

Supporting Information for

**Efficient and Selective Hydrogen Peroxide-Mediated Oxidation of Sulfides in Batch and
Segmented and Continuous Flow using a Peroxometalate-Based Polymer Immobilised Ionic
Liquid Phase Catalyst**

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Experimental

General Comments. All reagents were purchased from commercial suppliers and used without further purification. $[\text{NBu}_4]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{1-}$ and 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide were prepared as previously described² and $\text{H}_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$ was generated *in situ* immediately prior to use as previously described.³ ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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 ($\sim 25\text{ }^\circ\text{C}$) 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 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 $5\text{ }^\circ\text{C min}^{-1}$. 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. TEM images were acquired in bright field using a Tecnai 200 kV F20 Transmission Electron Microscope with a Field Emission Gun. A few drops of sample were pipetted onto an Agar holey carbon film copper TEM grids and the prepared grid was set aside for ca. 20 min prior to inserting it into the microscope, in order to allow the solvent to evaporate. Images were taken with a Gatan CCD digital camera attached to the microscope. 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 $5\text{ }\mu\text{m}$ Mixed D $300 \times 7.5\text{ mm}$ 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.). Flow reactions were performed using a Uniqsis FlowSyn Maxi all stainless steel platform with mandrels supplied by Uniqsis.

Ring opening metathesis polymerisation of 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide with cis-cyclooctene. A flame-dried three-neck round bottom flask under a nitrogen atmosphere was charged with chloroform (80 mL), *cis*-cyclooctene (3.0 mL, 23.0 mmol) and 1-benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide (4.23 g 11.7 mmol). To this was added a solution of [RuCl₂(PCy₃)₂(=CHPh)] (0.571 g, 0.694 mmol) in chloroform (*ca.* 10 mL) and the resulting mixture was heated at 40°C and left to stir for 19 h. Upon completion the reaction was allowed to cool to room temperature, ethyl vinyl ether (0.69 mL, 7.0 mmol) added and the solution stirred for an additional hour. The polymer was precipitated by slowly adding the reaction mixture portion wise to diethyl ether (*ca.* 600 mL) with vigorous stirring; after stirring for a further 60 minutes the polymer was isolated by filtration, using a sintered glass frit, washed with diethyl ether and dried to yield 5.2 g of a pale green solid. A solution of tris(hydroxymethyl)phosphine was prepared by degassing 2-propanol (90 mL) with nitrogen for 30 min prior to adding tetrakis(hydroxymethyl)phosphonium chloride (2.6 mL, 18 mmol). Potassium hydroxide (1.0 g, 18.0 mmol) was added slowly over 15 minutes to the vigorously stirred solution during which time a white precipitate formed. The mixture was allowed to stir for an additional 10 min and then added to a solution of the polymer in chloroform (*ca.* 100-150 mL). After heating at 60 °C for 19 h, NaBr (18.52 g, 180 mmol) was added and the mixture stirred for an additional 3 h at 60 °C. The mixture was then filtered, washed rigorously with distilled water (3 × 50 mL) and the resultant organic layer added dropwise to diethyl ether (*ca.* 500 mL) with vigorous stirring. After stirring for a minimum of 60 min the polymer was allowed to settle, isolated by filtration through a frit, washed with diethyl ether (2 × 50 mL) and dried under high vacuum to afford **1** as a buff brown solid in 61% yield (4.1 g). Anal. Calc for C₃₆H₅₆NBr: C, 74.20, H, 9.69, N, 2.40. Found: C, 73.82, H, 10.01, N, 2.35 (corresponding to a pyrrolidinium monomer content of 62.5 mol%, 1.72 mmol g⁻¹); GPC (average over 3 runs): $M_w = 9100$, $M_n = 8600$, PDI = 1.06 (Figure S1).

Figure S1 Differential refractive index (dRI) GPC trace of polymer **1** in DMF (0.6 mL/ min).

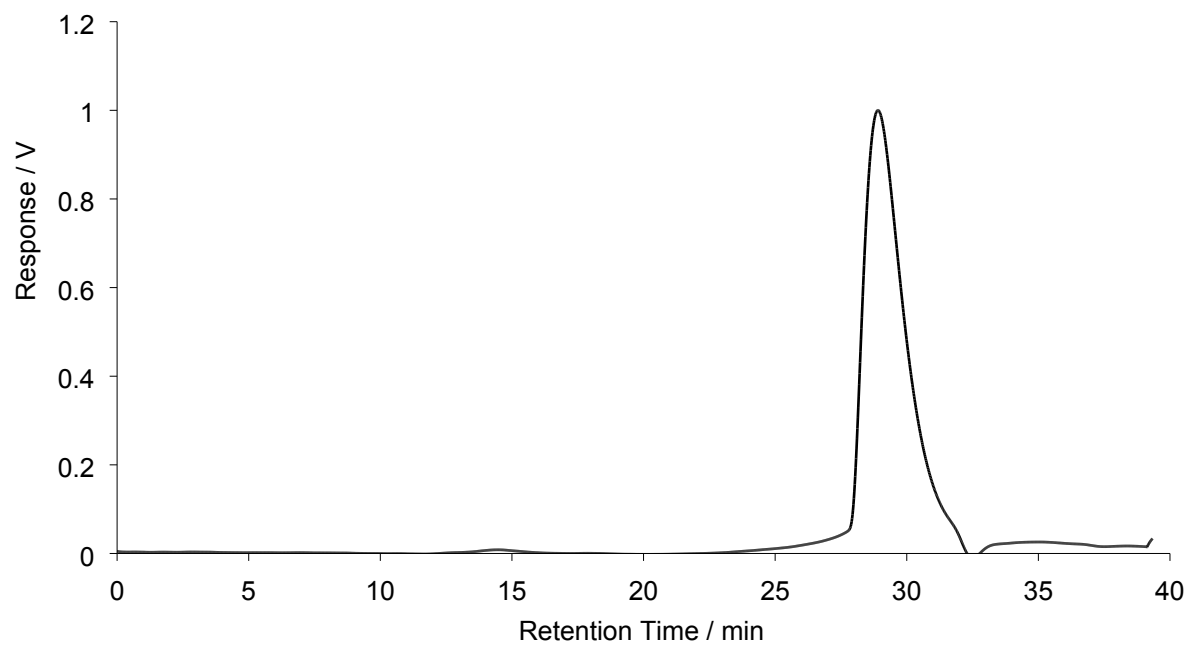
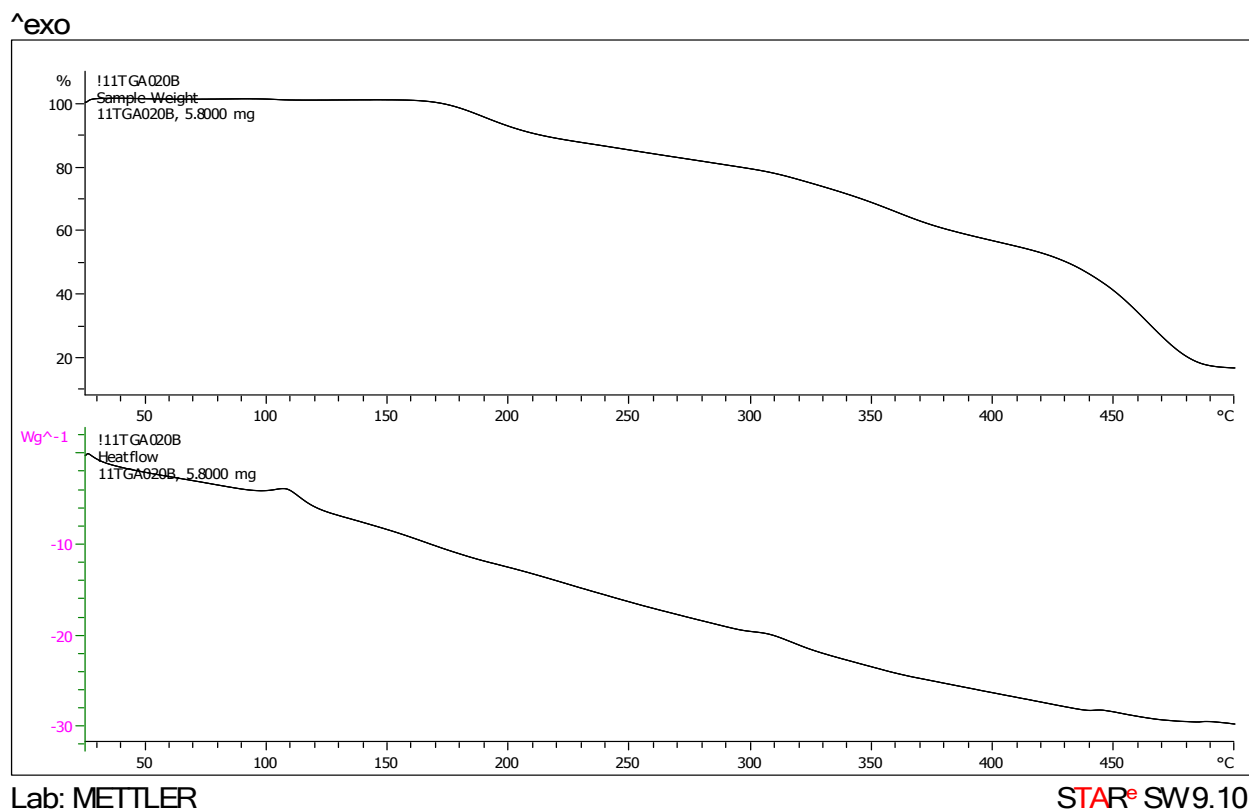


Figure S2 TGA and DSC curves for benzyl-1-((2-methylbicyclo[2.2.1]hept-5-en-2-yl)methyl)pyrrolidin-1-ium bromide-cis-cyclooctene copolymer **1**. The heating rate was 5 °C min⁻¹.



The heat flow plot (lower trace) of co-polymer **1** clearly shows an exotherm at 100 °C which could correspond to Hoffmann elimination with no loss in mass.

Synthesis of polymer immobilised peroxophosphotungstate 2. A hydrogen peroxide solution (35% w/w, 9.7 mL, 100 mmol) was added to phosphotungstic acid (1.73 g, 0.6 mmol) dissolved in a minimum volume of water and stirred at room temperature for 30 min. After this time, pyridine (0.145 mL, 1.8 mmol) was added followed by a solution of **1** (0.877 g, 1.8 mmol) in the minimum volume of ethanol, which resulted in the immediate precipitation of an amorphous white solid. The mixture was cooled to 0 °C, filtered through a sintered glass frit and the precipitate washed with water (2 × 10 mL) and diethyl ether (3 × 75 mL) and dried under vacuum to afford **6** in 84% yield. FT-IR (KBr plates): $\tilde{\nu}$ = 1087, 1058, 1028 (P-O), 956 (W=O), 837 (O-O), 585, 535 $W(O_2)_{sym,asym}$: Anal. Calc for $C_{108}H_{168}N_3O_{24}PW_4$: N, 1.58; W, 27.66. Found: N, 1.46; W, 26.31. Loading of tungsten 1.4 mmol g⁻¹.

Synthesis of $[nBu_4N]_3[PO_4\{WO(O_2)_2\}_4]/SiO_2$

A flame dried Schlenk flask was charged with $[nBu_4N]_3[PO_4\{WO(O_2)_2\}_4]$ (0.094 g, 0.05 mmol) and dichloromethane (6 mL) and the mixture stirred at room temperature for 15 min after which time 1.0 g of Geduran® Si60 (43-60 μm) was added and stirring continued for a further 2 h. The dichloromethane was removed under vacuum to afford a free flowing powder. FT-IR (KBr plates): $\tilde{\nu}$ = 1084, 1059, 1028 (P-O), 966 (W=O), 845 (O-O), 592, 532 $W(O_2)_{sym,asym}$. The tungsten loading was confirmed to be 0.19 mmol of W g⁻¹ of silica by ICP-OES analysis.

Figure S3a TEM image of freshly prepared polymer immobilised peroxophosphotungstate **2**

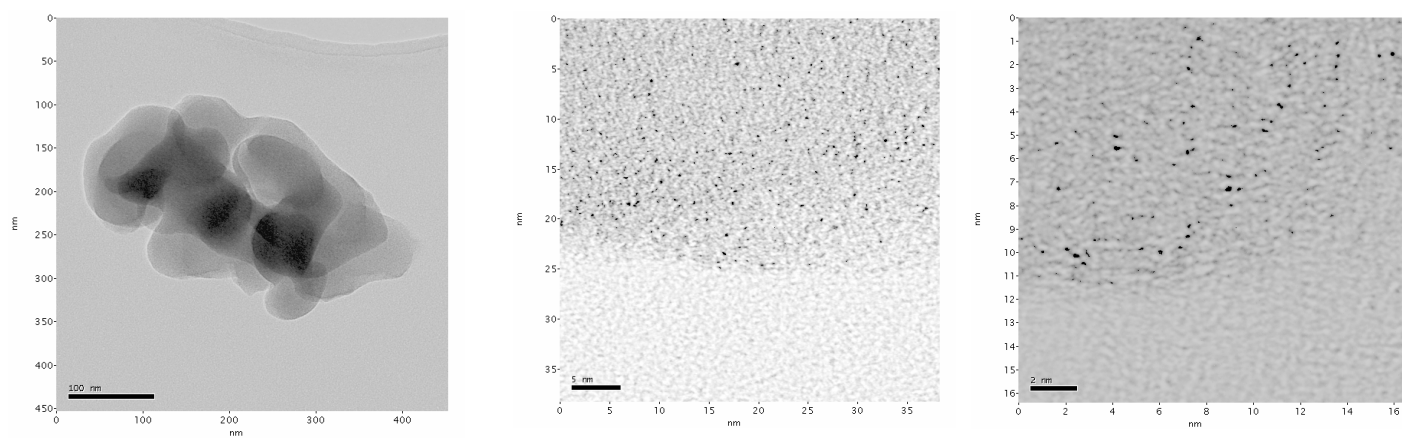
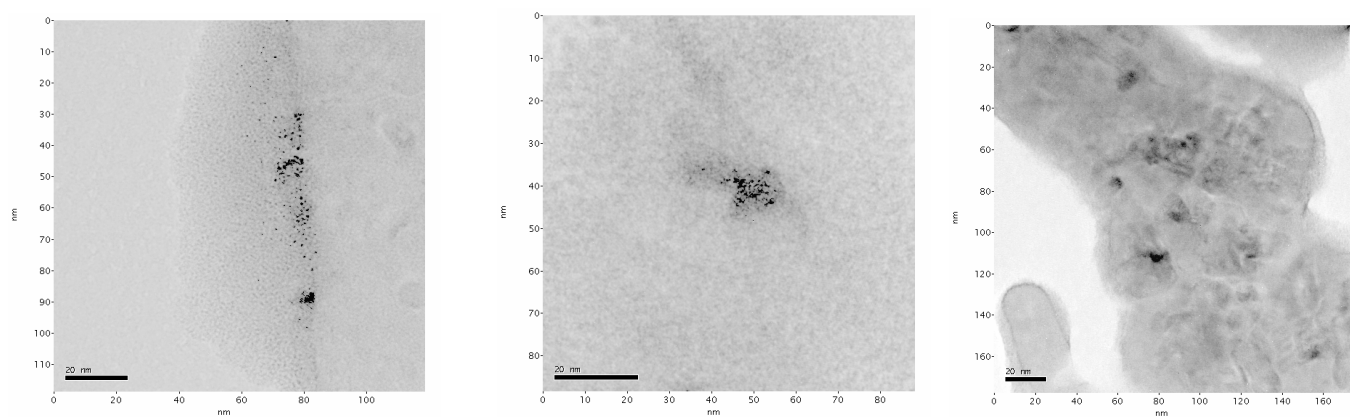


Figure S3b TEM image of polymer supported peroxophosphotungstate **2** recovered after use in catalysis



General Procedure for Catalytic Sulfoxidation in Batch

An oven-dried Schlenk flask was allowed to cool to room temperature and charged sequentially with sulfide (1.0 mmol), catalyst (0.013 g, 0.005 mmol) and solvent (3 mL), the reaction was then activated by the addition of 35% H₂O₂ (0.24 mL, 2.5 mmol) and allowed to stir at room temperature for 15 min. The reaction mixture was diluted with dichloromethane (25 mL), washed with water (*c.a.* 50 mL) and the organic extract dried over MgSO₄ and the solvent removed under reduced pressure. The resulting residue was analysed by either ¹H or ¹³C{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 Catalytic Sulfoxidation Recycle Studies

An oven-dried Schlenk flask was allowed to cool to room temperature and charged sequentially with sulfide (3.0 mmol), polymer immobilised catalyst **2** (0.039 g, 0.015 mmol) or [nBu₄N]₃[PO₄{WO(O₂)₂}₄]/SiO₂ (100 mg of a 6.5 wt%) and solvent (9 mL). The reaction was initiated by addition of 35% H₂O₂ (0.72 mL, 7.5 mmol) and the resulting mixture allowed to stir at room temperature for 20 min. After this time the solution was centrifuged (10 min, 12000 rpm), decanted using a pipette and the remaining catalyst washed with the reaction solvent and dried prior to reuse under the same conditions. The remaining solution was subject to the same work-up and analysis as described above. ICP analysis of a portion of the organic and aqueous phases between recycles was conducted using a Perkin Elmer Optima 4300DV ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer).

General Procedure for Catalytic Sulfoxidation Kinetic Studies

An oven-dried Schlenk flask was allowed to cool to room temperature and charged sequentially with sulfide (3.0 mmol), polymer immobilised catalyst **2** (0.039 g, 0.005 mmol) and solvent (9 mL). The reaction was initiated by addition of 35% H₂O₂ (0.72 mL, 7.5 mmol) and the resulting mixture stirred at room temperature for the 20 min during which time 0.5 mL aliquots were removed for work-up (as above) and analysis by ¹H NMR spectroscopy. After the final aliquot had been removed the remaining reaction mixture was decanted, the catalyst washed with diethyl ether, dried and replenished to account for losses arising from the sampling.

The recycle kinetic experiment was conducted by charging the Schlenk with fresh sulfide (3.0 mL), solvent (9 mL) and 35% H₂O₂ (0.72 mL, 7.5 mmol).

General Procedure for Segmented and Continuous Flow Catalytic Sulfoxidation

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 (25 mL, 0.6 M). A Uniqsis FlowSyn reactor was used to pump 1 mL of each reagent at total flow rates that varied between 0.293 mL min⁻¹ and 8.8 mL min⁻¹ (using the same solvent as stock) 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 x 100 mm) packed with 0.1 g of [PO₄{WO(O₂)₂}₄]@PIILP and 2.0 g of SiO₂ (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 (*c.a.* 15 mL), the organic extract dried over MgSO₄, the solvent removed under reduced pressure and the resulting residue analysed by ¹H NMR spectroscopy to quantify the composition of starting material and products.

Characterisation of Sulfoxides and Sulfones

Methyl phenyl sulfoxide.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 7.69-7.62 (m, 2H), 7.50-7.41 (m, 2H), 7.36-7.30 (m, 1H), 2.73 (s, 3H); ¹³C NMR (100.5 MHz, CDCl₃, δ): 145.42, 130.95, 128.63, 123.54, 43.93; LRMS (EI⁺) *m/z* 163 [M+Na]⁺.

Methyl phenyl sulfone.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 7.95-7.87 (m, 2H), 7.71-7.61 (m, 2H), 7.59-7.52 (m, 1H), 3.02 (s, 3H); ¹³C NMR (100.5MHz, CDCl₃, δ): 137.44, 133.21, 128.54, 126.23, 44.88; LRMS (EI⁺) *m/z* 179 [M+Na]⁺.

Ethyl phenyl sulfoxide.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 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); ¹³C NMR (100.5 MHz, CDCl₃, δ): 145.69, 131.47, 129.85, 125.42, 47.19, 10.39; LRMS (EI⁺) *m/z* 177 [M+Na]⁺.

Ethyl phenyl sulfone.^[4] ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100.5MHz, CDCl₃, δ): 138.31, 133.47, 128.92, 127.86, 50.28, 7.34; LRMS (EI⁺) *m/z* 193 [M+Na]⁺.

Allyl phenyl sulfoxide.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 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); ¹³C NMR (100.5 MHz, CDCl₃, 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.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 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); ¹³C NMR (100 MHz, CDCl₃, 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.^[5] ¹H NMR (400 MHz, CDCl₃, δ): 8.39 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 2.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, δ): 152.4, 150.0, 126.2, 125.8, 43.5; LRMS (EI⁺) *m/z* 205 [M+Na]⁺.

Methyl 4-nitrophenyl sulfone.^[6] ¹H NMR (400 MHz, CDCl₃, δ): 8.43 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 3.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, δ): 150.9, 145.9, 129.0, 124.6, 44.3. LRMS (EI⁺) *m/z* 224 [M+Na]⁺.

Dibenzothiophene sulfoxide.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 7.98-7.91 (m, 4H), 7.75-7.71 (m, 2H), 7.59-7.52 (m, 2H); ¹³C NMR (100.5 MHz, CDCl₃, δ): 143.33, 132.67, 129.83, 126.37, 124.16, 123.45; LRMS (EI⁺) *m/z* 223 [M+Na]⁺.

Dibenzothiophene sulfone.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 7.85-7.77 (m, 4H), 7.66-7.61 (m, 2H), 7.55-7.51 (m, 2H); ¹³C NMR (100.5 MHz, CDCl₃, δ): 137.62, 133.77, 131.53, 130.16, 121.97, 121.54; LRMS (EI⁺) *m/z* 239 [M+Na]⁺.

Homoallyl phenyl sulfoxide.^[7] ¹H NMR (300 MHz, CDCl₃, δ): 7.75-7.55 (m, 5H), 6.04-5.90 (m, 1H), 5.31-5.20 (m, 2H), 2.98-2.83 (m, 2H), 2.73-2.68 (m, 1H), 2.50-2.45 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, 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.^[8] ¹H NMR (400 MHz, CDCl₃, δ): 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); ¹³C NMR (100 MHz, CDCl₃, 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.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 7.55-7.42 (m, 2H), 7.36-7.17 (m, 3H), 7.11-6.63 (m, 5H), 3.98 (s, 2H); ¹³C NMR (100.5 MHz; CDCl₃, 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.^[4] ¹H NMR (400 MHz, CDCl₃, δ): 7.74-7.65 (m, 2H), 7.41-7.32 (m, 3H), 7.14-7.06 (m, 5H), 4.41 (s, 2H); ¹³C NMR (100.5 MHz; CDCl₃, δ): 137.49, 133.44, 130.53, 128.61, 128.47, 128.39, 128.31, 62.53; LRMS (EI⁺) *m/z* 255 [M+Na]⁺.

tert-Butyl methyl sulfoxide.^[9] ¹H NMR (300 MHz, CDCl₃, δ): 2.42 (s, 3H), 1.37 (s, 9H); ¹³C NMR (100 MHz; CDCl₃, δ): 57.80, 36.68, 26.60; LRMS (EI⁺) *m/z* 143 [M+Na]⁺.

tert-Butyl methyl sulfone.^[10] ¹H NMR (300 MHz, CDCl₃, δ): 2.70 (s, 3H), 1.41 (s, 9H); ¹³C NMR (100 MHz; CDCl₃, δ): 50.51, 32.05, 23.25. LRMS (EI⁺) *m/z* 137 [M+H]⁺.

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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- [4] (a) J. J. Boruah, S. P. Das, S. R. Ankireddy, S. R. Gogoi, N. S. Islam, *Green Chem.* 2013, **15**, 2944-2959. (b) X. Qu, X. Li, Y. Chai, Q. Yang, P. Li, Y. Yao, *Green Chem.*, 2013, **15**, 357–361.
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- [6] 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] B. J. McNelis, D. D. Sternbach, A. T. MacPhail, *Tetrahedron* 1994, **50**, 6767-6782.

Figure S4 ^1H NMR spectrum of the reaction mixture for the selective oxidation of thioanisole in methanol at RT for 15 min using 0.5 mol% **2**.

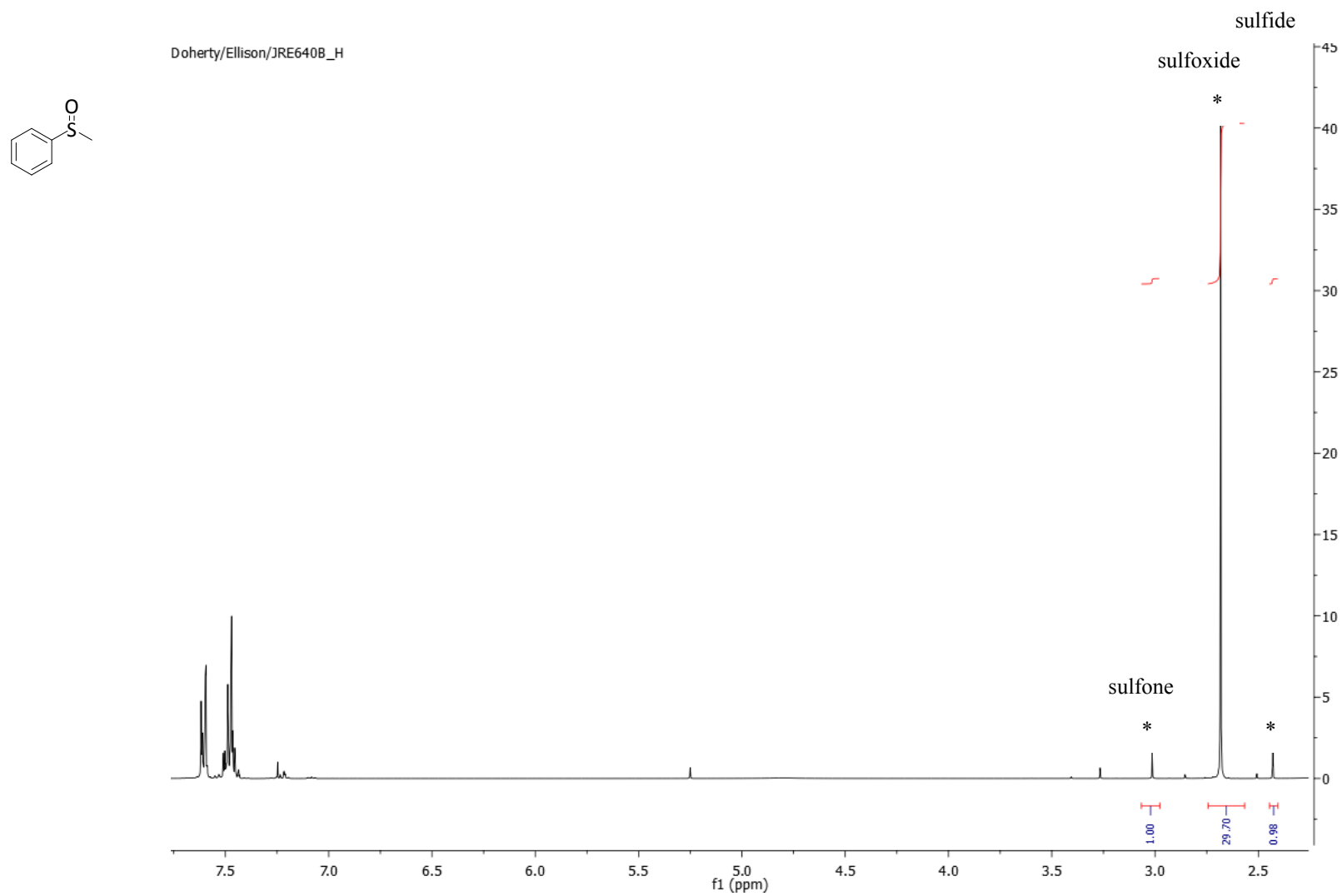


Figure S5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of thioanisole in methanol at RT for 15 min using 0.5 mol% **2**.

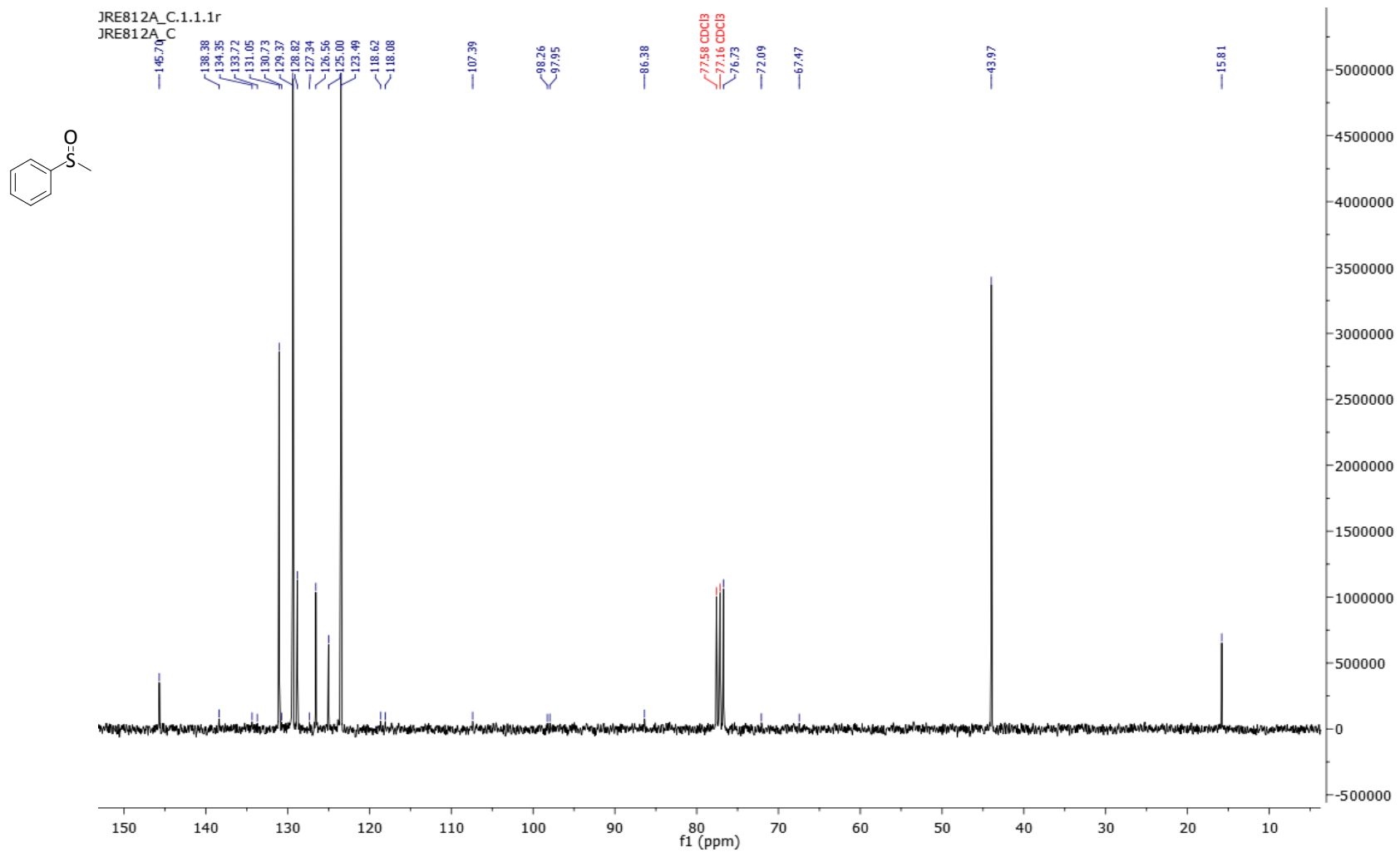


Figure S6 ^1H NMR spectrum of methyl phenyl sulfone obtained from the oxidation of thioanisole in MeCN using 0.5 mol% **2**.

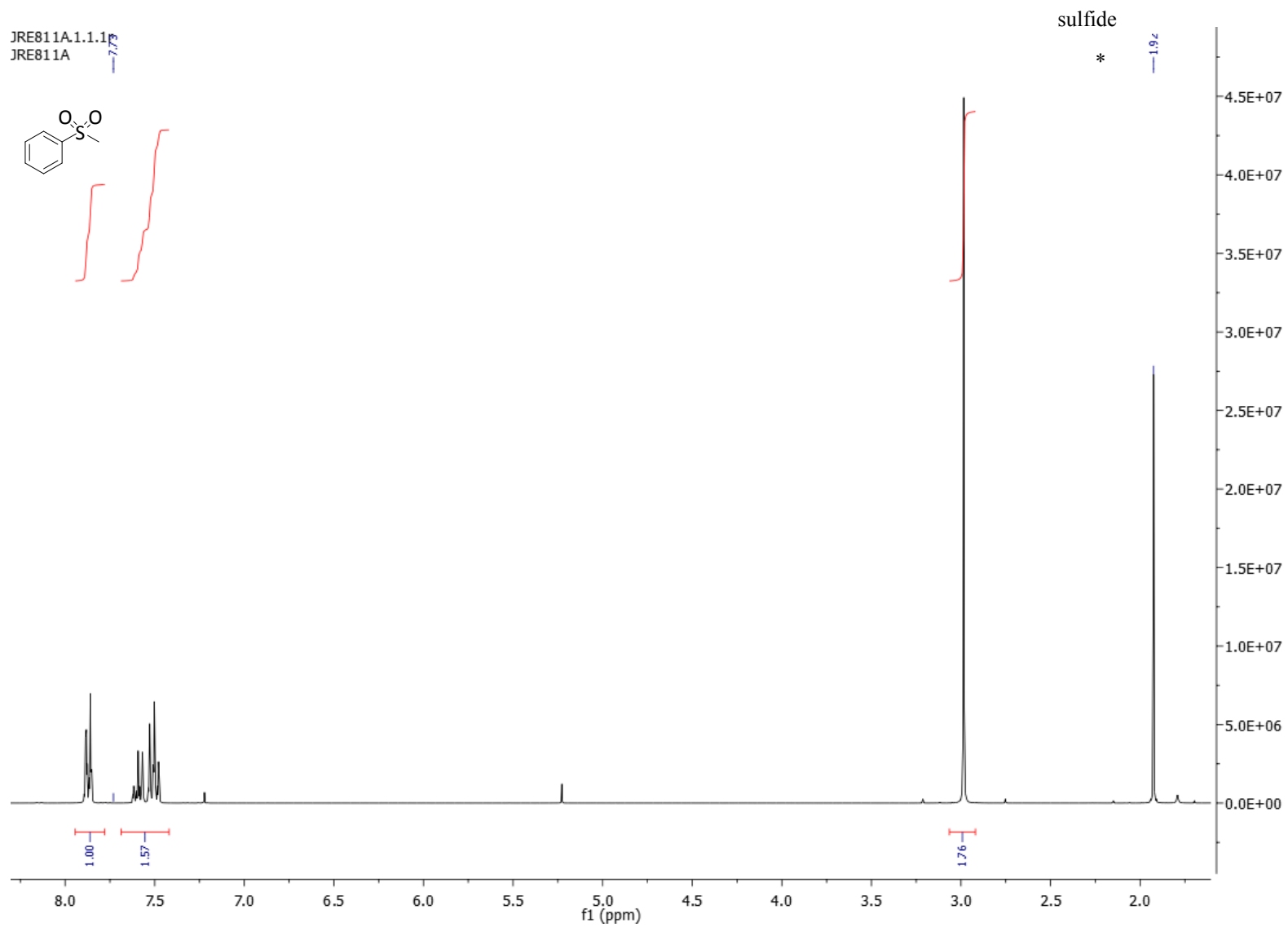


Figure S7 ^{13}C NMR spectrum of methyl phenyl sulfone obtained from the oxidation of thioanisole in MeCN using 0.5 mol% **2**.

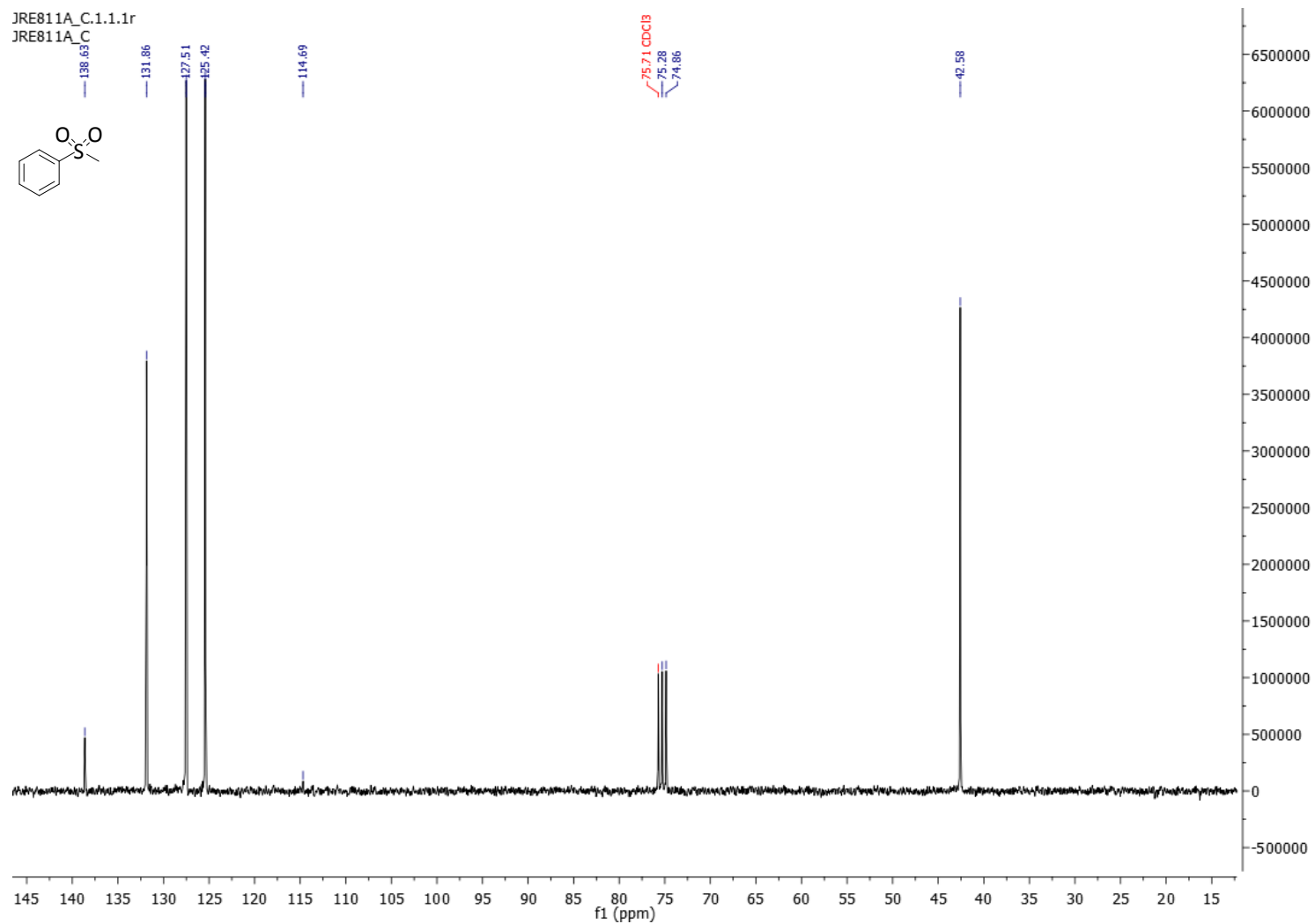


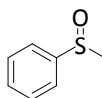
Figure S8 Mass Spectra for methyl phenyl sulfoxide (left) and methyl phenyl sulfone (right)

Elemental Composition Report

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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:

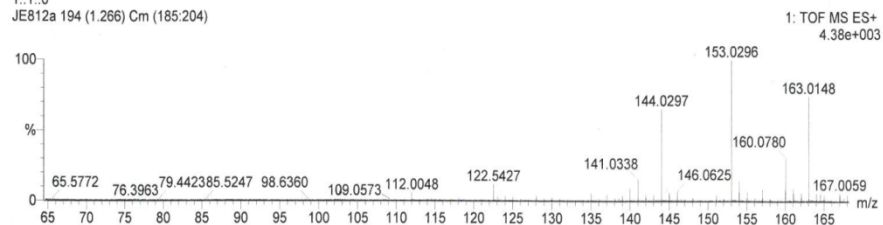
C: 8-8 H: 10-10 O: 2-2 23Na: 0-1 S: 1-1

direct

22-Oct-2014

1:1:0

JE812a 194 (1.266) Cm (185:204)



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

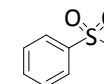
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
163.0148	---						

Elemental Composition Report

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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:

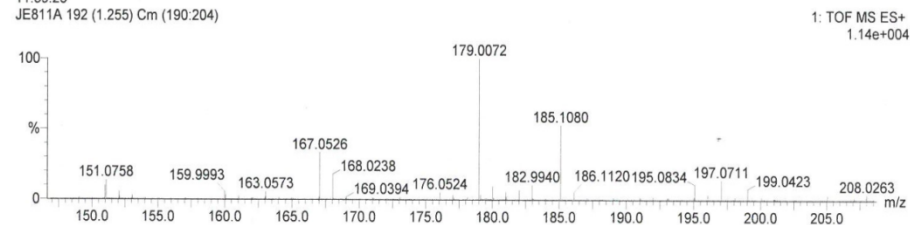
C: 7-7 H: 8-8 O: 2-2 23Na: 0-1 S: 1-1

direct

22-Oct-2014

11:39:23

JE811A 192 (1.255) Cm (190:204)



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 S9 ^1H NMR spectrum of the reaction mixture for the selective oxidation of ethyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

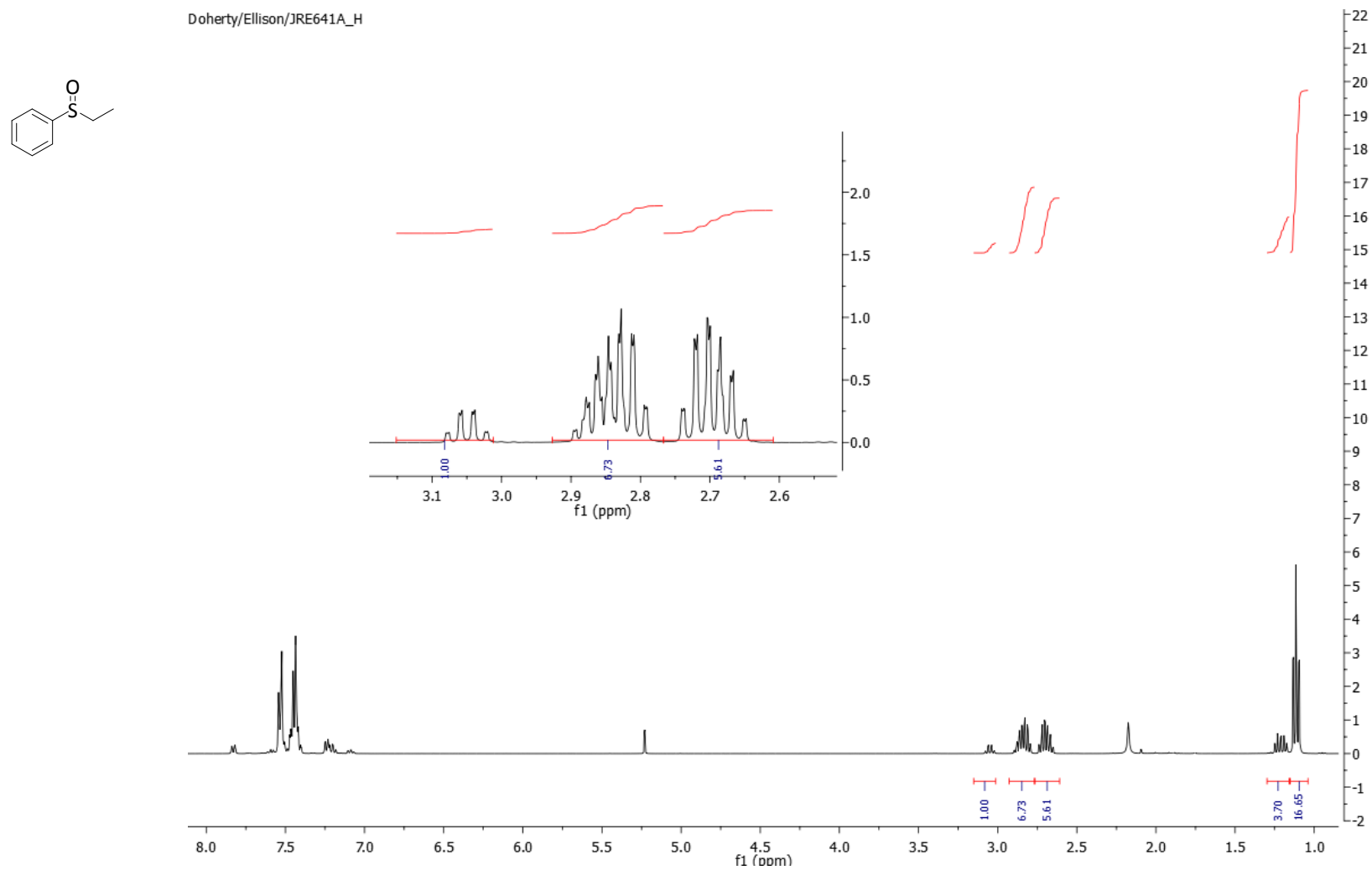


Figure S10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of ethyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

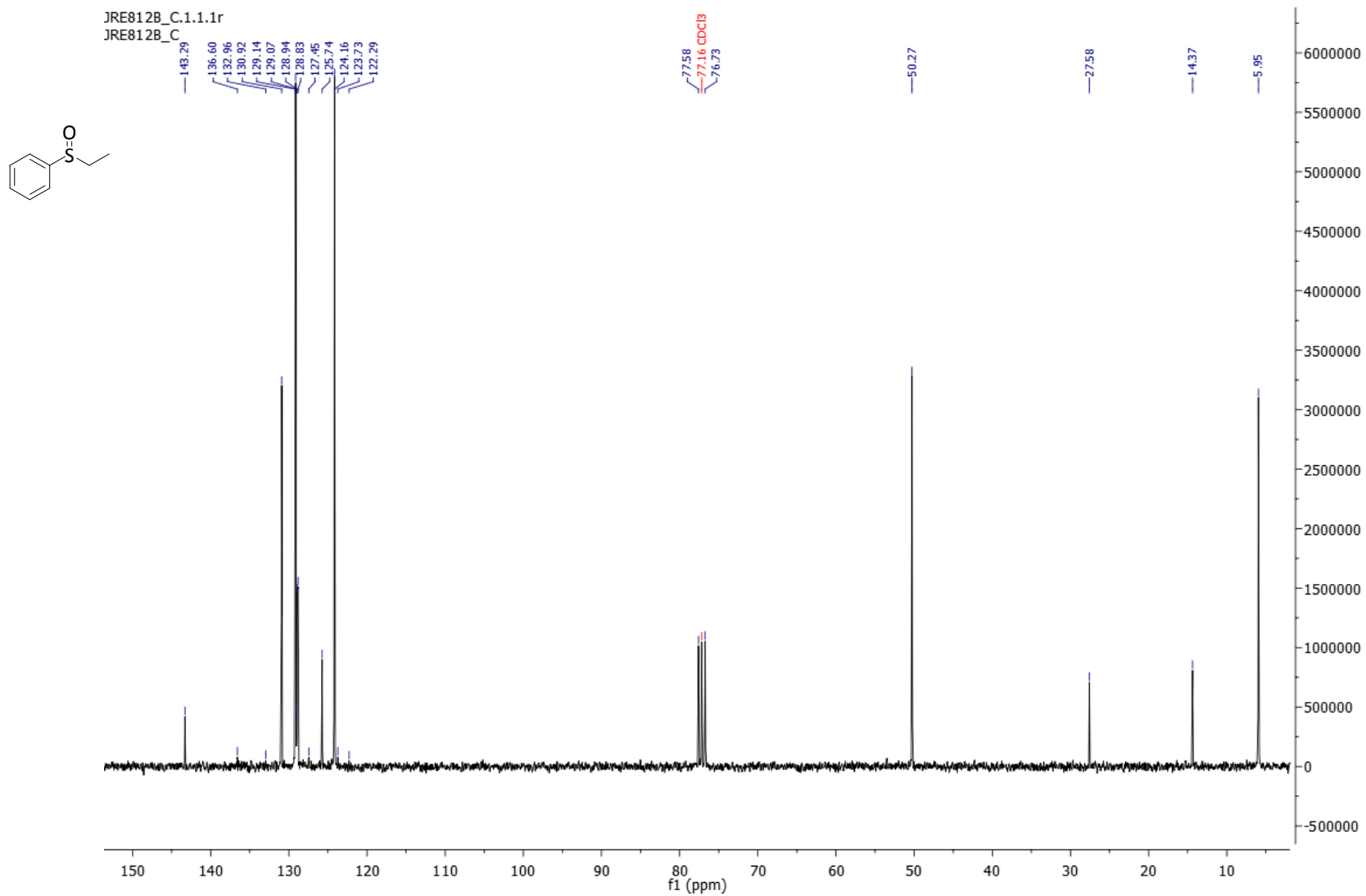


Figure S11 ^1H NMR spectrum of ethyl phenyl sulfone obtained from the oxidation of ethyl phenyl sulfide in MeCN using 0.5 mol% **2**.

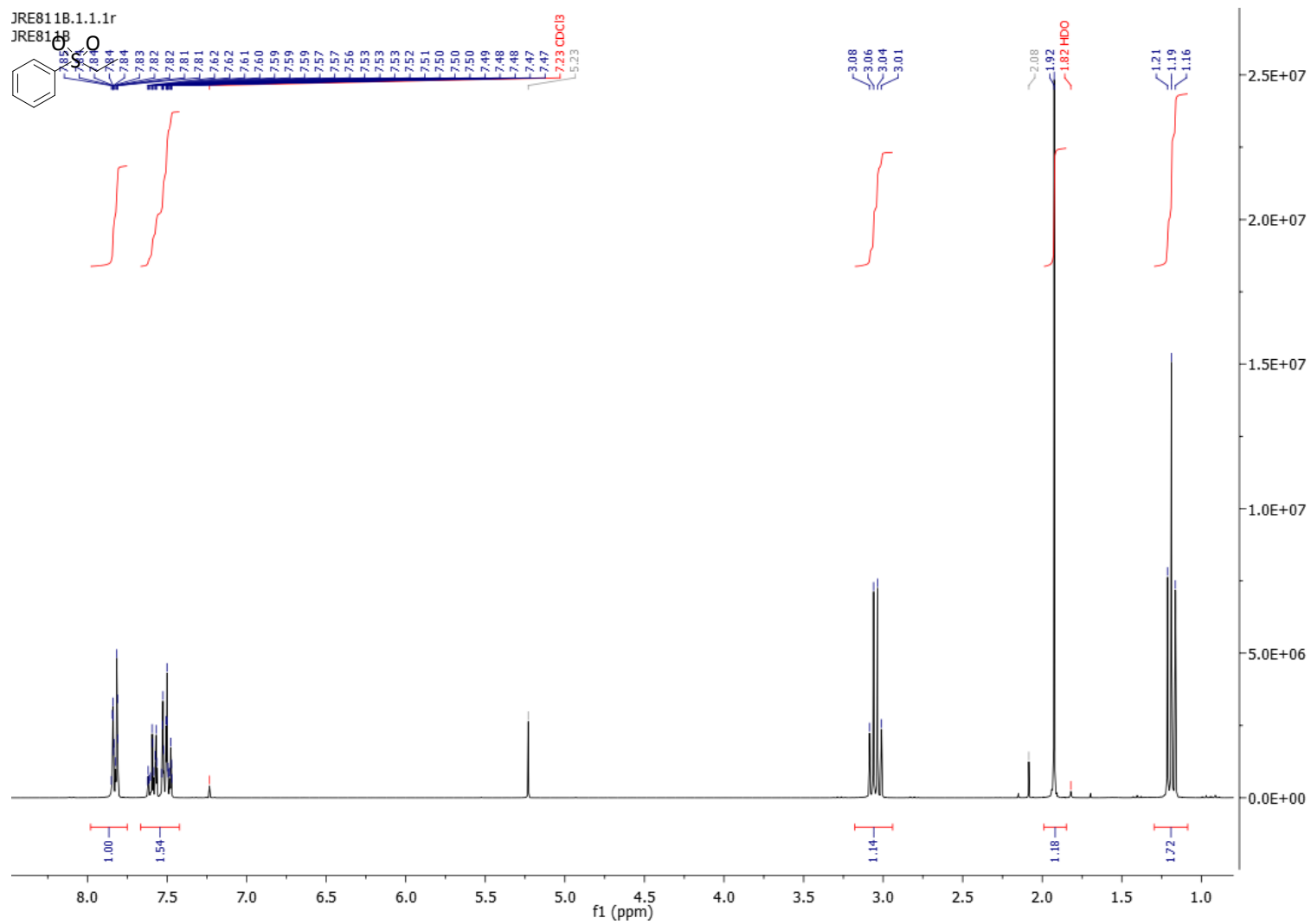


Figure S12 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of ethyl phenyl sulfone obtained from the oxidation of ethyl phenyl sulfide in MeCN using 0.5 mol% **2**.

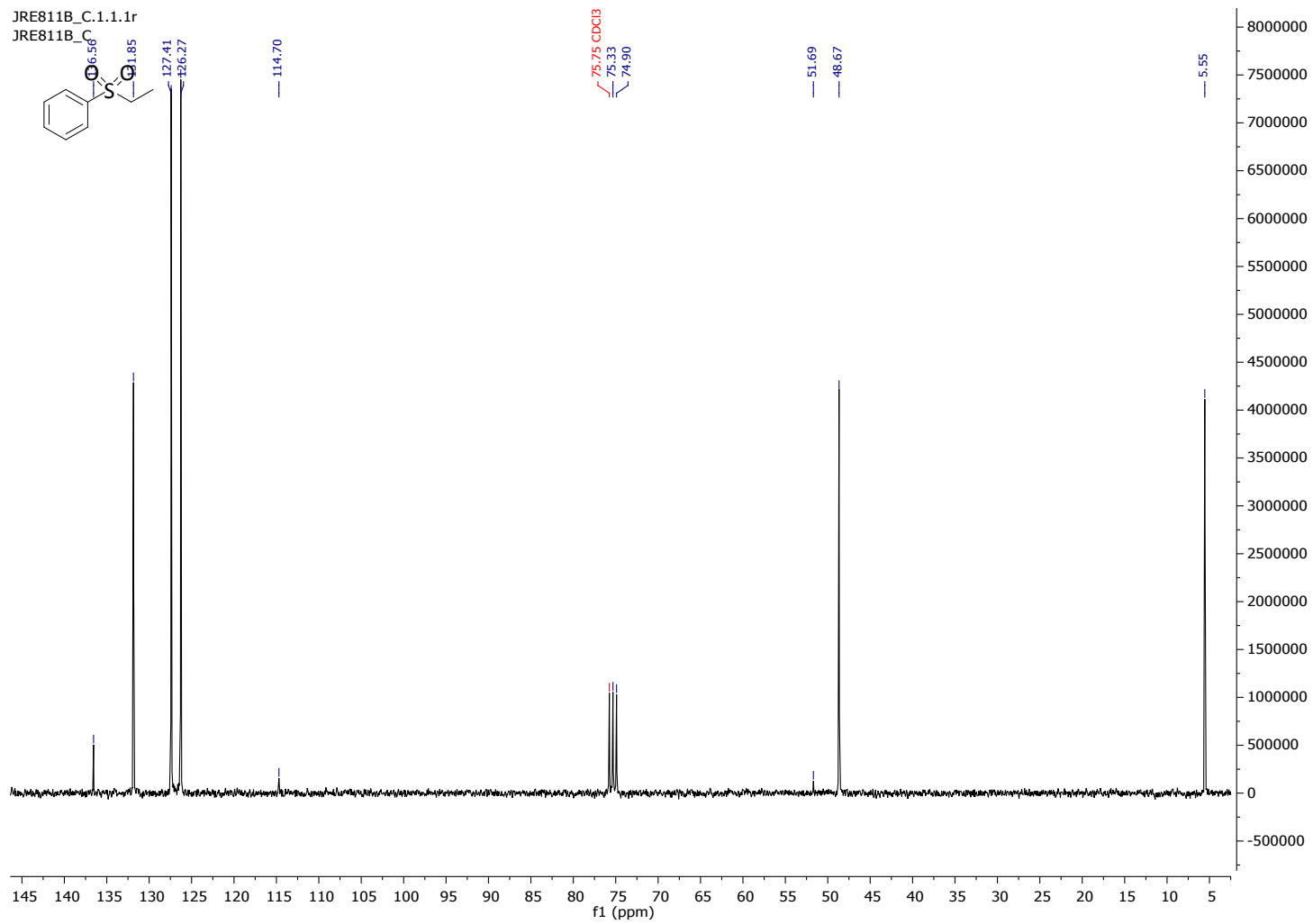


Figure S13 Mass Spectra for ethyl phenyl sulfoxide (right) and ethyl phenyl sulfone (left)

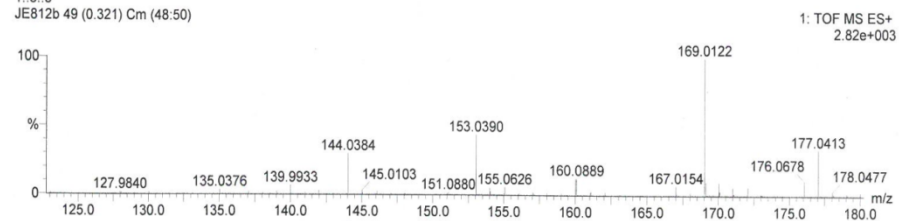
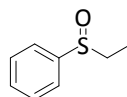
Elemental Composition Report

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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
 11:49:38
 JE812b 49 (0.321) Cm (48:50)



1: TOF MS ES+
2.82e+003

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

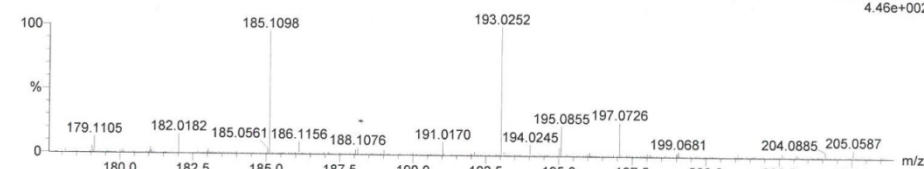
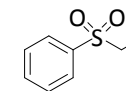
Elemental Composition Report

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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
 11:49:38
 JE811B 174 (1.141)



1: TOF MS ES+
4.46e+002

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

Figure S14 ^1H NMR spectrum of the reaction mixture for the selective oxidation of allyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

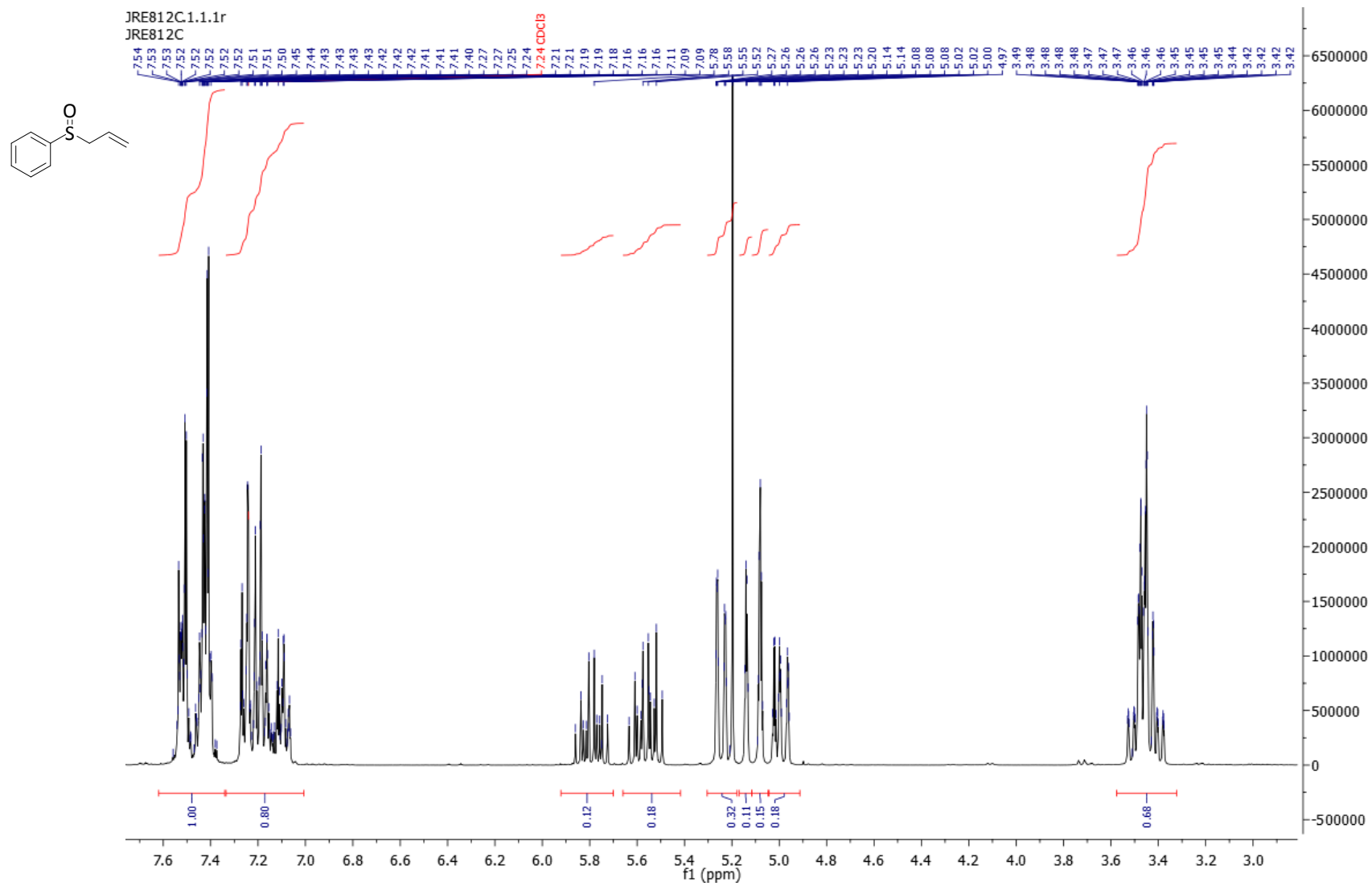


Figure S15 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of allyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

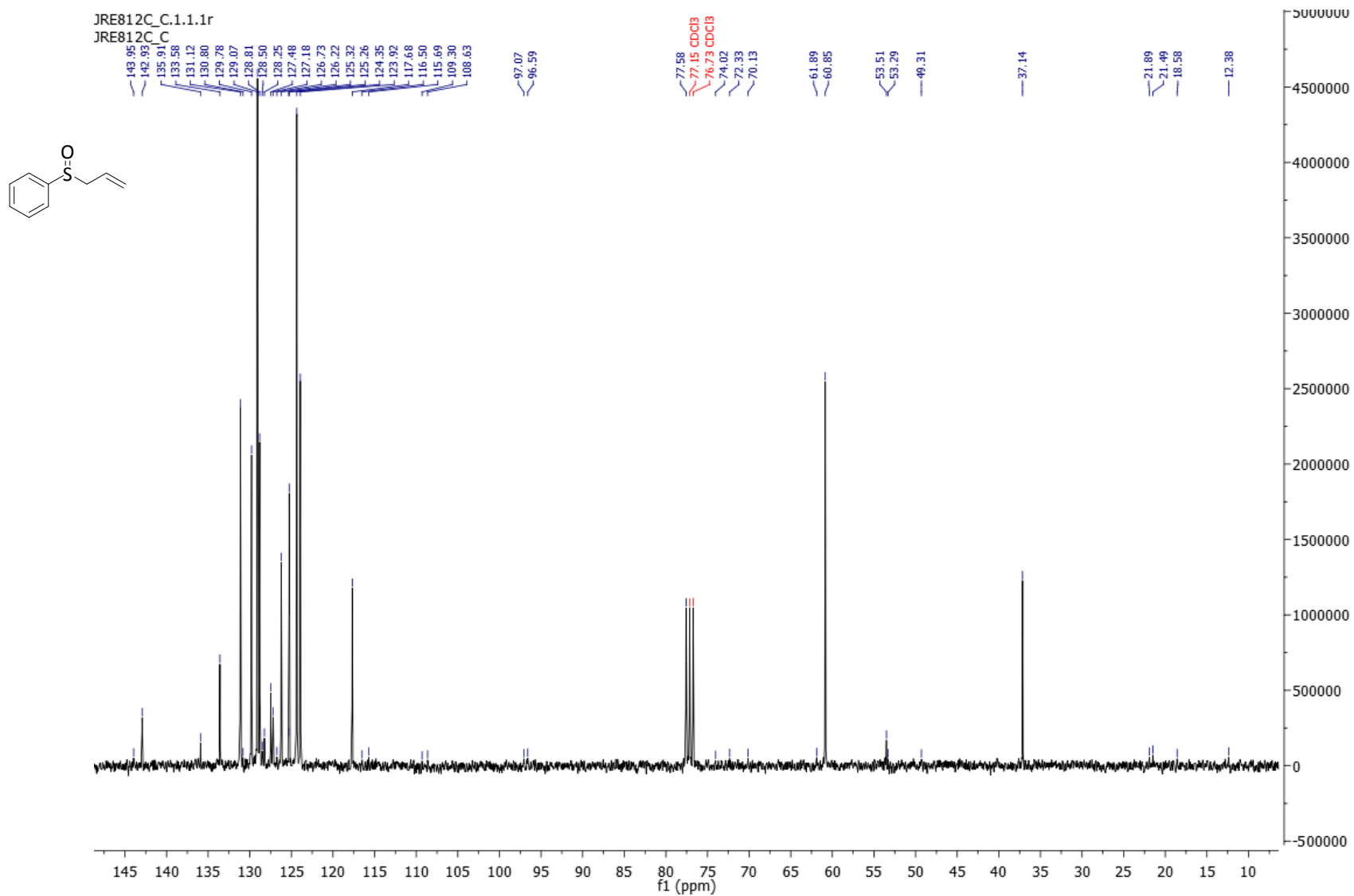


Figure S16 ^1H NMR spectrum of allyl phenyl sulfone obtained from the oxidation of allyl phenyl sulfide in MeCN using 0.5 mol% **2**.

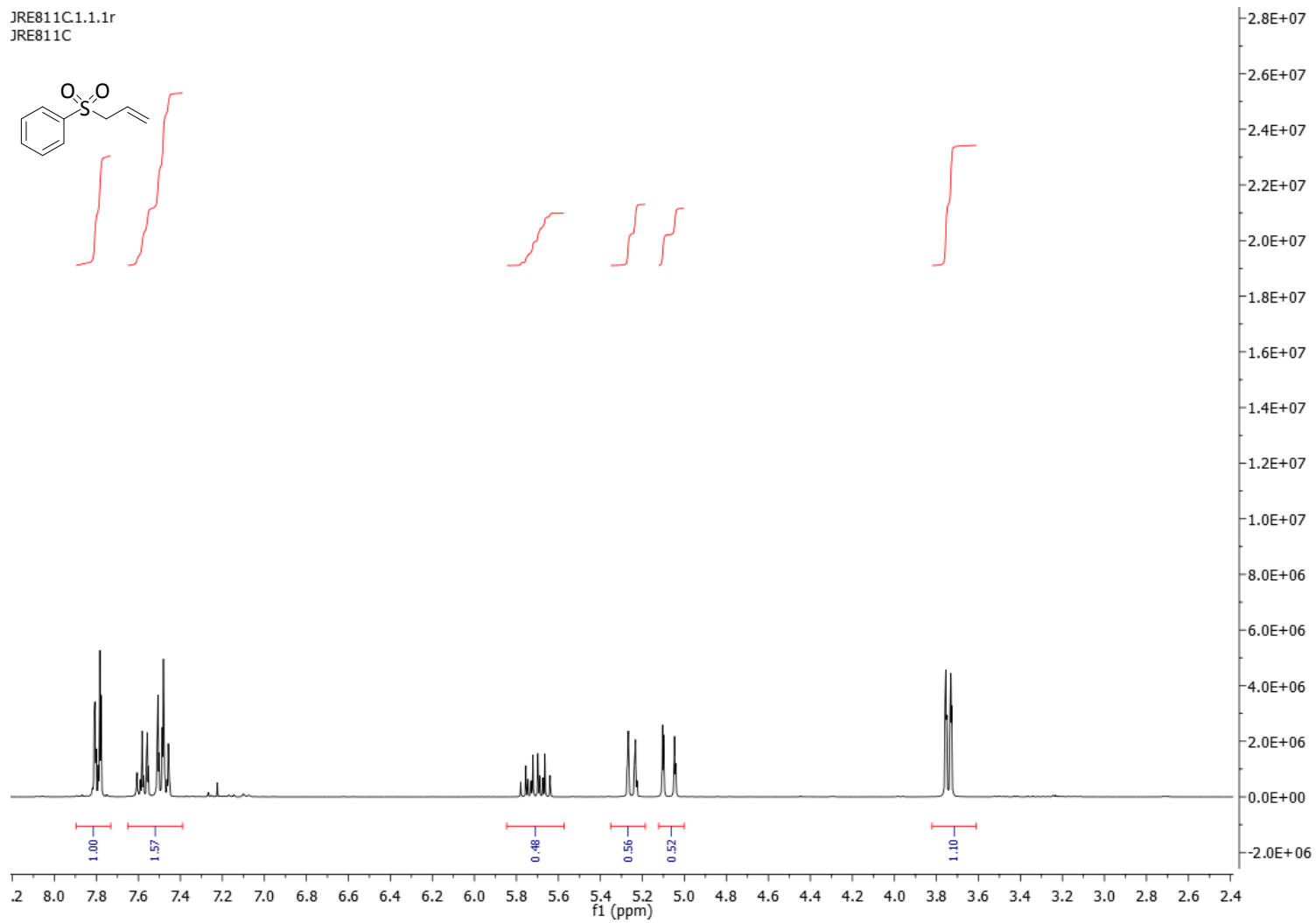


Figure S17 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of allyl phenyl sulfone obtained from the oxidation of allyl phenyl sulfide in MeCN using 0.5 mol% **2**.

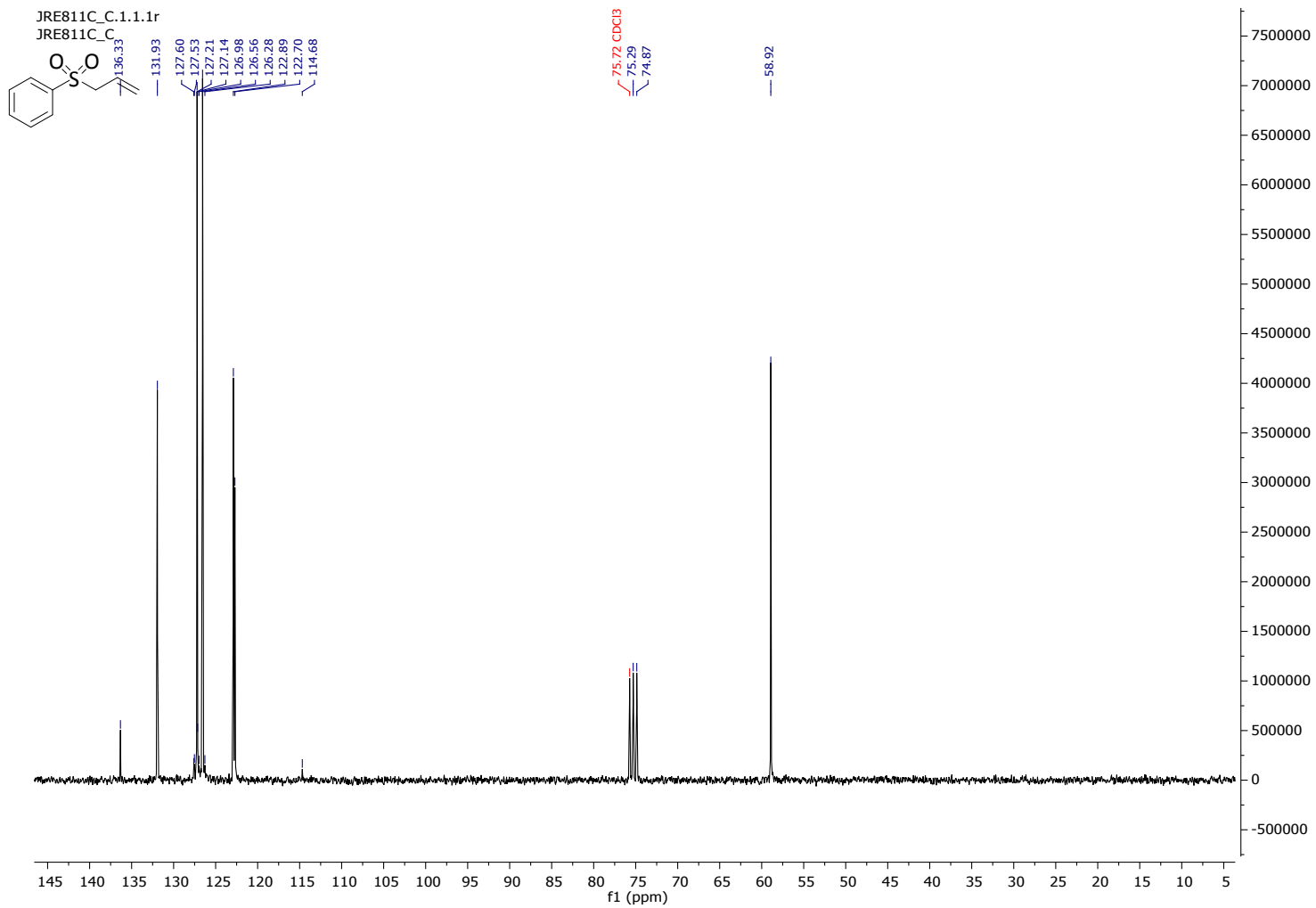


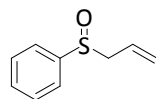
Figure S18 Mass spectra for allyl phenyl sulfoxide (left) and allyl phenyl sulfone (right)

Elemental Composition Report

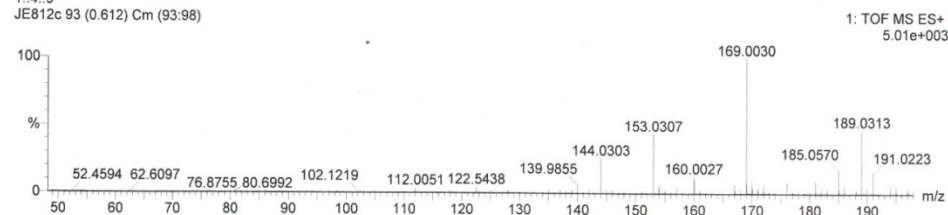
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Single Mass Analysis

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
 1:4:9
 JEB12c 93 (0.612) Cm (93:98)



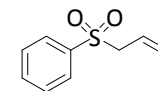
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
189.0313	---						

Elemental Composition Report

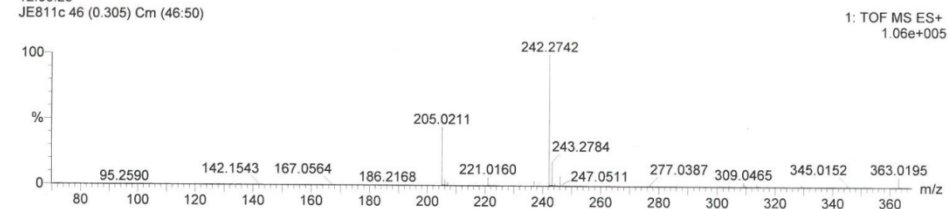
Page 1 of 1

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
 12:06:25
 JEB11c 46 (0.305) Cm (46:50)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
205.0211	---						

Figure S19 ^1H NMR spectrum of the reaction mixture for the selective oxidation of 4-nitrothioanisole in methanol at RT for 15 min using 0.5 mol% **2**.

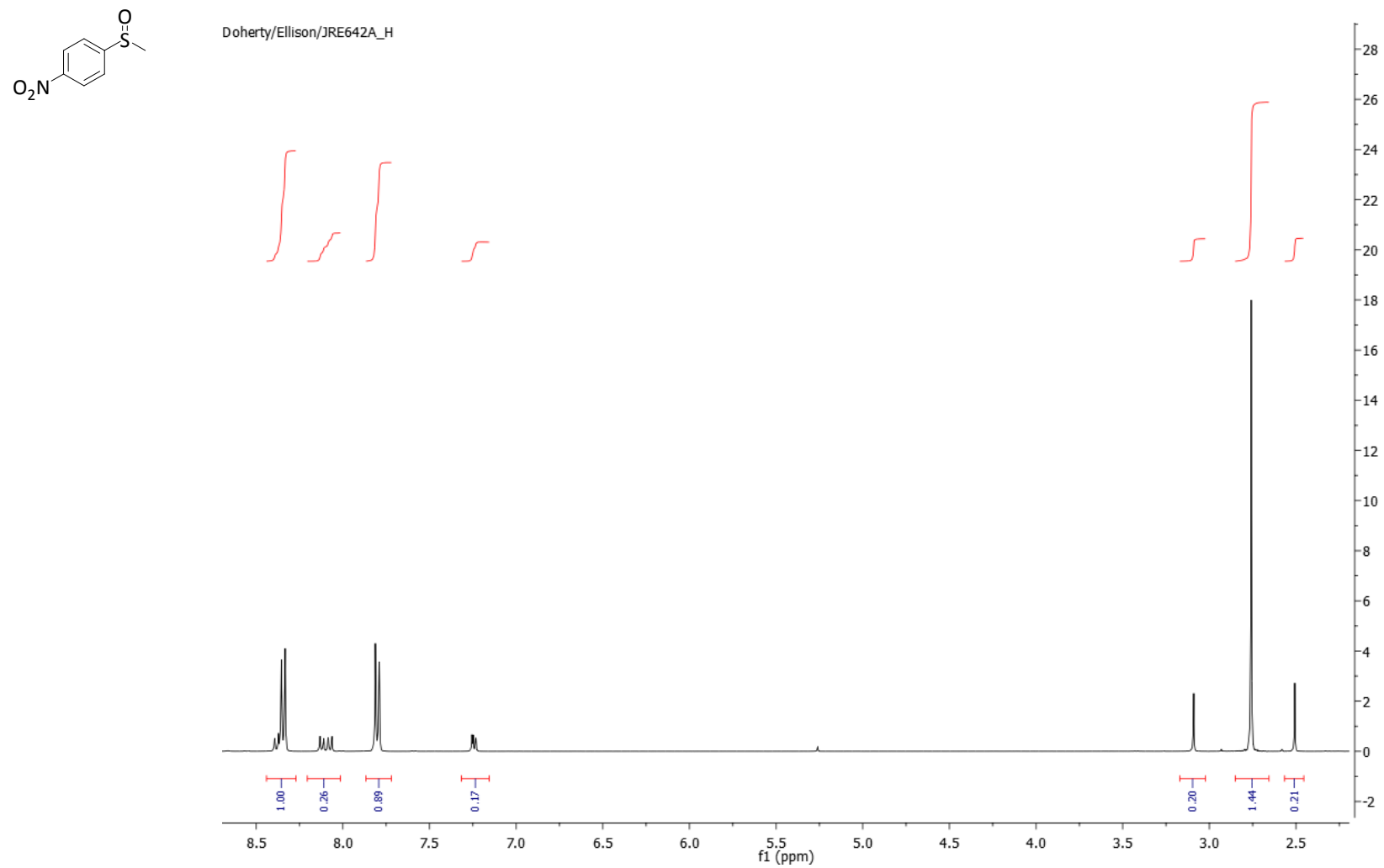


Figure S20 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of 4-nitrothioanisole in methanol at RT for 15 min using 0.5 mol% **2**.

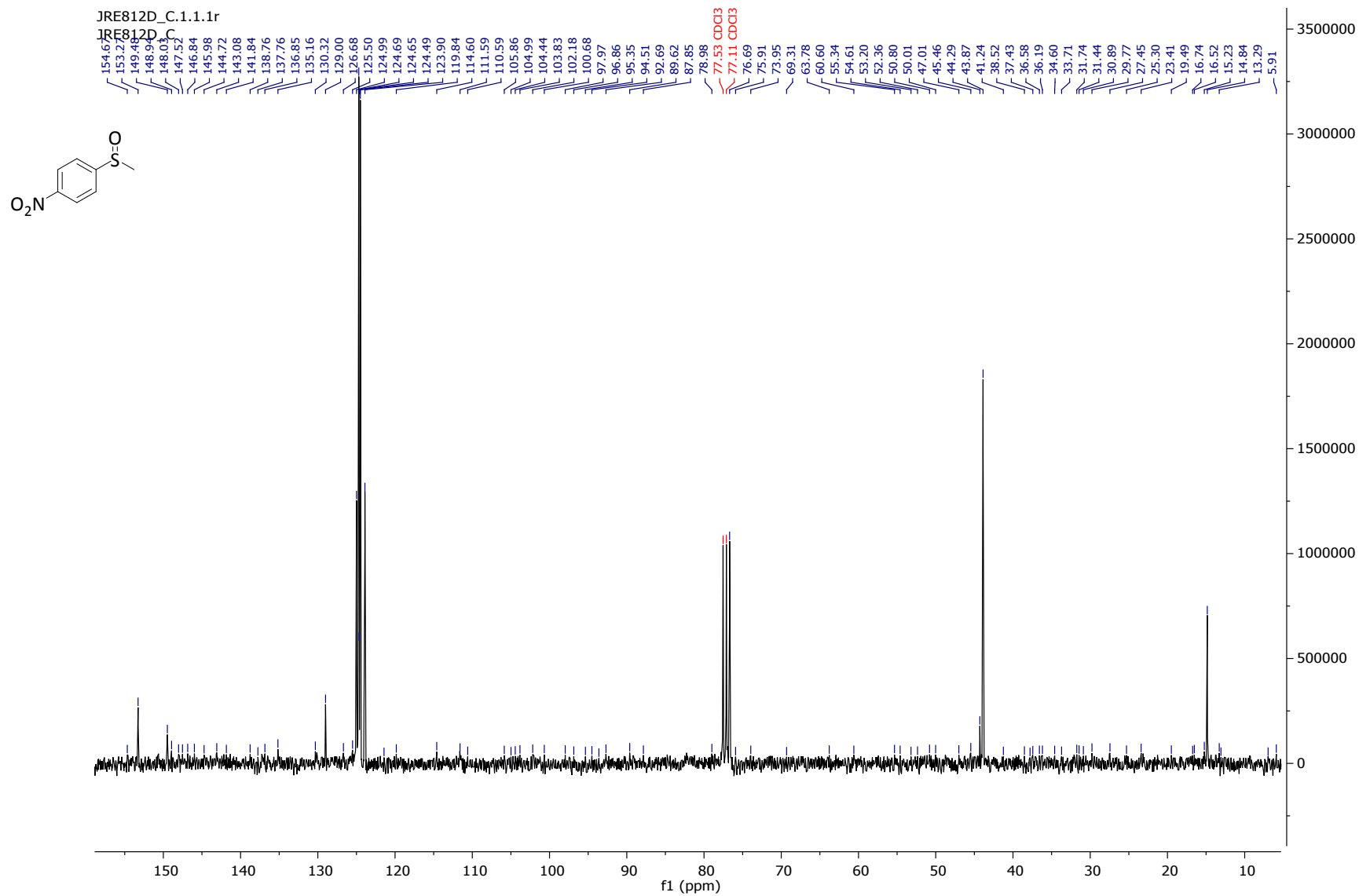


Figure S21 ^1H NMR spectrum of methyl 4-nitrophenyl sulfone obtained from the oxidation of 4-nitrothioanisole in MeCN using 0.5 mol% **2**.

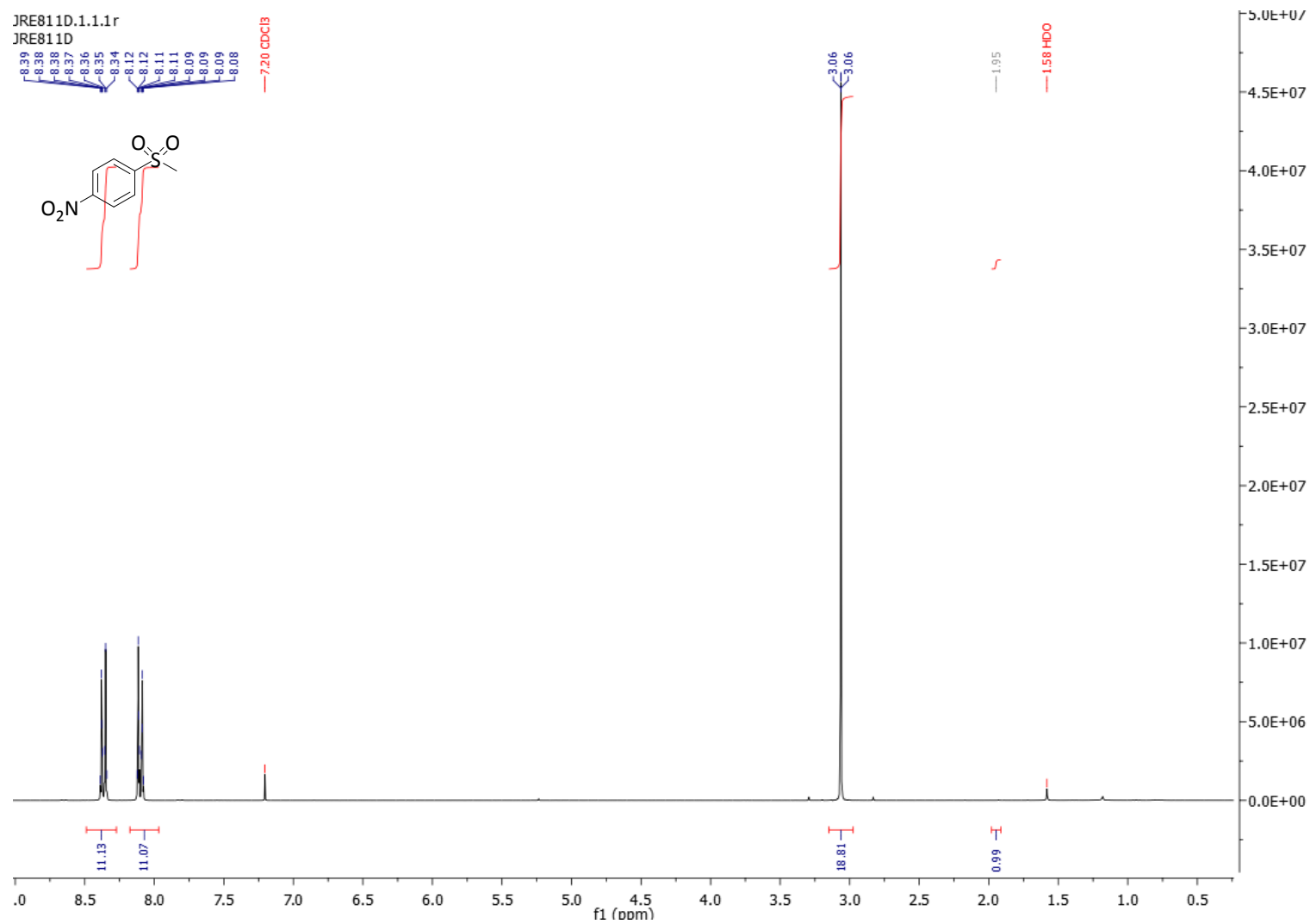


Figure S22 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of methyl 4-nitrophenyl sulfone obtained from the oxidation of 4-nitrothioanisole in MeCN using 0.5 mol% **2**.

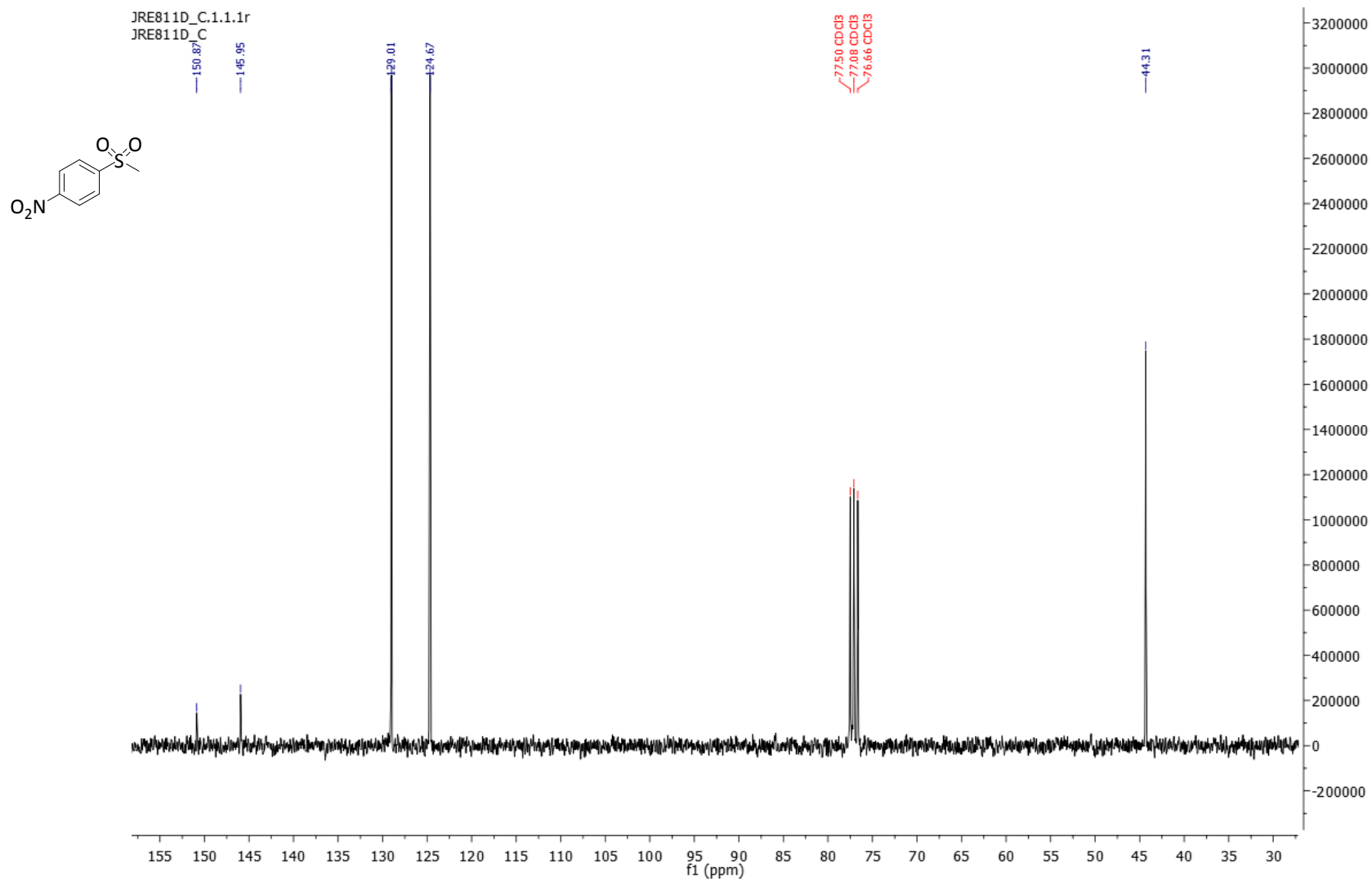


Figure S23 Mass spectra for methyl 4-nitrophenyl sulfoxide (left) and methyl 4-nitrophenyl sulfone (right)

Elemental Composition Report

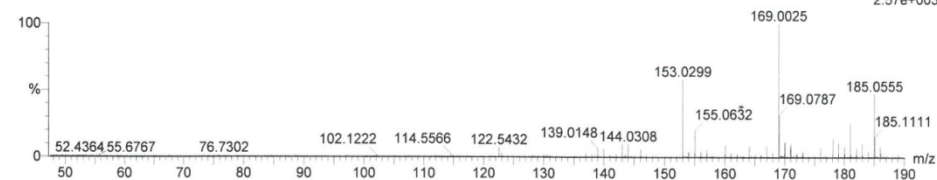
Single Mass Analysis

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)

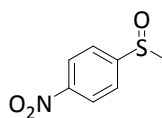
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direct
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 10:36:39
 JE812d 237 (1.558) Cm (235:243)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
185.0555	---						

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Elemental Composition Report

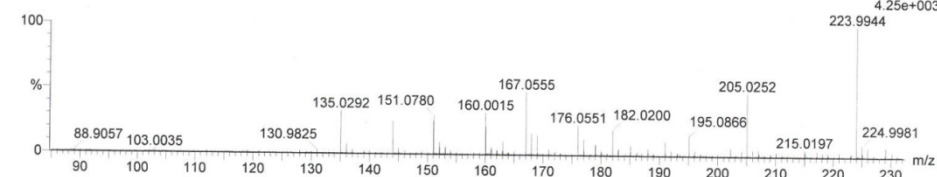
Single Mass Analysis

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
 12:14:23
 JE811d 62 (0.401) Cm (60:67)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
223.9944	---						

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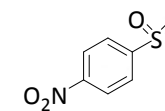


Figure S24 ^1H NMR spectrum of the reaction mixture for the selective oxidation of dibenzothiophene in methanol at RT for 15 min using 0.5 mol% **2**.

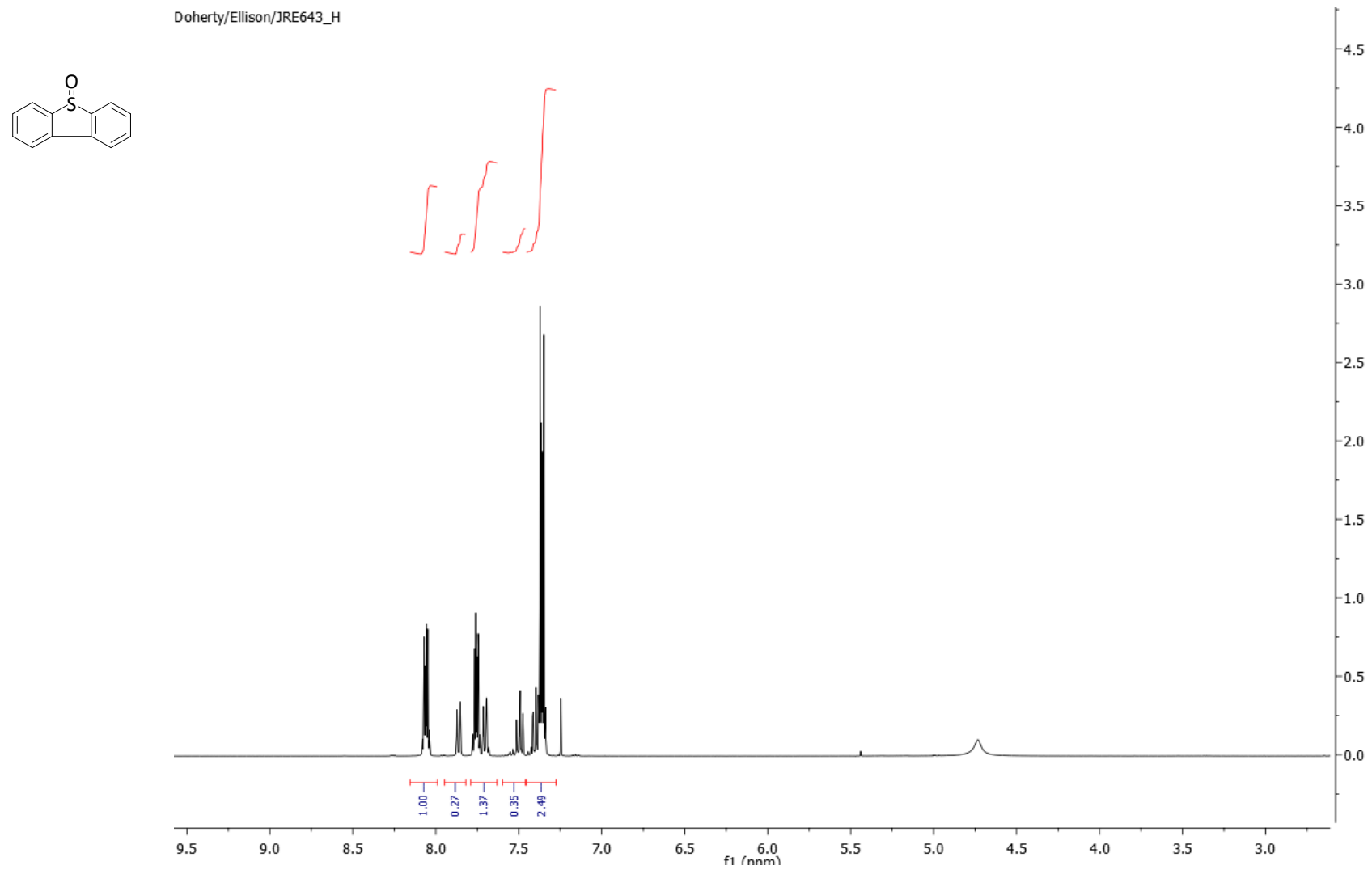


Figure S25 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of dibenzothiophene in methanol at RT for 15 min using 0.5 mol% **2**.

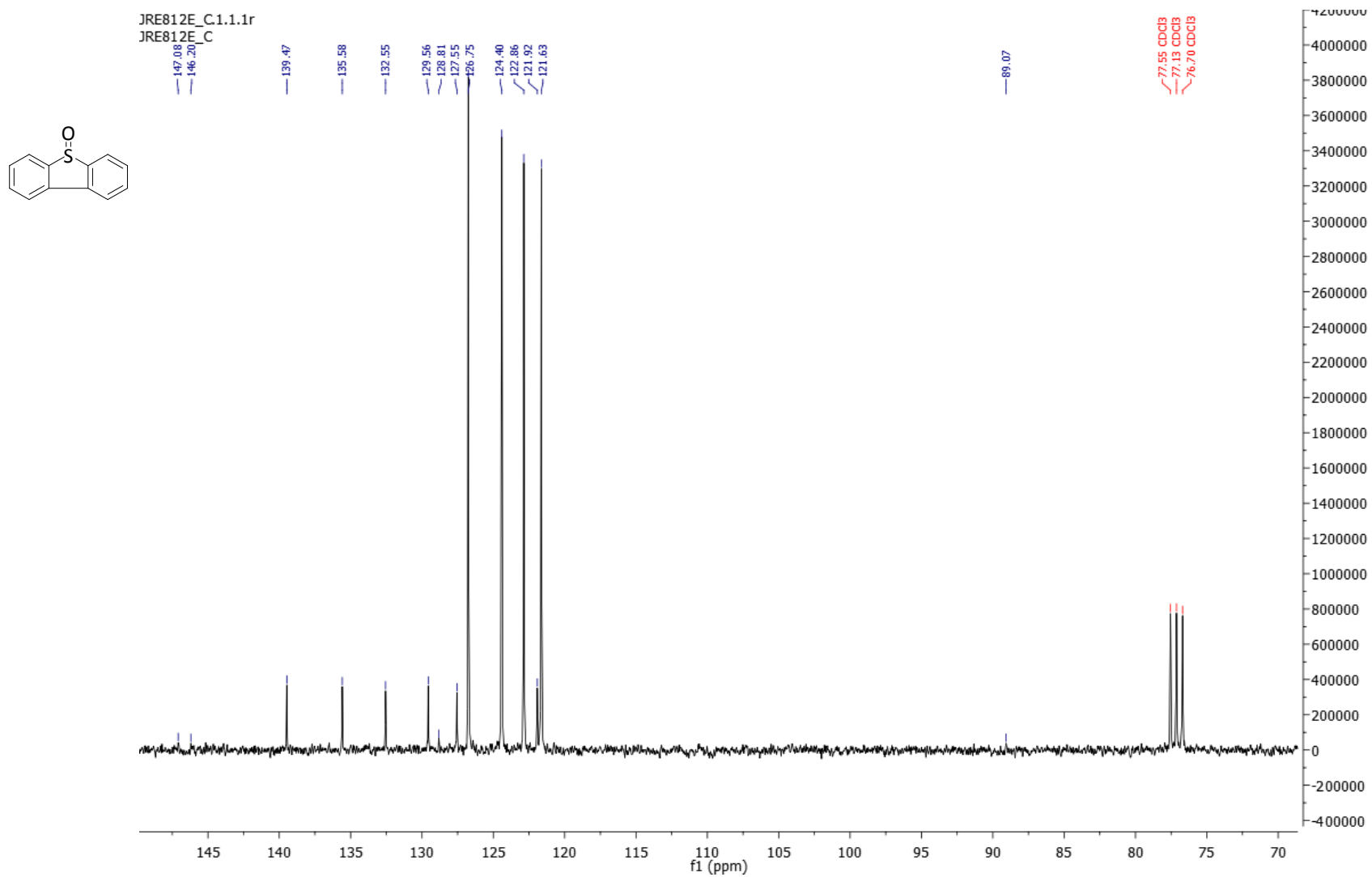


Figure S26 ^1H NMR spectrum of dibenzothiophene sulfone obtained from the oxidation of dibenzothiophene in MeCN using 0.5 mol% **2**.

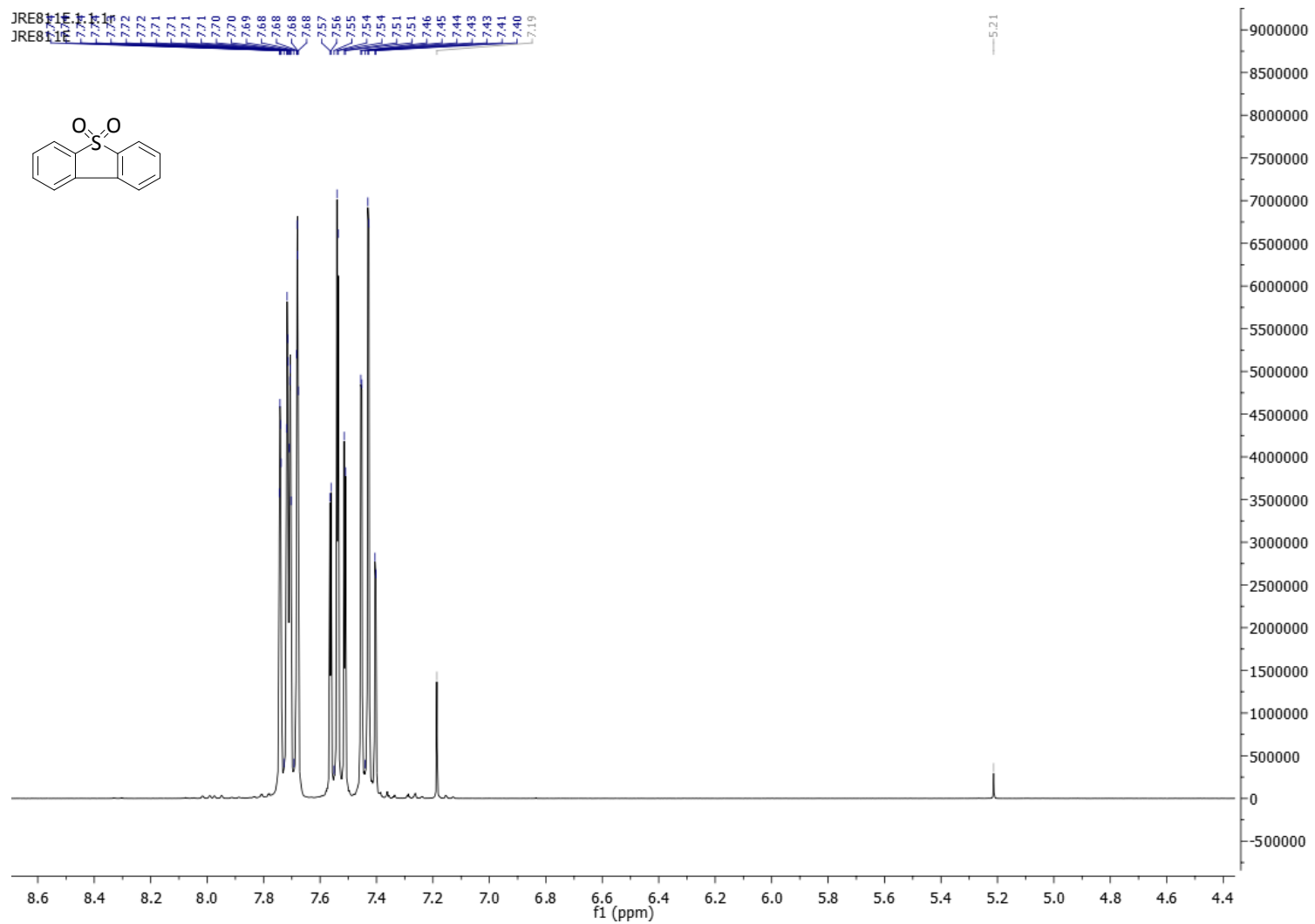


Figure S27 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of dibenzothiophene sulfone obtained from the oxidation of dibenzothiophene in MeCN using 0.5 mol% **2**.

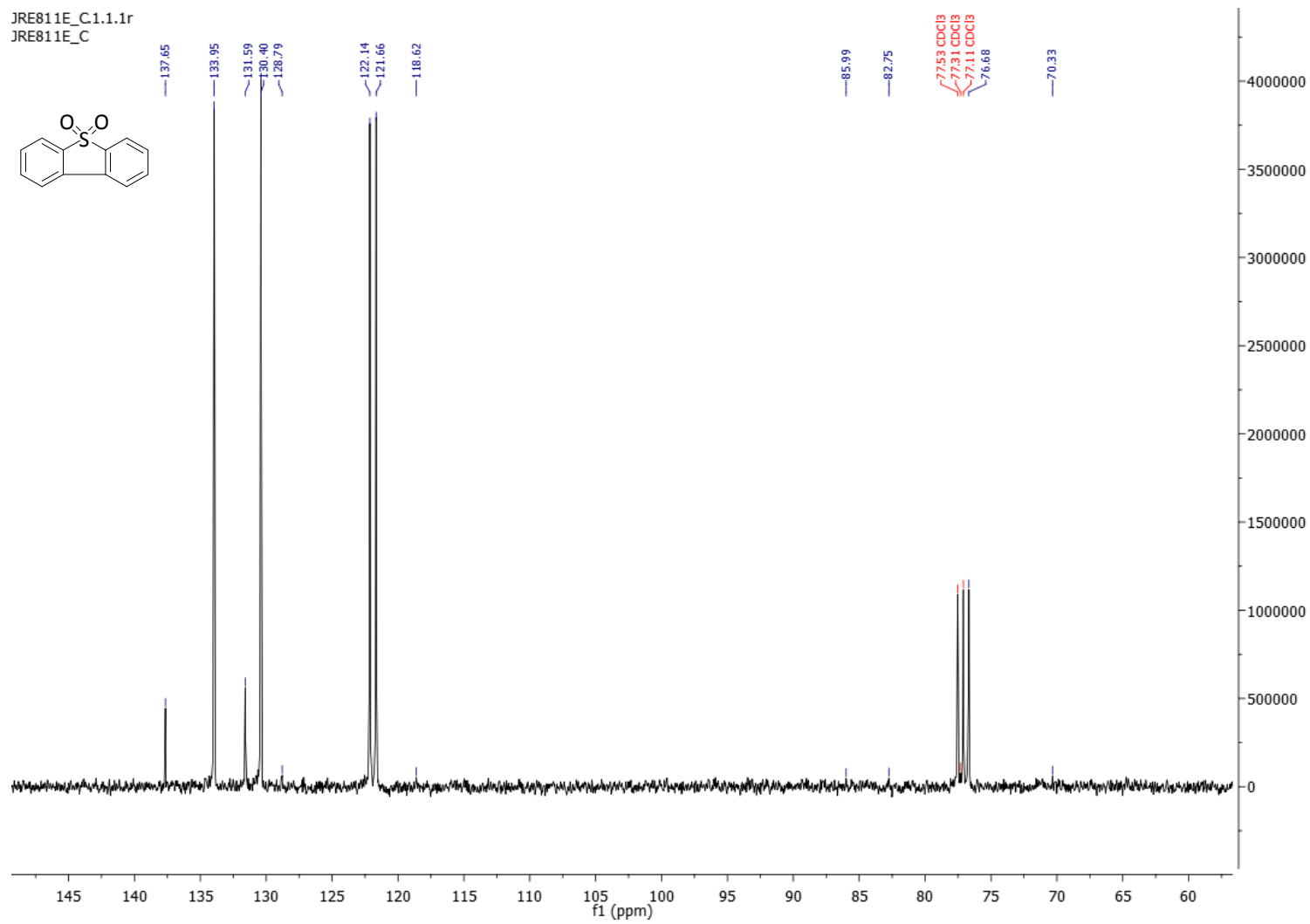


Figure S28 Mass spectra for dibenzothiophene sulfoxide (left) and dibenzothiophene sulfone (right)

Elemental Composition Report

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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:

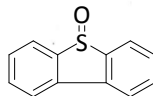
C: 8-8 H: 10-10 O: 2-2 ²³Na: 0-1 S: 1-1

direct

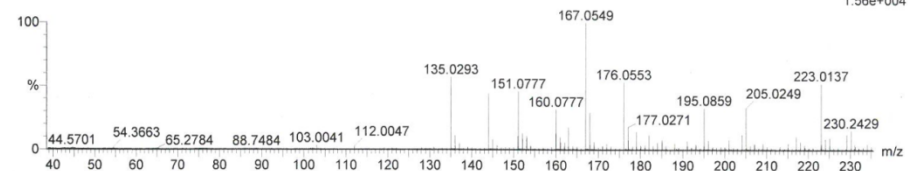
22-Oct-2014

12:22:07

JE812e 205 (1.338) Cm (181:230)



1: TOF MS ES+
1.56e+004



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
------	------------	-----	-----	-----	-------	--------------	---------

223.0137	---						
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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:

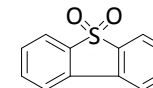
C: 8-8 H: 10-10 O: 2-2 ²³Na: 0-1 S: 1-1

direct

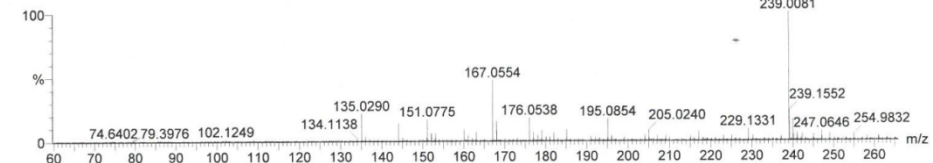
22-Oct-2014

12:30:12

JE811e 303 (1.980)



1: TOF MS ES+
5.32e+002



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
------	------------	-----	-----	-----	-------	--------------	---------

239.0081	---						
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Figure S29 ^1H NMR spectrum of the reaction mixture for the selective oxidation of homoallyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

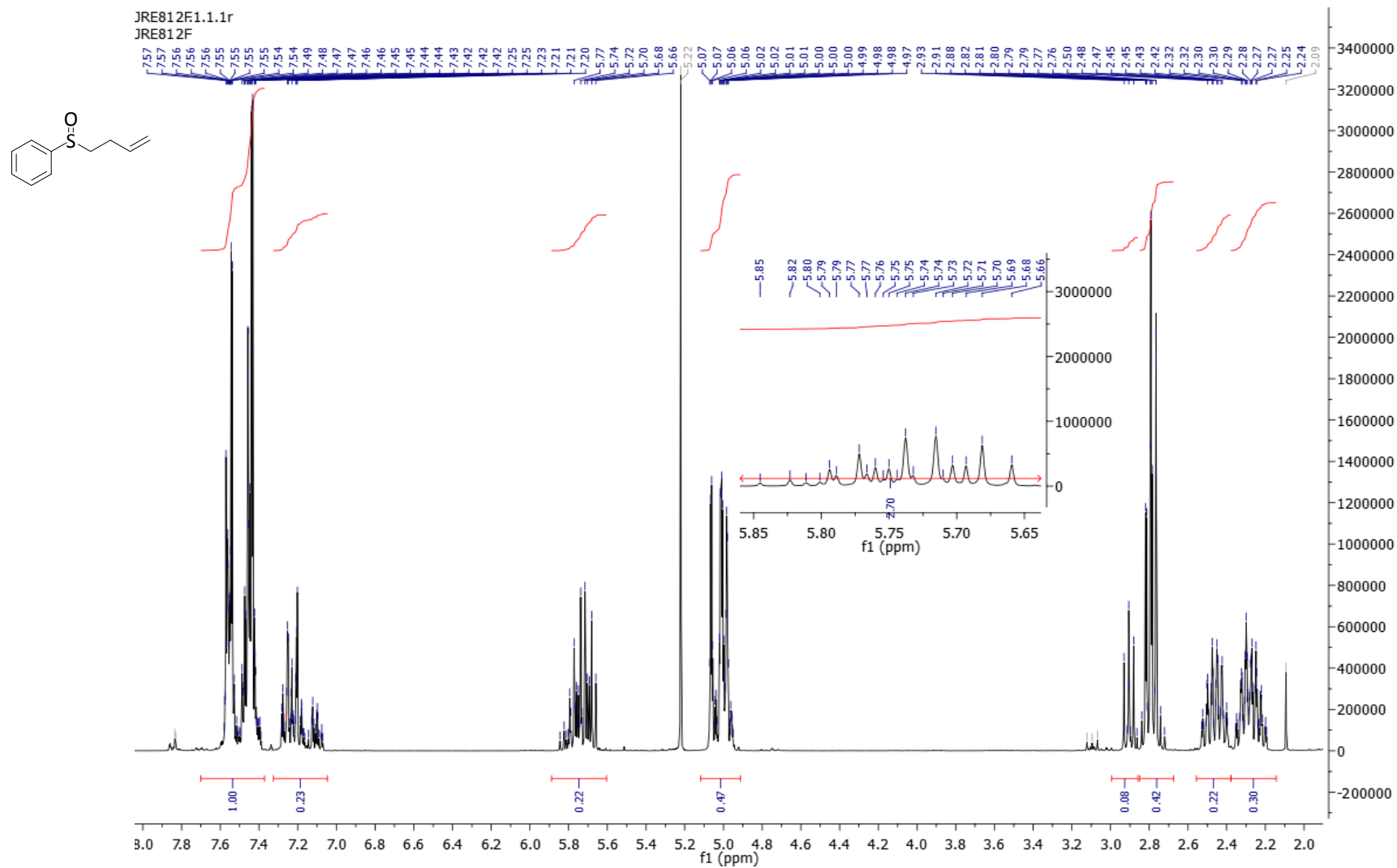


Figure S30 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of homoallyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

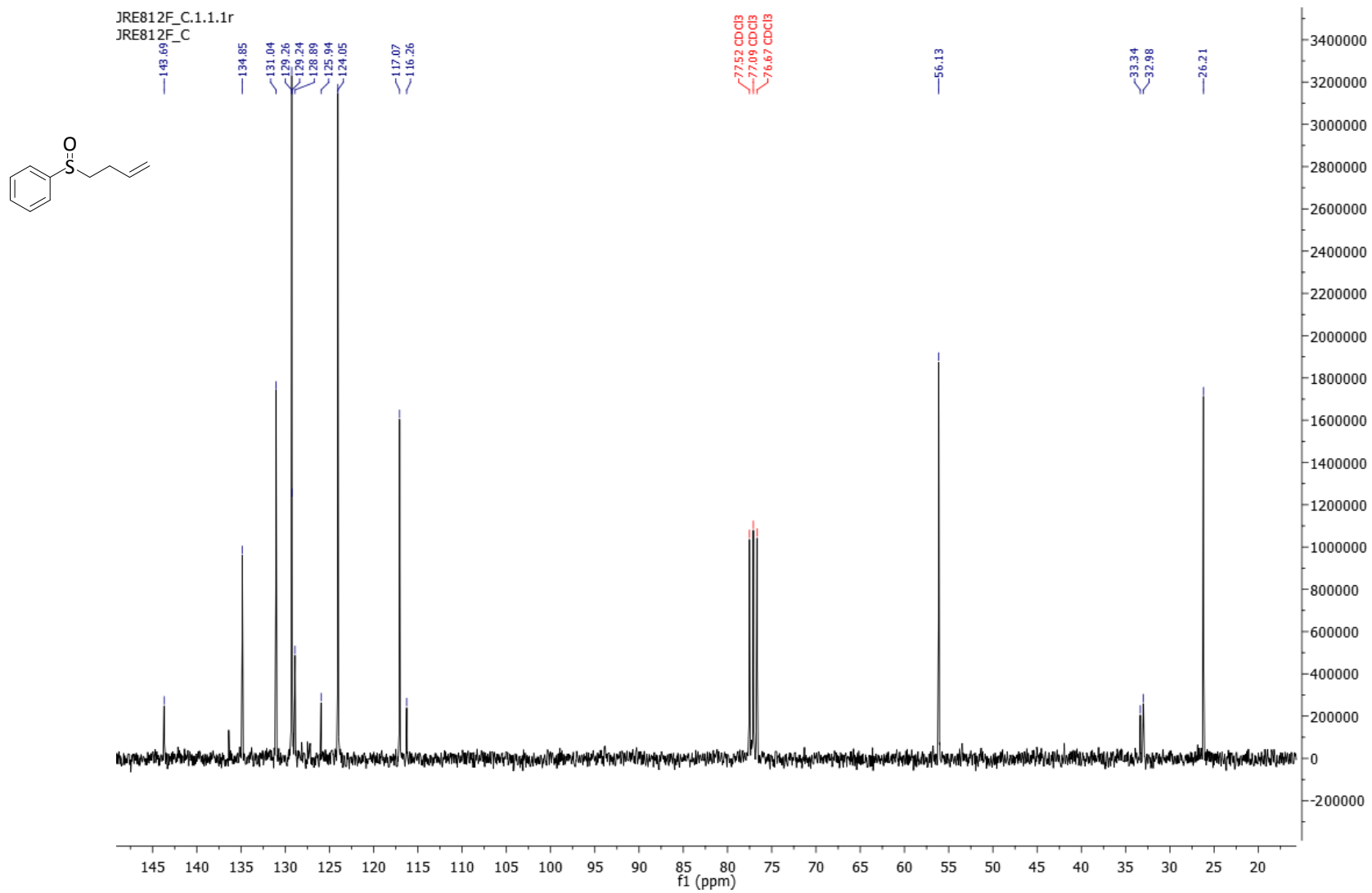


Figure S31 ^1H NMR spectrum of homoallyl phenyl sulfone obtained from the oxidation of dibenzothiophene in MeCN using 0.5 mol% **2**.

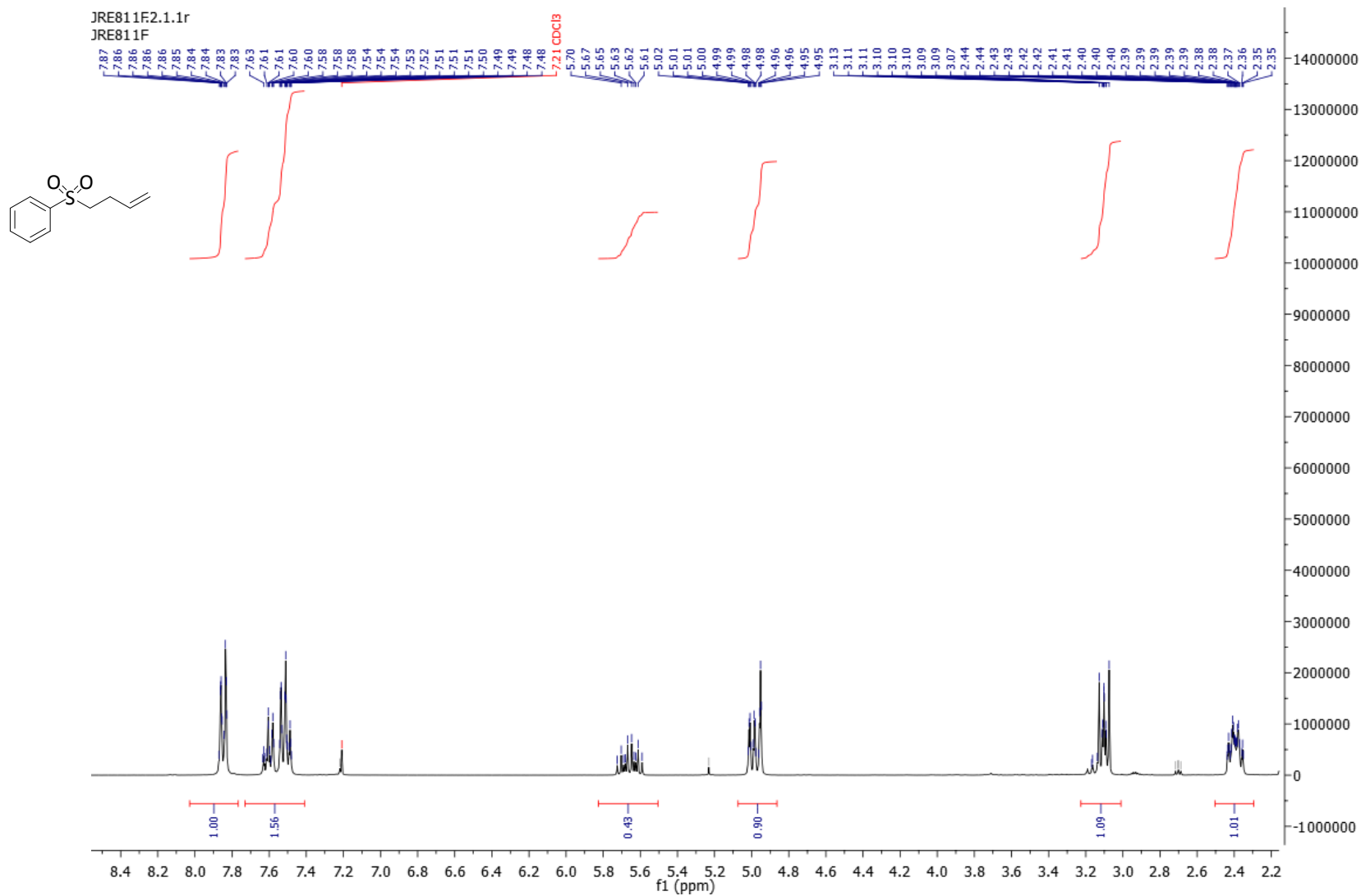


Figure S32 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of homoallyl phenyl sulfone obtained from the oxidation of dibenzothiophene in MeCN using 0.5 mol% **2**.

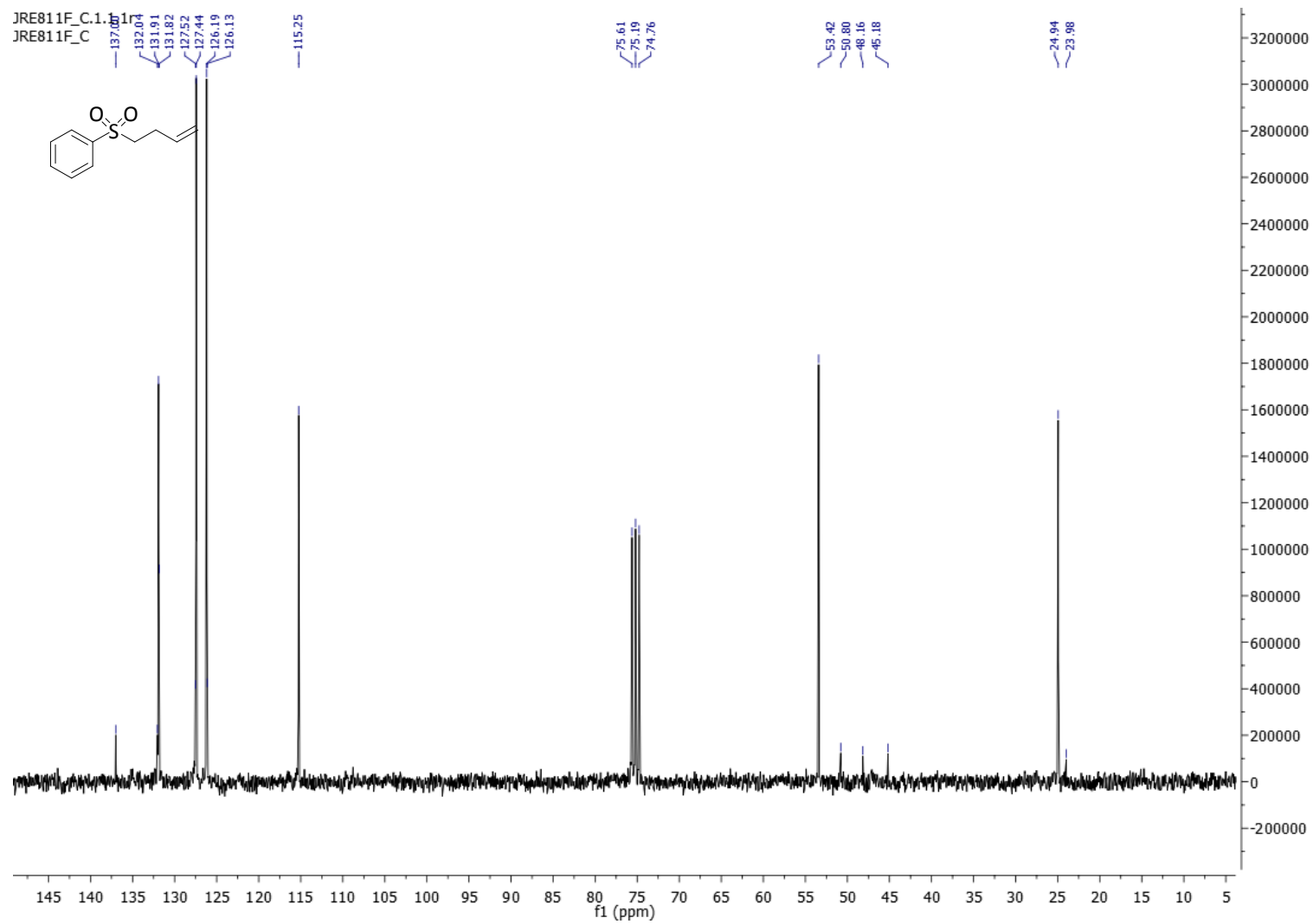


Figure S33 Mass spectra for homoallyl phenyl sulfoxide (left) and homoallyl phenyl sulfone (right)

Elemental Composition Report

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

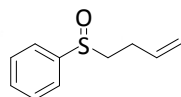
Monoisotopic Mass, Even Electron Ions

1 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)

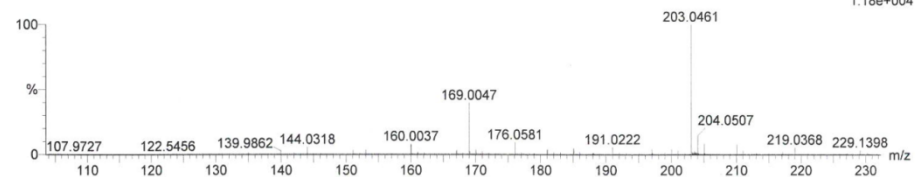
Elements Used:

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



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
203.0461	---						

Elemental Composition Report

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

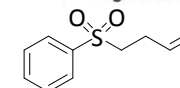
Monoisotopic Mass, Even Electron Ions

2 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)

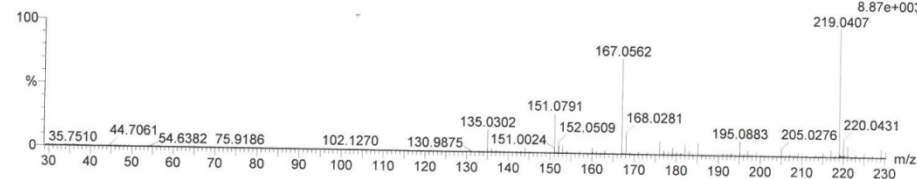
Elements Used:

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 S34 ^1H NMR spectrum of the reaction mixture for the selective oxidation of benzyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

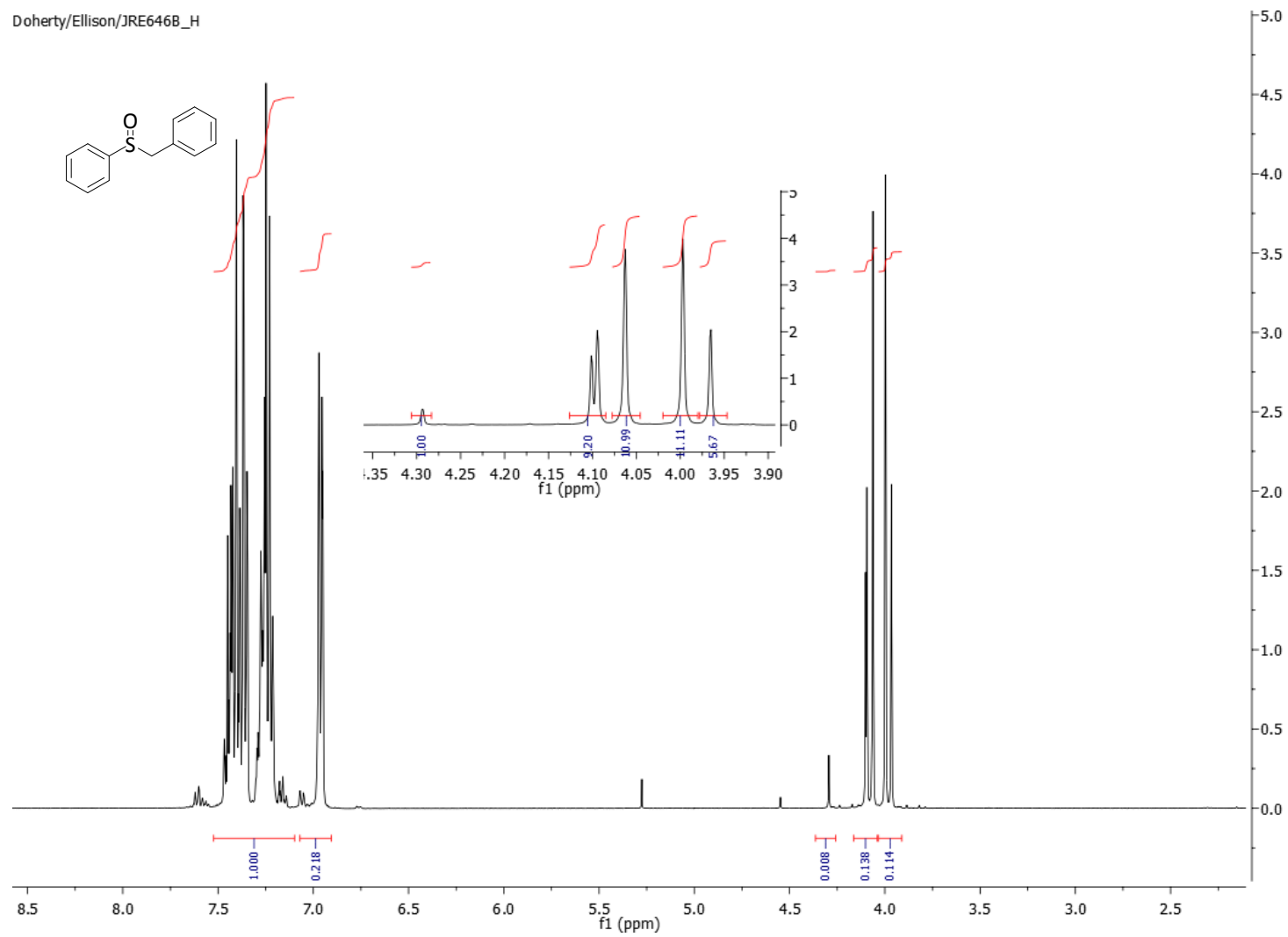


Figure S35 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of benzyl phenyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

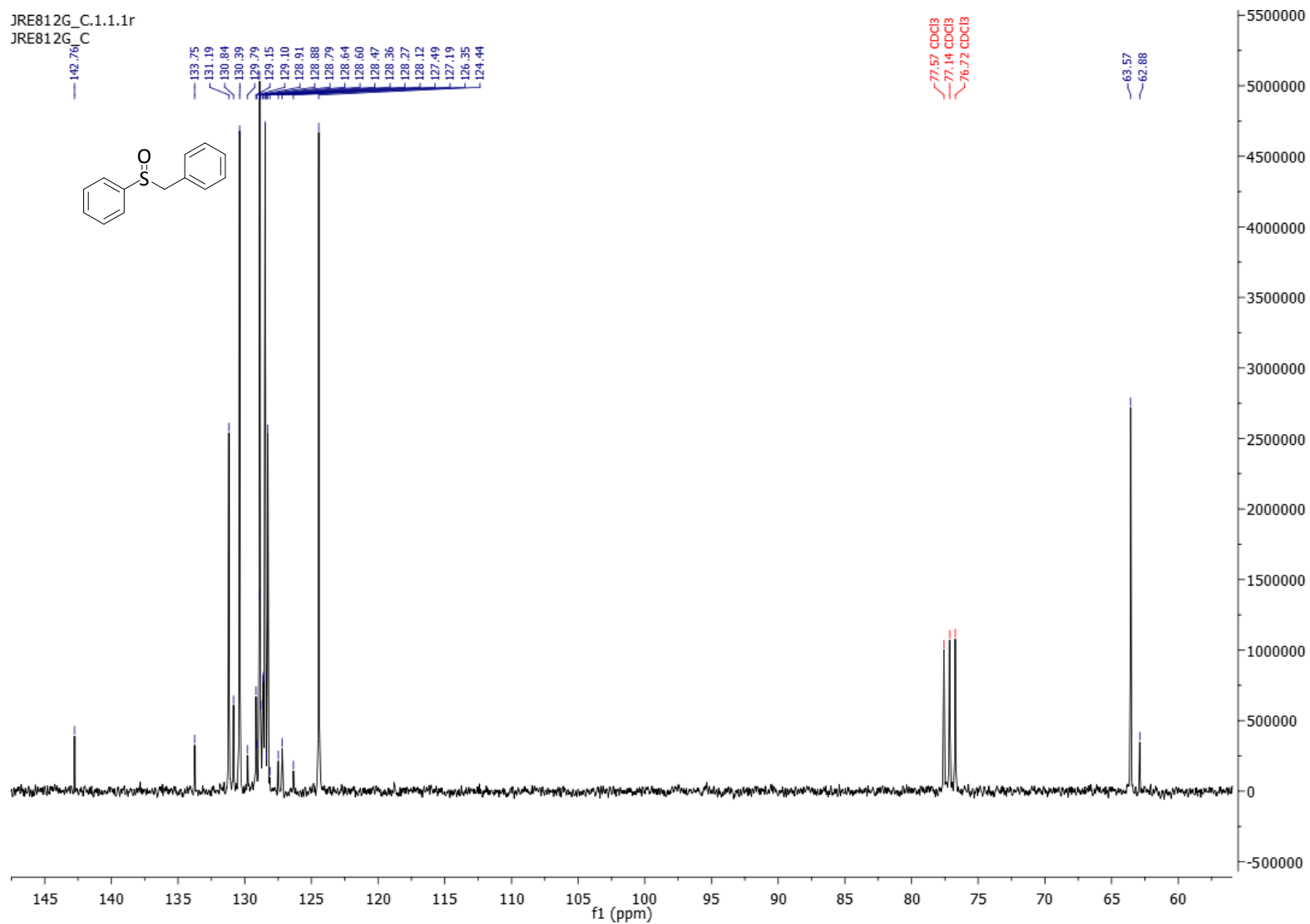


Figure S36 ^1H NMR spectrum of benzyl phenyl sulfone obtained from the oxidation of benzyl phenyl sulfide in MeCN using 0.5 mol% **2**.

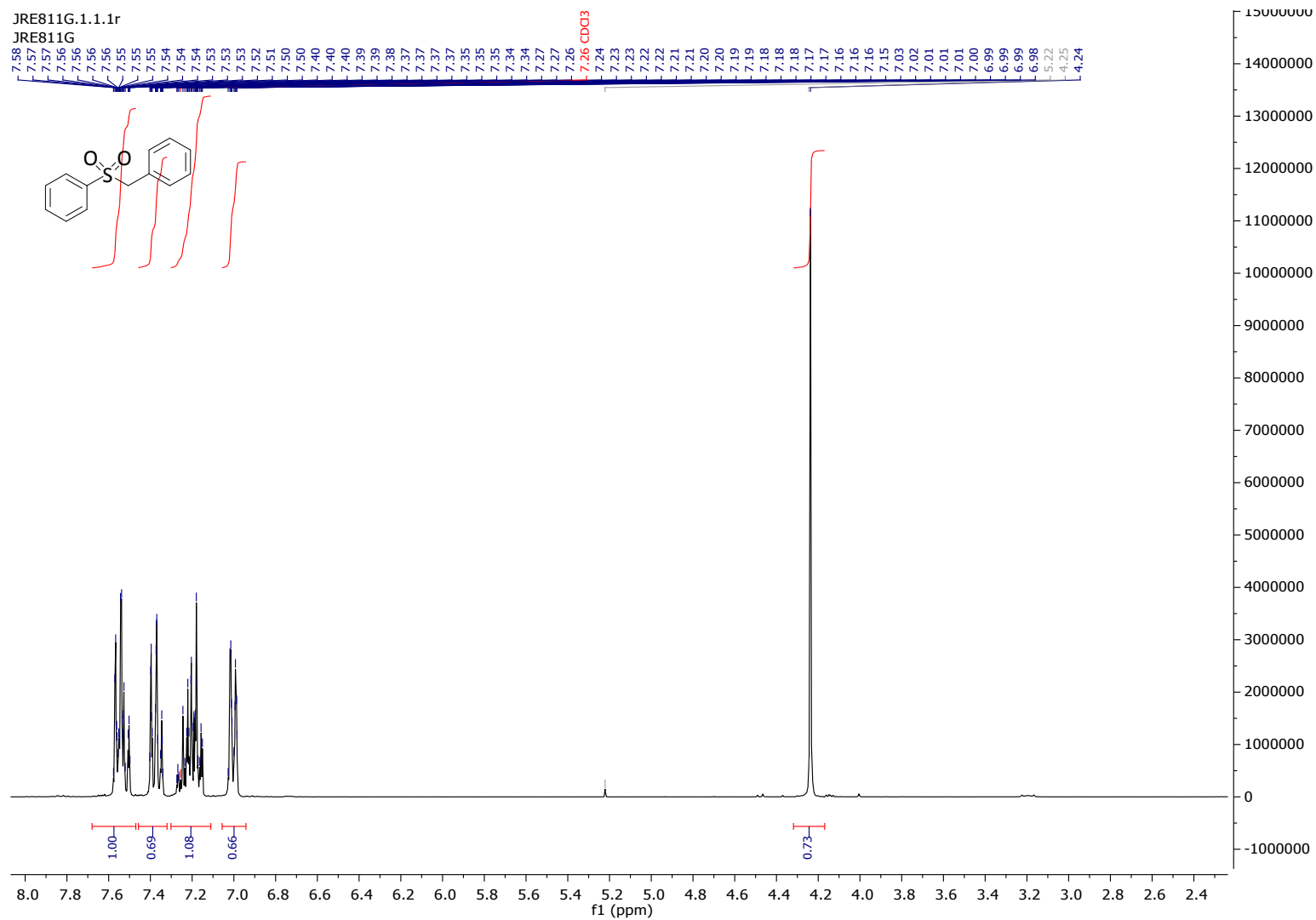


Figure S37 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of benzyl phenyl sulfone obtained from the oxidation of benzyl phenyl sulfide in MeCN using 0.5 mol% **2**.

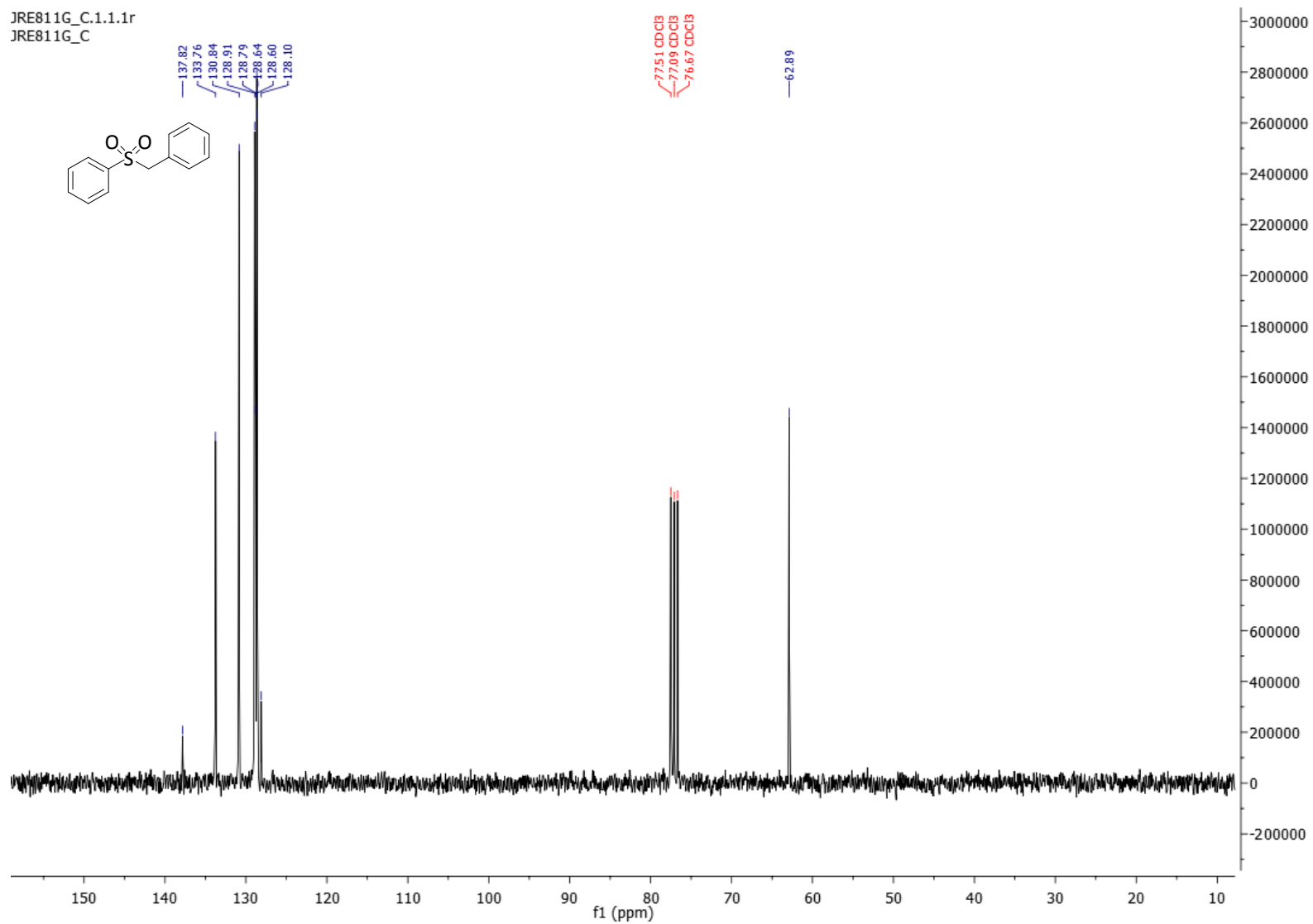


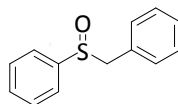
Figure S38 Mass spectra for benzyl phenyl sulfoxide (left) and benzyl phenyl sulfone (right)

Elemental Composition Report

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Single Mass Analysis

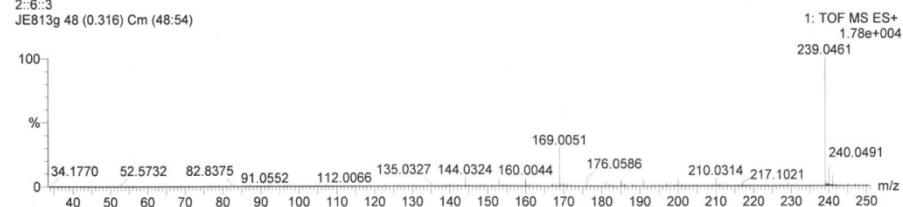
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3



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: 50.0

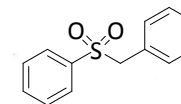
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
239.0461	---						

Elemental Composition Report

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Single Mass Analysis

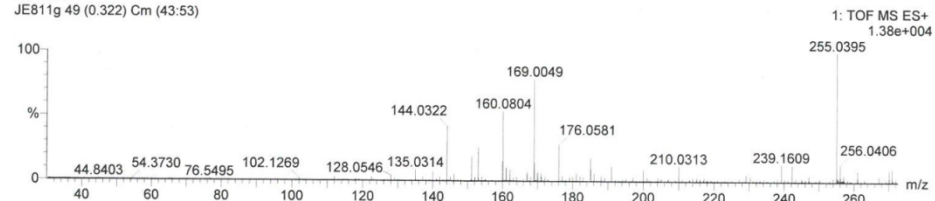
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3



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: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
255.0395	---						

Figure S39 ^1H NMR spectrum of the reaction mixture for the selective oxidation of *tert*-butyl methyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

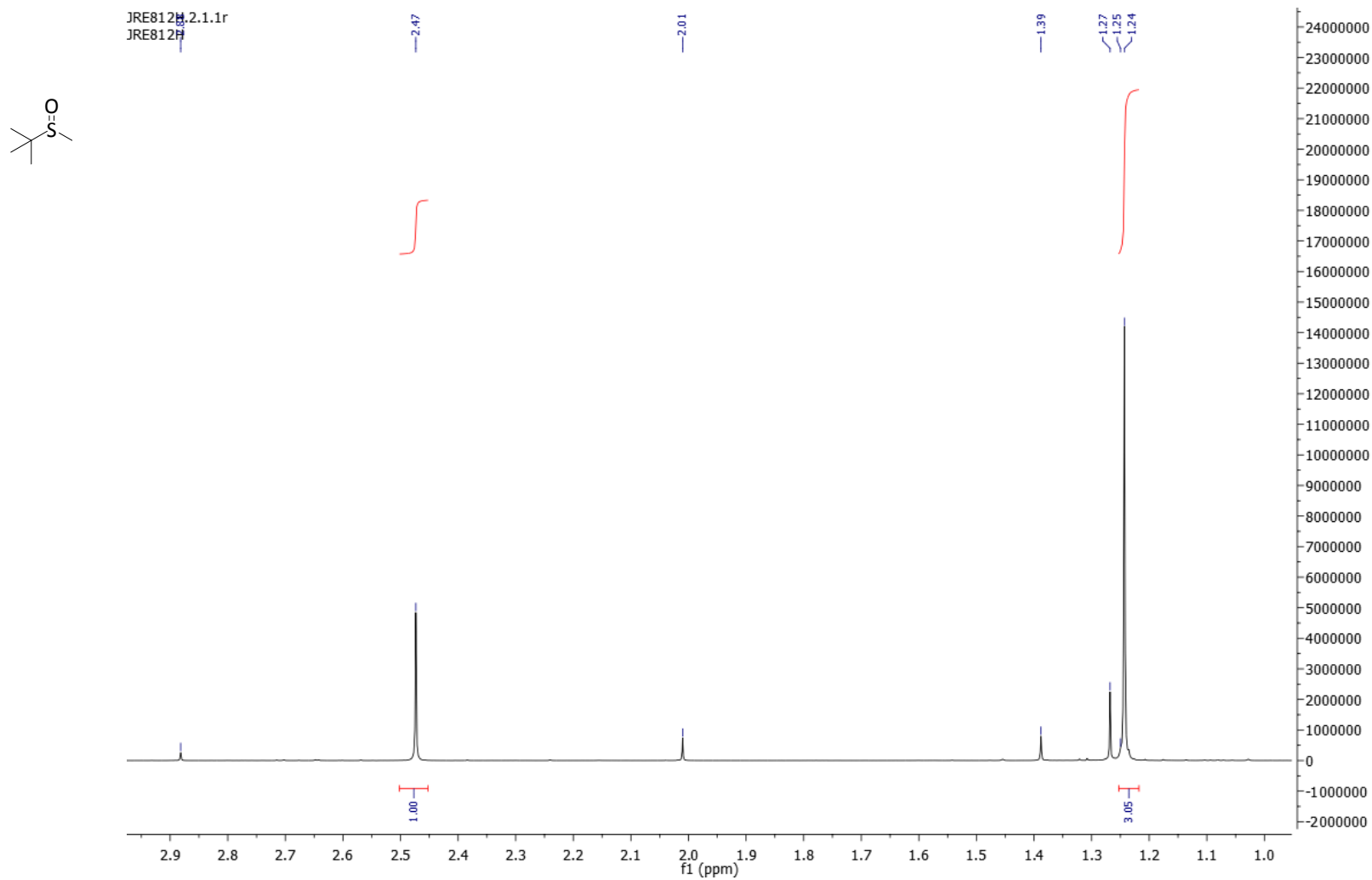


Figure S40 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture for the selective oxidation of *tert*-butyl methyl sulfide in methanol at RT for 15 min using 0.5 mol% **2**.

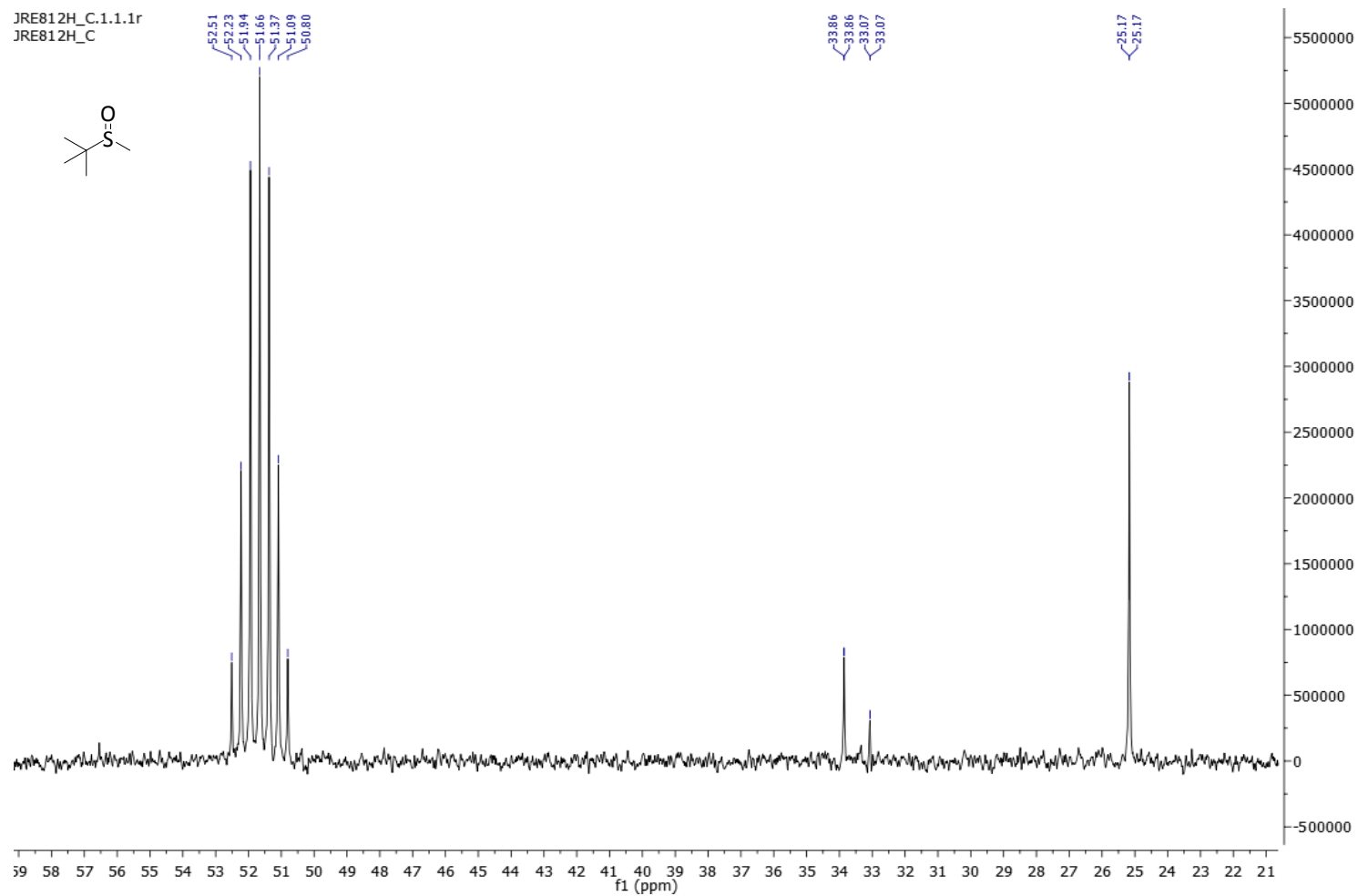


Figure S41 ^1H NMR spectrum of *tert*-butyl methyl sulfone obtained from the oxidation of *tert*-butyl methyl sulfide in MeCN using 0.5 mol% **2**.

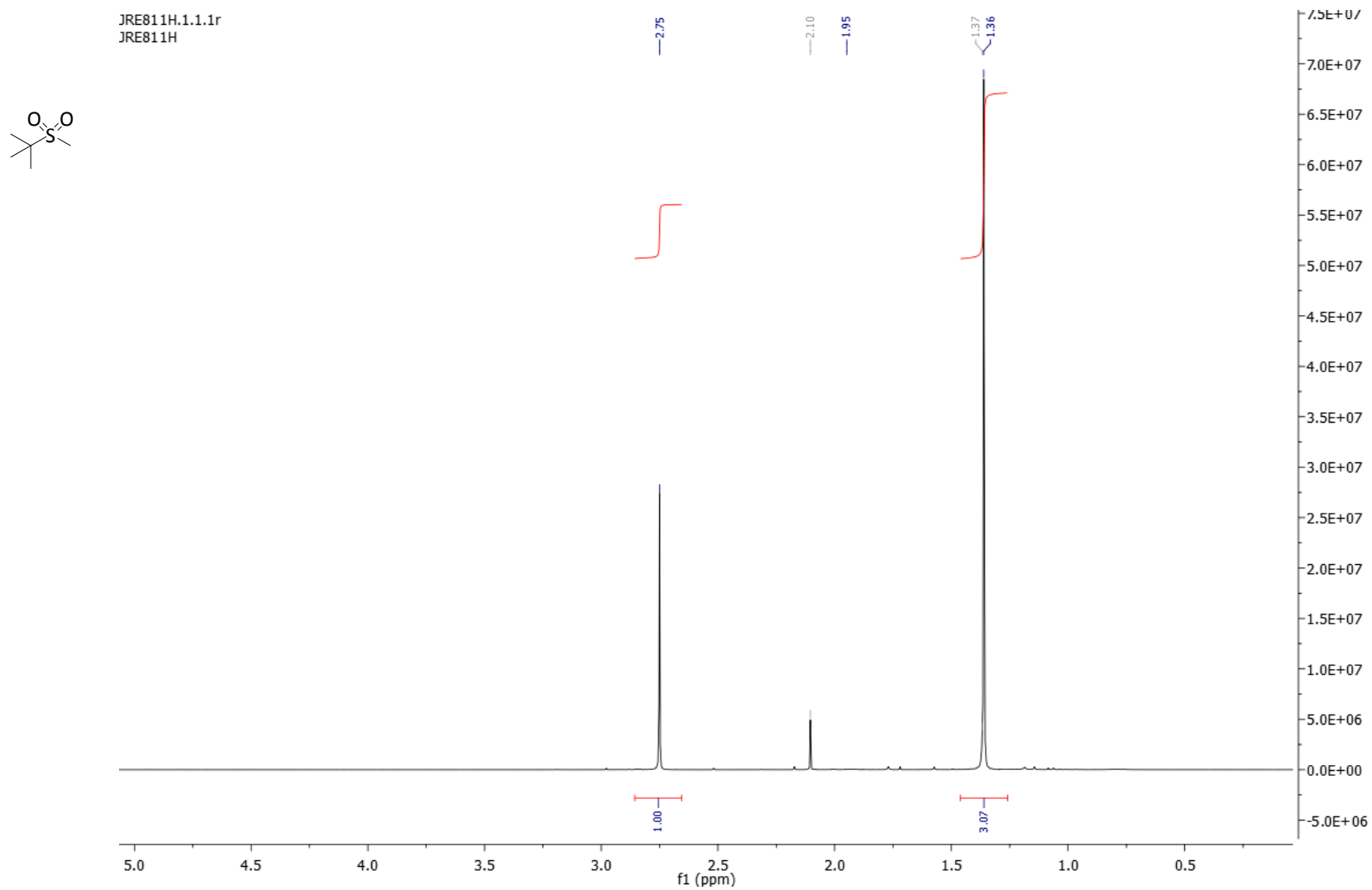


Figure S42 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *tert*-butyl methyl sulfone obtained from the oxidation of *tert*-butyl methyl sulfide in MeCN using 0.5 mol% 2.

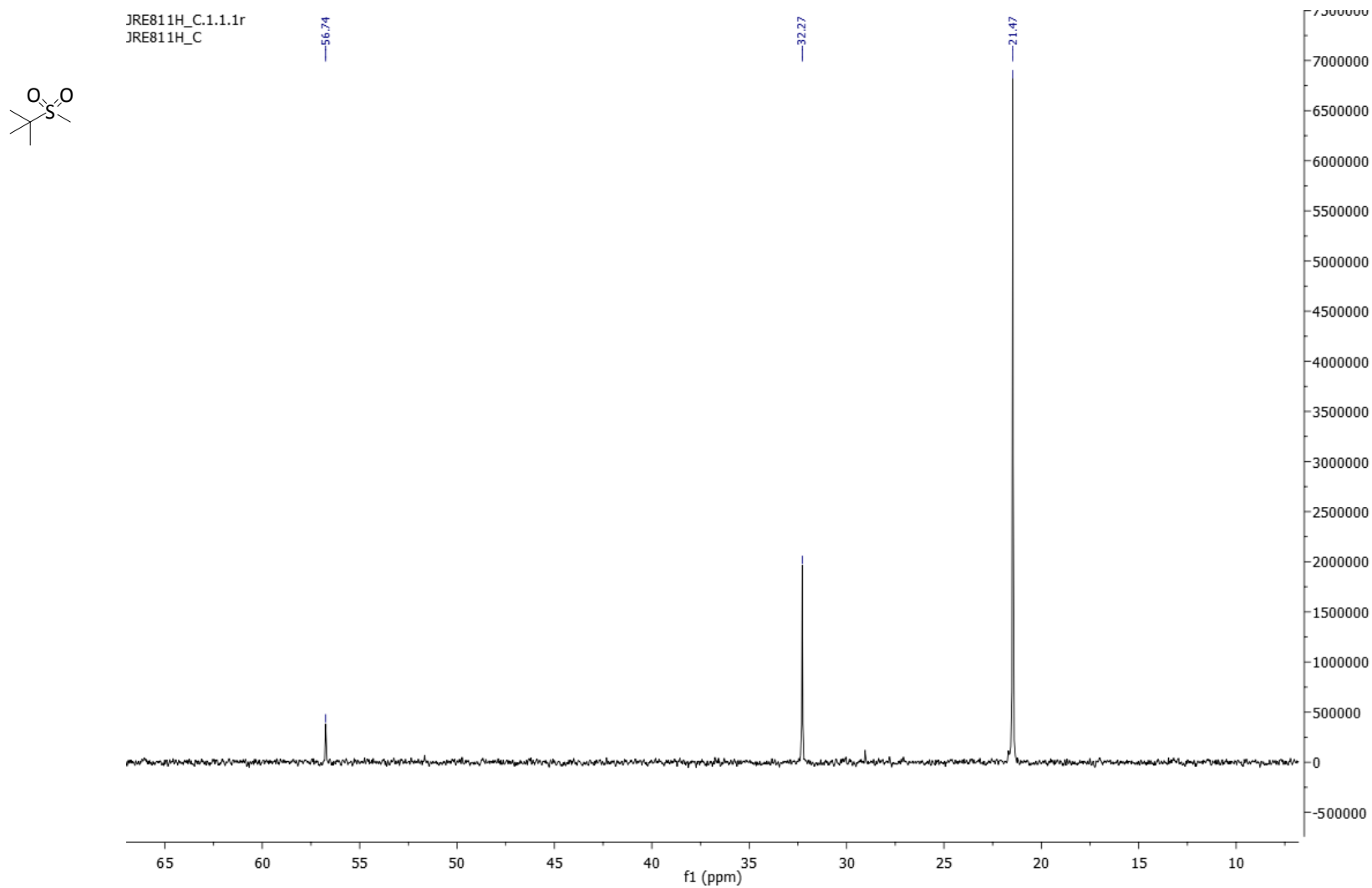


Figure S43 Mass spectra for *tert*-butyl methyl sulfoxide (left) and *tert*-butyl methyl sulfone (right)

Elemental Composition Report

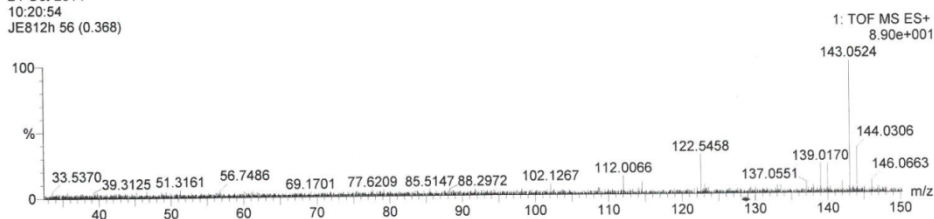
Single Mass Analysis

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
 24-Oct-2014
 10:20:54
 JE812h 56 (0.368)



Minimum:	Maximum:	Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
		143.0524	---						

Elemental Composition Report

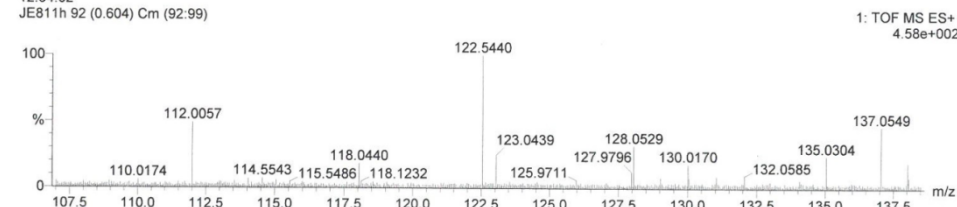
Single Mass Analysis

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
 12:54:02
 JE811h 92 (0.604) Cm (92.99)



Minimum:	Maximum:	Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
		139.9849	---						

Figure S44 FT-IR Spectra of (a) fresh $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ (**2**) and (b) catalyst isolated after the 6th run of a methanol recycle experiment.

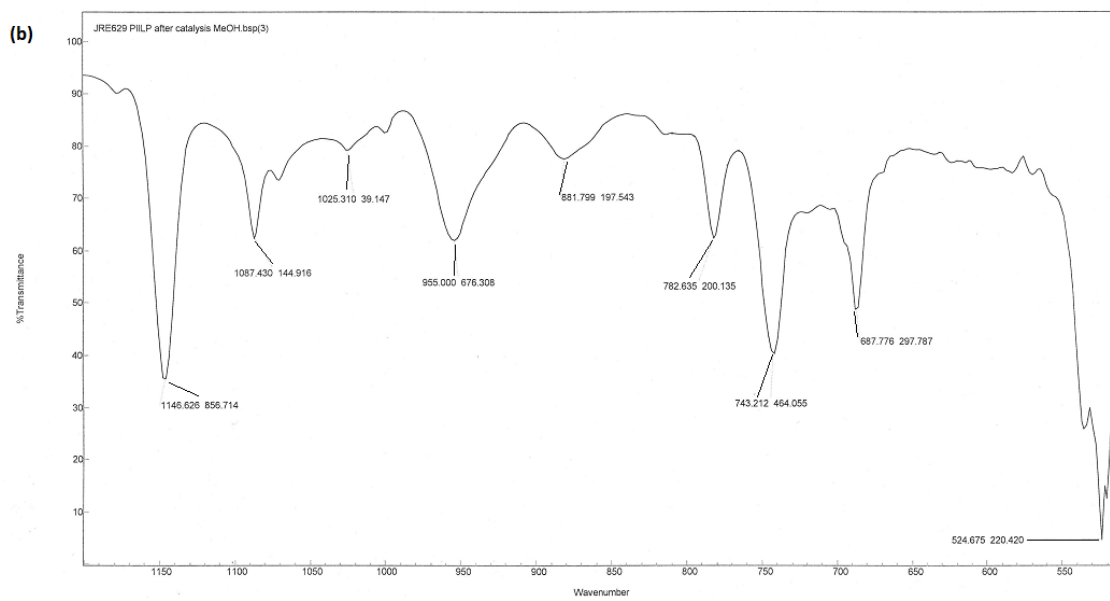
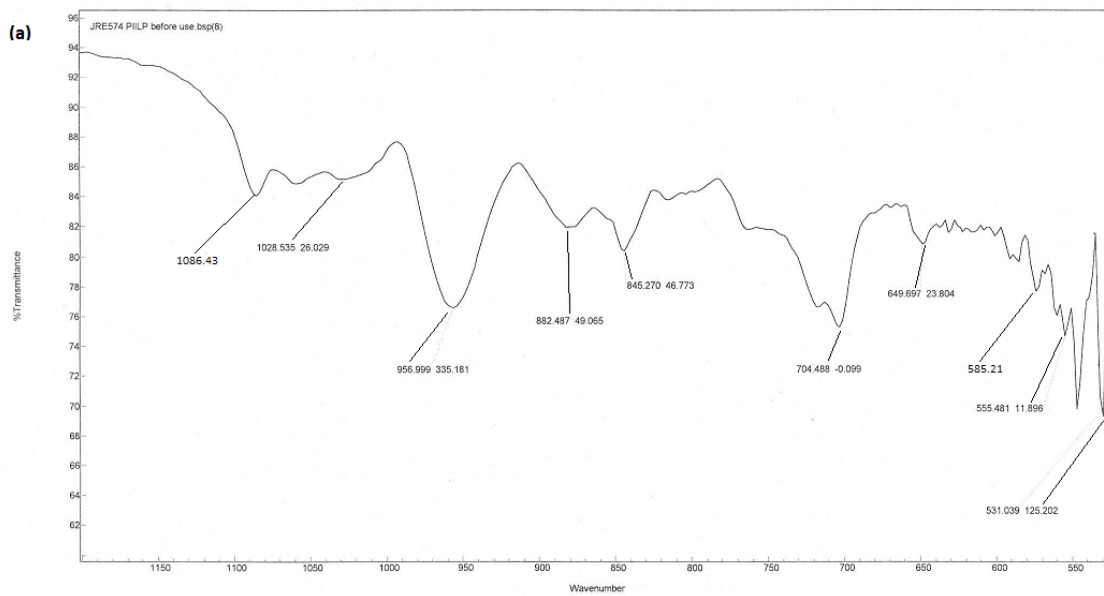


Figure S45 Conversion-selectivity profile as a function of temperature for the continuous flow $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalysed sulfoxidation of thioanisole in acetonitrile with a residence time of 4 min

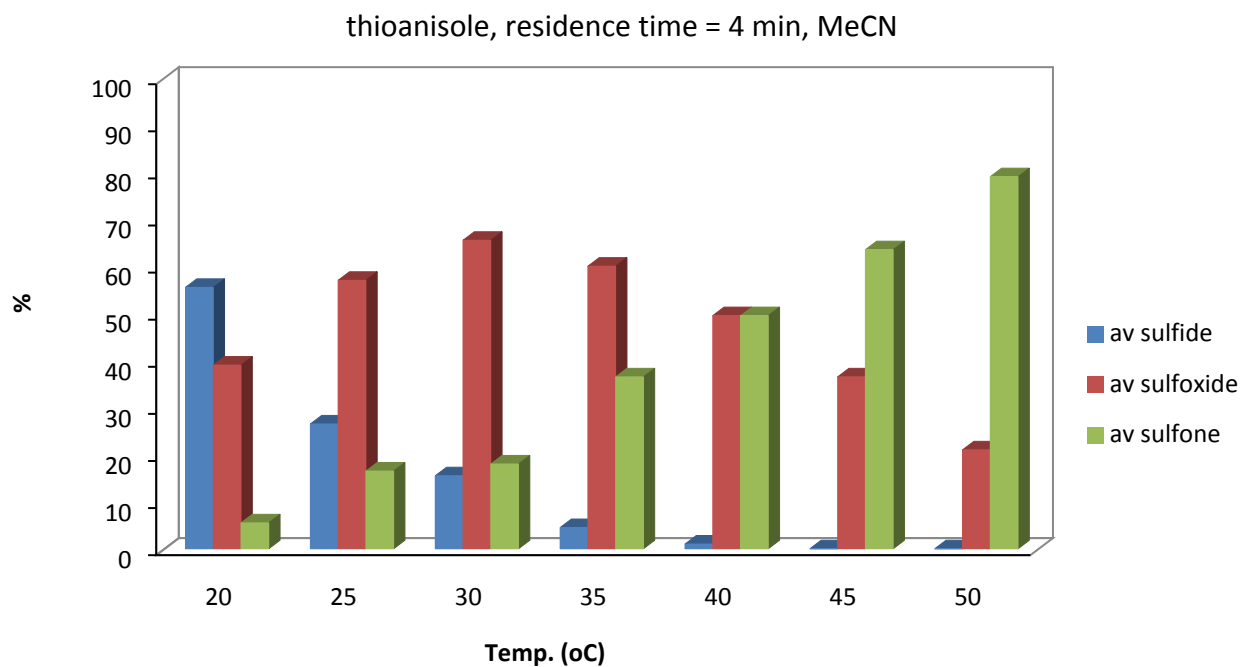


Figure S46 Conversion-selectivity profile as a function of temperature for the continuous flow $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalysed sulfoxidation of thioanisole in methanol with a residence time of 4 min

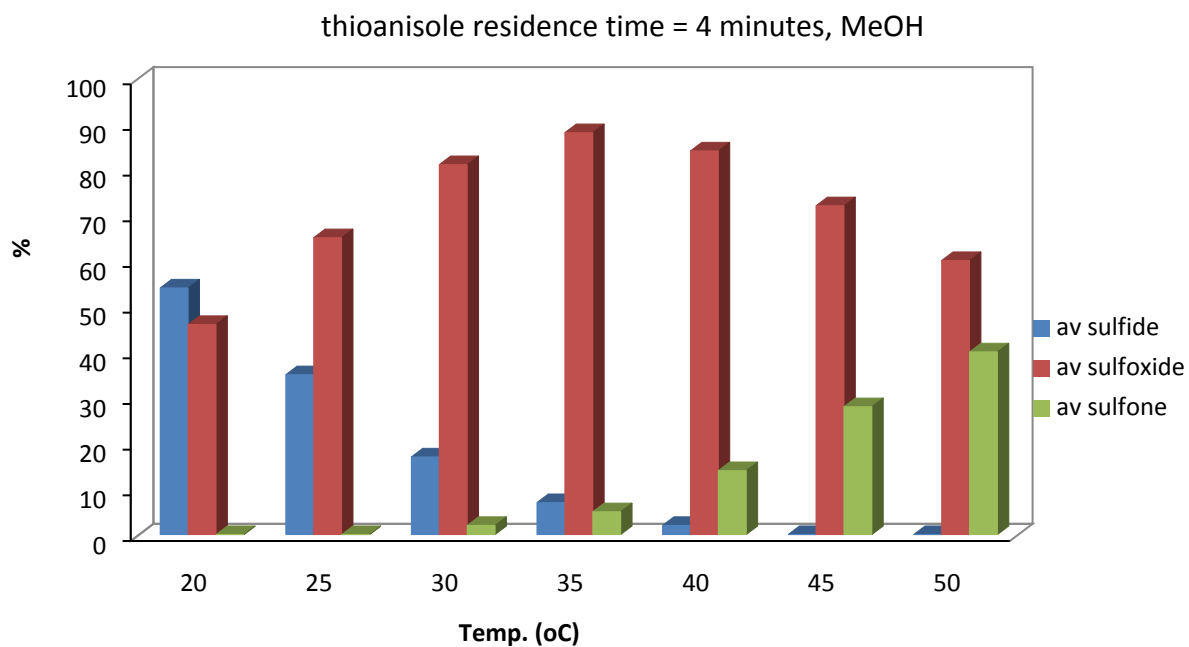


Figure S47 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in acetonitrile at 30 °C.

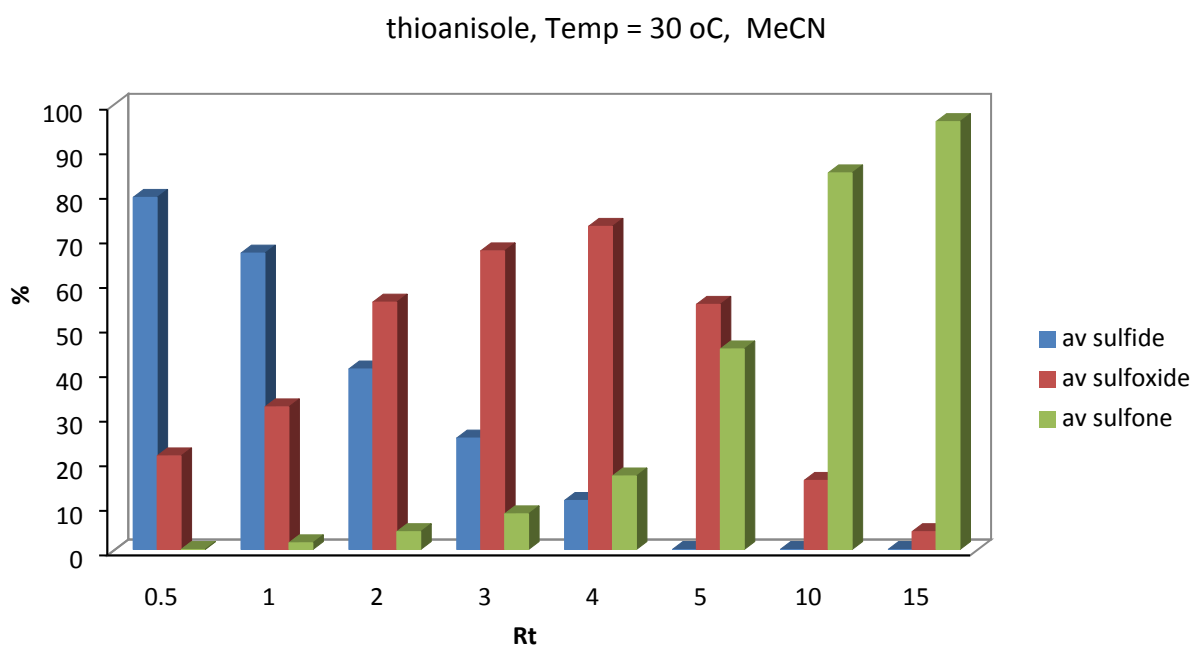


Figure S48 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol at 30 °C.

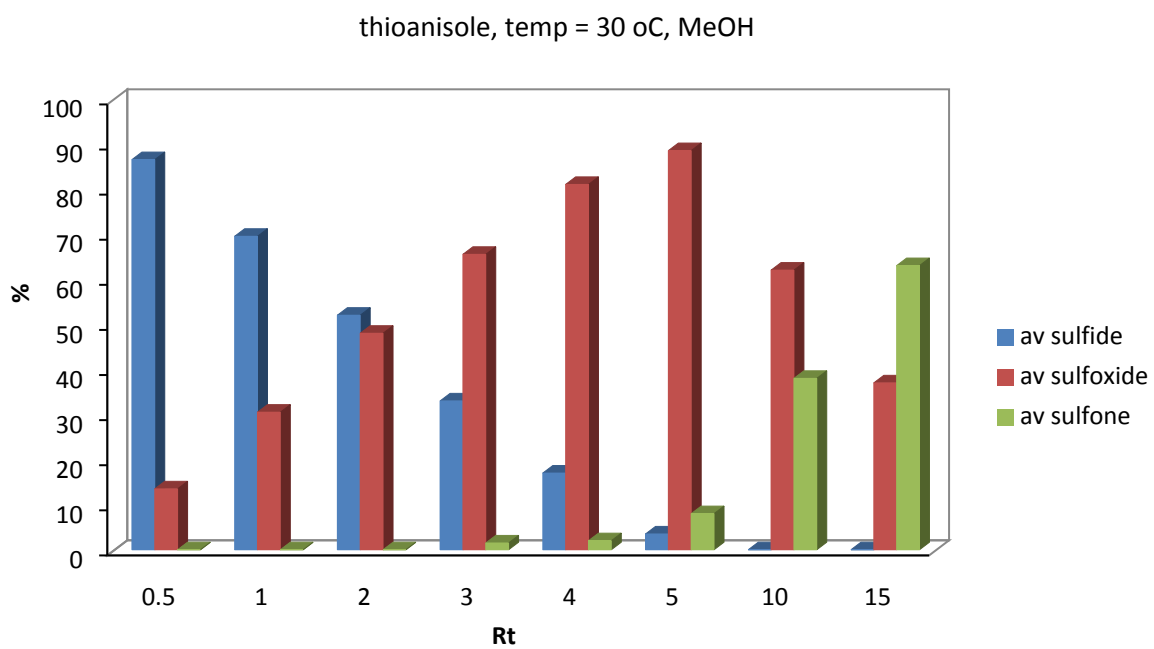


Figure S49 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in acetonitrile at 30 °C with 2 equivalents of H_2O_2

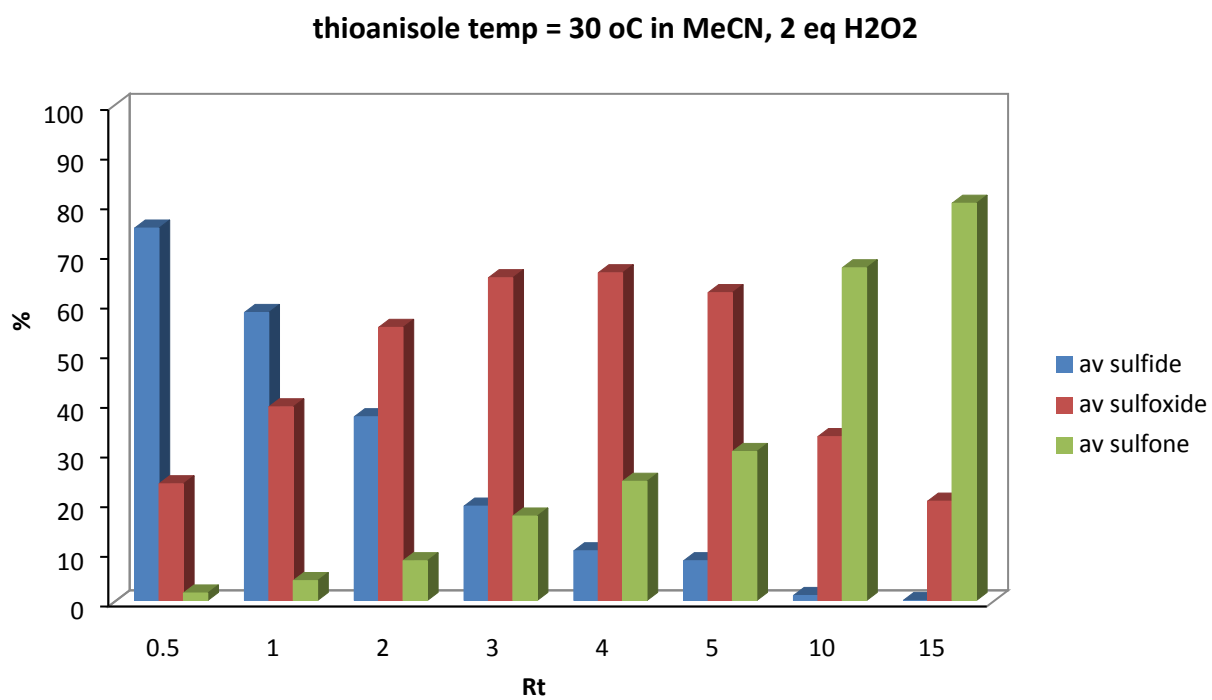


Figure S50 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in acetonitrile at 30 °C with 3 equivalents of H_2O_2

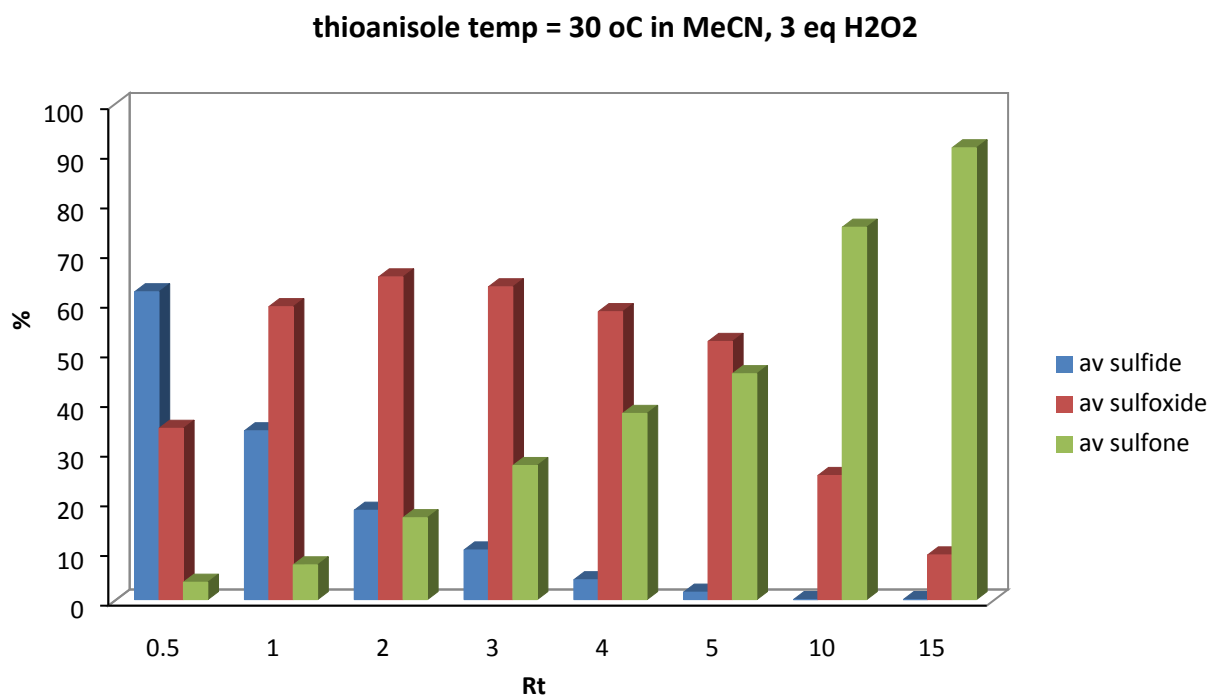


Figure S51 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in acetonitrile at 30 °C with 6 equivalents of H_2O_2

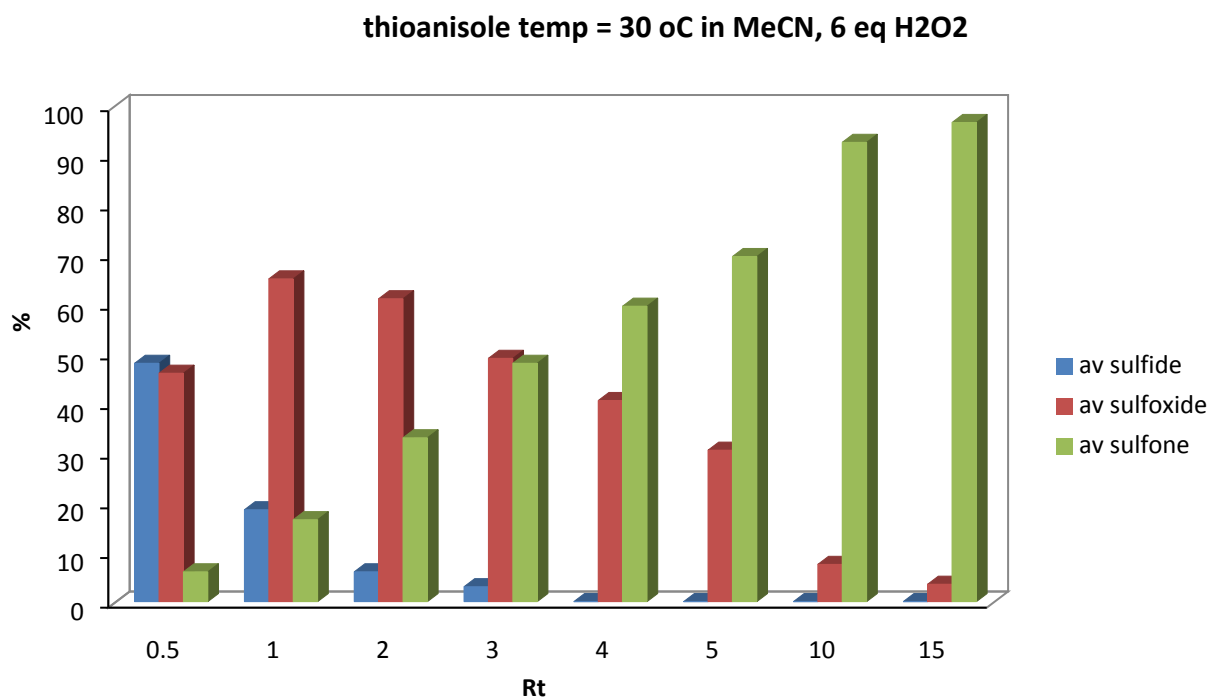


Figure S52 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in acetonitrile at 30 °C with 12 equivalents of H_2O_2

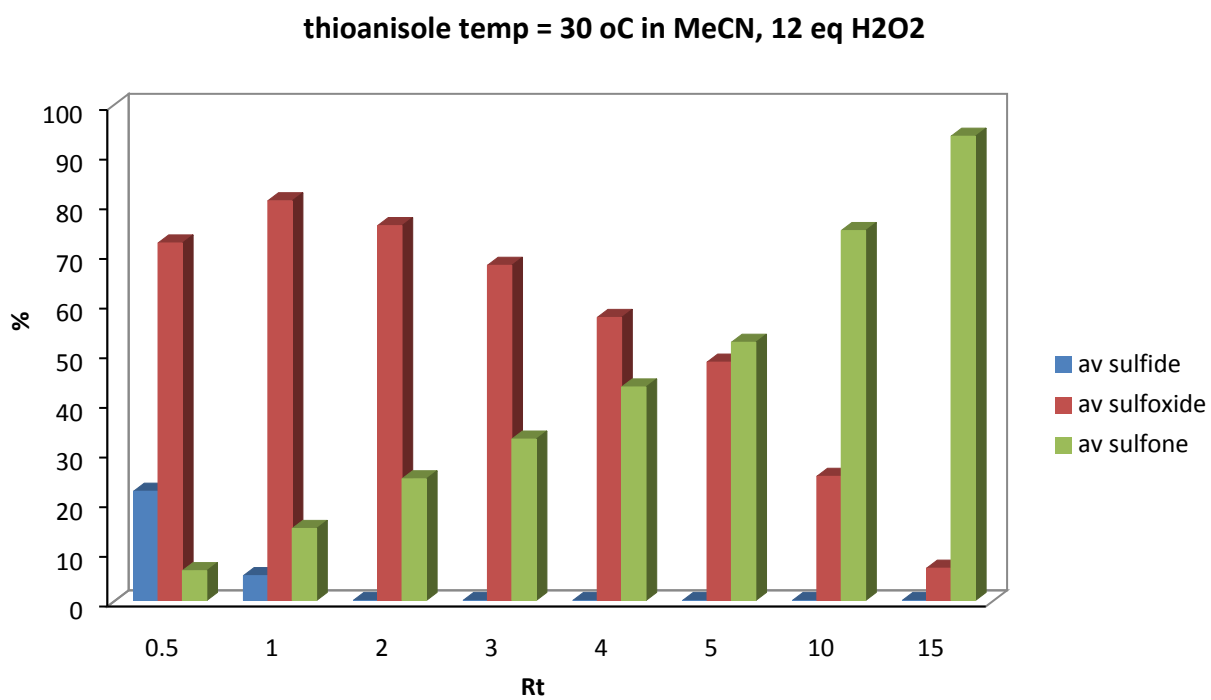
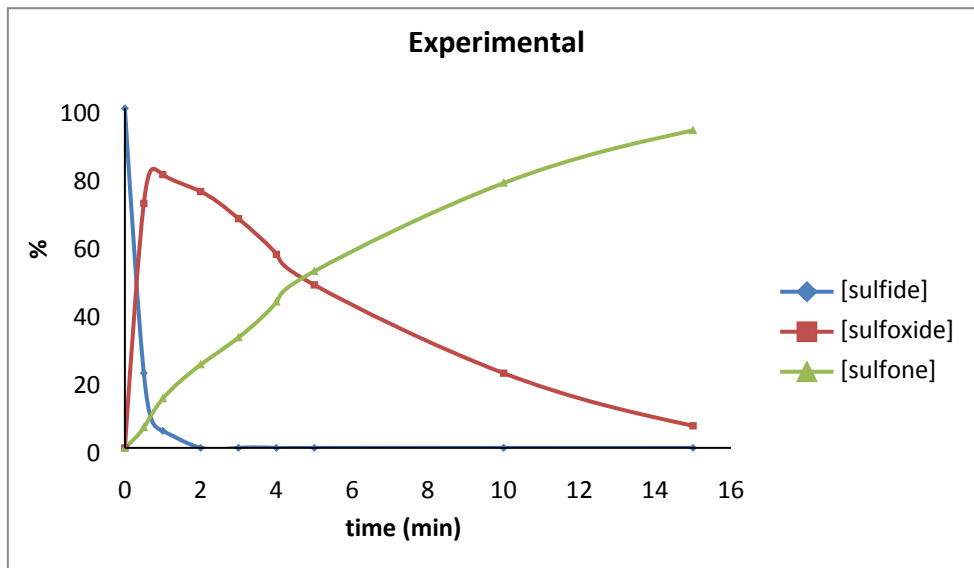
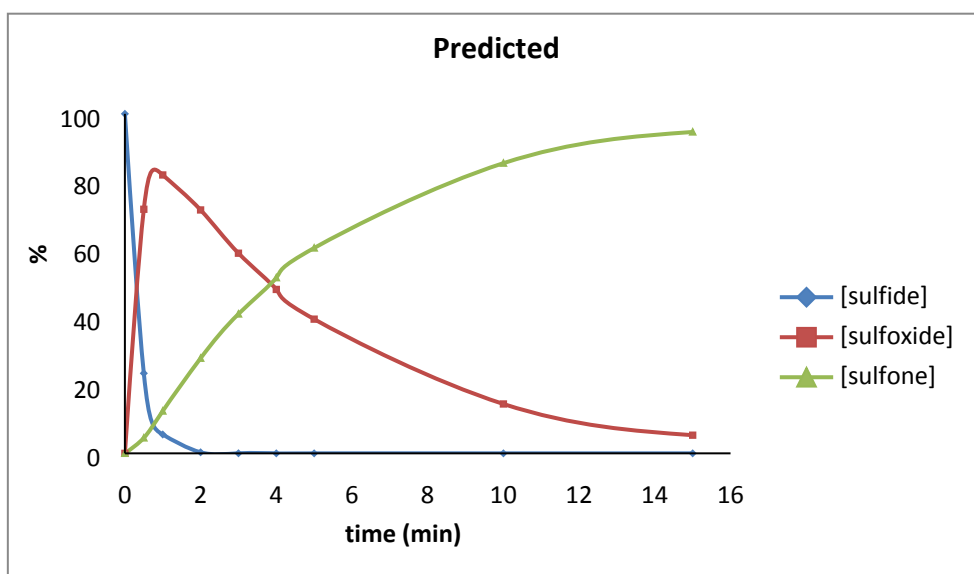


Figure S53a,b Determination of rate constants for the formation of methyl phenyl sulfoxide (k_a) and methyl phenyl sulfone (k_b) in acetonitrile with 12 equivalents of H_2O_2 by fitting the concentration-time profile for the consumption of sulfide and the formation of product.

(a)



(b)



k_a (min^{-1})	k_b (min^{-1})
2.89	0.2

Figure S54 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in acetonitrile at 30 °C with 20 equivalents of H_2O_2

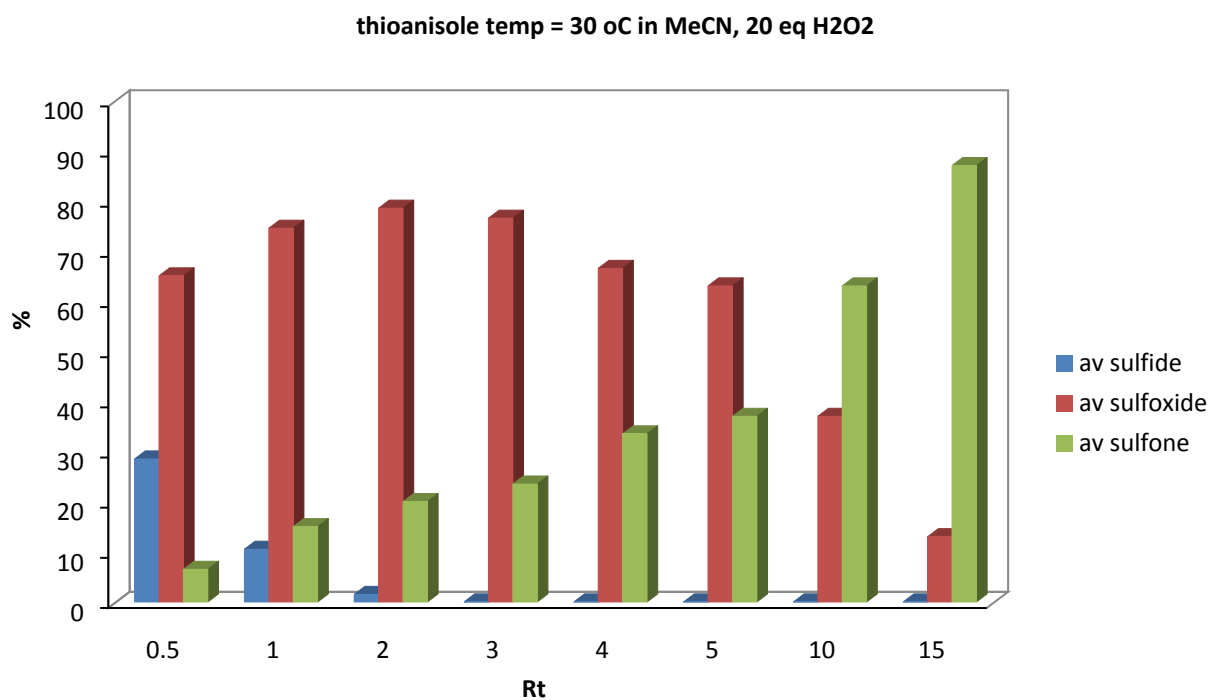
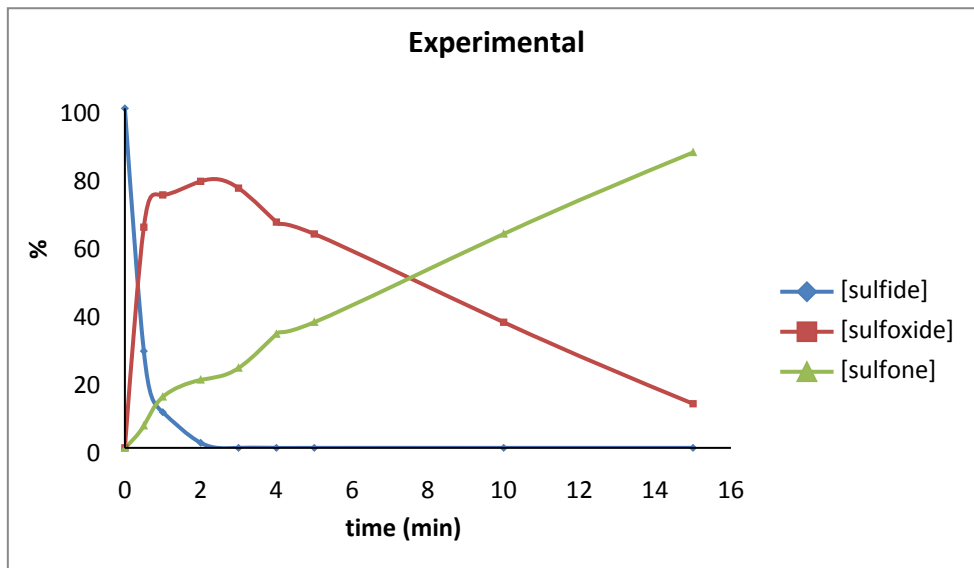
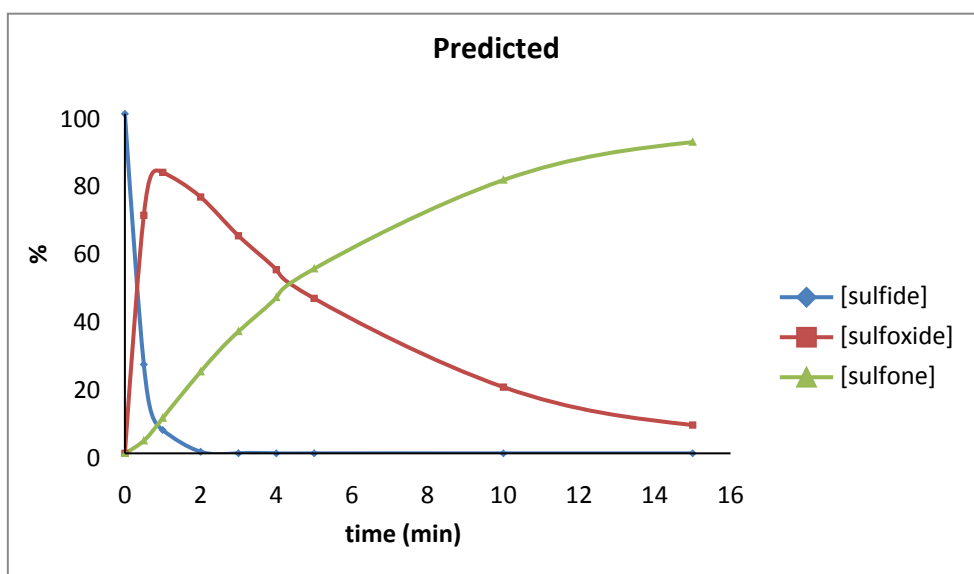


Figure S55a,b Determination of rate constants for the formation of methyl phenyl sulfoxide (k_a) and methyl phenyl sulfone (k_b) in acetonitrile with 20 equivalents of H_2O_2 by fitting the concentration-time profile for the consumption of sulfide and the formation of product.

(a)



(b)



k_a (min^{-1})	k_b (min^{-1})
2.68	0.17

Figure S56 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol at 30 °C with 2 equivalents of H_2O_2

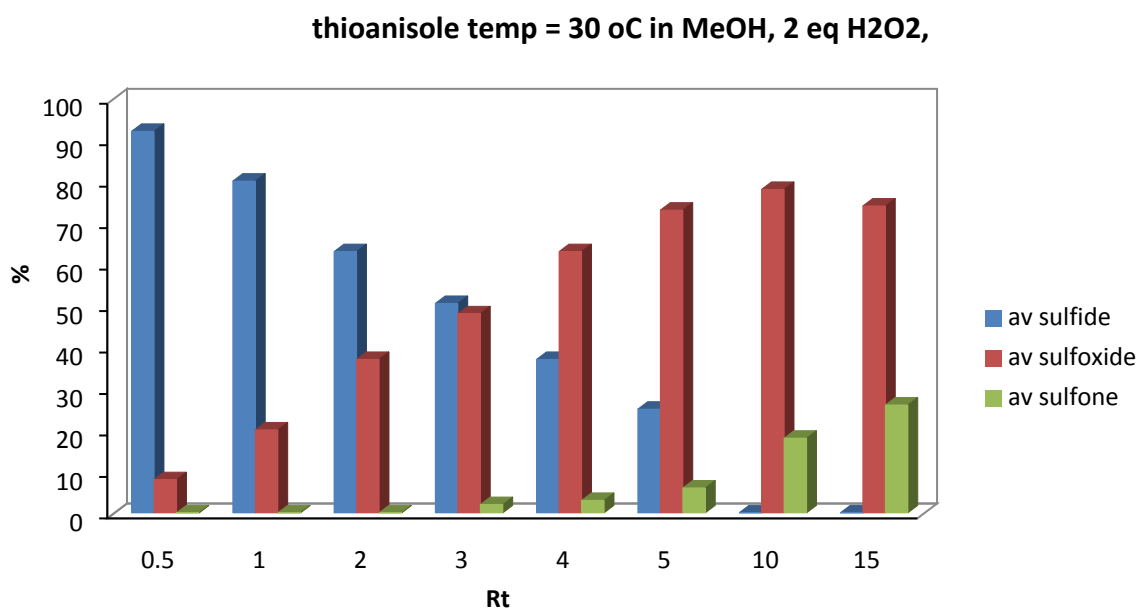


Figure S57 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol at 30 °C with 3 equivalents of H_2O_2

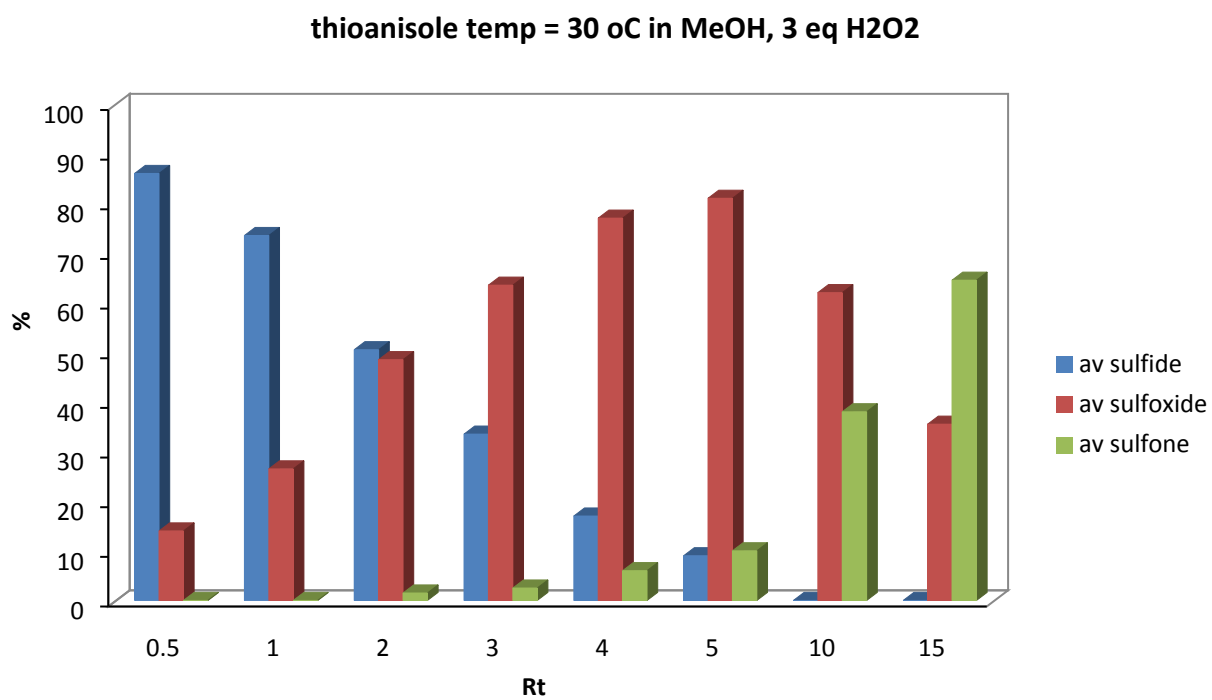


Figure S58 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol at 30 °C with 6 equivalents of H_2O_2

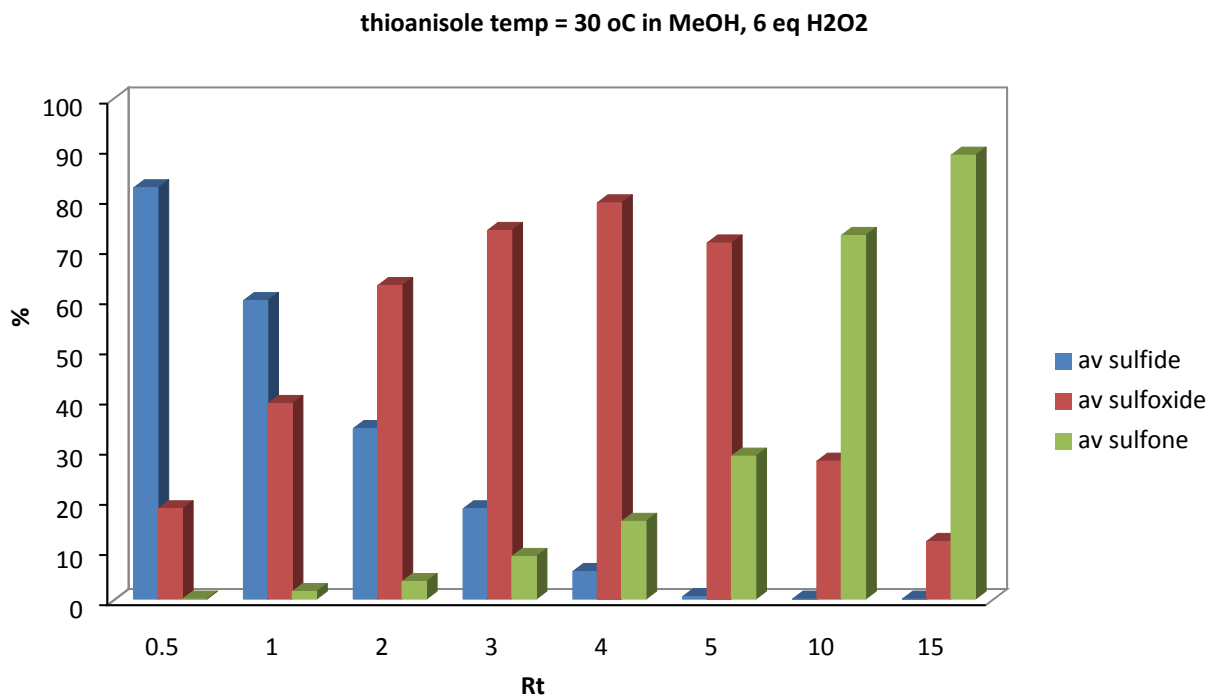


Figure S59 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol at 30 °C with 12 equivalents of H_2O_2

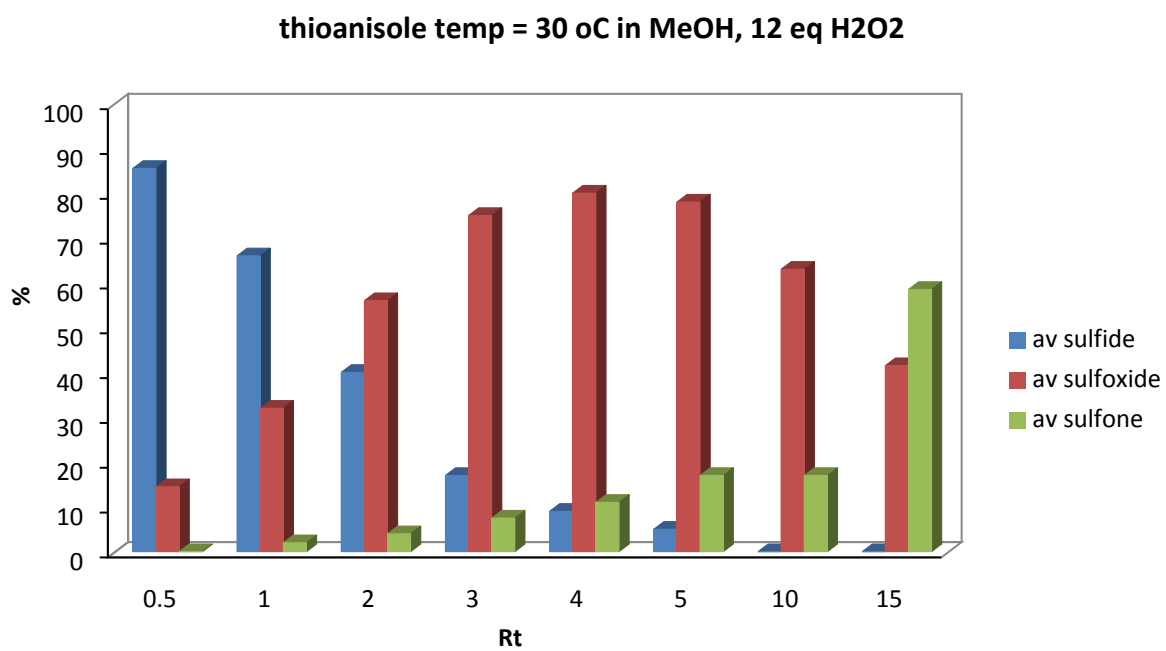
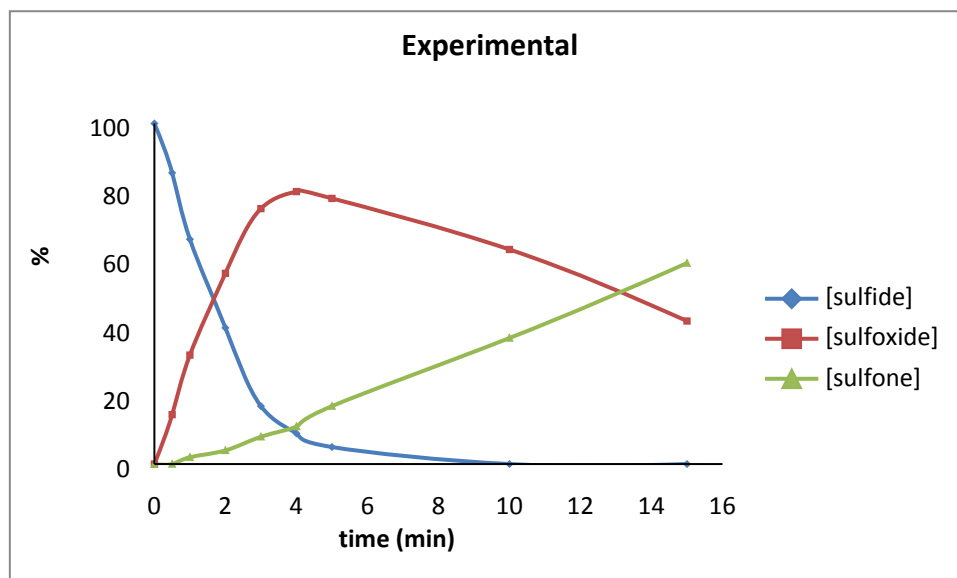
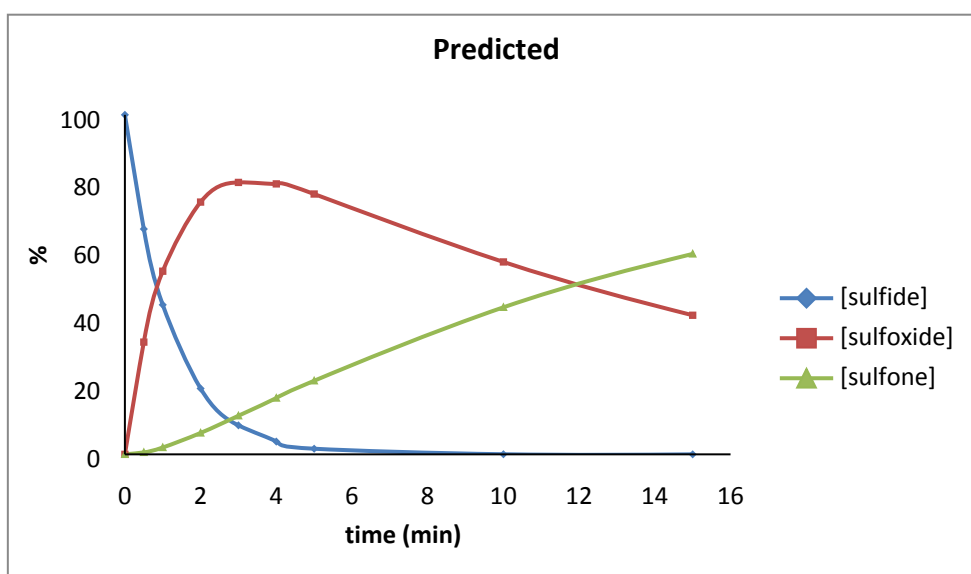


Figure S60a,b Determination of rate constants for the formation of methyl phenyl sulfoxide (k_a) and methyl phenyl sulfone (k_b) in methanol with 12 equivalents H_2O_2 by fitting the concentration-time profile for the consumption of sulfide and the formation of product.

(a)



(b)



k_a (min^{-1})	k_b (min^{-1})
0.82	0.065

Figure S61 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol at 30 °C with 20 equivalents of H_2O_2

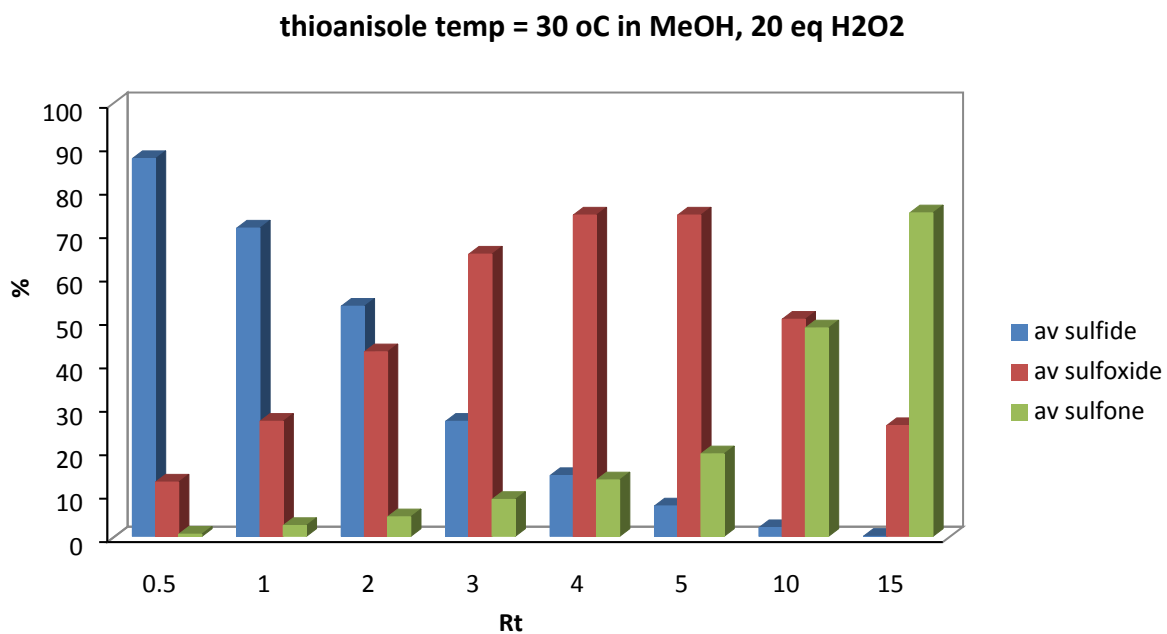
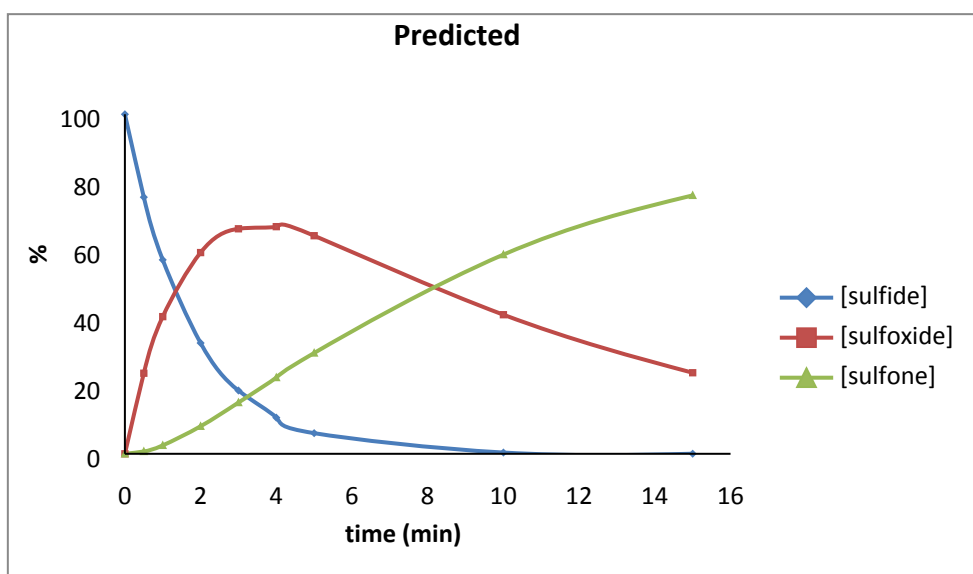
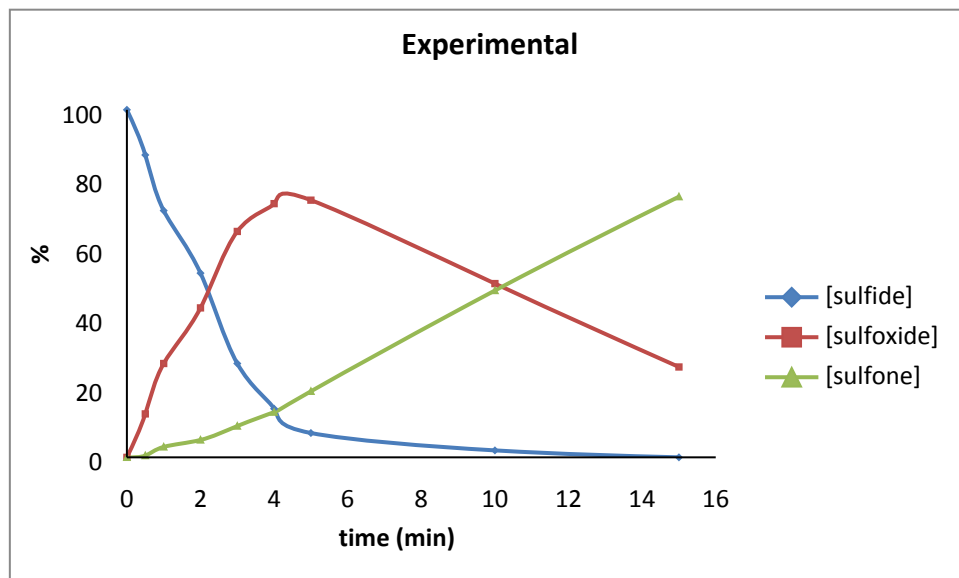


Figure S62a,b Determination of rate constants for the formation of methyl phenyl sulfoxide (k_a) and methyl phenyl sulfone (k_b) in methanol with 20 equivalents H_2O_2 by fitting the concentration-time profile for the consumption of sulfide and the formation of product.



k_a (min^{-1})	k_b (min^{-1})
0.56	0.11

Figure S63 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in acetonitrile at 30 °C with 3 equivalents of H_2O_2 and doped with water

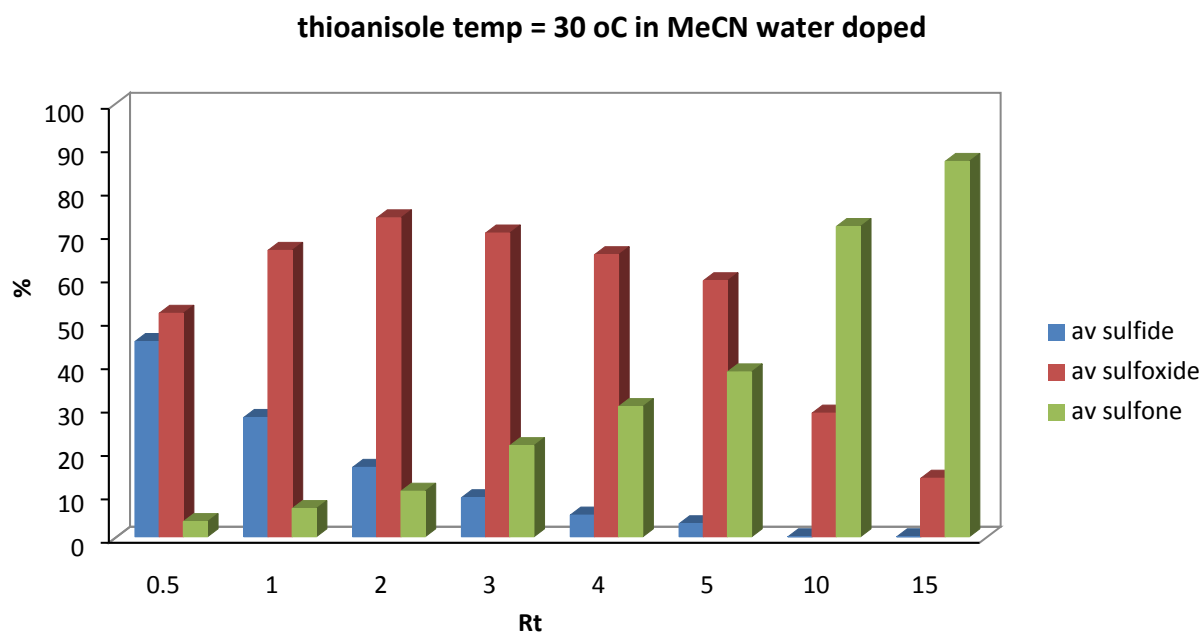


Figure S64 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol at 30 °C with 3 equivalents of H_2O_2 and doped with water

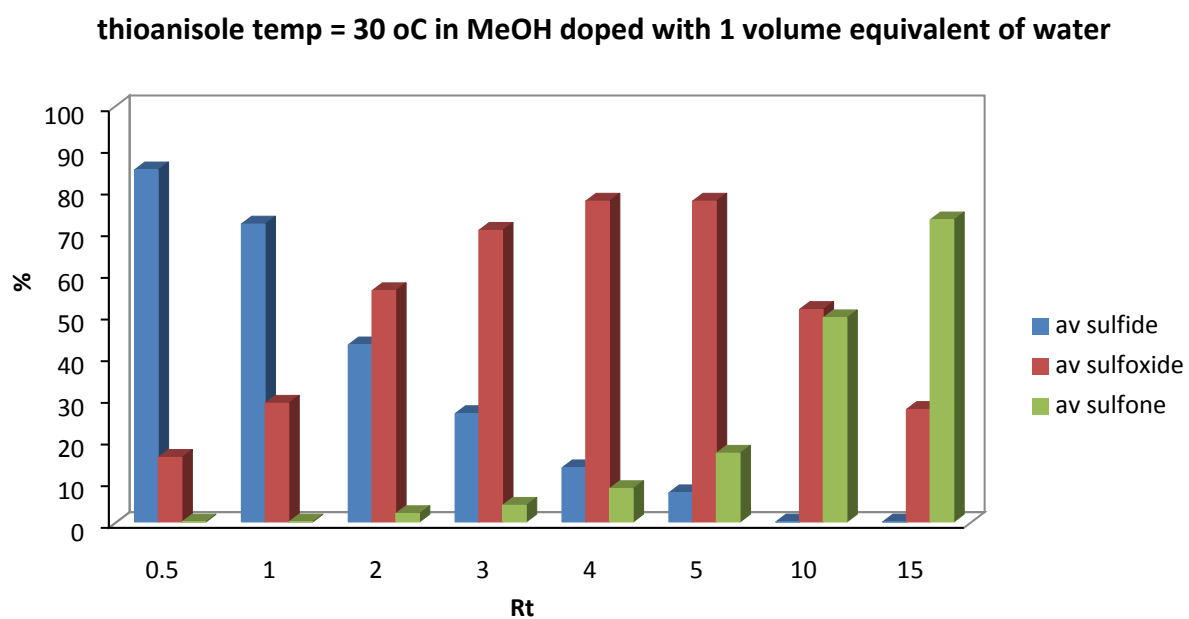


Figure S65 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of thioanisole in methanol-water (1:1, v/v) at 30 °C with 3 equivalents of H_2O_2

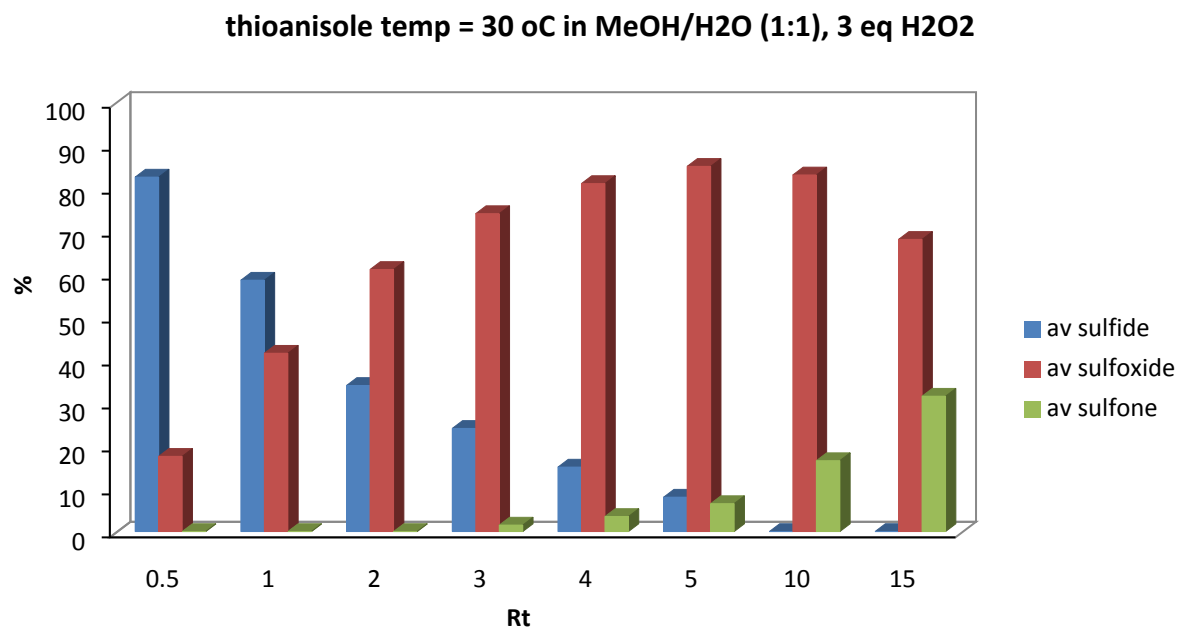


Figure S66 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of benzyl phenyl sulfide in acetonitrile at 30 °C.

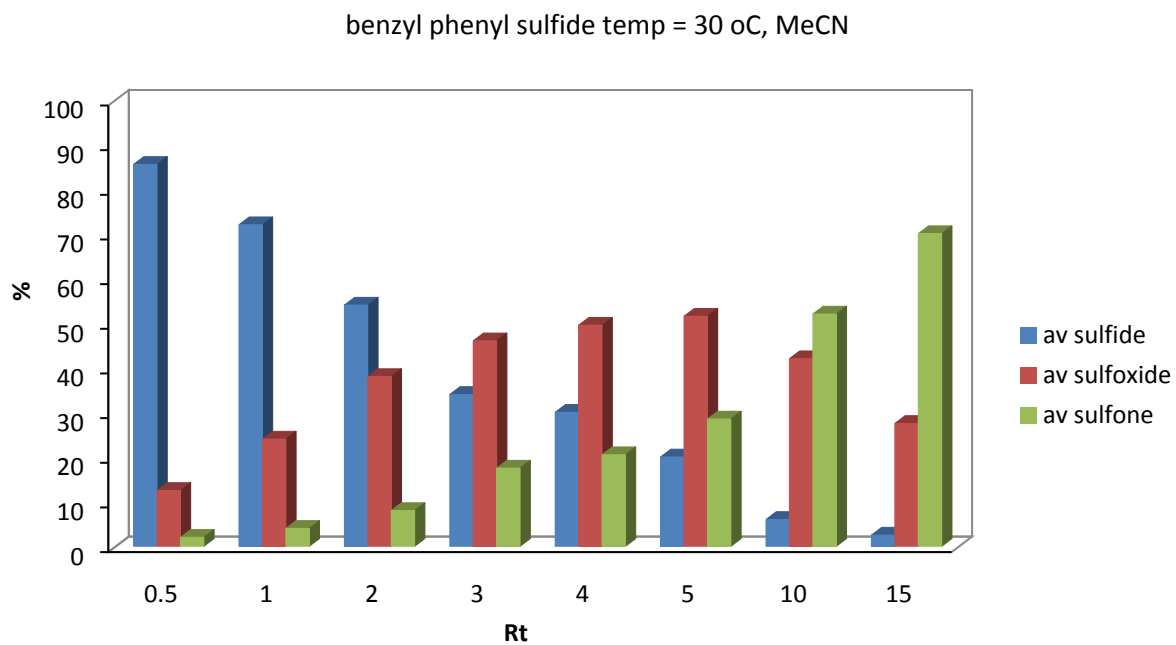


Figure S67 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of benzyl phenyl sulfide in methanol at 30 °C.

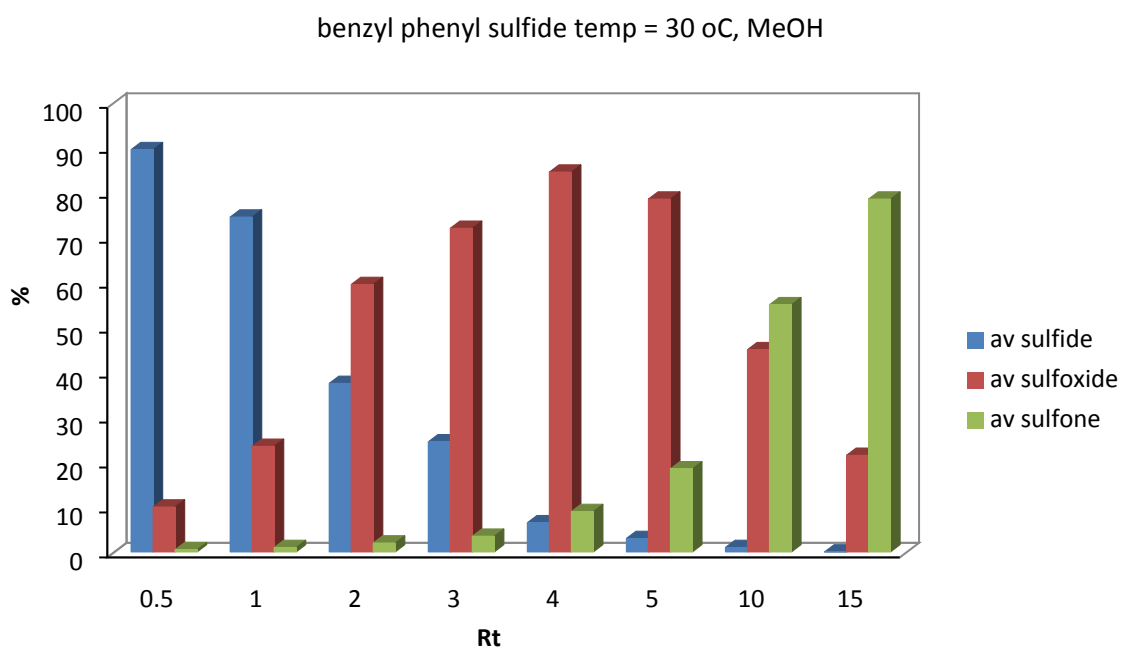


Figure S68 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of nitrothioanisole in acetonitrile at 30 °C.

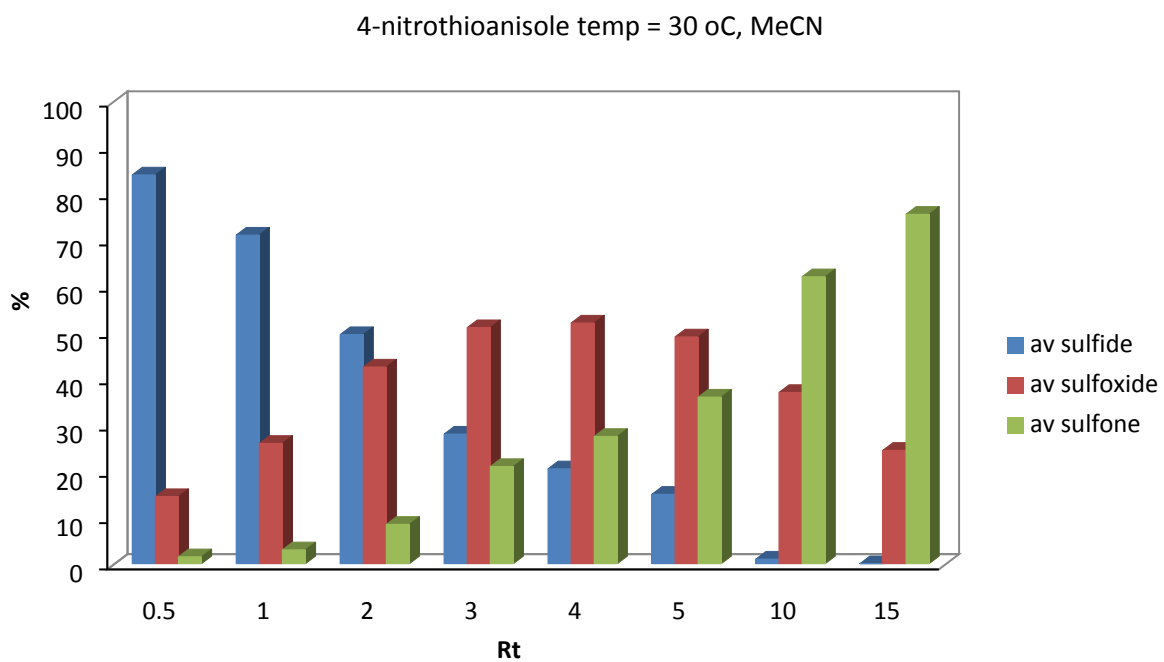


Figure S69 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of nitrothioanisole in methanol at 30 °C.

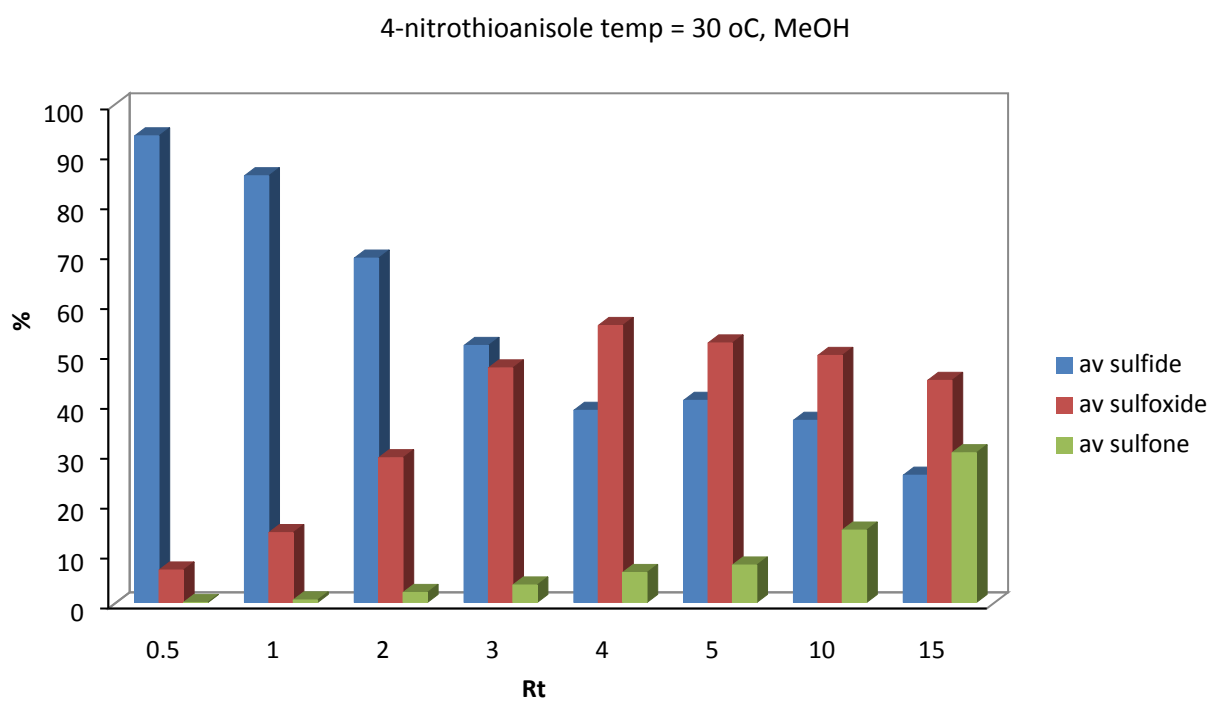


Figure S70 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of homoallylphenyl sulfide in acetonitrile at 30 °C.

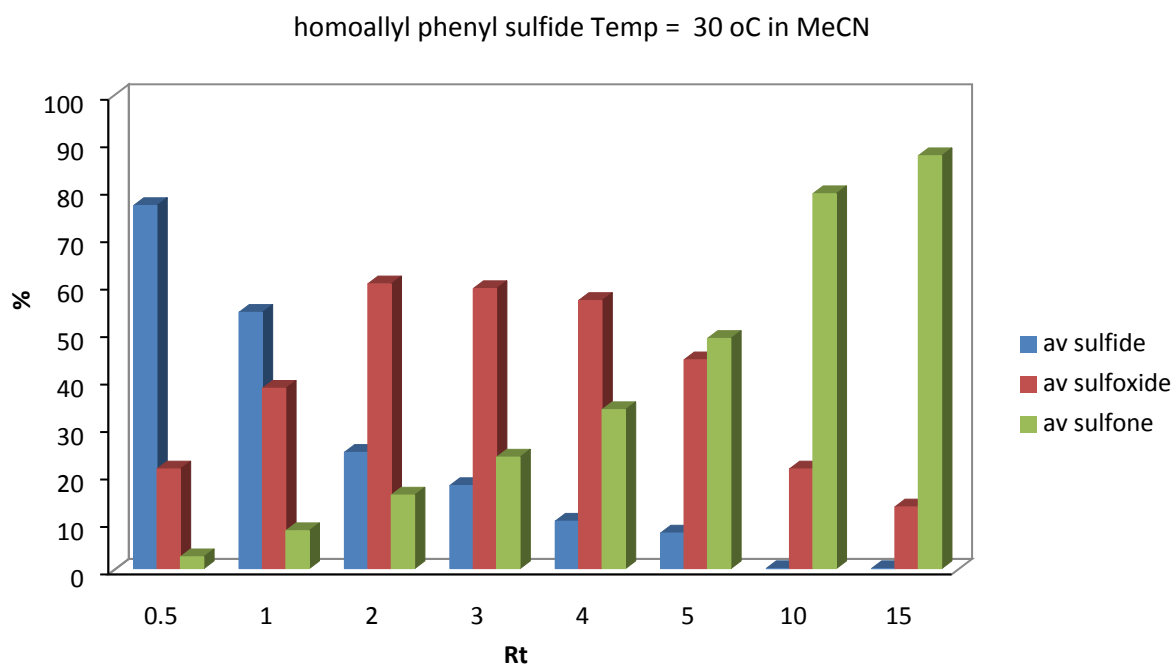


Figure S71 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of homoallylphenyl sulfide in methanol at 30 °C.

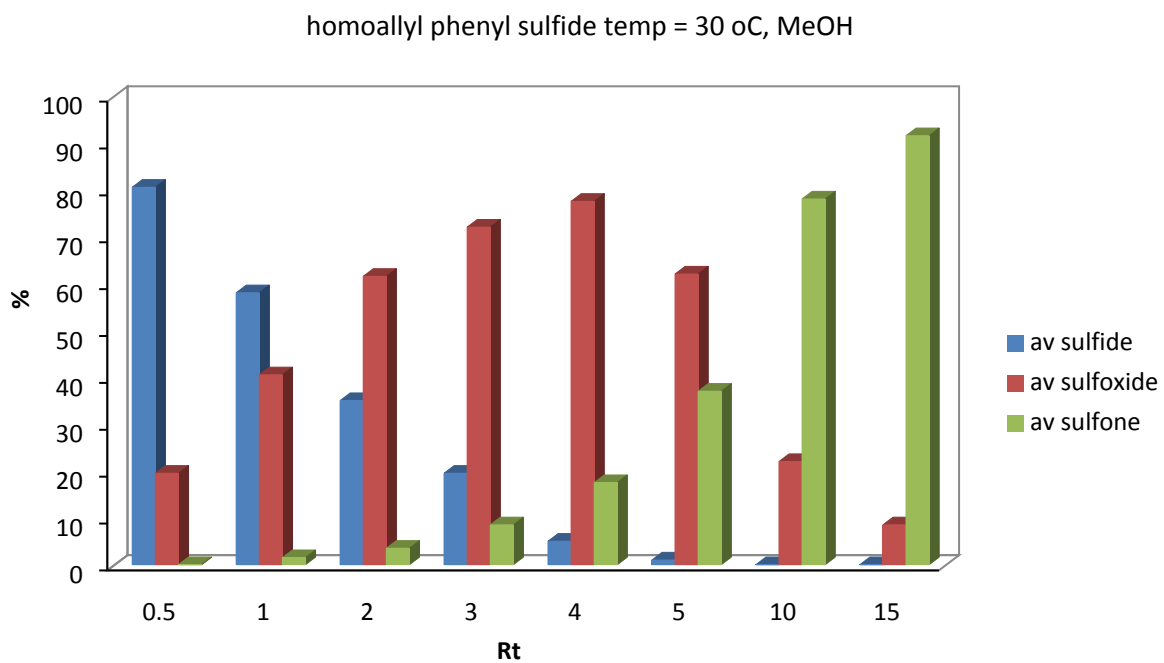


Figure S72 Conversion-selectivity profile as a function of residence time for the $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalyzed sulfoxidation of dibenzothiophene in acetonitrile at 30 °C.

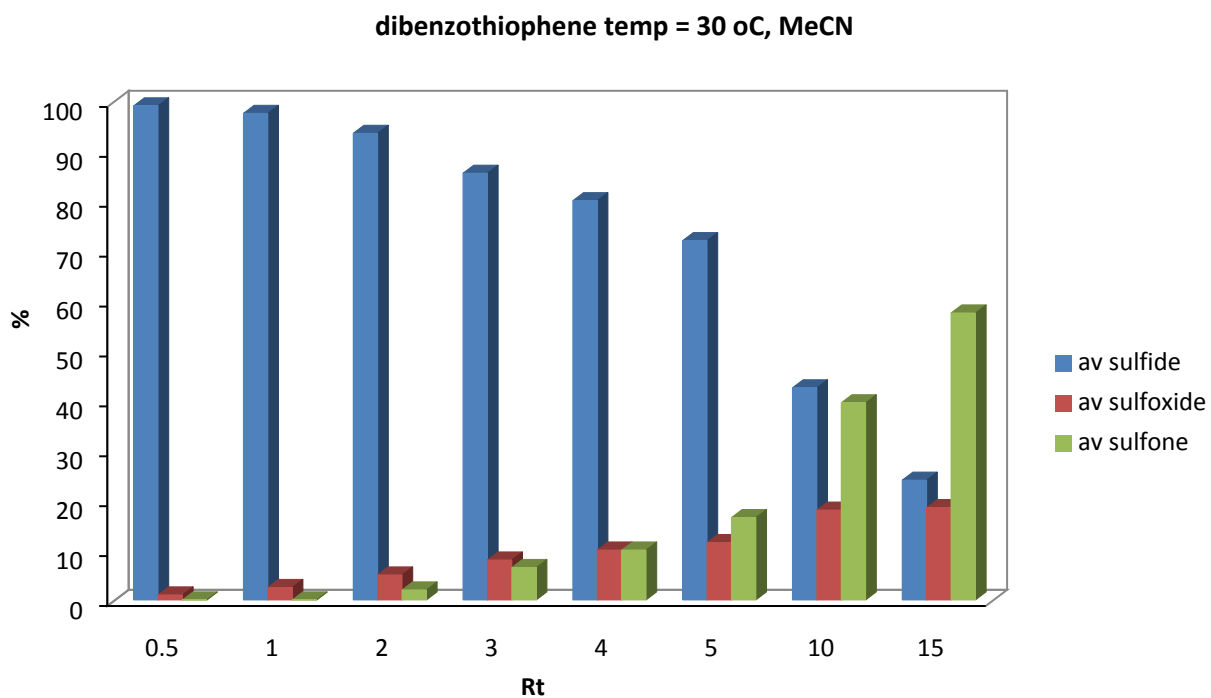


Figure S73 Conversion-selectivity profile as a function of time for an 8 h continuous flow $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalysed sulfoxidation of thioanisole at 30 °C with a residence time of 4 min in acetonitrile at 30 °C

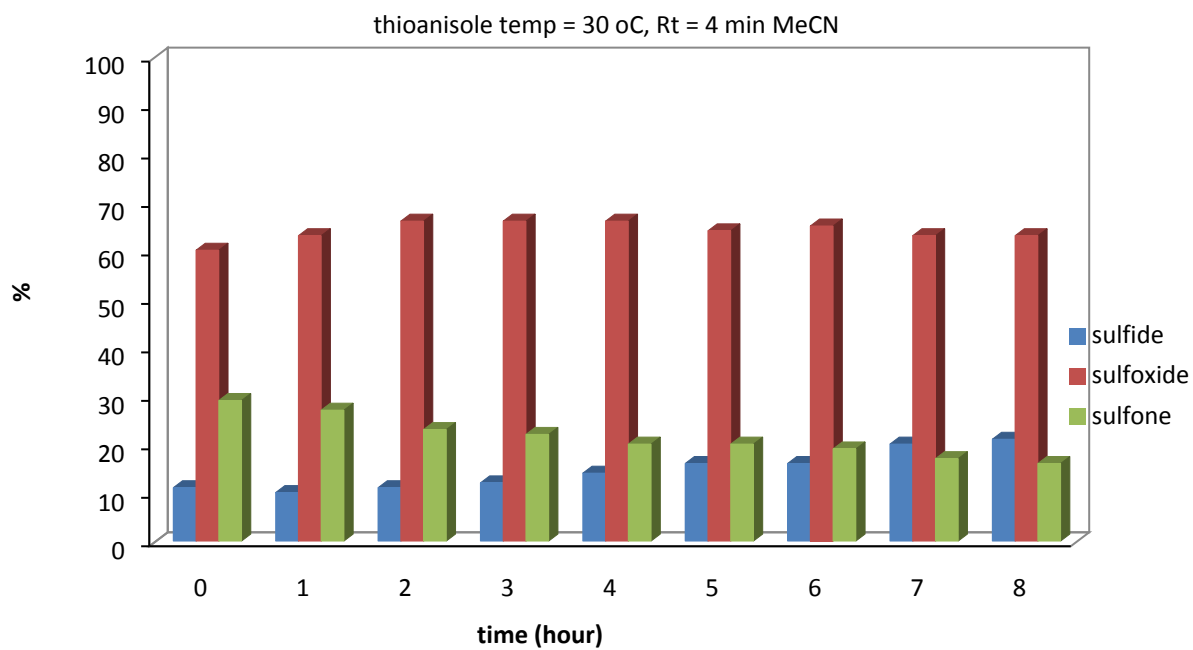


Figure S74 Conversion-selectivity profile as a function of time for an 8 h continuous flow $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalysed sulfoxidation of thioanisole at 30 °C with a residence time of 4 min in acetonitrile at 30 °C, with the H_2O_2 reservoir replenished after 4 h (*)

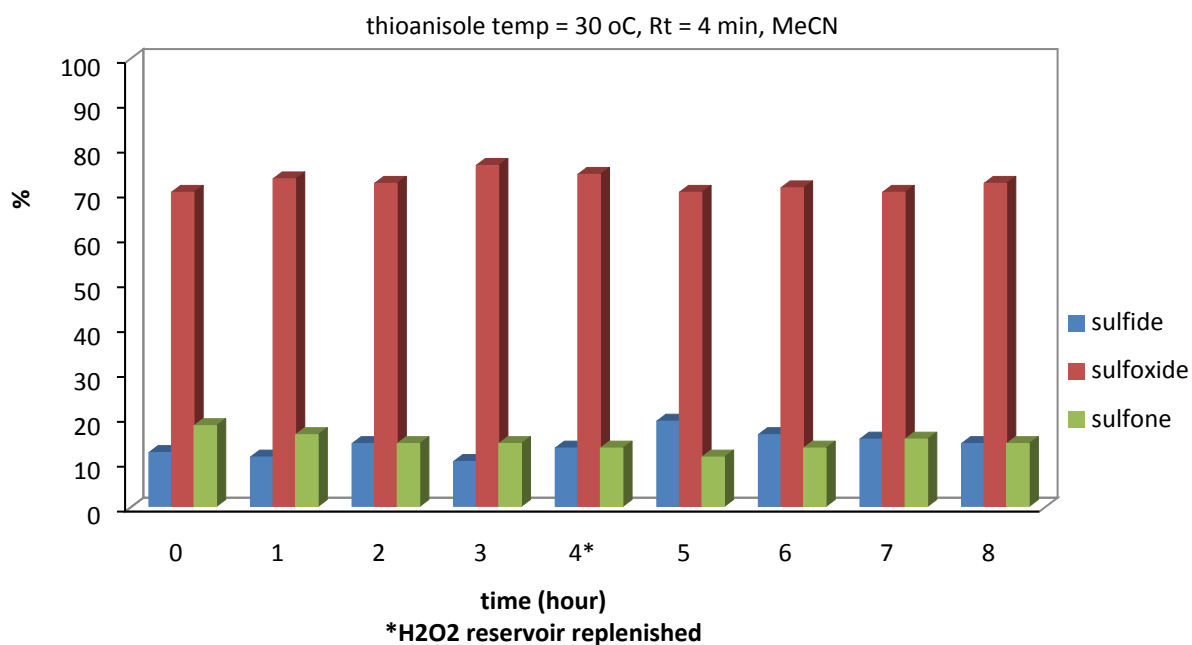


Figure S75 Conversion-selectivity profile as a function of time for an 8 h continuous flow $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalysed sulfoxidation of thioanisole at 30 °C with a residence time of 4 min in methanol at 30 °C

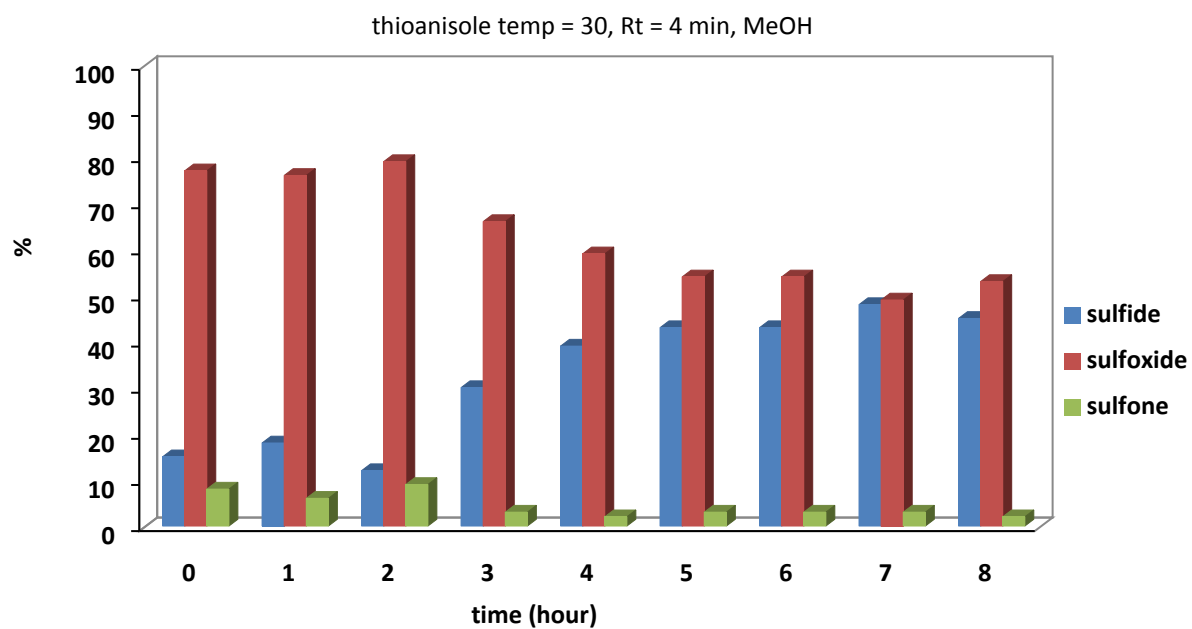


Figure S76 Conversion-selectivity profile as a function of time for an 8 h continuous flow $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]@\text{PIILP}$ -catalysed sulfoxidation of thioanisole at 30 °C with a residence time of 4 min in methanol at 30 °C, with the H_2O_2 reservoir replenished after 4 h (*)

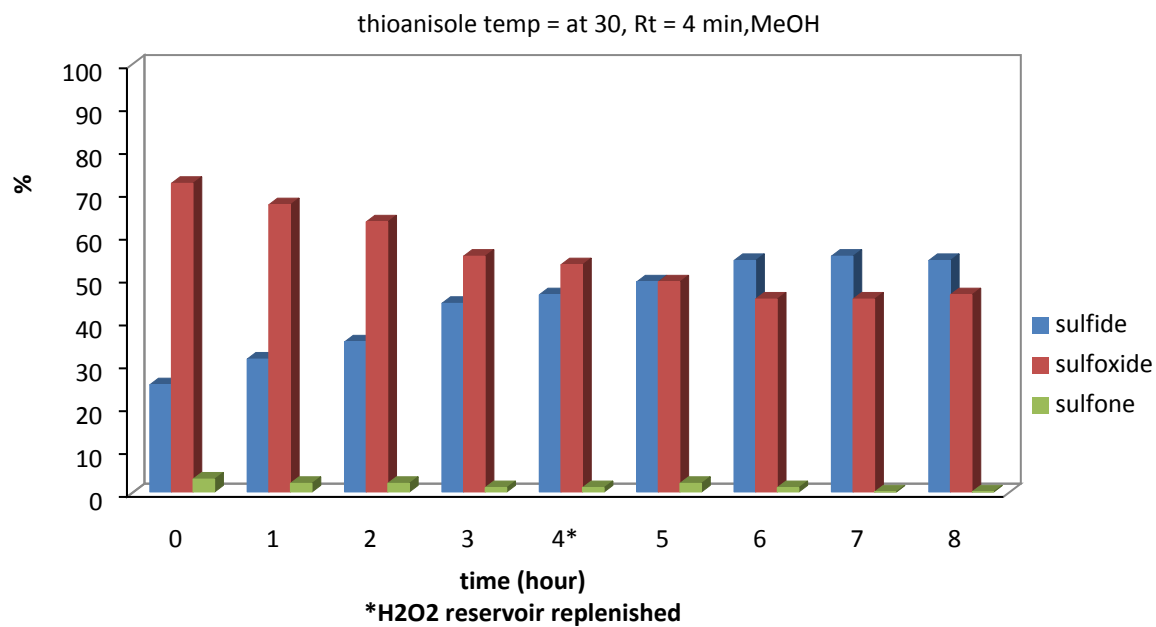


Figure S77 Conversion-selectivity profile as a function of time for an 8 h continuous flow sulfoxidation of thioanisole using $[n\text{Bu}_4\text{N}]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$ as catalyst at 30 °C with a residence time of 4 min in acetonitrile, with the H_2O_2 reservoir replenished after 4 h (*)

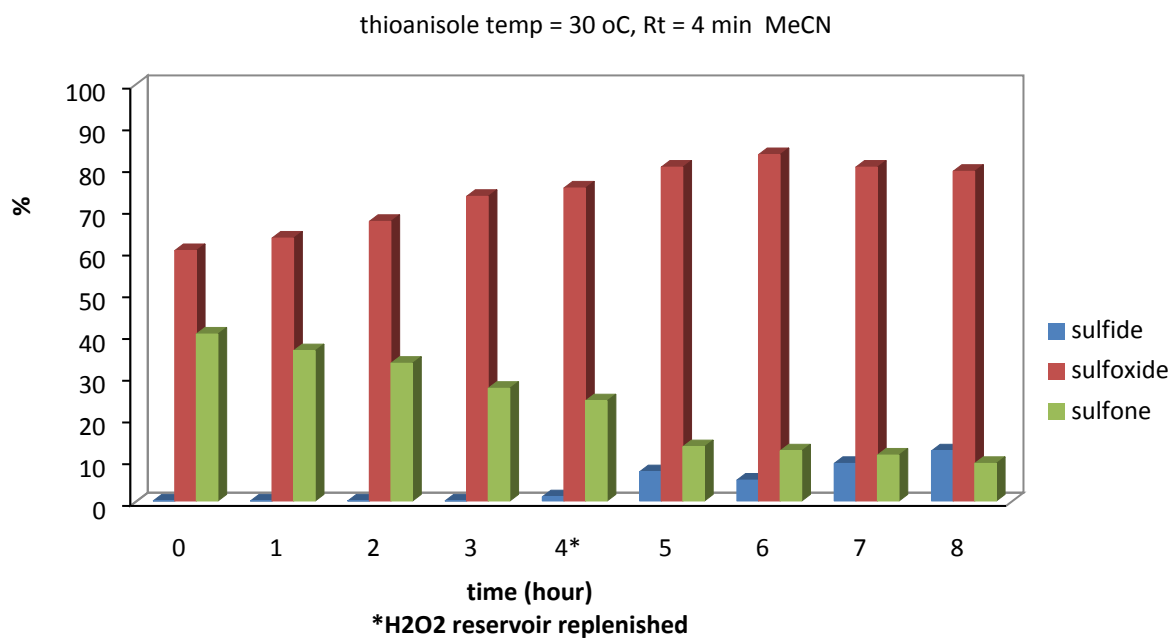


Figure S78 Conversion-selectivity profile as a function of time for an 8 h continuous flow sulfoxidation of thioanisole using $[n\text{Bu}_4\text{N}]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$ as catalyst at 30 °C with a residence time of 4 min in methanol, with the H_2O_2 reservoir replenished after 4 h (*)

