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Supplementary Information

p-Cymenesulphonyl Chloride: A Bio-Based Activating Group and Protecting Group for Greener Organic Synthesis

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Reagents

p-Cymene (99% purity) and 2-octanol (97% purity) were purchased from Acros Organics. Chlorosulphonic acid (99% purity), 1-octanol (99% purity) and all other reagents were obtained from Sigma-Aldrich. All chemicals were used as received without further purification.

Experimental and analytical techniques

The activating reagent *p*-cymene sulphonic acid was synthesized, isolated and characterized as documented in the main article. All subsequent activated compounds were used crude in following reactions. Spectra corresponding to these intermediate compounds are supplied in this document, as are key spectral assignments (^{1}H NMR, MS) of the major isomer of each activated compound in the crude reaction mixture. These compounds can be considered as crude, and were not purified. The authors recommend applying one-pot reactions for the activation and functionalization of substrates. For the purpose of this work a two stage synthesis was applied only to emphasise the formation of the sulphonate esters. Characterisation of the final products is provided also.

The direct infusion mass spectrometer used a time of flight (TOF) detector with electron impact (EI +) ionisation. The infusion was generally prepared in dichloromethane as the solvent. The GC-MS was a Perkin Elmer Clarus 500 gas chromatograph (GC) and Perkin Elmer Clarus 5605 mass spectrometer, quadrupole detector and EI + ionisation: the injection volume was 1 μL; injector temperature was 300 °C, and the solvent delay was 2.50 min for samples dissolved in dichloromethane and 3.10 min for samples dissolved in toluene. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained on a Perkin Elmer Spectrometer 400. The GC-FID used an Agilent 6890N GC and detector: the injection volume was 1 μL; injector temperature was 290 °C; detector temperature was 340 °C. All NMR spectroscopy was performed in a 400 MHz Jeol spectrometer, all samples prepared as solutions in deuterated chloroform.

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1-Octyl-*p*-cymene-α-sulphonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 3H, CH_3), 1.25 (m, 16H, CH_3 and CH_2), 1.63 (m, 2H, CH_2), 2.59 (s, 3H, Ar–CH_3), 2.93 (m, 1H, CH), 4.00 (t, 2H, CH_2O), 7.18-7.29 (m, 1H, Ar–H), 7.35 (m, 1H, Ar–H), 7.67-7.89 (m, 1H, Ar–H); MS (EI +) *m/z* 326 $[M]^+$.

1-Octyl-*p*-toluenesulphonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 3H, *J* 6.95 Hz, CH_3), 1.13-1.33 (m, 10H, CH_2), 1.53-1.70 (m, 2H, CH_2), 2.44 (s, 3H, Ar–CH_3), 4.00 (t, 2H, *J* 6.59 Hz), 7.33 (d, 2H, *J* 8.42 Hz, Ar–H), 7.78 (d, 2H, *J* 8.42 Hz, Ar–H); MS (EI +) *m/z* 173 $[M - C_8H_{15}]^+$, 112 $[M - C_7H_8O_3S]^+$, 91 $[M - C_8H_{17}O_3S]^+$.

2-Octyl-*p*-cymene-α-sulphonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, 3H, *J* 7.14 Hz), 1.10-1.22 (m, 5H, CH_3 and CH_2), 1.23-1.30 (m, 12H, Ar–CH_3 and CH_2), 1.60 (m, 2H, CH_2), 2.60 (s, 3H, Ar–CH_3), 2.94 (m, 1H, Ar–CH), 4.60 (m, 1H, CH–O), 7.24 (d, 1H, *J* 8.41 Hz, Ar–H), 7.34 (dd, 1H, *J* 1.48, 8.41 Hz, Ar–H), 7.82 (d, 1H, *J* 1.48 Hz, Ar–H); MS (EI +) *m/z* 326 $[M]^+$, 214 $[M - C_8H_{16}]^+$, 199 $[M - C_9H_{19}]^+$.

2-Octyl-*p*-toluenesulphonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, 3H, *J* 6.95 Hz, CH_3), 1.01-1.22 (m, 8H, CH_2), 1.22-1.32 (m, 3H, CH_3), 1.40-1.71 (m, 2H, CH_2), 2.43 (s, 3H, Ar–CH_3), 4.58 (m,

1H, CH–O), 7.31 (d, 2H, *J* 8.05 Hz, Ar–H), 7.78 (d, 2H, *J* 8.05 Hz, Ar–H); MS (EI +) *m/z* 173 $[M - C_8H_{15}]^+$, 155 $[M - C_8H_{17}O]^+$, 91 $[M - C_8H_{17}O_3S]^+$.

Phenyl-*p*-cymene-α-sulphonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (d, 6H, *J* 6.59 Hz, CH_3), 2.69 (s, 3H, Ar–CH_3), 4.09 (m, 1H, Ar–CH), 6.85-7.03 (m, 2H, Ar–H), 7.14-7.24 (m, 4H, Ar–H), 7.40 (m, 1H, Ar–H), 7.61 (s, 1H, Ar–H); MS (EI +) *m/z* 290 $[M]^+$.

N,N-1,5-Pentylene-*p*-cymene-α-sulphonamide

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14-1.26 (m, 8H, Ar–CH_3 and CH_2), 1.55 (m, 4H, CH_2), 2.53 (s, 3H, Ar–CH_3), 3.08 (m, 4H, N–CH_2), 4.06 (m, 1H, Ar–CH), 7.13-7.20 (m, 1H, Ar–H), 7.22-7.31 (m, 1H, Ar–H), 7.69 (s, 1H, Ar–H); MS (EI +) *m/z* 281 $[M]^+$.

1-Octyl methyl ether

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* 6.95 Hz, CH_3), 1.23-1.31 (m, 10H, CH_2), 1.55 (m, 2H, CH_3), 3.31 (s, 3H, O–CH_3), 3.35 (t, 2H, *J* 6.77 Hz, O–CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 23.9, 26.2, 29.3, 29.7, 31.9, 58.6, 73.1; MS (EI +) *m/z* 145 $[M + H]^+$, 112 $[M - CH_4O]^+$.

2-Octyl methyl ether

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* 6.59 Hz, CH_3), 1.10 (d, 3H, *J* 5.12 Hz, CH_2), 1.22-1.32 (m, 8H, CH_3), 3.26 (m, 1H, O–CH), 3.29 (s, 3H, O–CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 19.1, 22.7, 25.5, 29.5, 31.9, 33.8, 36.4, 56.0, 68.2; MS (EI +) *m/z* 129 $[M - CH_3]^+$, 112 $[M - CH_4O]^+$.

N-1-Octyl morpholine

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, 3H, *J* 6.41 Hz, CH_3), 1.18-1.33 (m, 10H, CH_2), 1.44 (m, 2H, CH_2), 2.29 (m, 2H, N–CH_2), 2.39 (m, 4H, N–CH_2), 3.68 (t, 4H, *J* 4.76 Hz, O–CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 26.6, 27.7, 29.3, 29.6, 31.9, 53.8, 59.4, 67.0; MS (EI +) *m/z* 199 $[M]^+$.

N-2-Octyl morpholine

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 3H, *J* 6.95 Hz, CH_3), 0.95 (d, 3H, *J* 6.60 Hz, CH_2), 1.18-1.32 (m, 10H, CH_2), 1.48 (m, 1H, N–CH_2), 2.34-2.59 (m, 4H, N–CH_2), 3.67 (m, 4H, O–CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.7, 26.8, 29.6, 31.9, 33.4, 49.0, 53.5, 59.5, 67.6; MS (EI +) *m/z* 199 $[M]^+$.

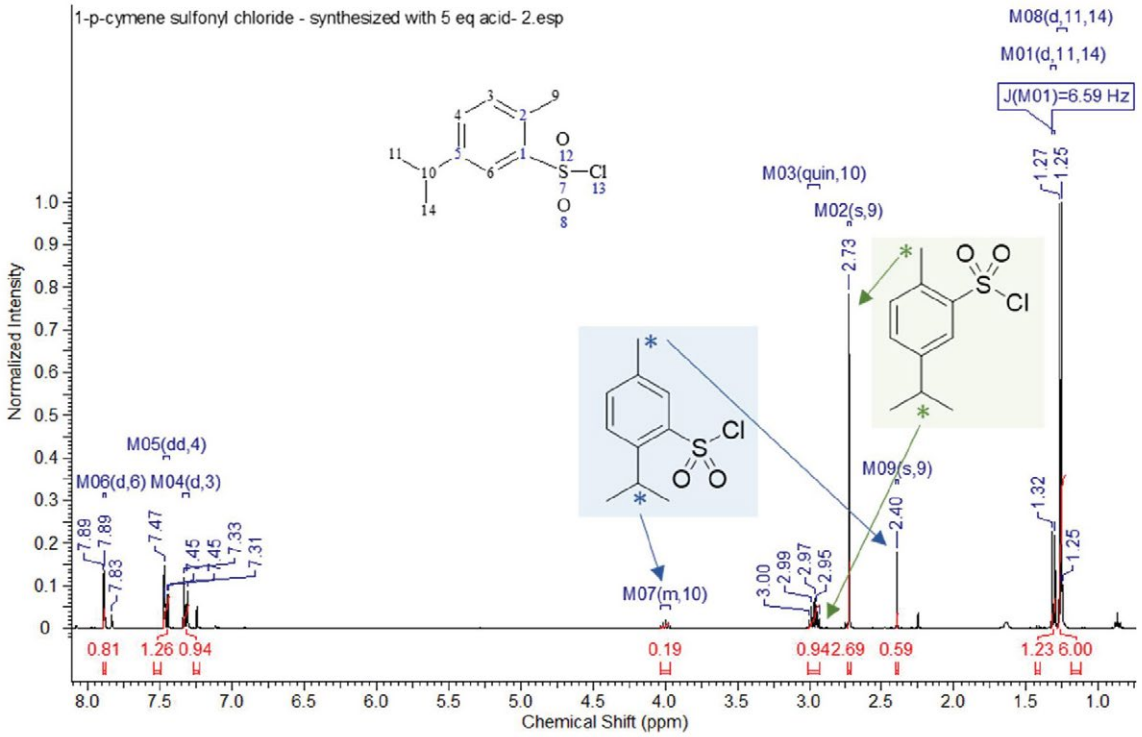

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *p*-cymenesulphonyl chloride (with characteristic signals for the two regioisomers indicated).

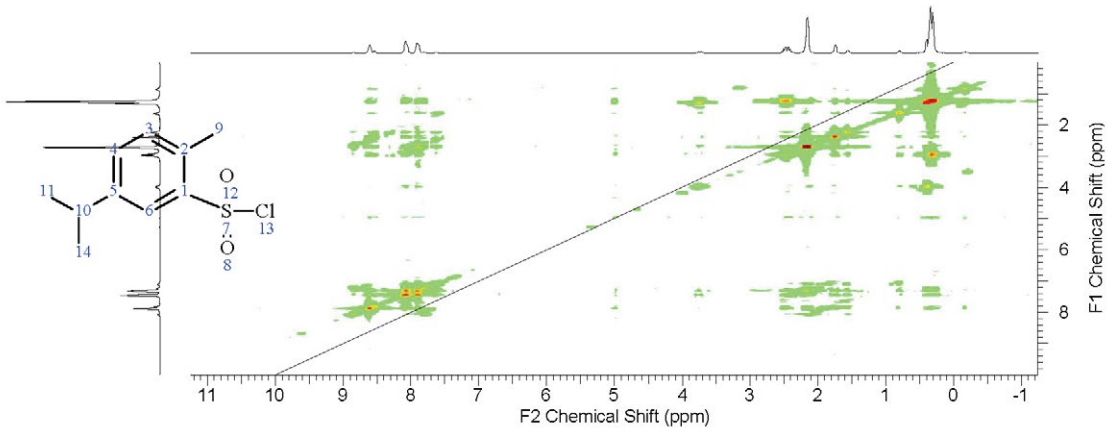

Figure S2. ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$) of *p*-cymenesulphonyl chloride.

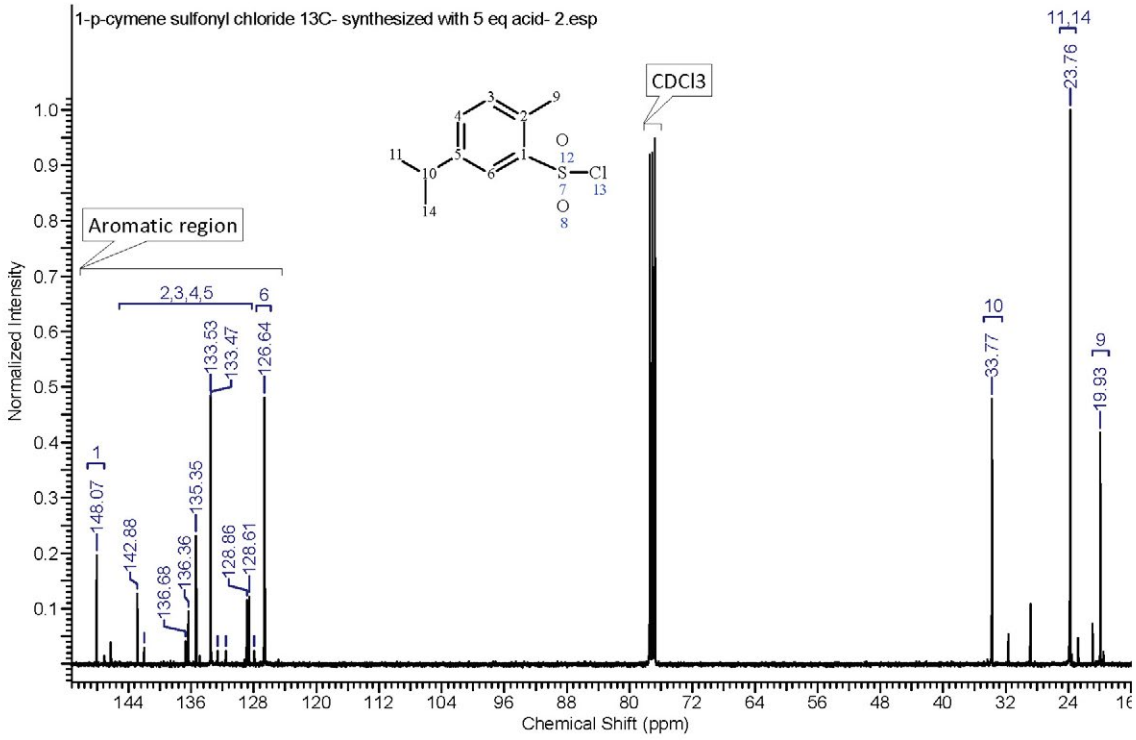

Figure S3. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of *p*-cymenesulphonyl chloride.

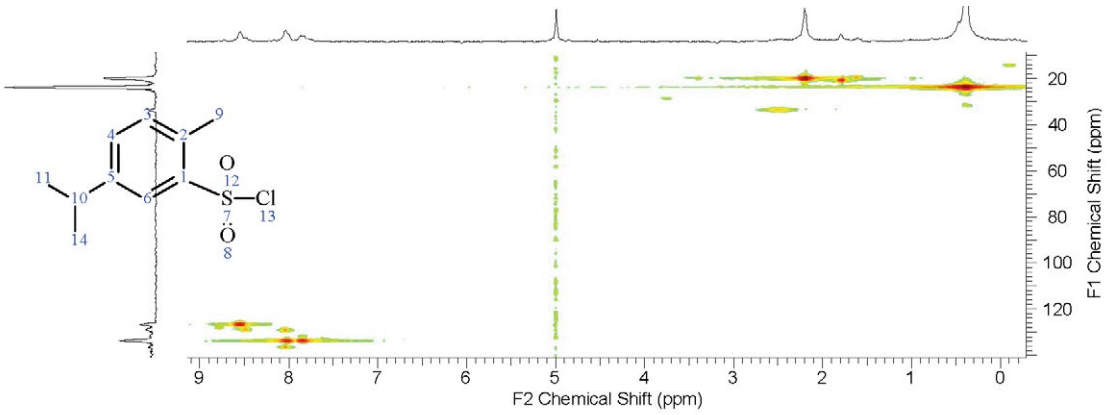

Figure S4. ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) of *p*-cymenesulphonyl chloride.

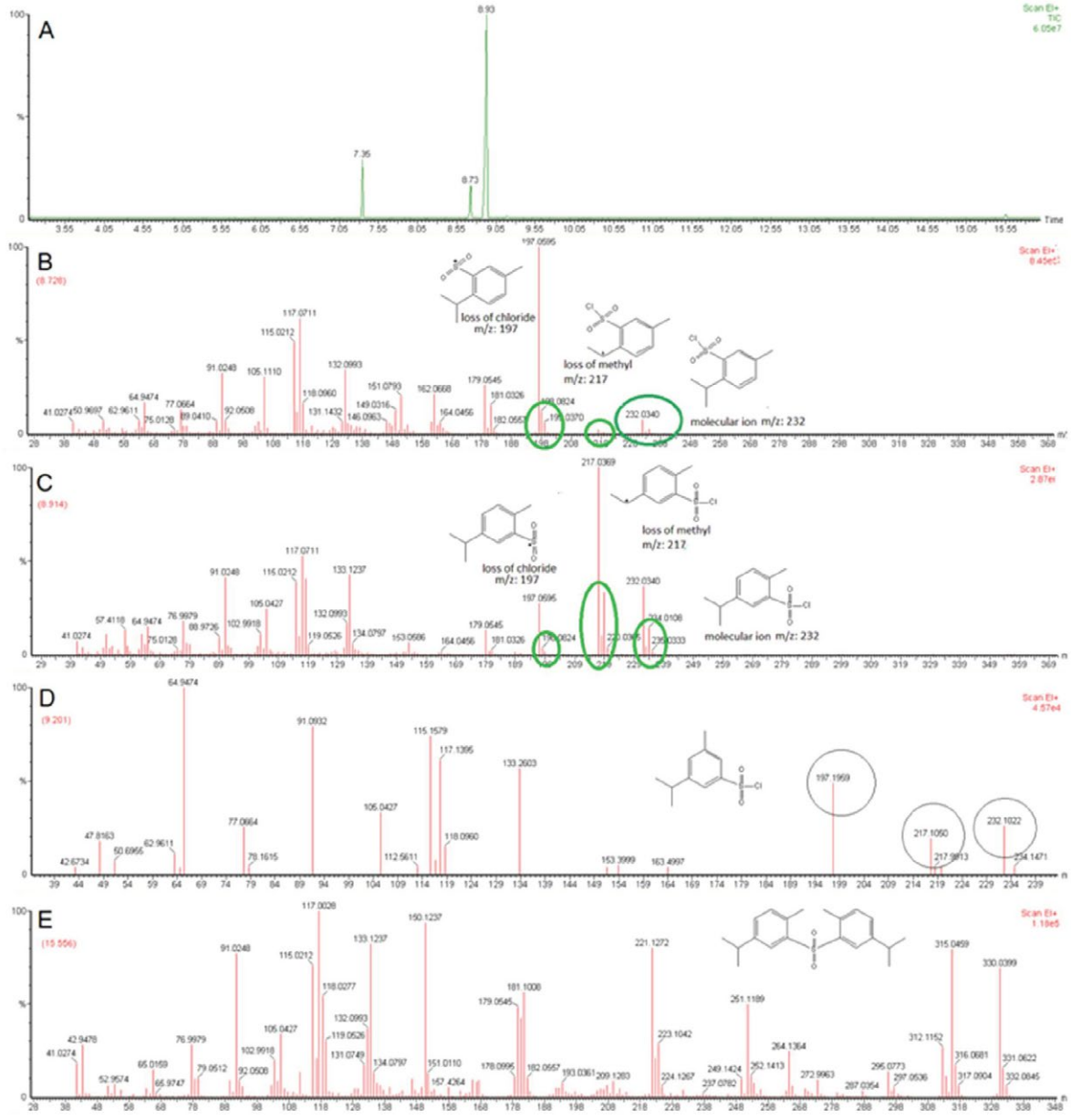

Figure S5. GC-MS chromatogram and mass spectra of *p*-cymenesulphonyl chloride.

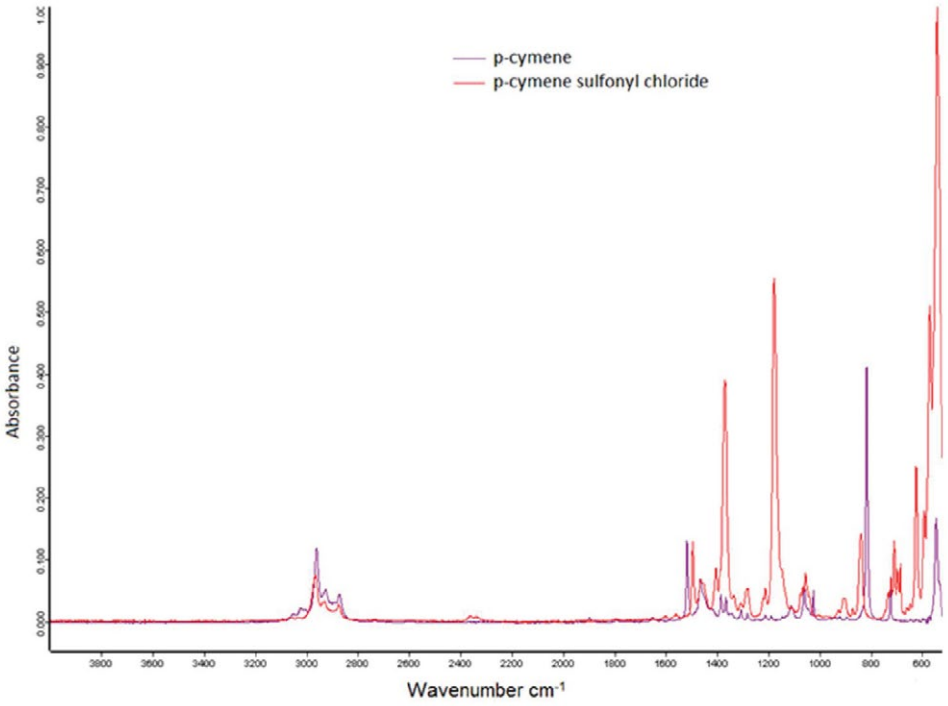

Figure S6. FTIR spectrum (ATR) of *p*-cymene and *p*-cymenesulphonyl chloride.

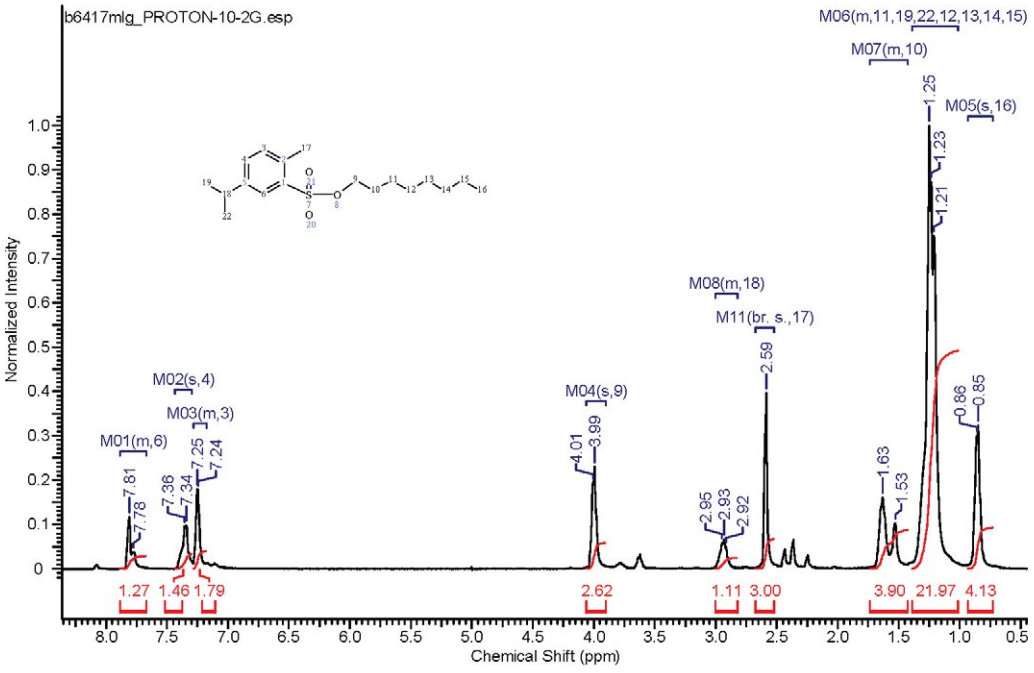

Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude intermediate 1-octyl-*p*-cymene sulphonate.

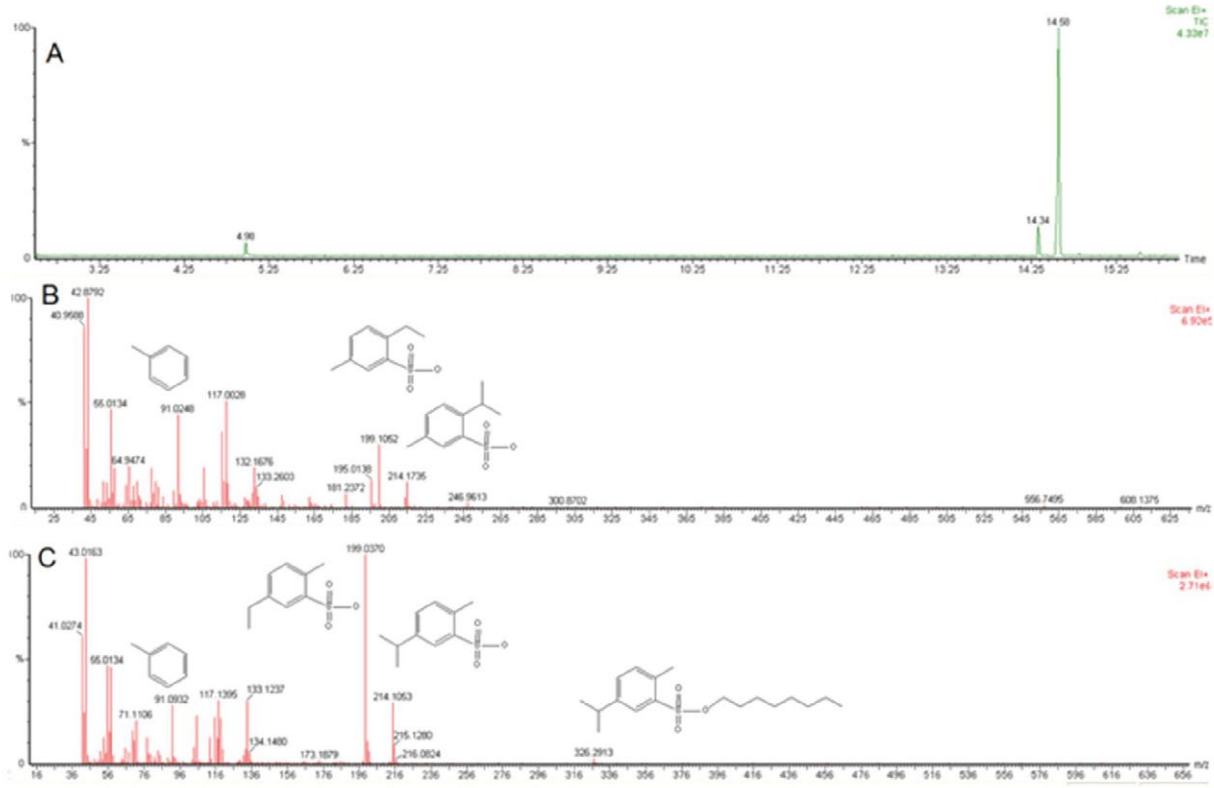

Figure S8. GC-MS chromatogram and mass spectra of crude intermediate 1-octyl-*p*-cymene sulphonate.

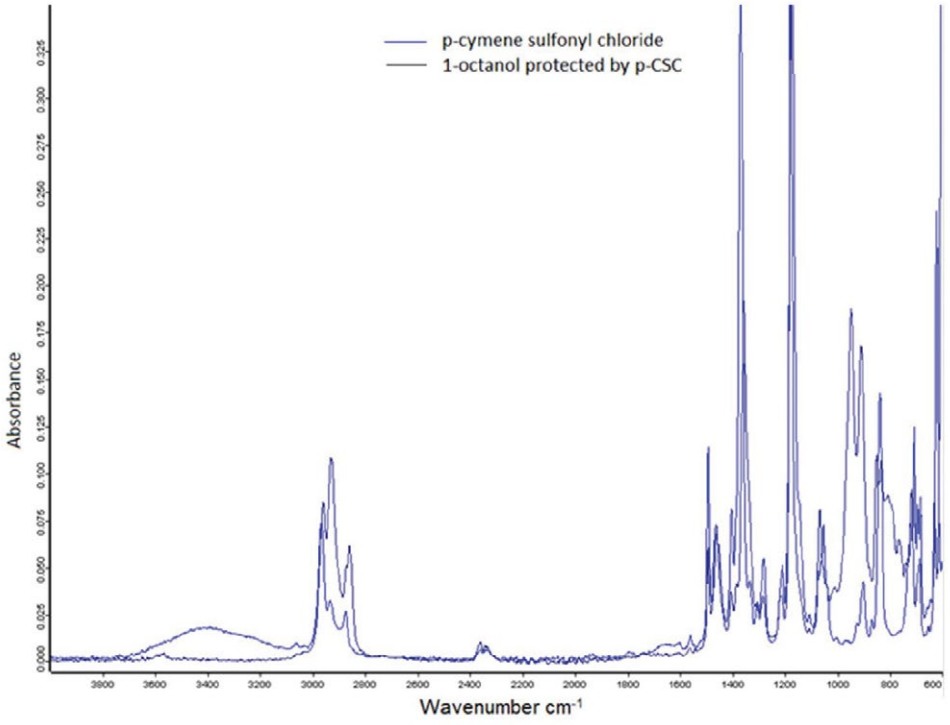

Figure S9. FTIR spectrum (ATR) of the crude intermediates *p*-cymenesulphonyl chloride and 1-octyl-*p*-cymene sulphonate.

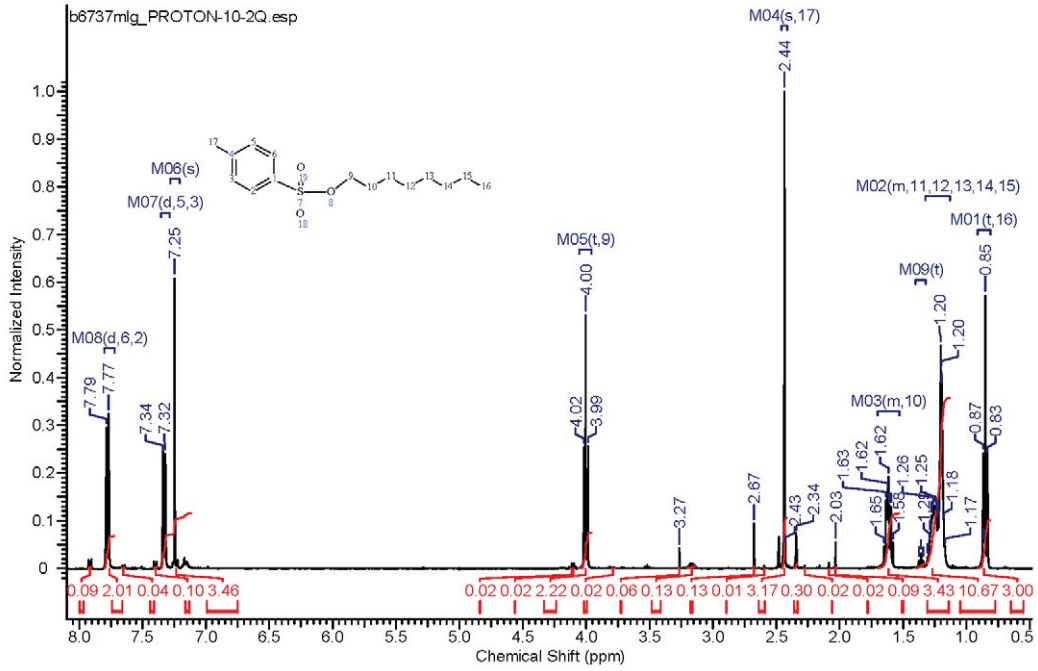

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude intermediate 1-octyl-*p*-toluenesulphonate.

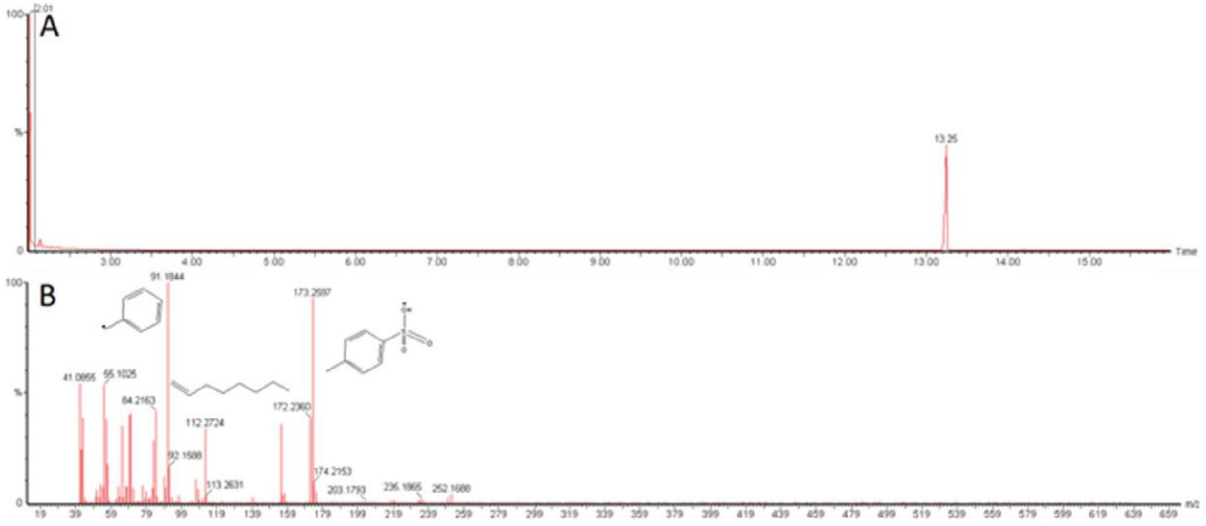

Figure S11. GC-MS chromatogram and mass spectrum of crude intermediate1-octyl-*p*-toluenesulphonate.

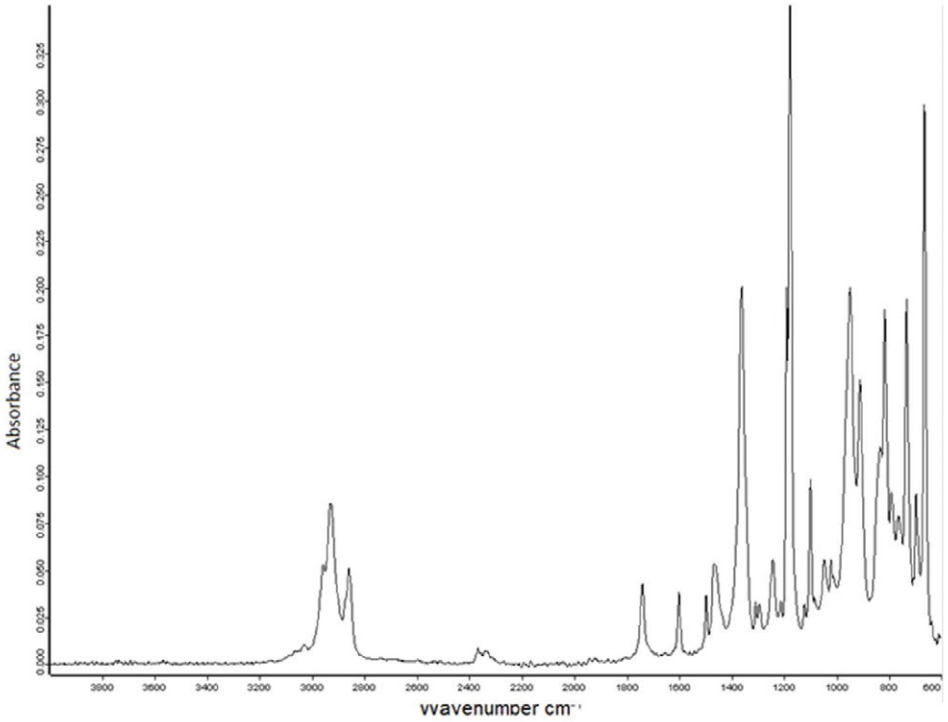

Figure S12. FTIR spectrum (ATR) of crude intermediate 1-octyl-*p*-toluenesulphonate.

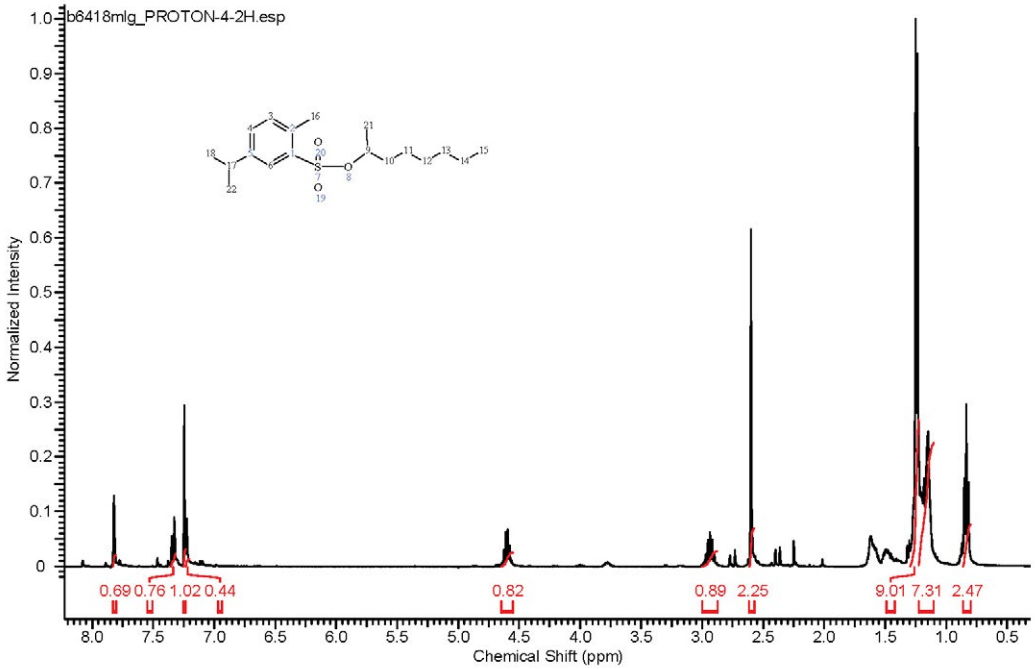

Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude intermediate 2-octyl-*p*-cymenesulphonate.

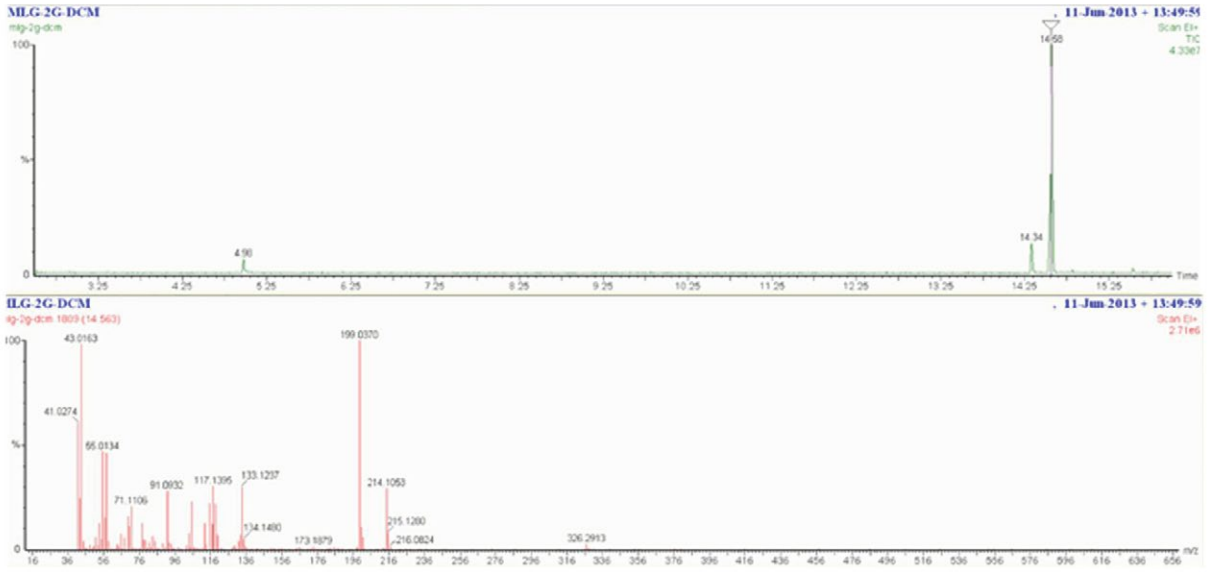

Figure S14. GC-MS chromatogram and mass spectrum of crude intermediate 2-octyl-*p*-cymenesulphonate.

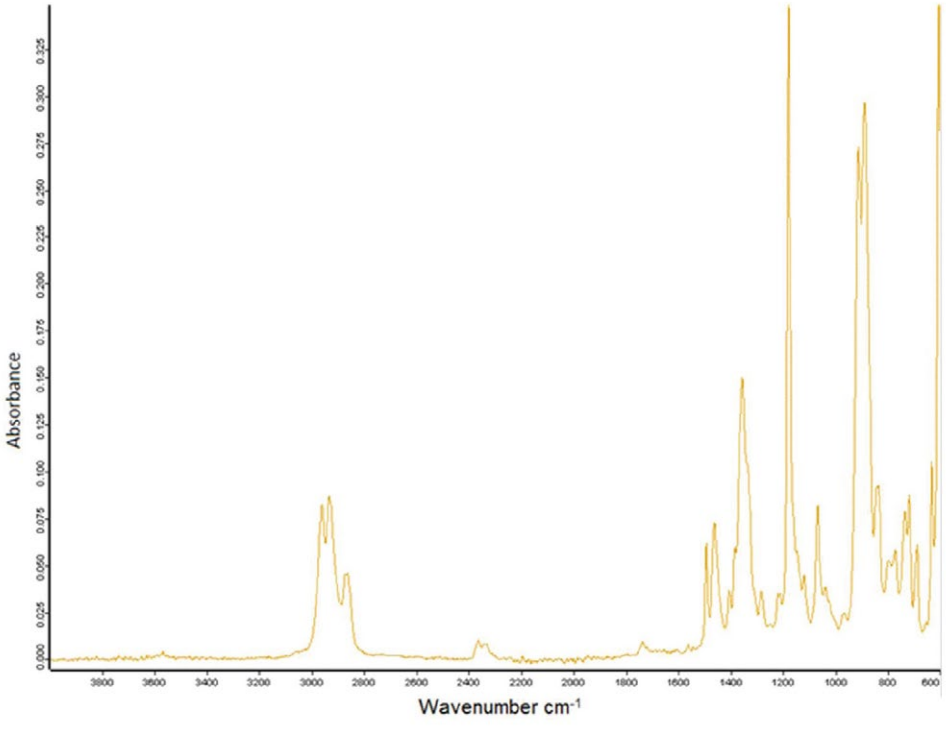

Figure S15. FTIR spectrum (ATR) of crude intermediate 2-octyl-*p*-cymenesulphonate.

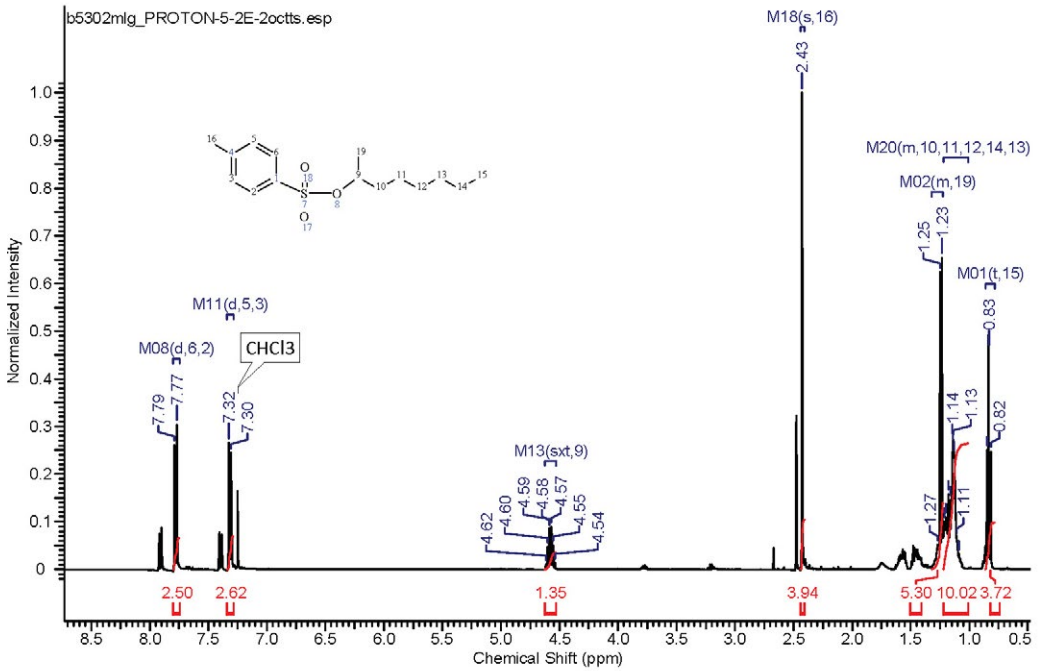

Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude intermediate 2-octyl-*p*-toluenesulphonate.

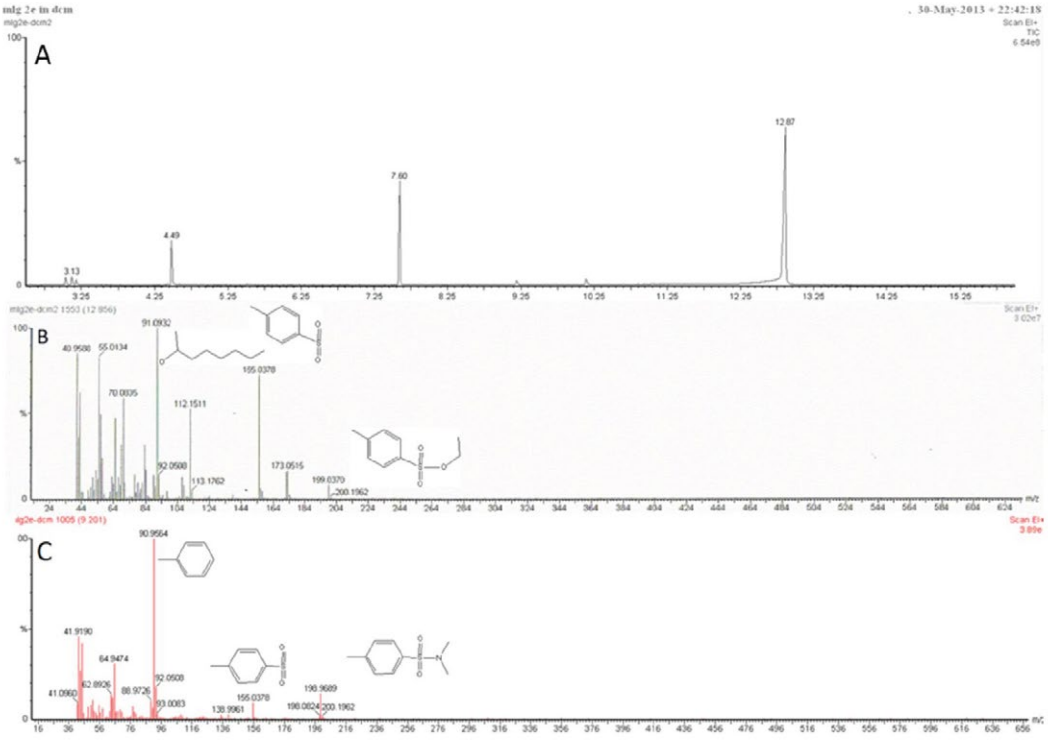

Figure S17. GC-MS chromatogram and mass spectrum of crude intermediate 2-octyl-*p*-toluenesulphonate.

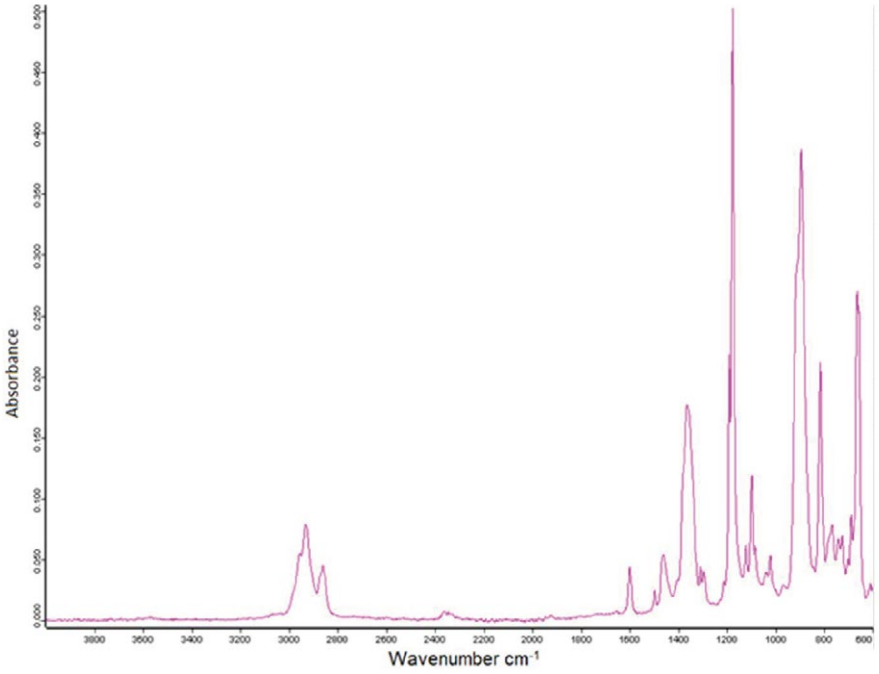

Figure S18. FTIR spectrum (ATR) of crude intermediate 2-octyl-*p*-toluenesulphonate.

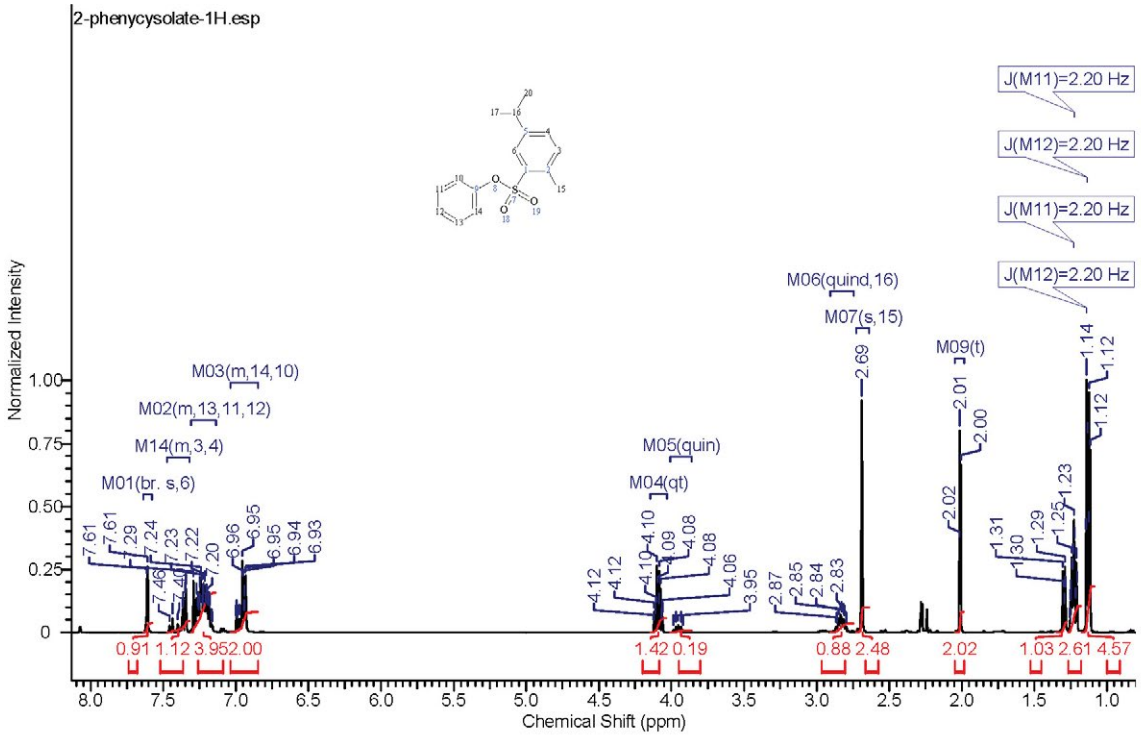

Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude intermediate phenyl-*p*-cymenesulphonate.

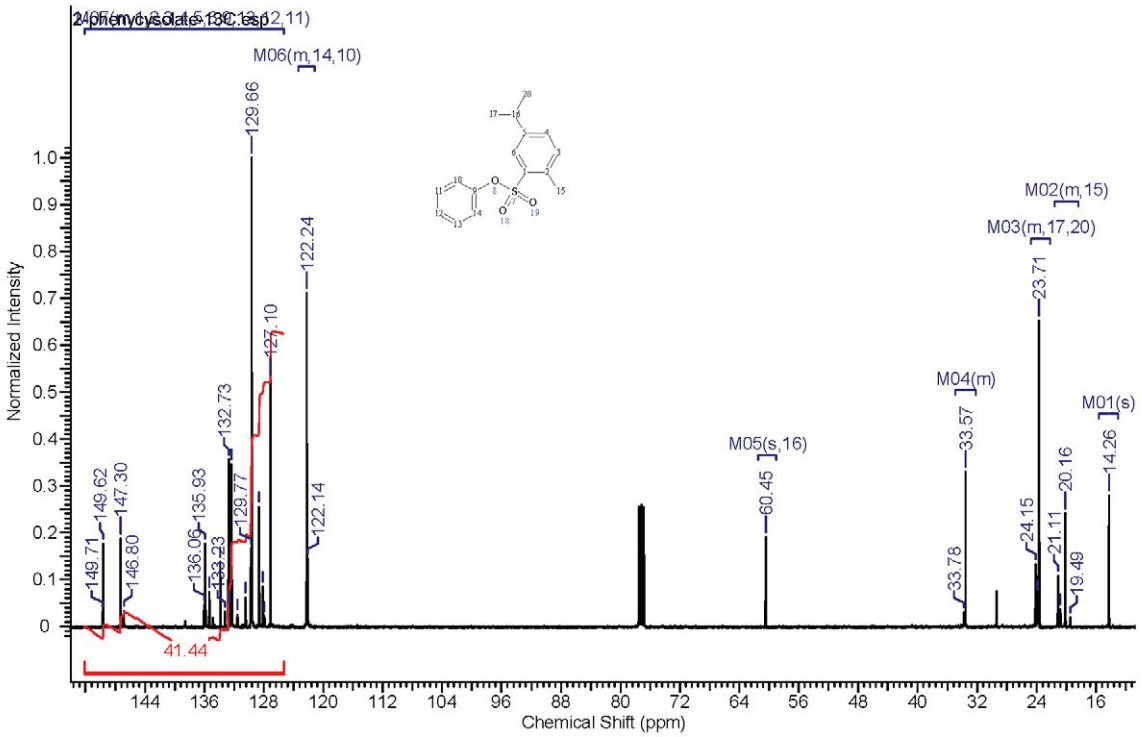

Figure S20. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of crude intermediate phenyl-*p*-cymenesulphonate.

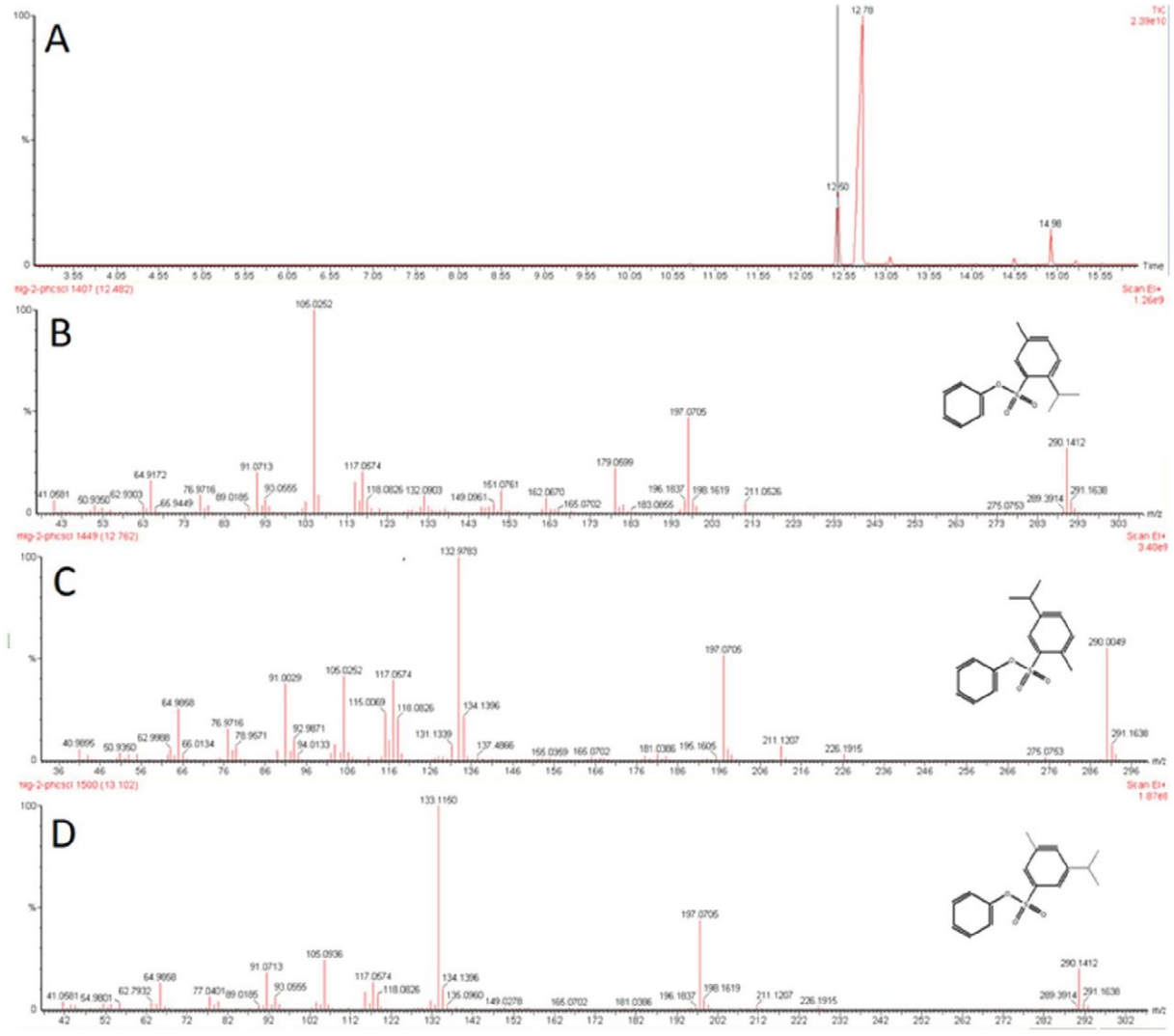

Figure S21. GC-MS chromatogram and mass spectra of crude intermediate phenyl-*p*-cymenesulphonate.

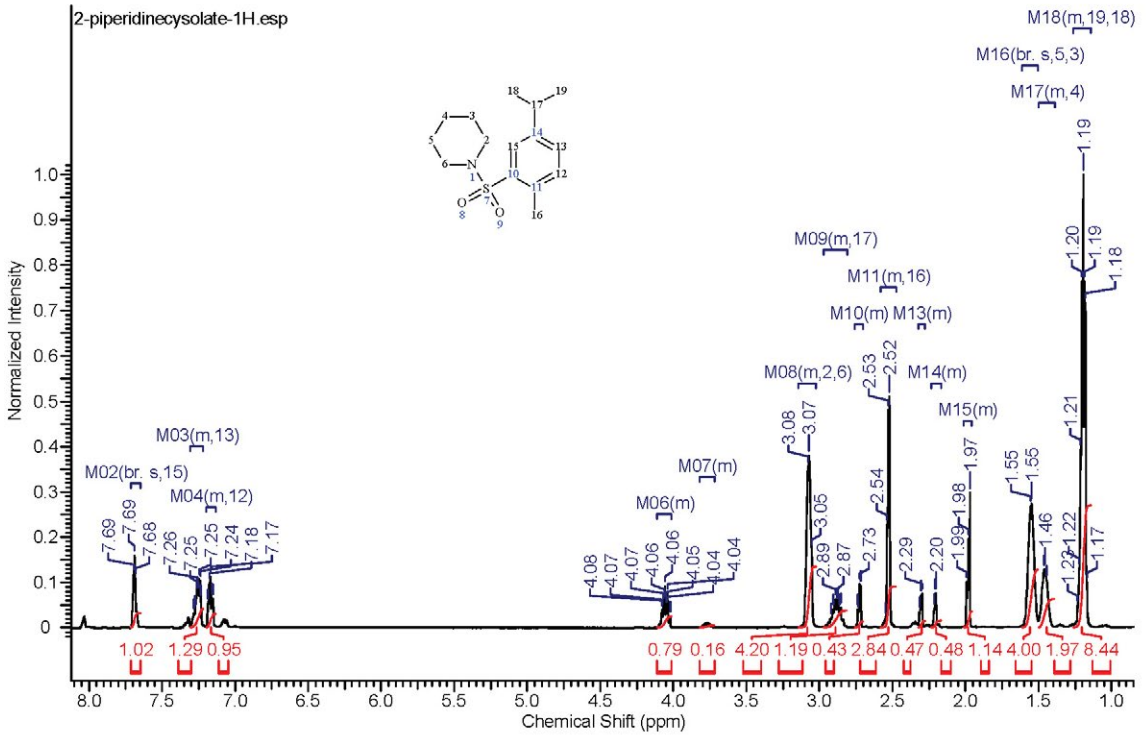

Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude intermediate *N*,*N*-1,5-pentylene-*p*-cymenesulphonamide.

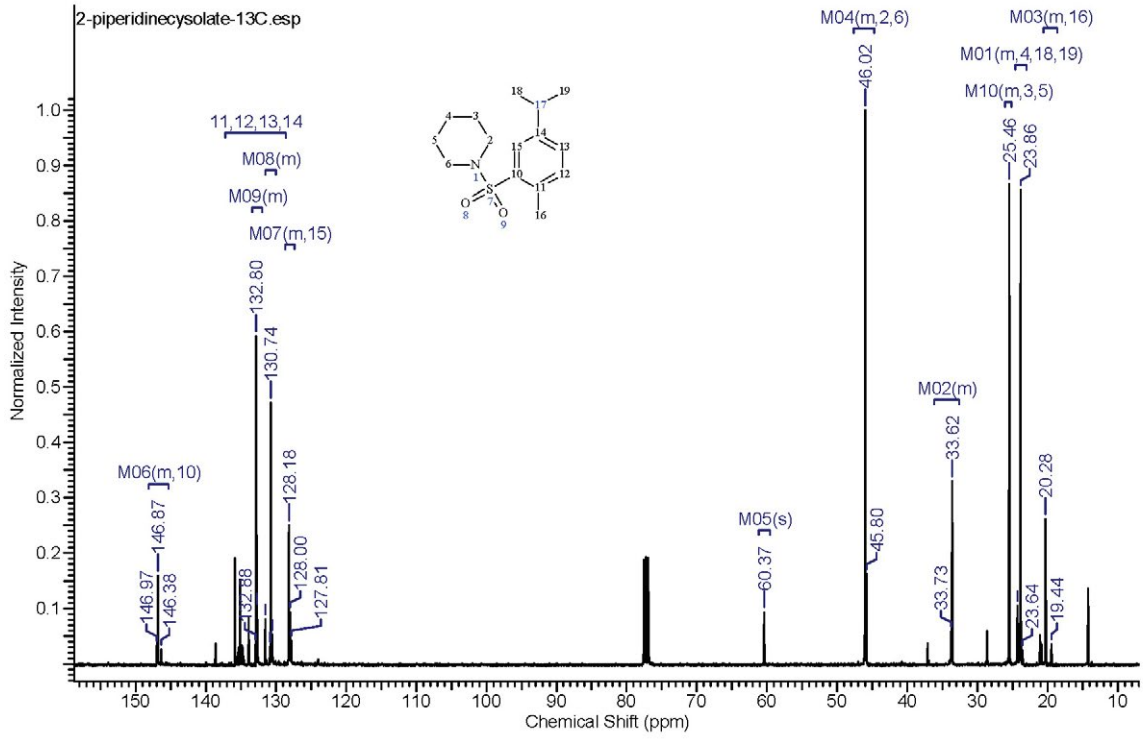

Figure S23. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of crude intermediate *N*,*N*-1,5-pentylene-*p*-cymenesulphonamide.

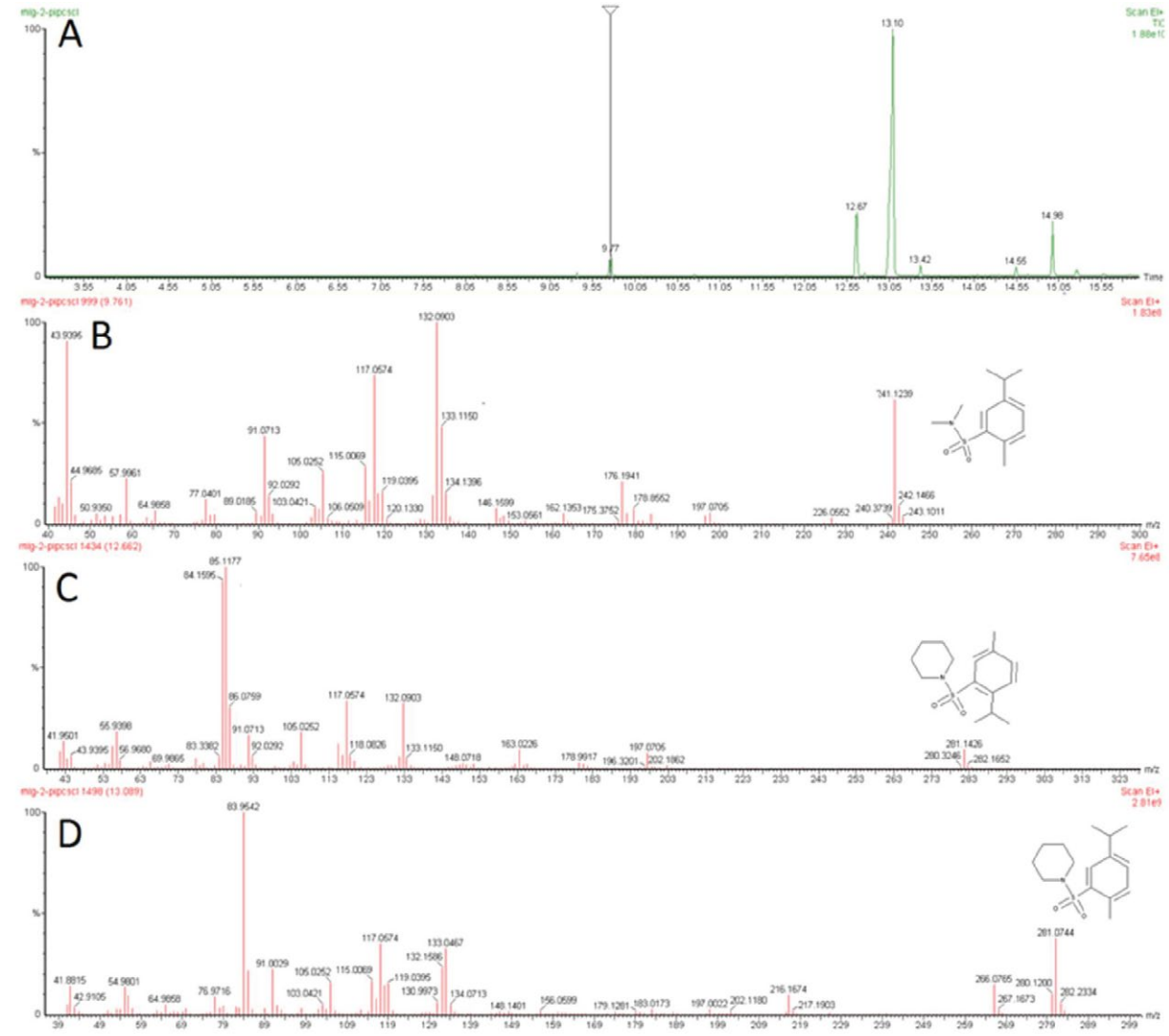

Figure S24. GC-MS chromatogram and mass spectra of crude intermediate *N*,*N*-1,5-pentylene-*p*-cymenesulphonamide.

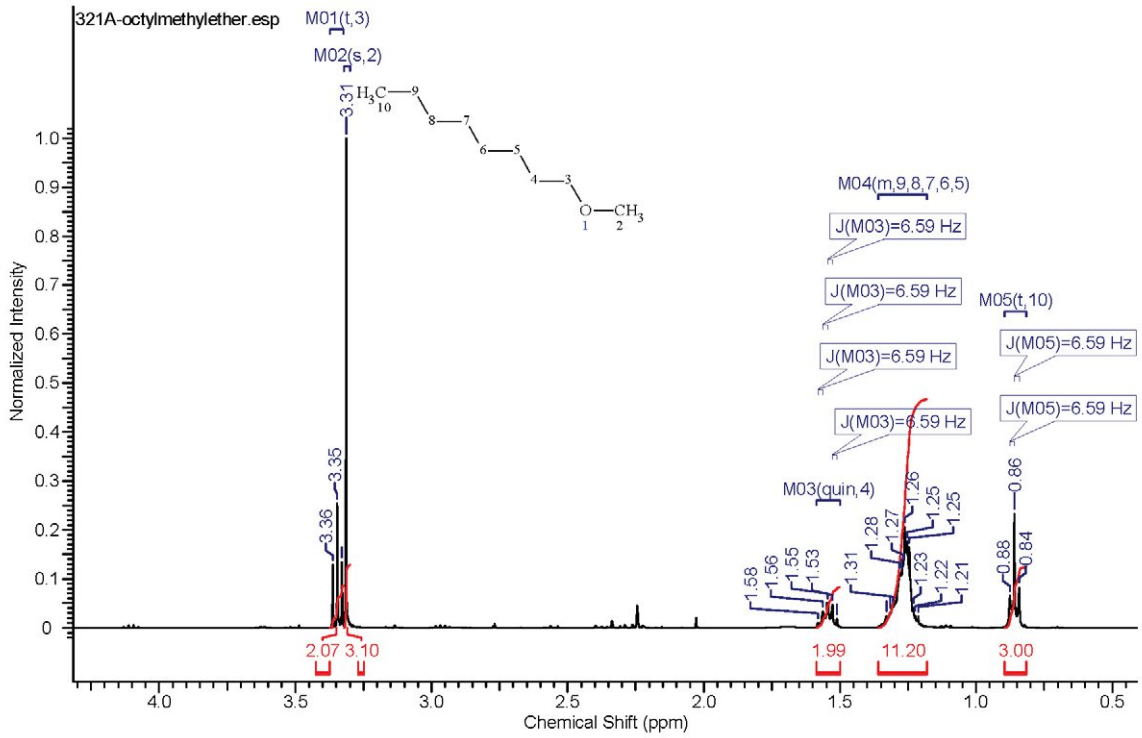

Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1-octyl methyl ether (made from 1-octyl-*p*-cymenesulphonate).

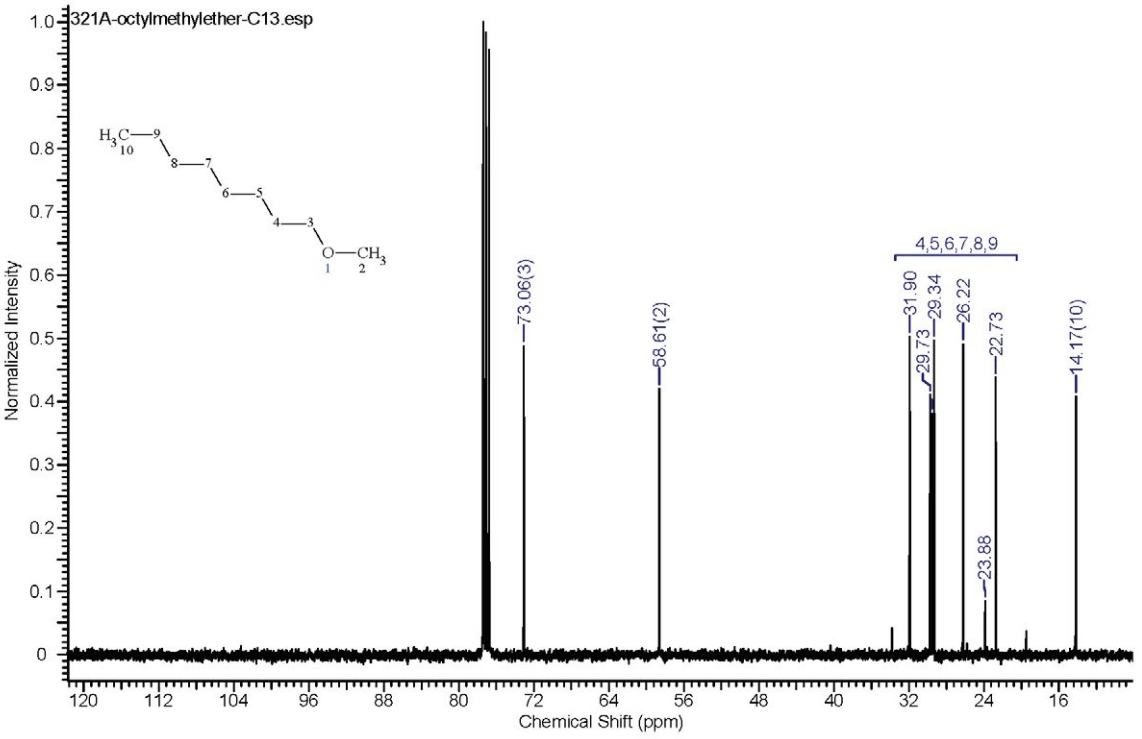

Figure S26. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 1-octyl methyl ether (made from 1-octyl-*p*-cymenesulphonate).

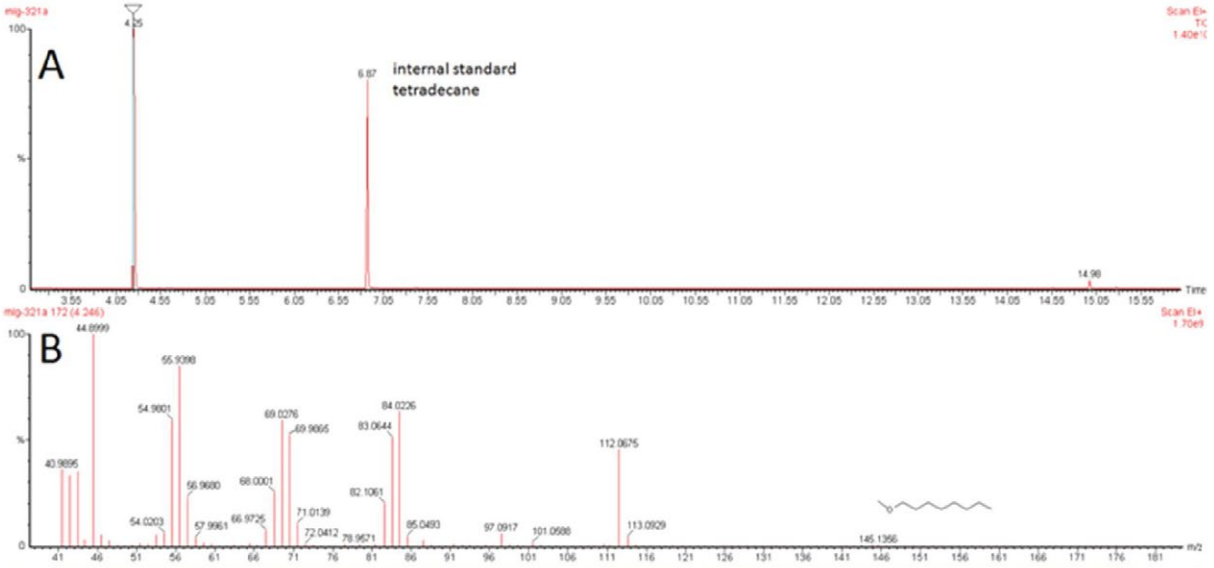

Figure S27. GC-MS chromatogram and mass spectrum of 1-octyl methyl ether (made from 1-octyl-*p*-cymenesulphonate).

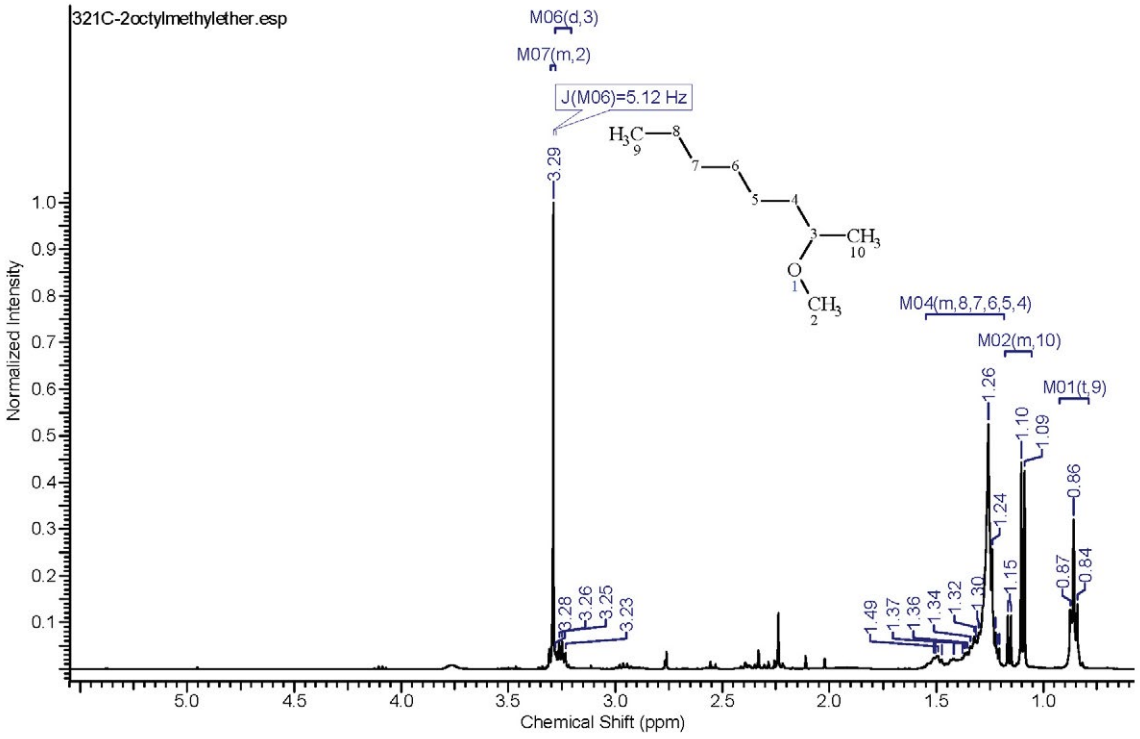

Figure S28. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-octyl methyl ether (made from 2-octyl-*p*-cymenesulphonate).

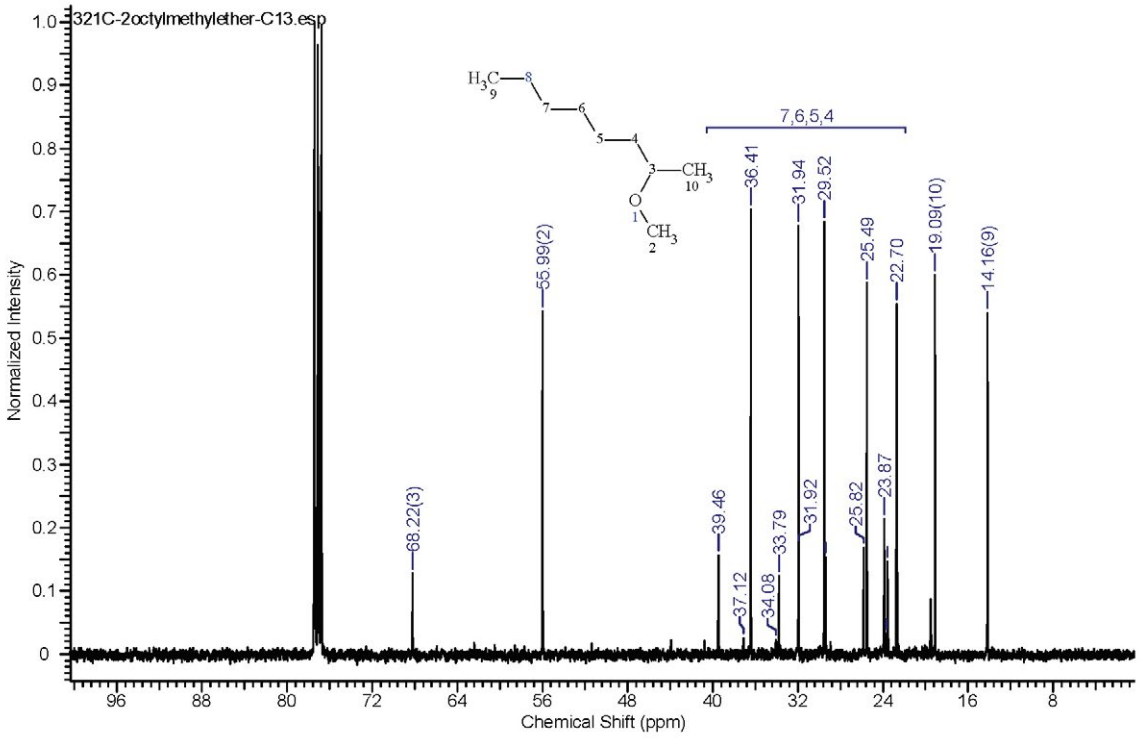

Figure S29. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of 2-octyl methyl ether (made from 2-octyl-*p*-cymenesulphonate).

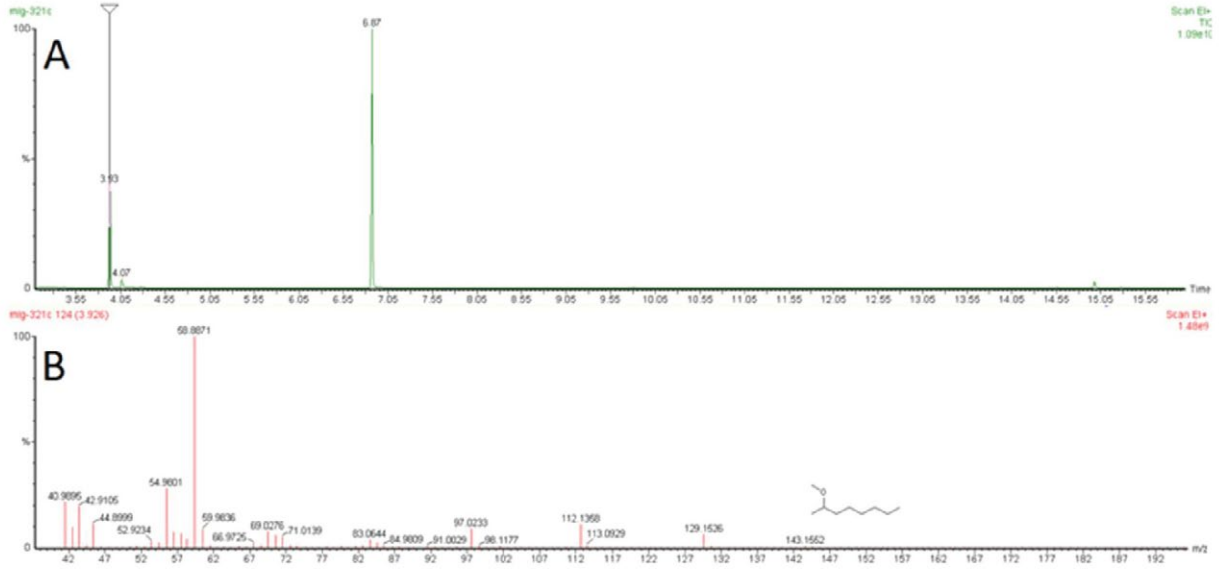

Figure S30. GC-MS chromatogram and mass spectrum of 2-octyl methyl ether (made from 2-octyl-*p*-cymenesulphonate).

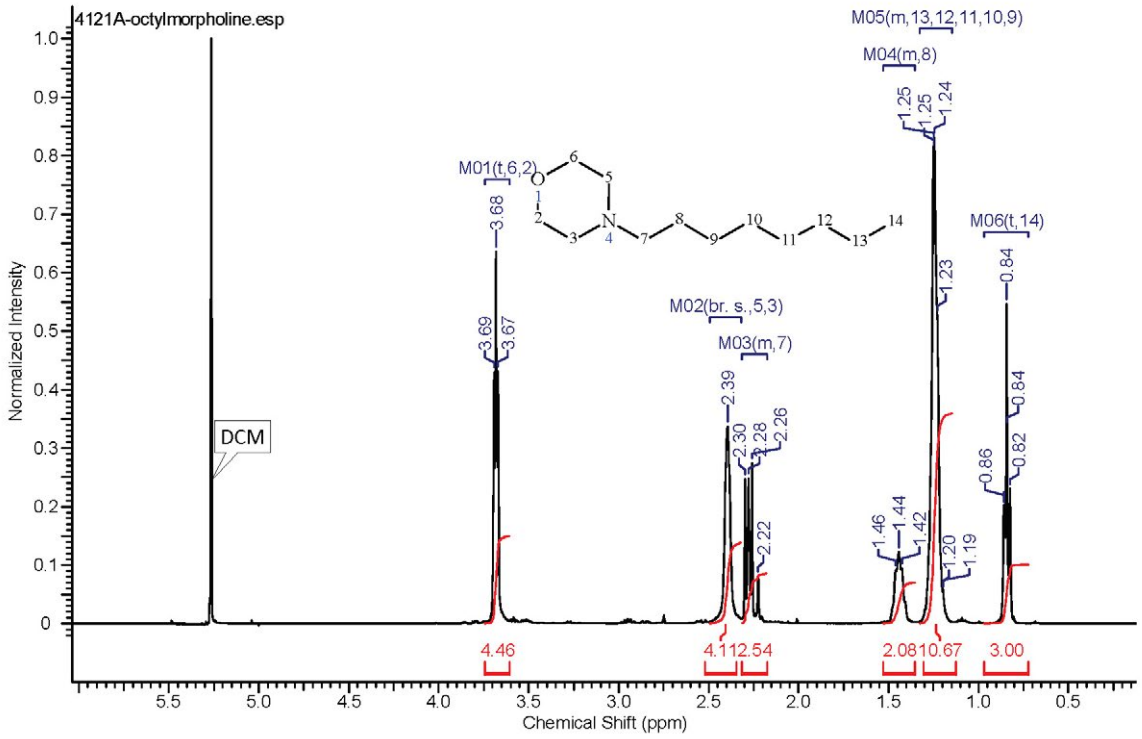

Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-1-octyl morpholine (made from 1-octyl-*p*-cymenesulphonate).

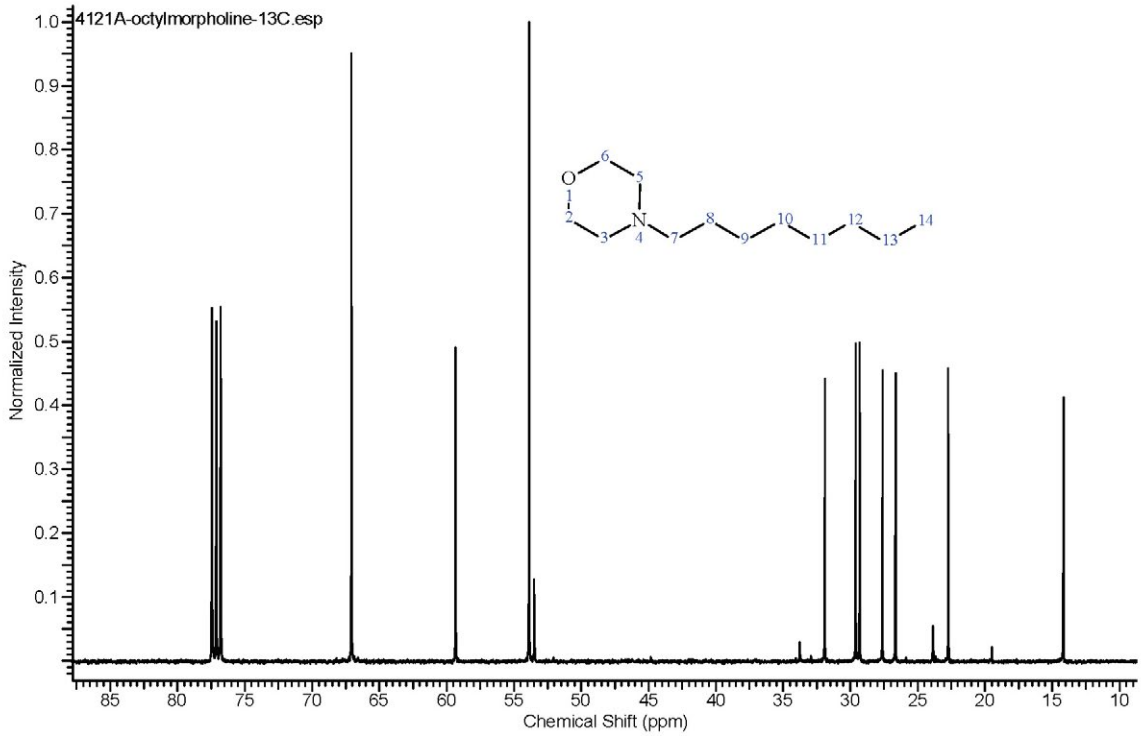

Figure S32. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of *N*-1-octyl morpholine (made from 1-octyl-*p*-cymenesulphonate).

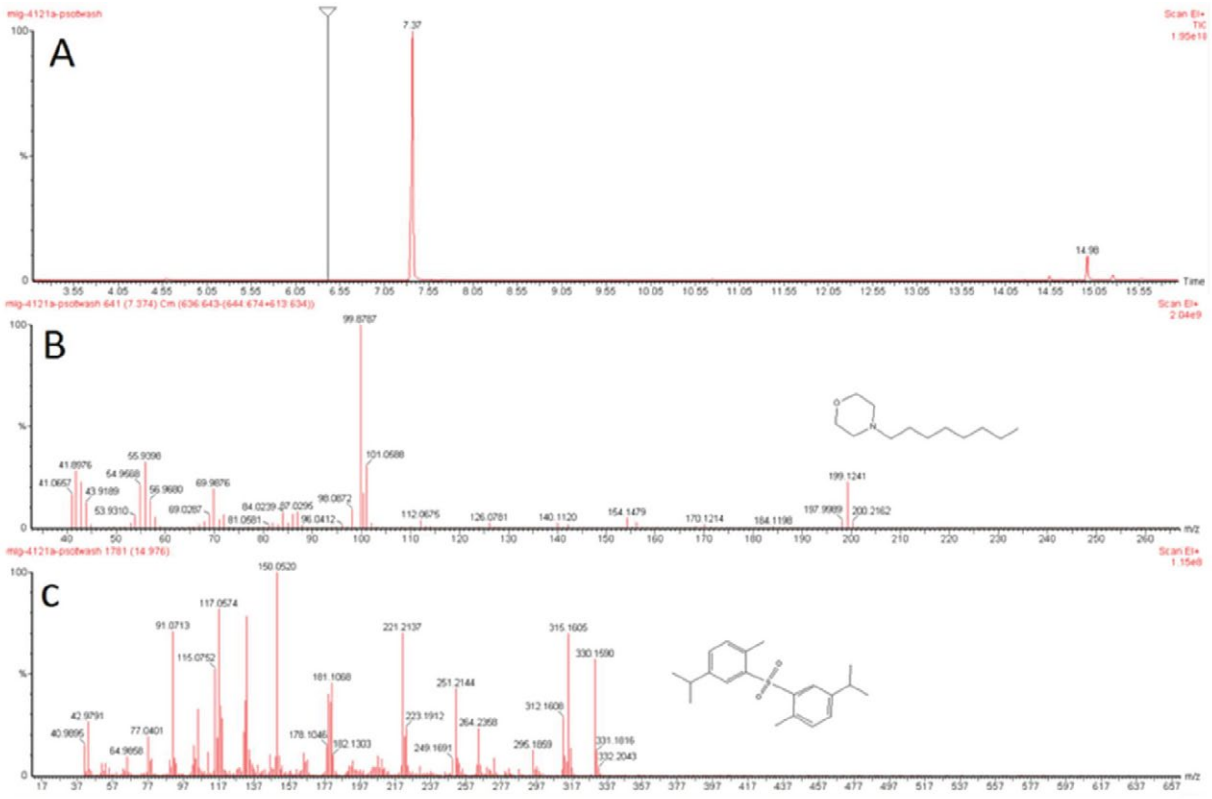

Figure S33. GC-MS chromatogram and mass spectrum of *N*-1-octyl morpholine (made from 1-octyl-*p*-cymenesulphonate).

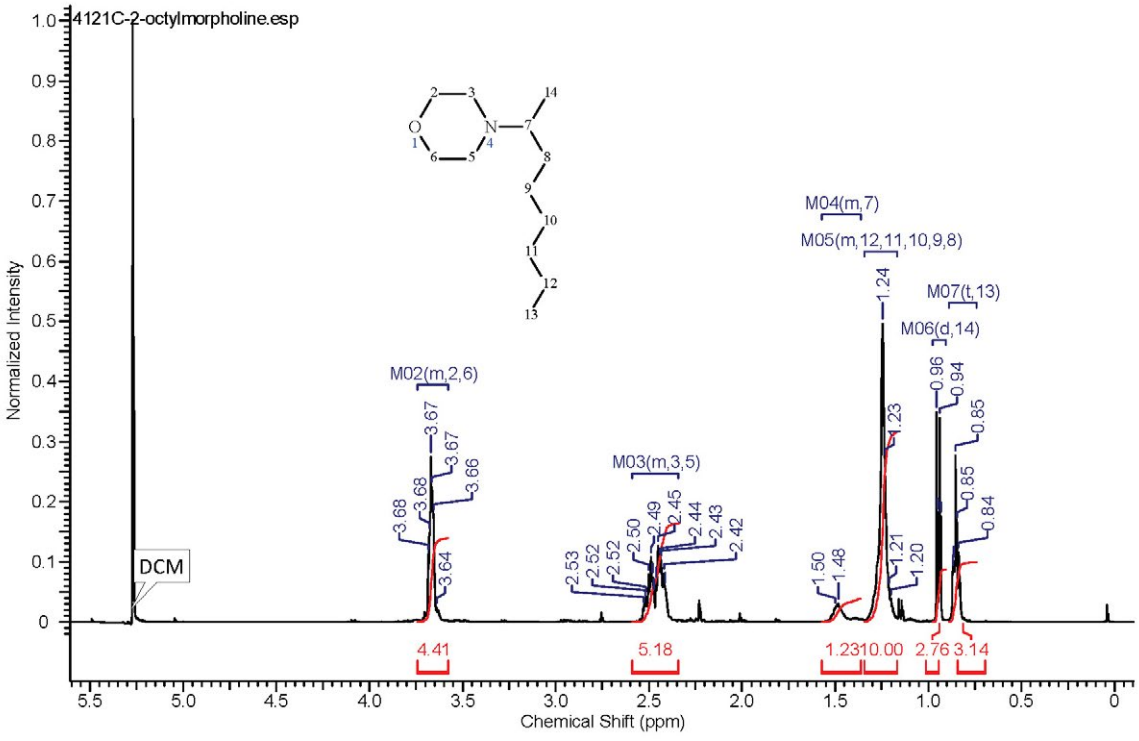

Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-2-octyl morpholine (made from 2-octyl-*p*-cymenesulphonate).

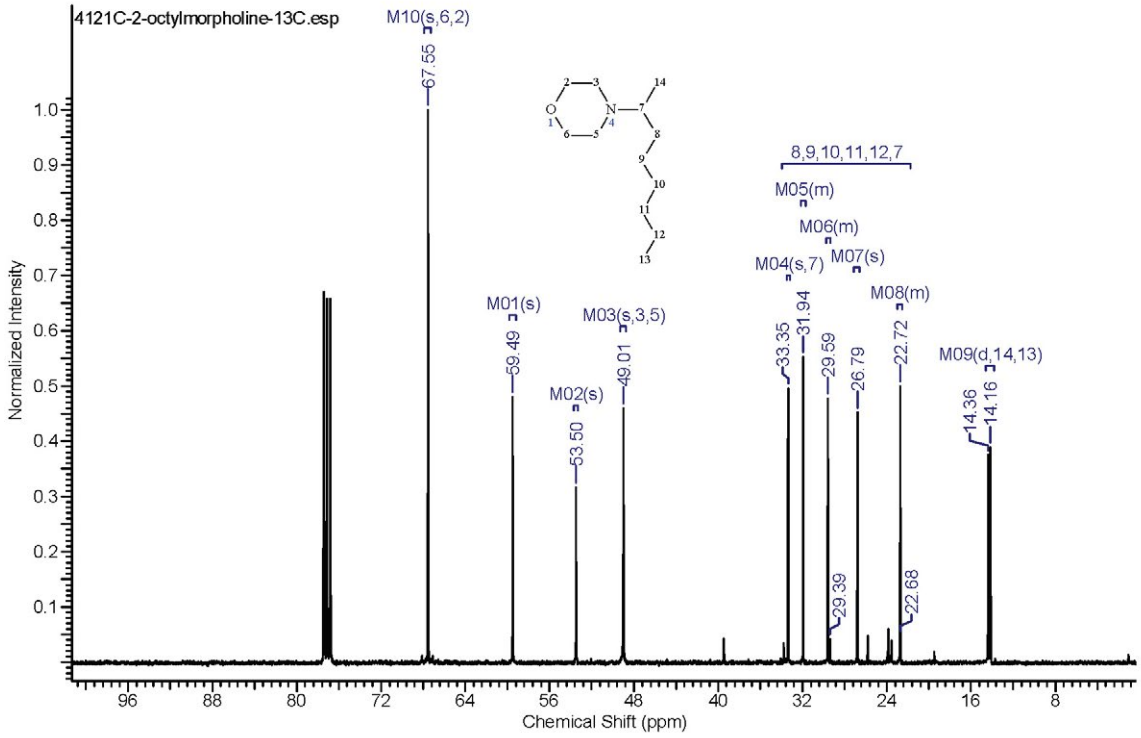

Figure S35. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of *N*-2-octyl morpholine (made from 2-octyl-*p*-cymenesulphonate).

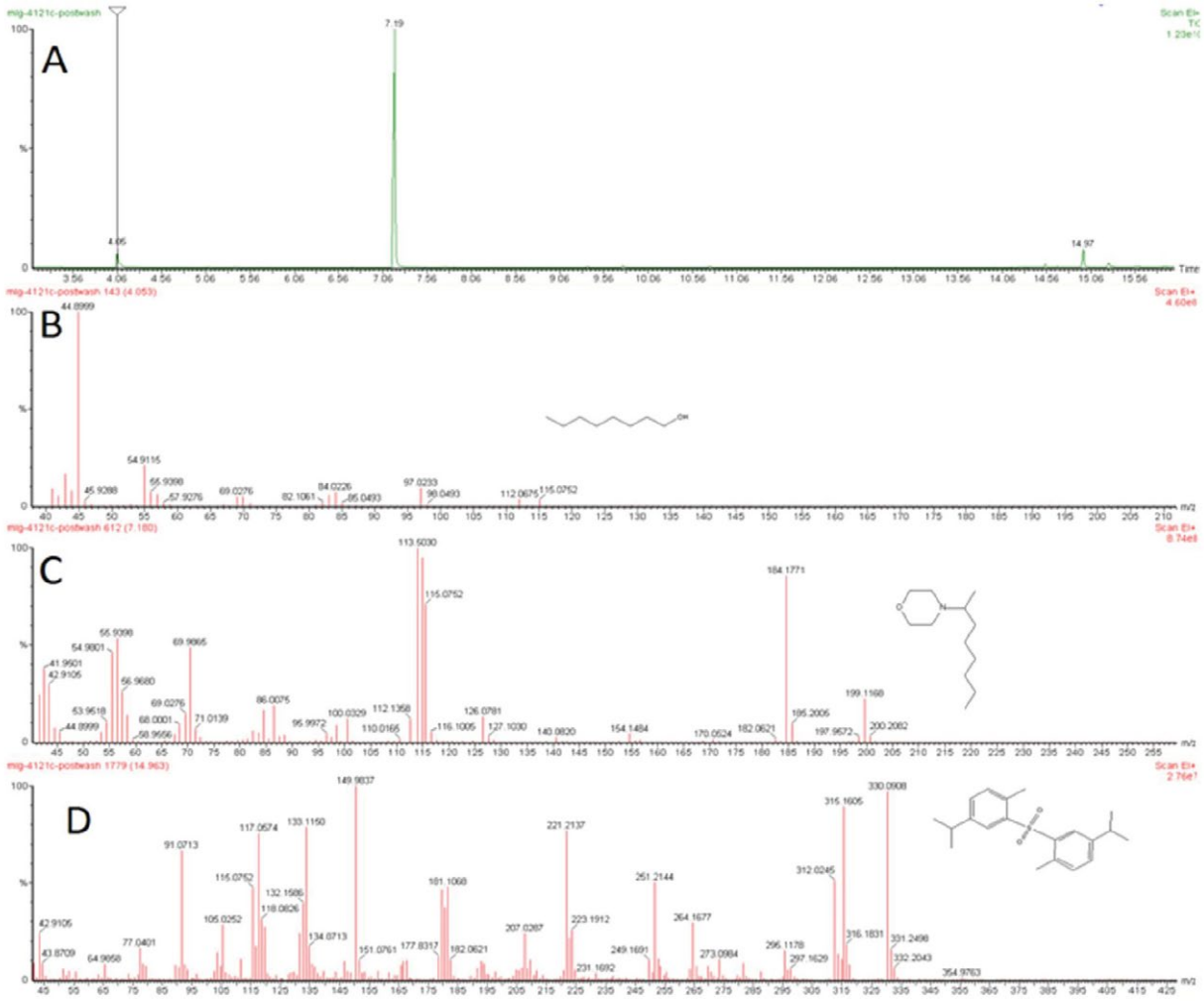

Figure S36. GC-MS chromatogram and mass spectrum of *N*-2-octyl morpholine (made from 2-octyl-*p*-cymenesulphonate).