Supplementary Information for

Simple low cost porphyrinic photosensitizers for large scale chemoselective oxidation of sulfides to sulfoxides under green conditions: Targeted protonation of porphyrins

Aida G. Mojarrad and Saeed Zakavi*

[a]Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran. E-mail: zakavi@iasbs.ac.ir

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S1a: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data for H_2TPP.

H_2TPP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.77 (2H, br, s, NH), 7.77-7.84 (8H_m and 4H_p, m), 8.26-8.27 (8H_o, d), 8.90 (8H_β, s); ^{13}C NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 120.18 (C_{meso}), 142.20 (C_1), 134.60 (C_2, C_6), 126.73 (C_3, C_5), 127.75 (C_4), 131.5 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 417 (5.79), 513 (4.58), 548 (4.38), 590 (4.30), 647 (4.29).

S1b: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data for $H_4TPP(CF_3COO)_2$.

$H_4TPP(CF_3COO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 0.276 (4H, br, s, NH), 7.99-8.043 (8H_m and 4H_p, m), 8.616-8.652 (8H_o, m), 8.616-8.652 (8H_β, m); ^{13}C NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 122.77 (C_{meso}), 139.90 (C_1), 138.52 (C_2, C_6), 128.31 (C_3, C_5), 130.01 (C_4), 145.72 (C_α), 128.31 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 437 (5.83), 600 (4.46), 652 (4.93).

S1c: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data for $H_4TPP(Cl_2CHCOO)_2$.

$H_4TPP(Cl_2CHCOO)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.99-8.07 (8H_m and 4H_p, m), 8.64-8.66 (8H_o, m), 8.71 (8H_β, s), -0.41 (4H, br, s, NH); ^{13}C NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 123.16 (C_{meso}), 139.57 (C_1), 138.62 (C_2, C_6), 128.96 (C_3, C_5), 130.34 (C_4), 145.78 (C_α), 128.56 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 439 (4.59), 600 (3.30), 652 (3.73).

S1d: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data for $H_4TPP(ClO_4)_2$.

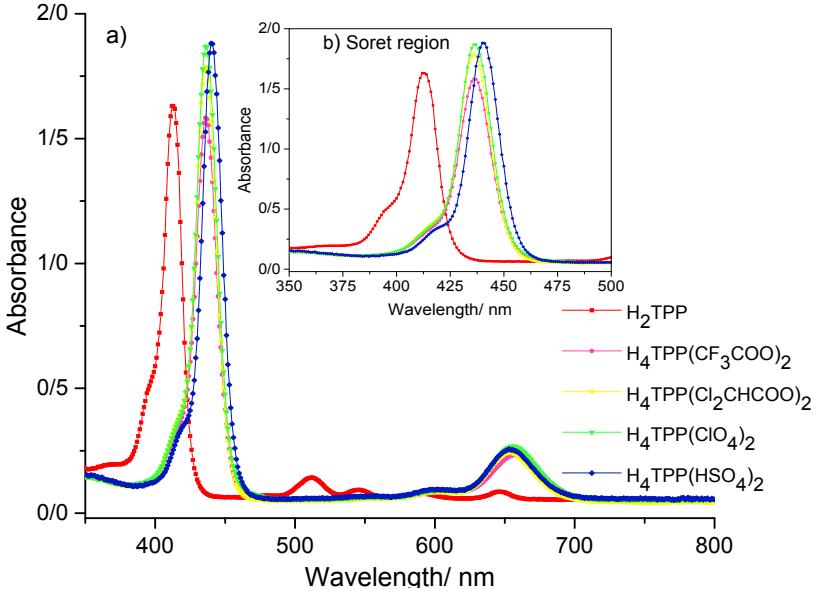
$H_4TPP(ClO_4)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 8.021-8.098 (8H_m and 4H_p, m), 8.65-8.67 (8H_o, d), 8.838 (8H_β, s), no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (400MHz, $CDCl_3$,

TMS), δ/ppm: 123.38 (C_{meso}), 139.50 (C_1), 138.72 (C_2, C_6), 128.56 (C_3, C_5), 130.46 (C_4), 146.21 (C_α), 129.76(C_β); UV-vis in CH_2Cl_2, λ_{max}/nm(logε): 439 (4.64), 600 (3.36), 655 (3.79).

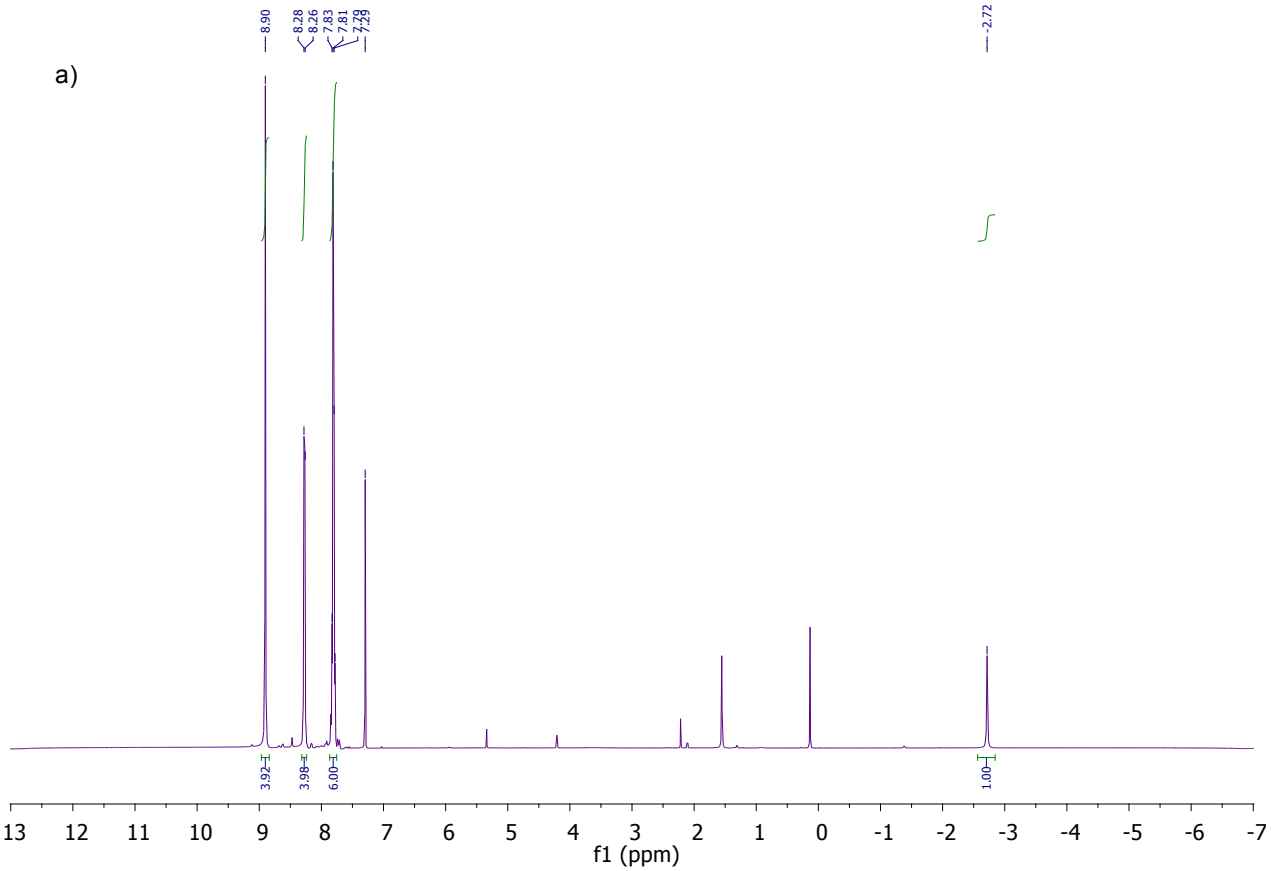
S1e: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data for $H_4TPP(HSO_4)_2$.

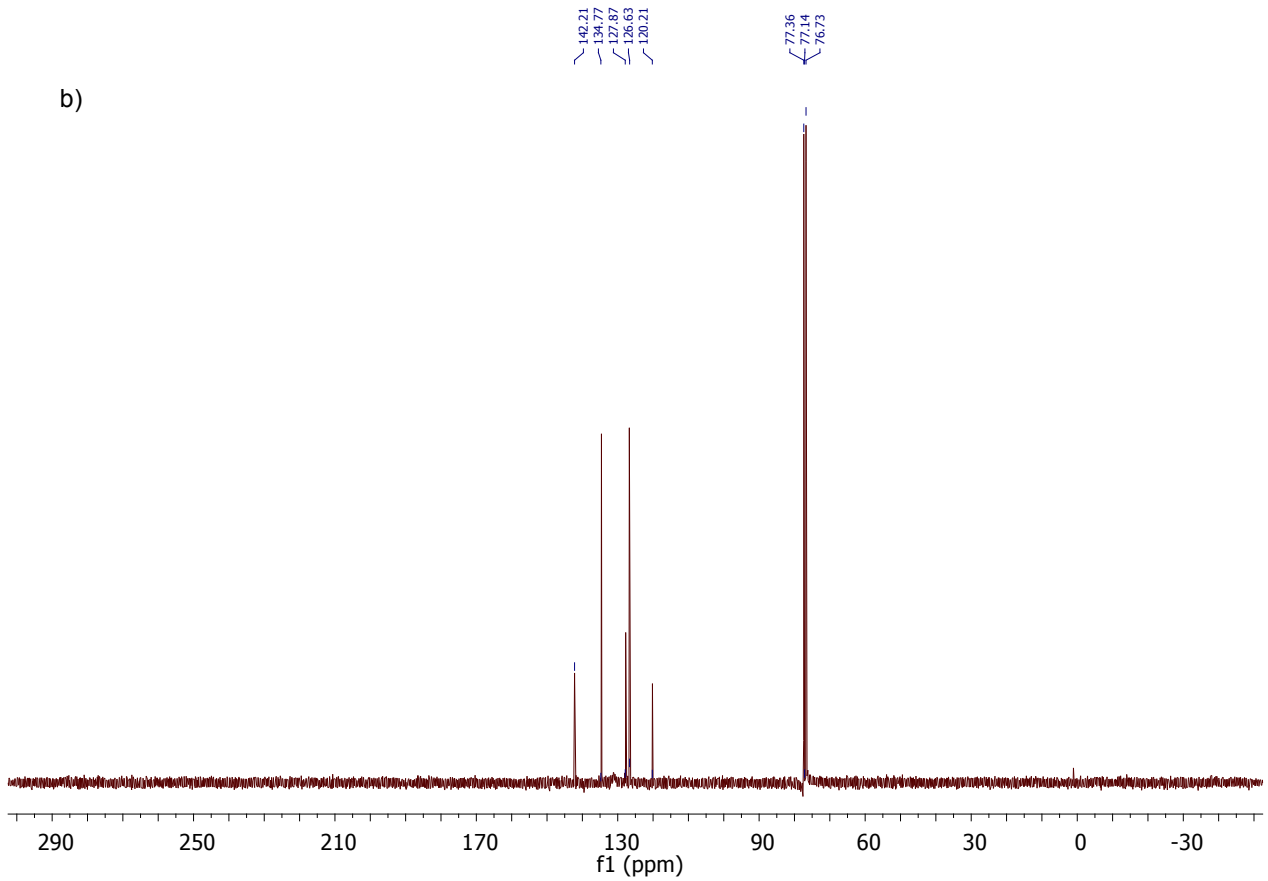
$H_4TPP(HSO_4)_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.984-8.074 ($8H_m$ and $4H_p$, m), 8.626-8.663 ($8H_o$, m), 8.626-8.663 ($8H_\beta$, m), no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 122.63 (C_{meso}), 139.93 (C_1), 139.05 (C_2, C_6), 128.12 (C_3, C_5), 130.01 (C_4), 146.05 (C_α), 128.40(C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 445 (5.70), 611 (3.43), 662 (3.77).

S2: UV-Vis spectra of H_2TPP and diacid species with CF_3COOH, $Cl_2CHCOOH$, $HClO_4$ and H_2SO_4.

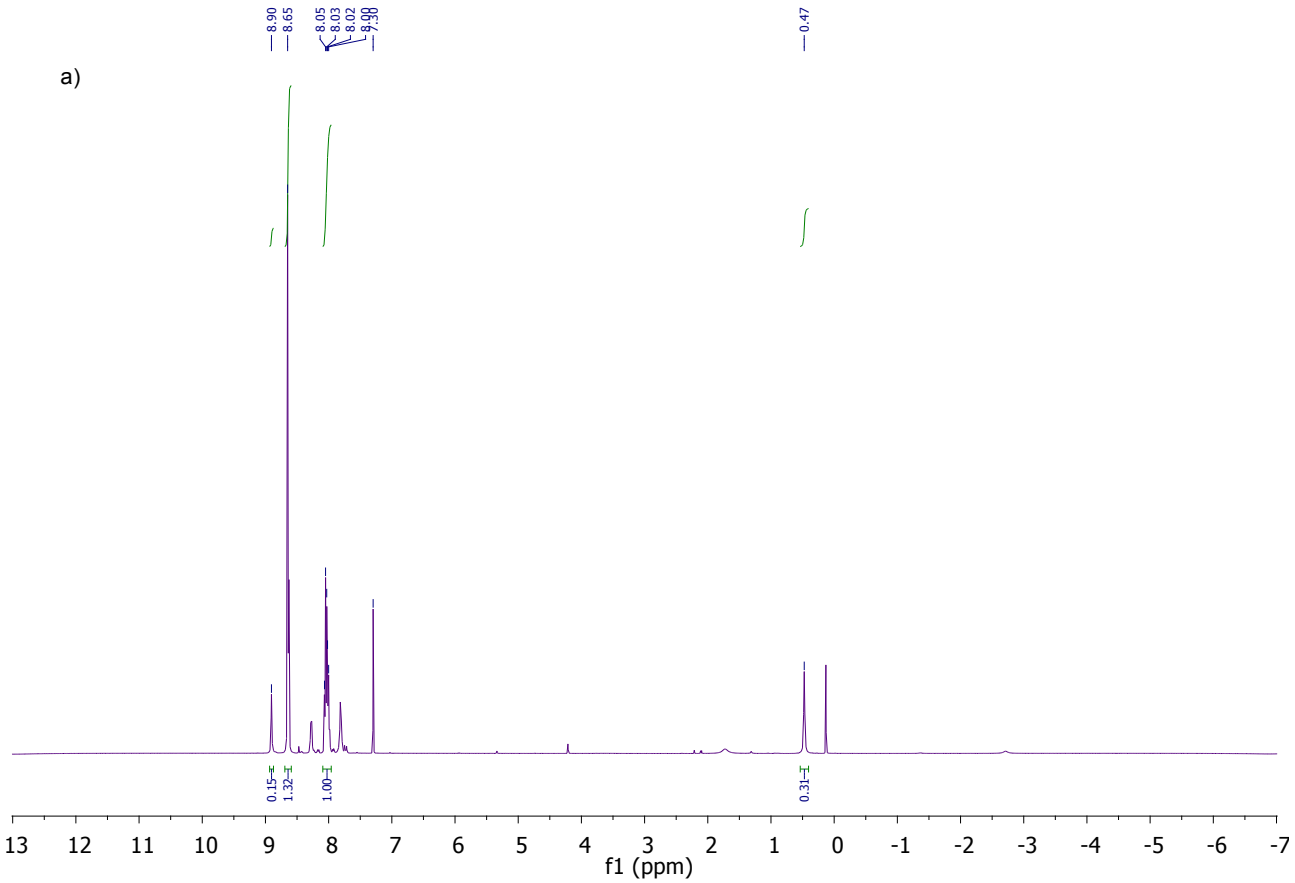


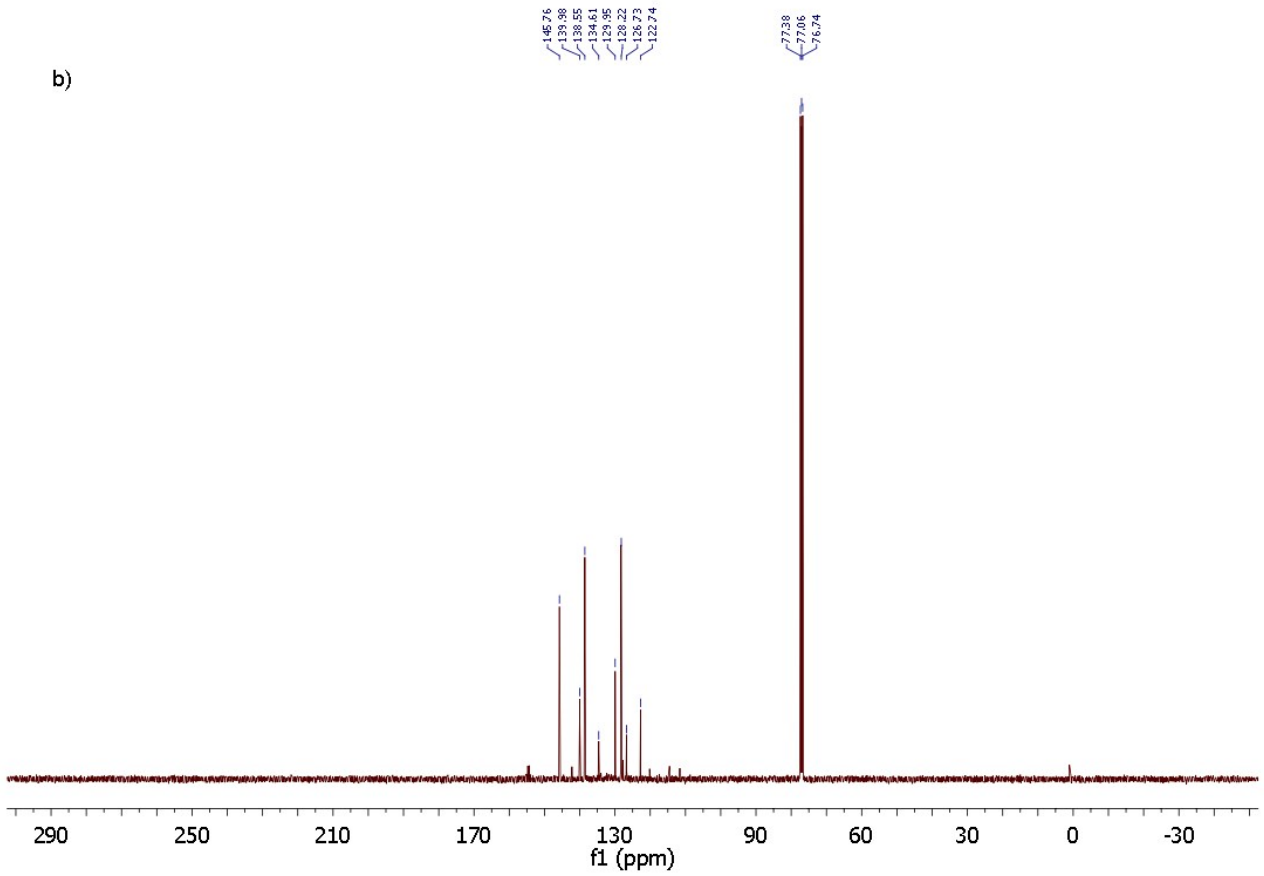
S3 (a,b): ^{1}H NMR and ^{13}C NMR spectra of H_2TPP.



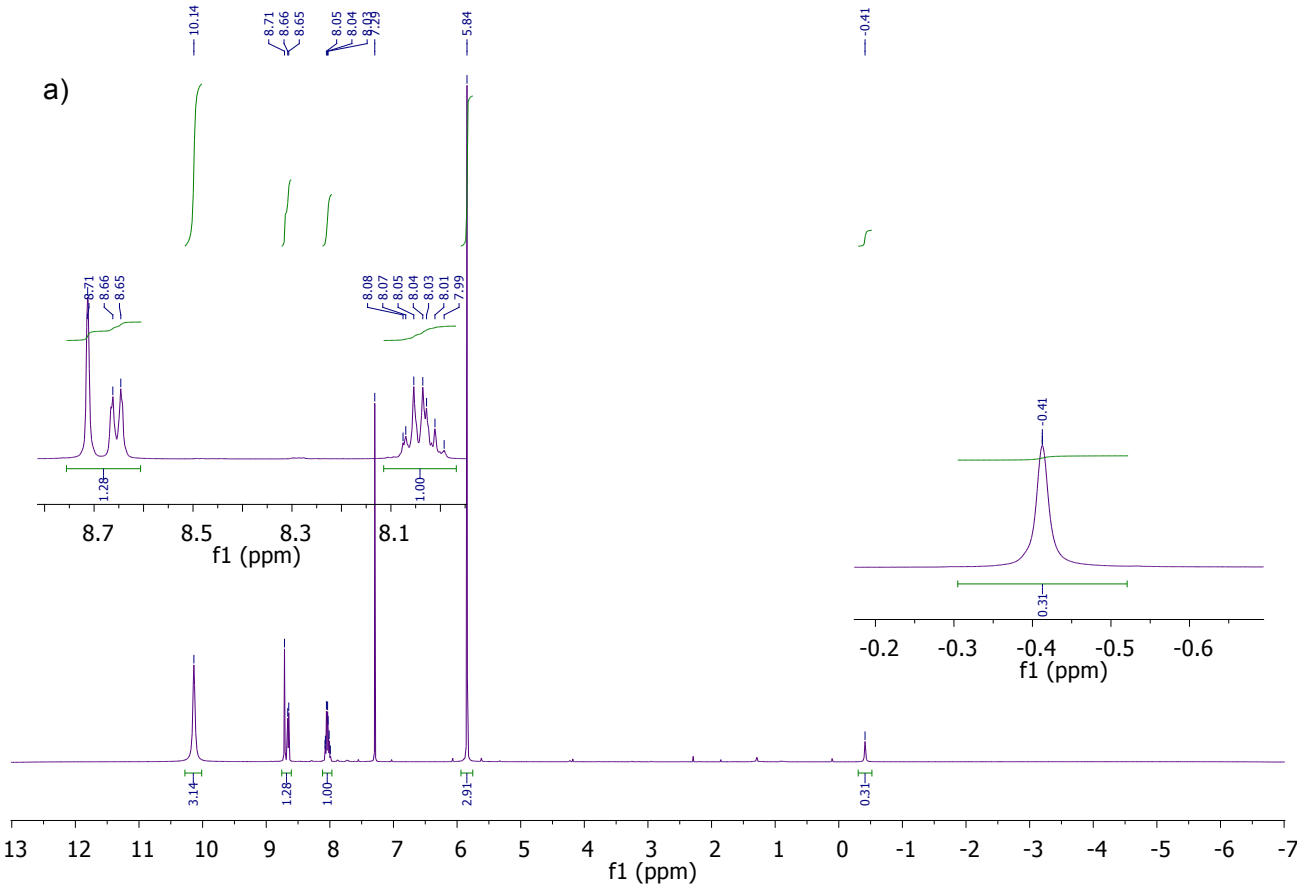


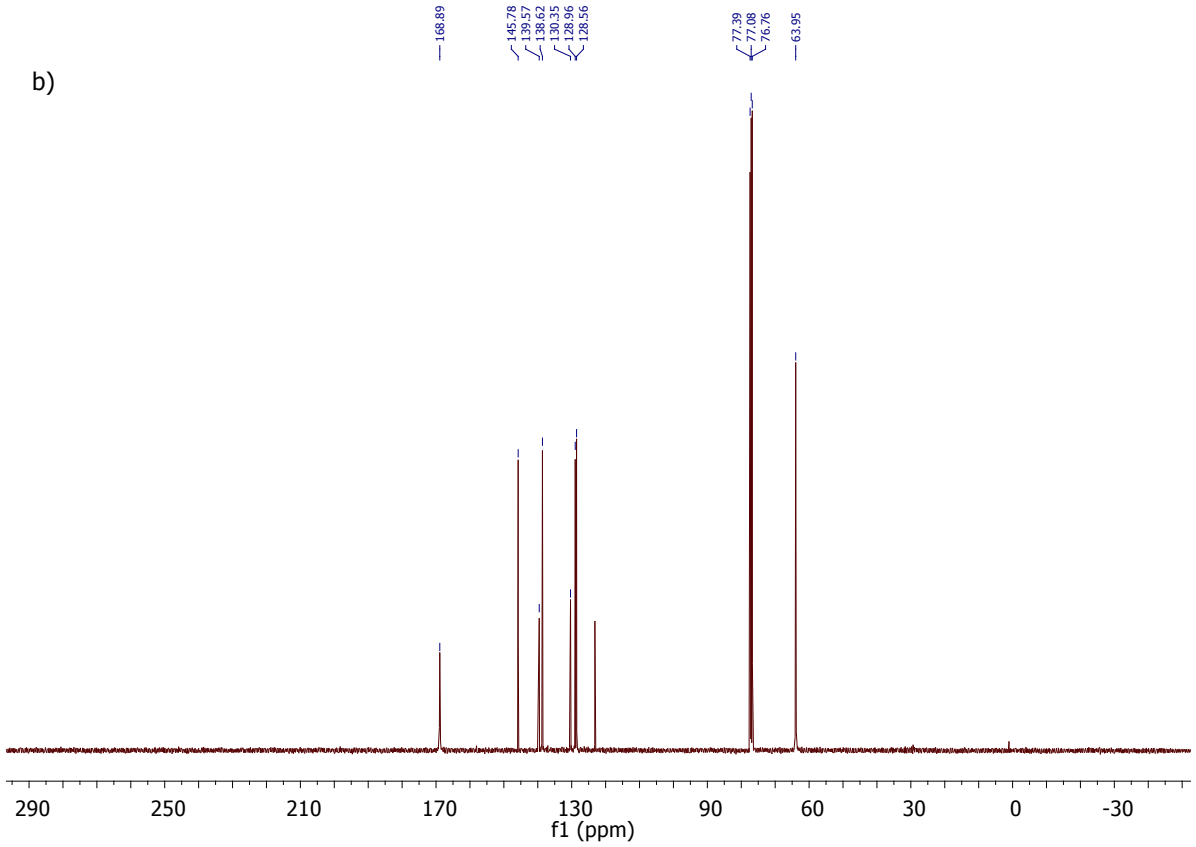
S4 (a,b): ^{1}H NMR and ^{13}C NMR spectra of $H_4TPP(CF_3COO)_2$.



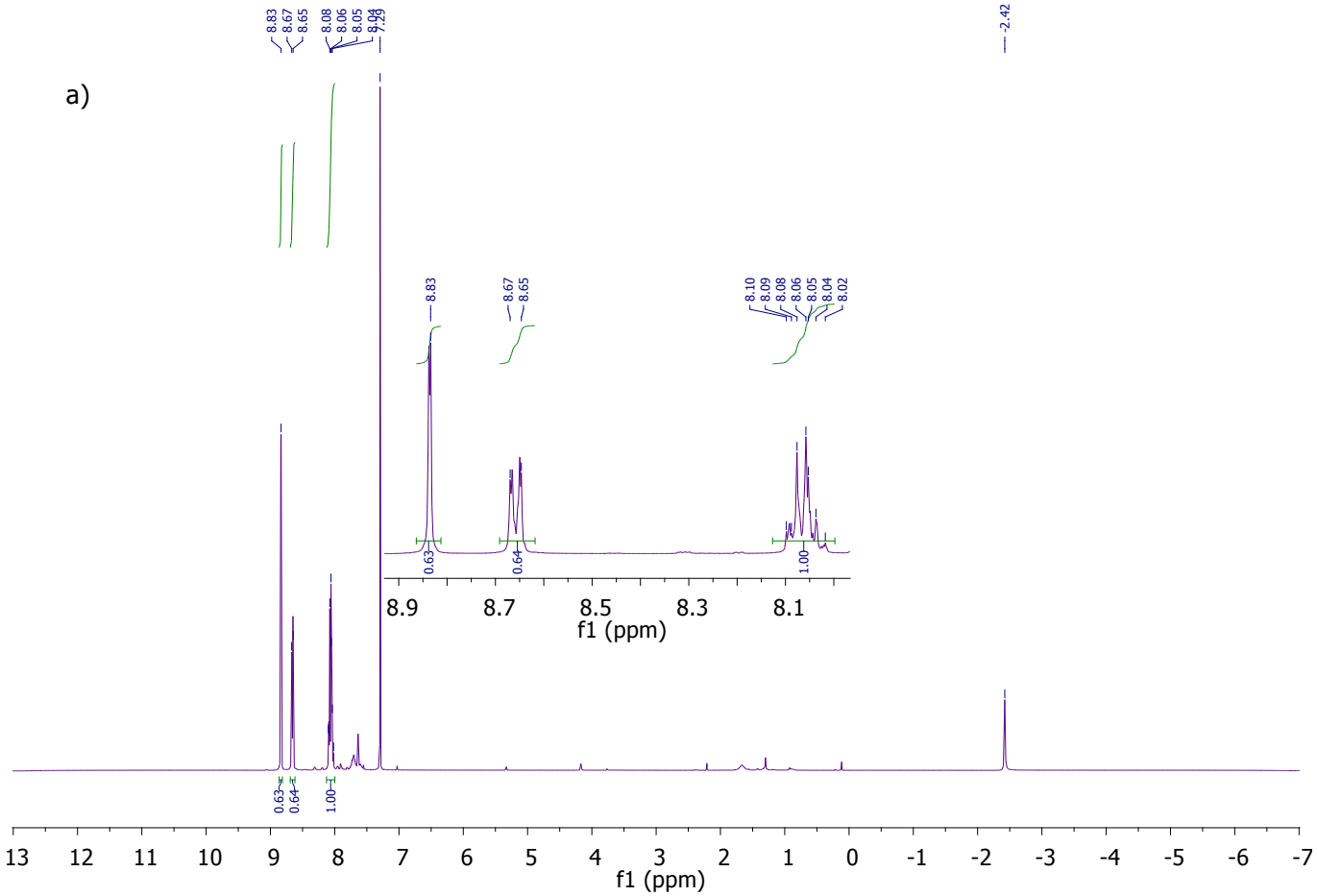


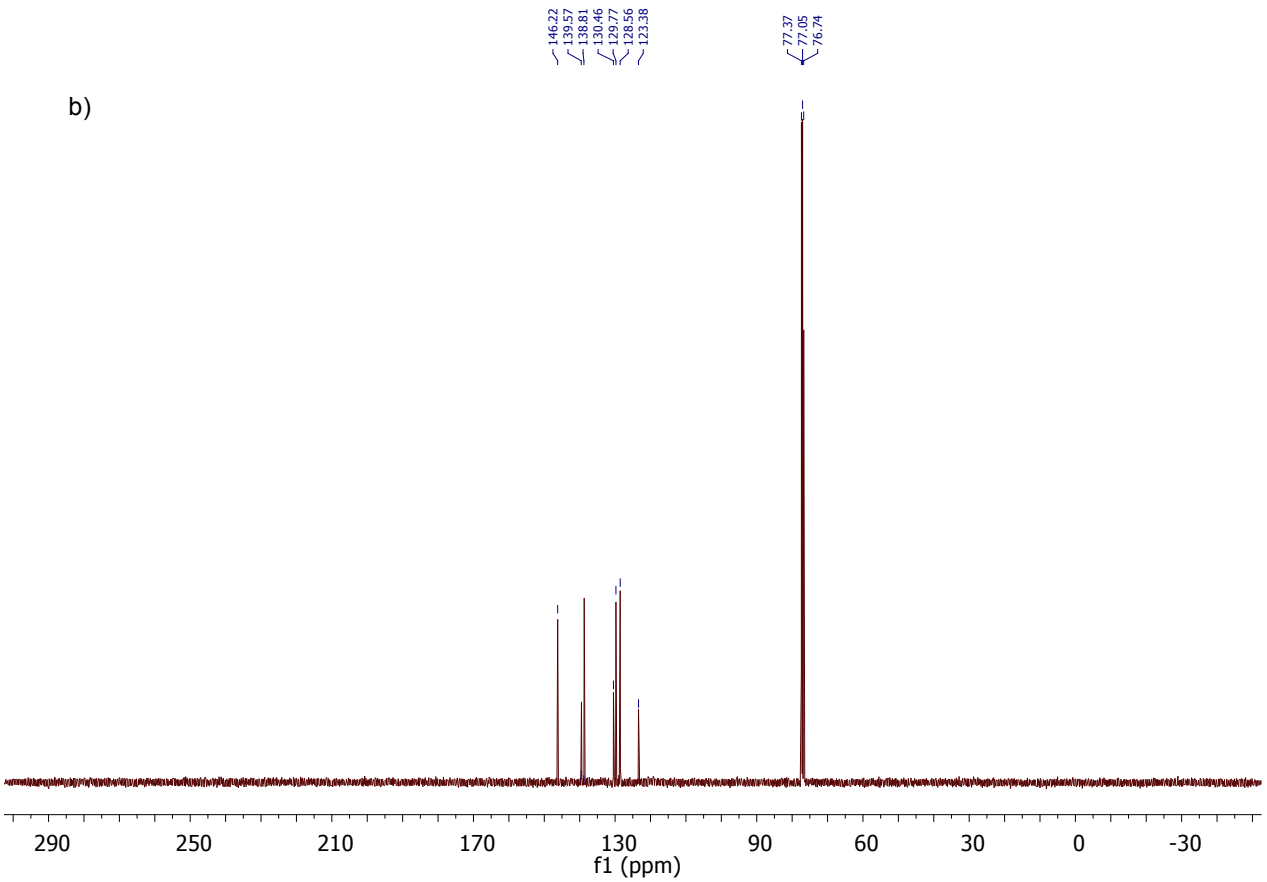
S5 (a,b): ^{1}H NMR and ^{13}C NMR spectra of $H_4TPP(Cl_2CHCOO)_2$.



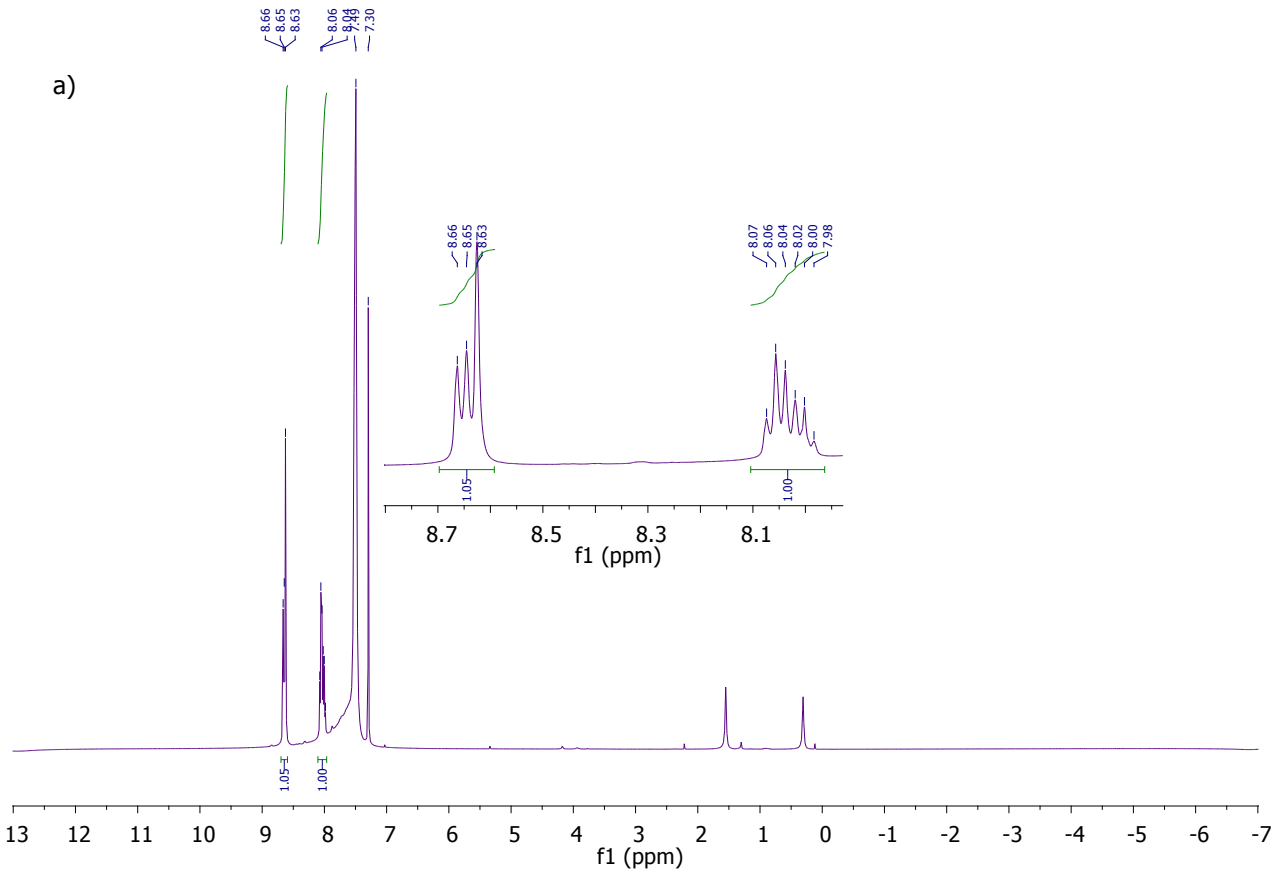


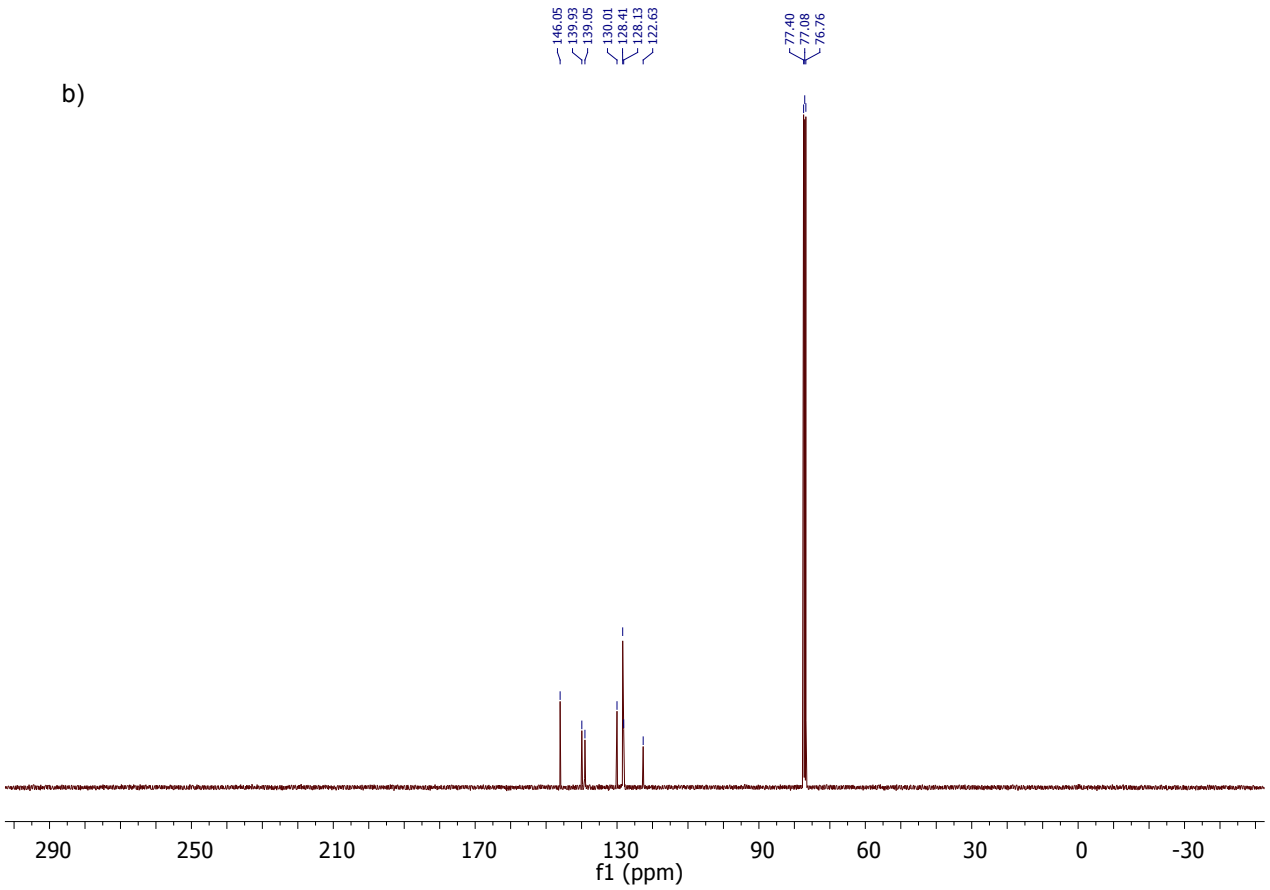
S6 (a,b): ^{1}H NMR and ^{13}C NMR spectra of $H_4TPP(ClO_4)_2$.





S7 (a,b): ^{1}H NMR and ^{13}C NMR spectra of $H_4TPP(HSO_4)_2$.





S8a: ^{1}H NMR, ^{13}C NMR spectral data for Methyl(phenyl)sulfane **(1a)**.

Methyl(phenyl)sulfane (1a).^{1}H NMR (400 MHz, chloroform-*d*): δ = 2.52 ppm (–CH_3, 3H, s), 7.16-7.18 (H_o, 2H, m), 7.18-7.20 (H_m, 2H, m), 7.31-7.33 (H_p, t); ^{13}C NMR (400 MHz, chloroform-*d*): δ = 16.08 ppm (–CH_3), 138.26 (–CS–), 126.75 (C_o), 128.56 (C_m), 125.13 (C_p).

S8b: ^{1}H NMR, ^{13}C NMR spectral data for Ethyl(phenyl)sulfane **(2a)**.

Ethyl(phenyl)sulfane (2a). ^{1}H NMR (400 MHz, chloroform-*d*): δ=1.33-1.37 ppm (–CH_3, 3H, t), 2.96-3.00 (–CH_2 , 2H, quartet), 7.18-7.19 (H_p, t), 7.32-7.38 (H_o, 2H, m), 7.21-7.22 (H_m, quartet) ; ^{13}C NMR (400 MHz, chloroform-*d*): δ=14.47 ppm (–**C**H_3), 27.77 (–**C**H_2–), 136.66 (–**C**S–), 125.79 (C_p), 129.04 (C_o), 128.82 (C_m).

S8c: ^{1}H NMR, ^{13}C NMR spectral data for Butyl(phenyl)sulfane **(3a)**.

Butyl(phenyl)sulfane (3a). ^{1}H NMR (400 MHz, chloroform-*d*): δ=0.95-0.98 ppm (–CH_3, 3H, t), 1.45-1.54 (–C**H_2**CH_3, 2H, m), 1.64-1.72 (–C**H_2**C_2H_5, 2H, quintet), 2.95-2.98 (–C**H_2**S–, 2H, t), 7.32 (H_m, 2H, quartet), 7.36-7.38 (H_o, 2H, d), 7.18-7.22 (H_p, t); ^{13}C NMR (400 MHz, chloroform-*d*): δ=13.62 ppm (–CH_3), 21.91 (–**C**H_2CH_3), 31.25 (–**C**$H_2C_2H_5$), 33.28 (–**C**H_2S–), 137.02 (–**C**S–), 125.65 (C_p), 128.84-128.86 (C_m, C_o).

S8d: ^{1}H NMR, ^{13}C NMR spectral data for Methyl(p-tolyl)sulfane **(5a)**.

Methyl(p-tolyl)sulfane (5a). ^{1}H NMR (400 MHz, chloroform-*d*): δ=2.51 ppm (C**H_3**S , 3H, s), 2.36 (C**H_3**Ph , 3H, s), 7.14-7.16 (H_m, 2H, d), 7.22-7.24 (H_o, 2H, d); ^{13}C NMR (400 MHz, chloroform-*d*): δ=20.92 ppm (**C**H_3Ph–), 16.57 (**C**H_3S–), 135.09 (**C**S), 127.32 (C_o), 129.62 (C_m), 134.72 (C_p).

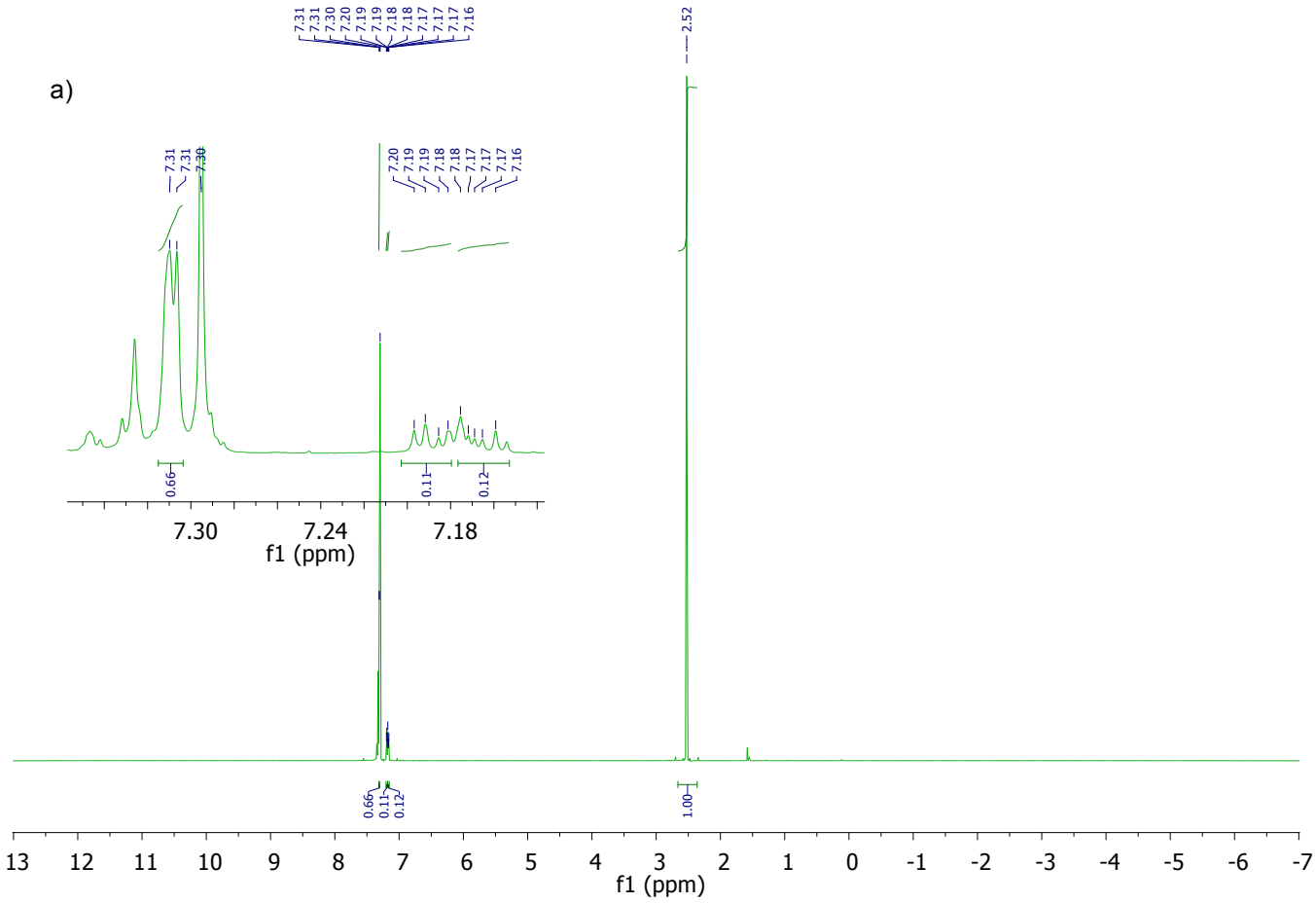
S8e: ^{1}H NMR, ^{13}C NMR spectral data for Ethyl(p-tolyl)sulfane **(6a)**.

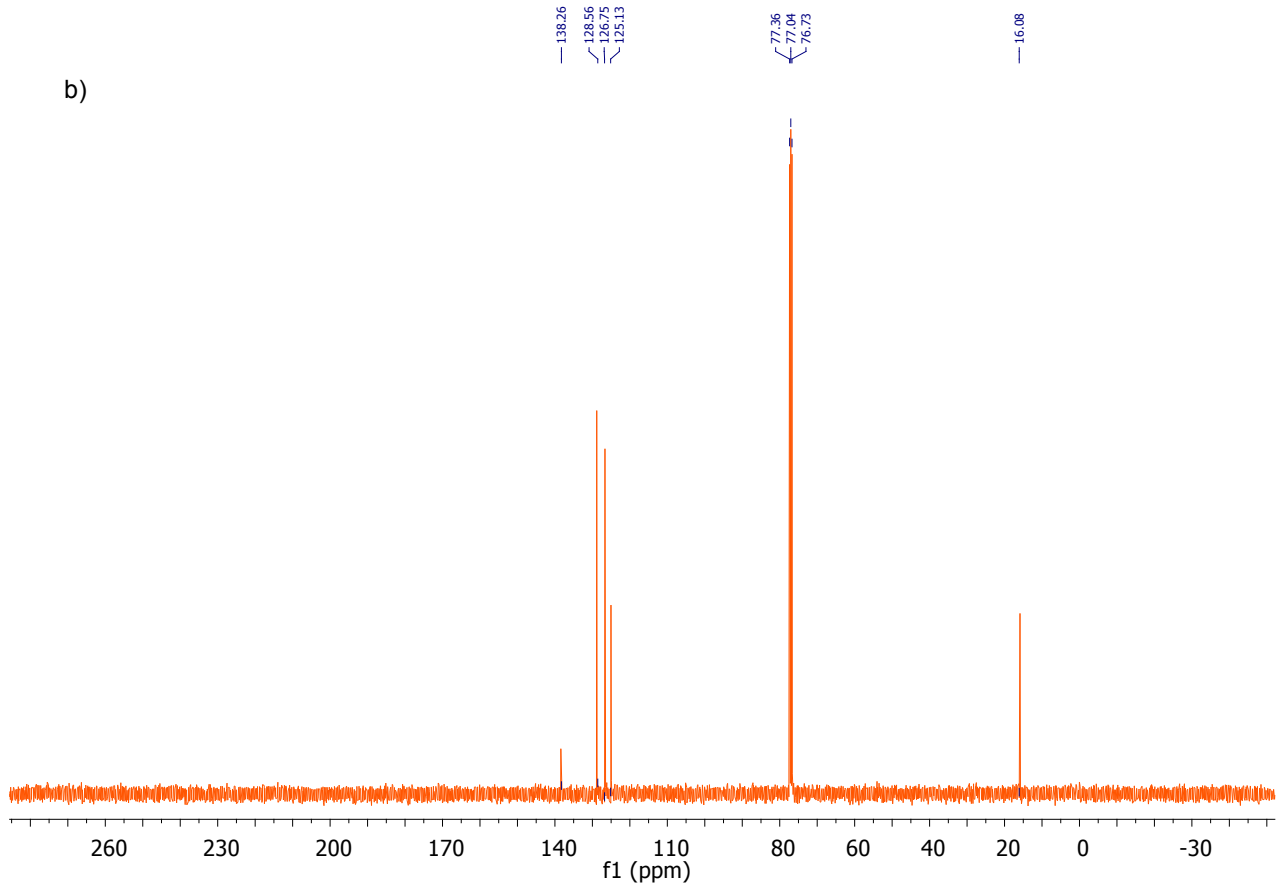
Ethyl(p-tolyl)sulfane (6a). ^{1}H NMR (400 MHz, chloroform-*d*): δ=1.31-1.35 ppm (C**H$_3$**CH$_2$, 3H, t), 2.36 (–C**H$_3$**Ph , 3H, s), 2.90-2.97 (–C**H$_2$**S–, 2H, quartet), 7.29-7.31 (H_o, 2H, d), 7.13-7.15 (H_m, 2H, d); ^{13}C NMR (400 MHz, chloroform-*d*): δ=14.52 ppm (**C**H$_3$CH$_2$–), 20.96 (**C**H$_3$Ph–), 28.36 (–**C**H$_2$S), 132.72 (–**C**S), 136.0 (C_p), 129.64 (C_o), 129.99 (C_m).

S8f: ^{1}H NMR, ^{13}C NMR spectral data for Butyl(p-tolyl)sulfane **(7a)**.

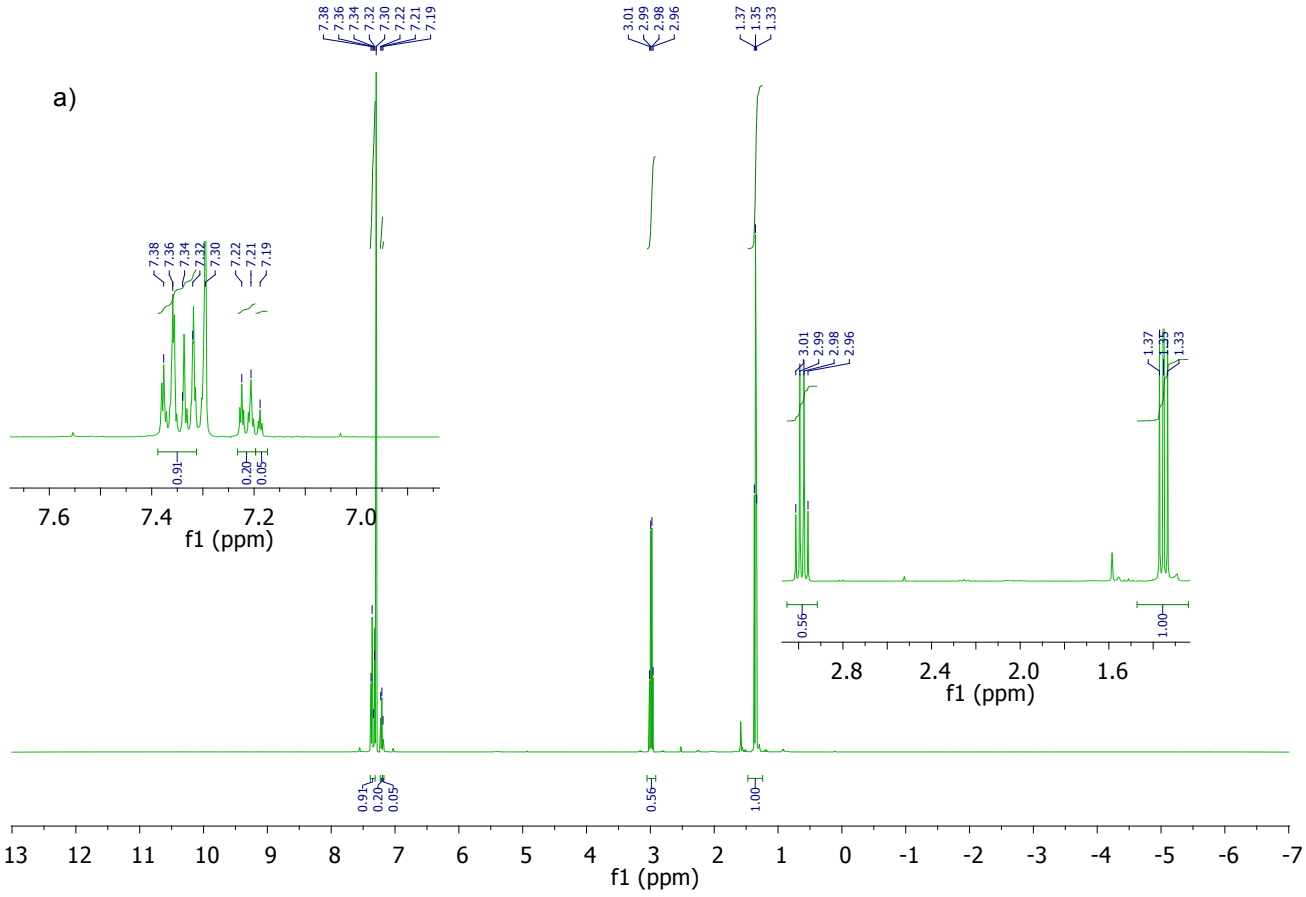
Butyl(p-tolyl)sulfane (7a). ^{1}H NMR (400 MHz, chloroform-*d*): δ=0.94-0.98 ppm (C**H$_3$**CH$_2$, 3H, t), 1.44-1.53 (–C**H$_2$**CH$_3$, 2H, m), 1.62-1.69 (–C**H$_2$**C$_2$H$_5$, 2H, m), 2.36 (C**H$_3$**Ph , 3H, s), 2.91-2.94 (–C**H$_2$**S , 2H, t), 7.13-7.15 (H_m, 2H, d), 7.28-7.30 (H_o, 2H, d); ^{13}C NMR (400 MHz, chloroform-*d*): δ=13.73 ppm (**C**H$_3$CH$_2$–), 21.01 (–**C**H$_2$CH$_3$), 22.0 (**C**H$_3$Ph–), 31.37 (–**C**H$_2$C$_2$H$_5$), 34.06 (–**C**H$_2$S–), 133.18 (–**C**S–), 135.86 (C_p), 129.79 (C_m), 129.62 (C_o).

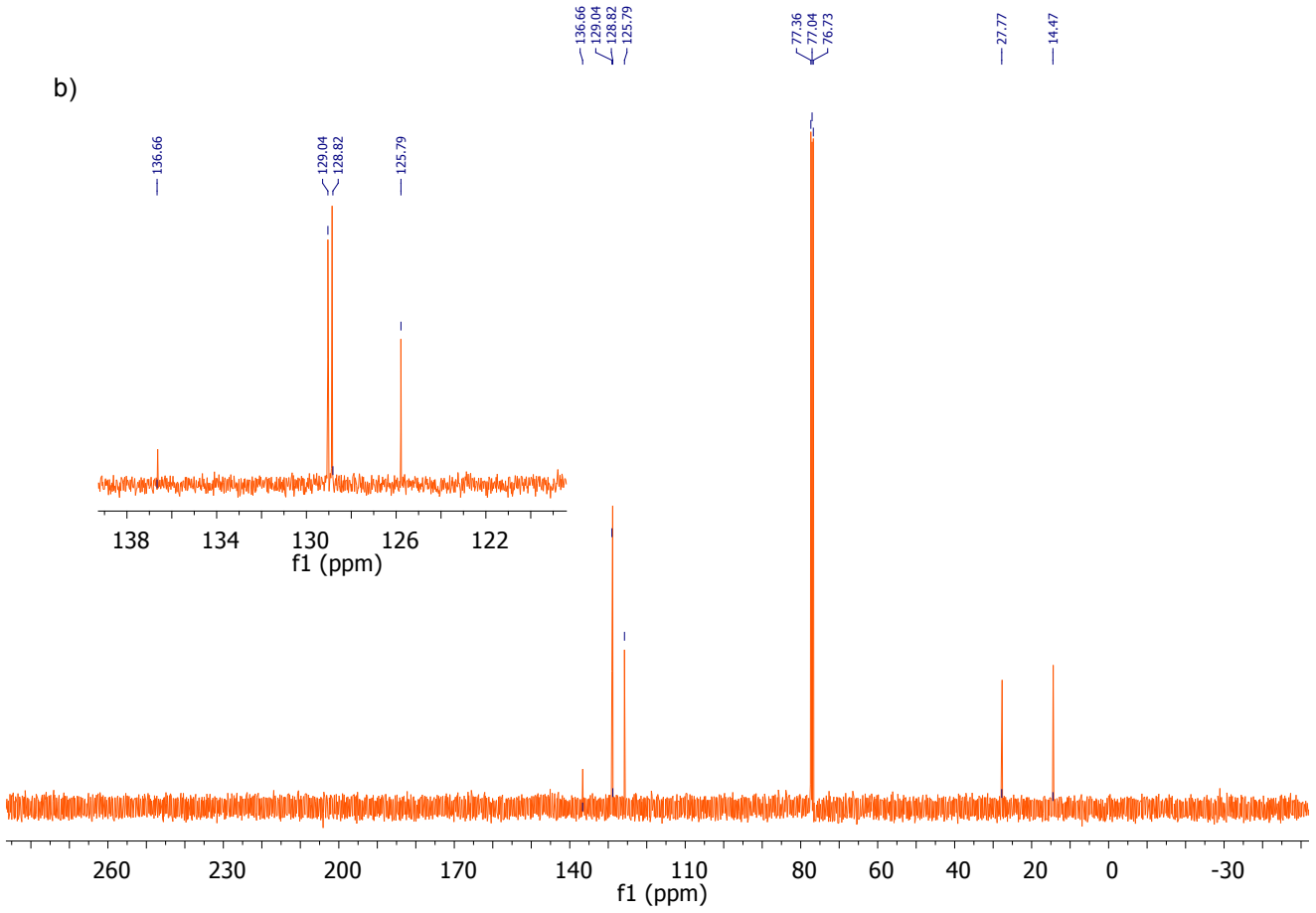
S9 (a,b): ^{1}H NMR, ^{13}C NMR spectra for Methyl(phenyl)sulfane **(1a)**.



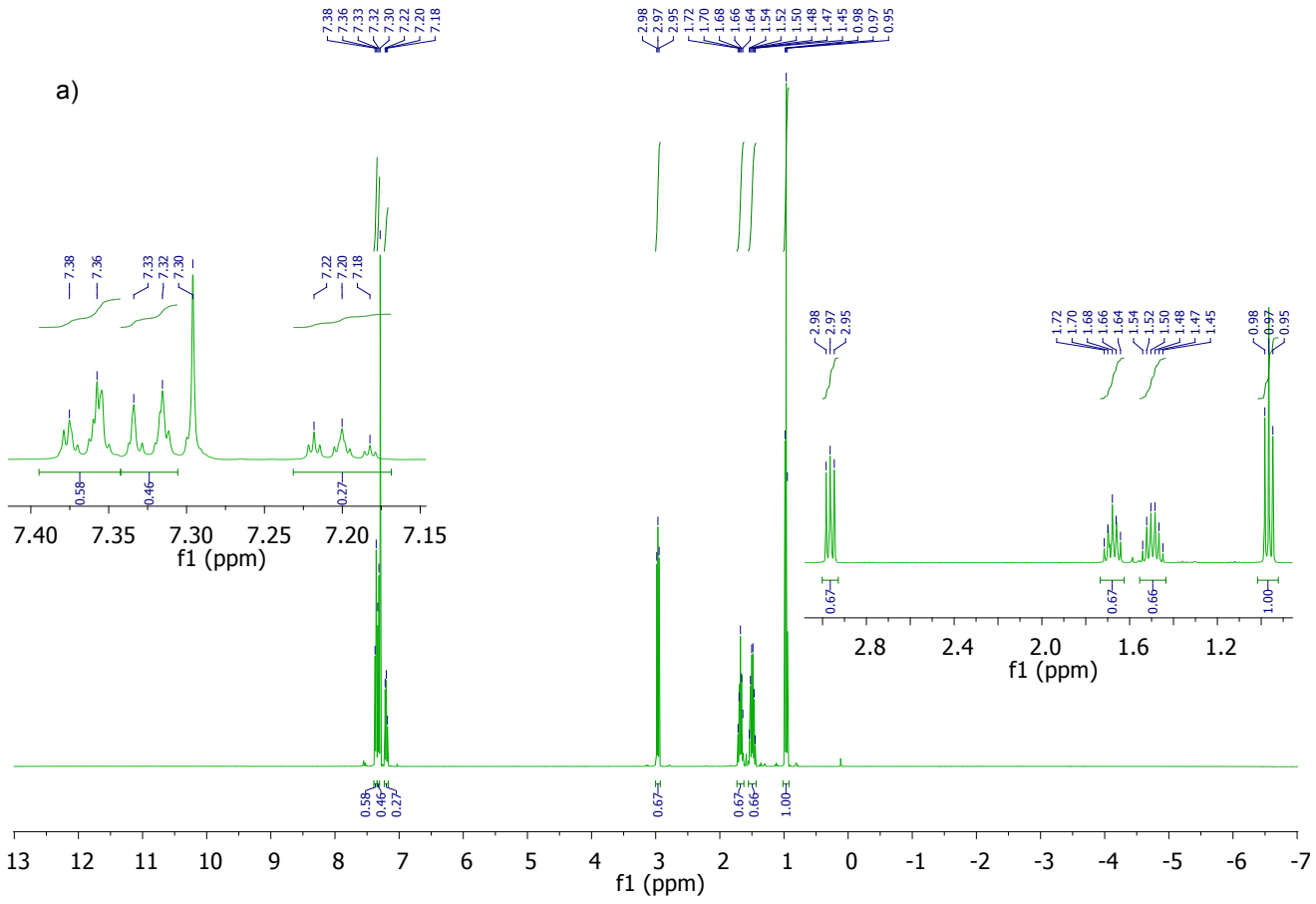


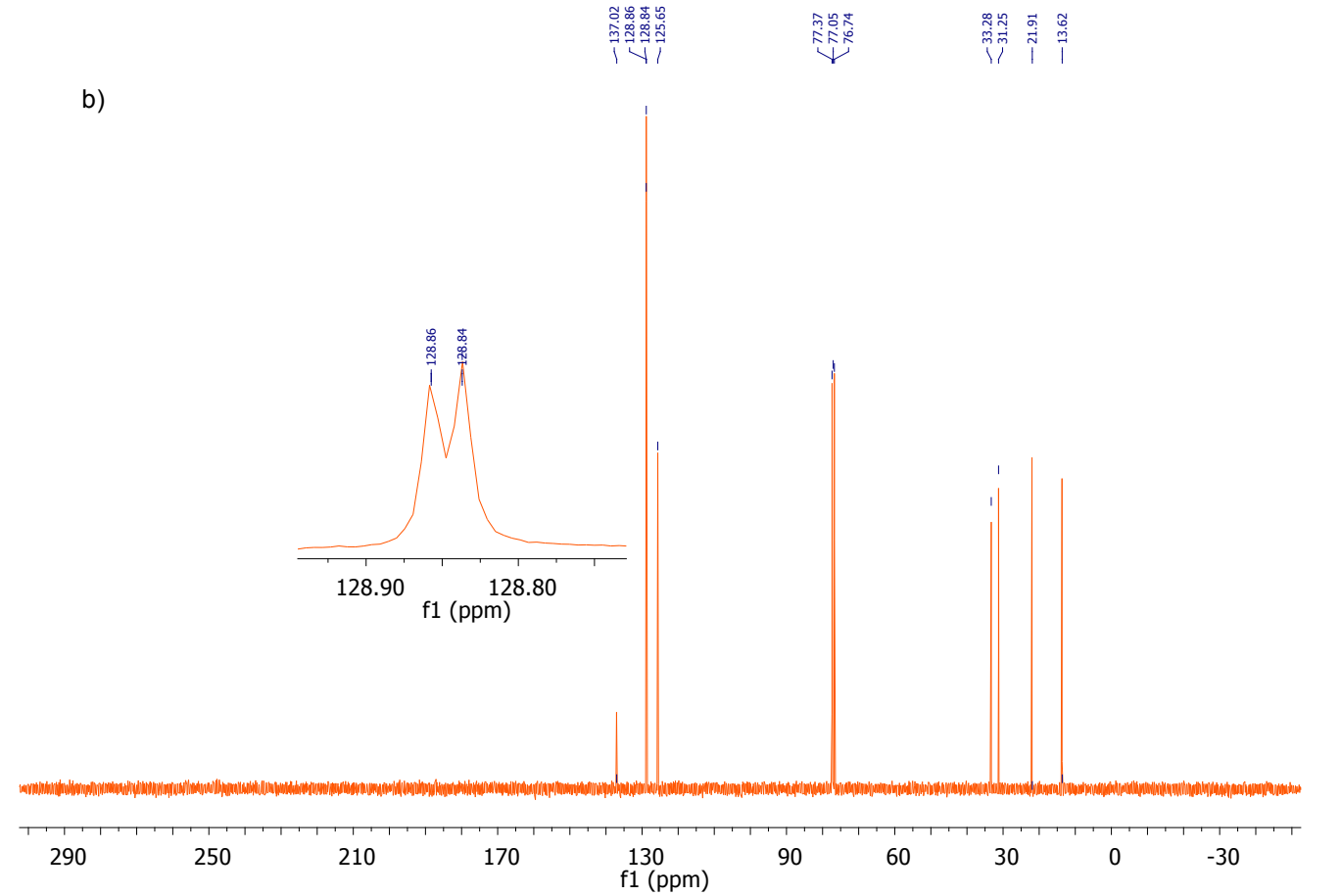
S10 (a,b): ^{1}H NMR, ^{13}C NMR spectra for Ethyl(phenyl)sulfane **(2a)**.



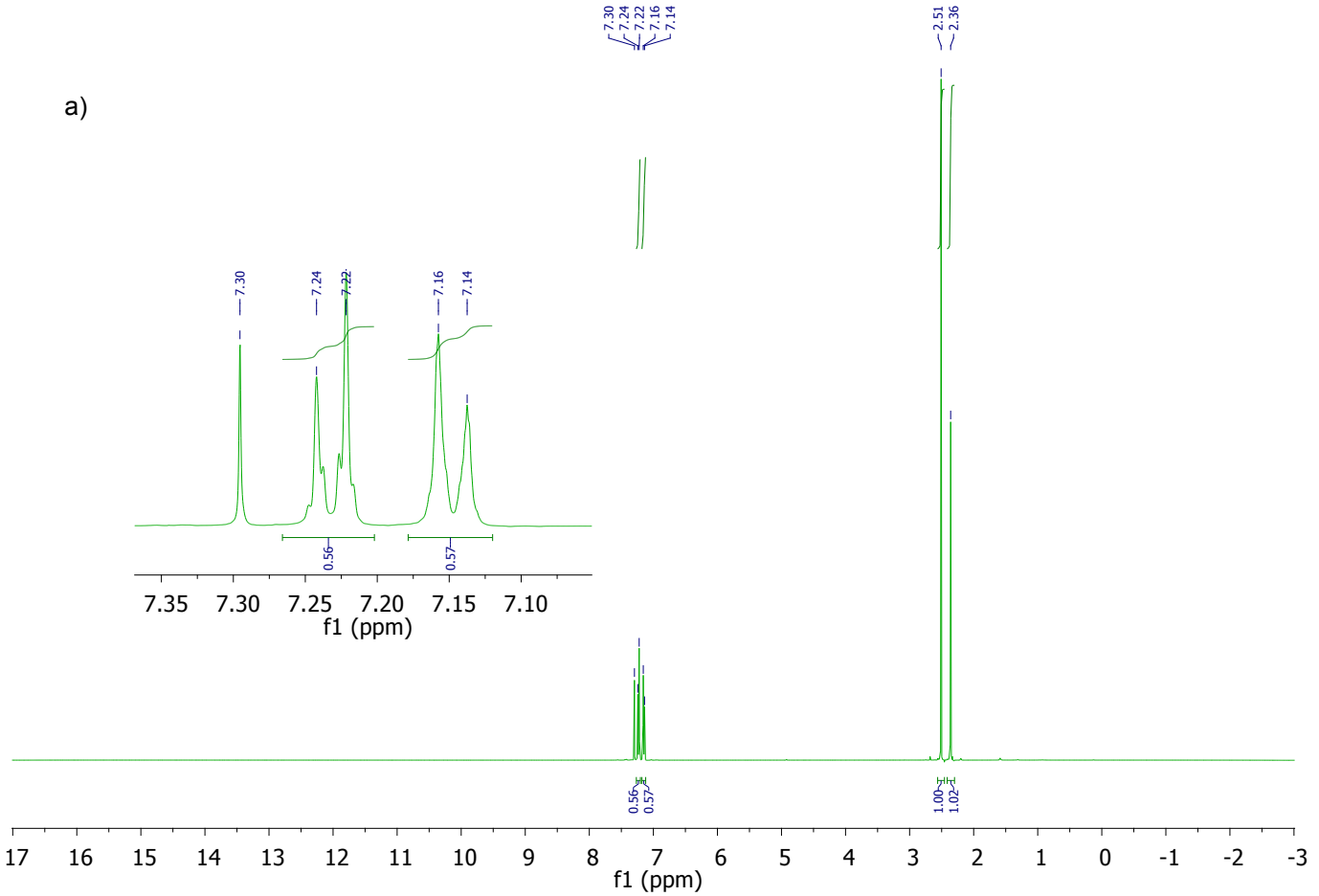


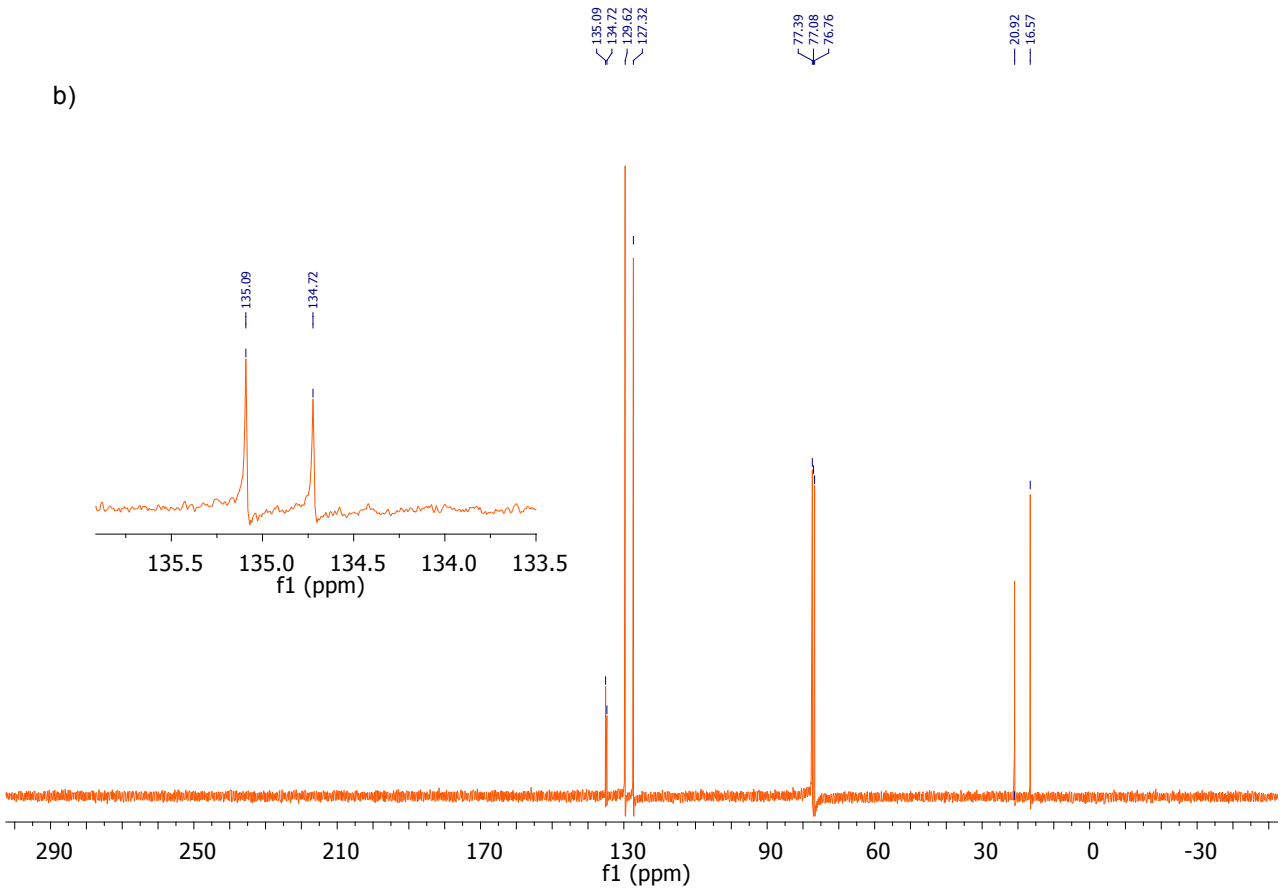
S11 (a,b): ^{1}H NMR, ^{13}C NMR spectra for Butyl(phenyl)sulfane **(3a)**.



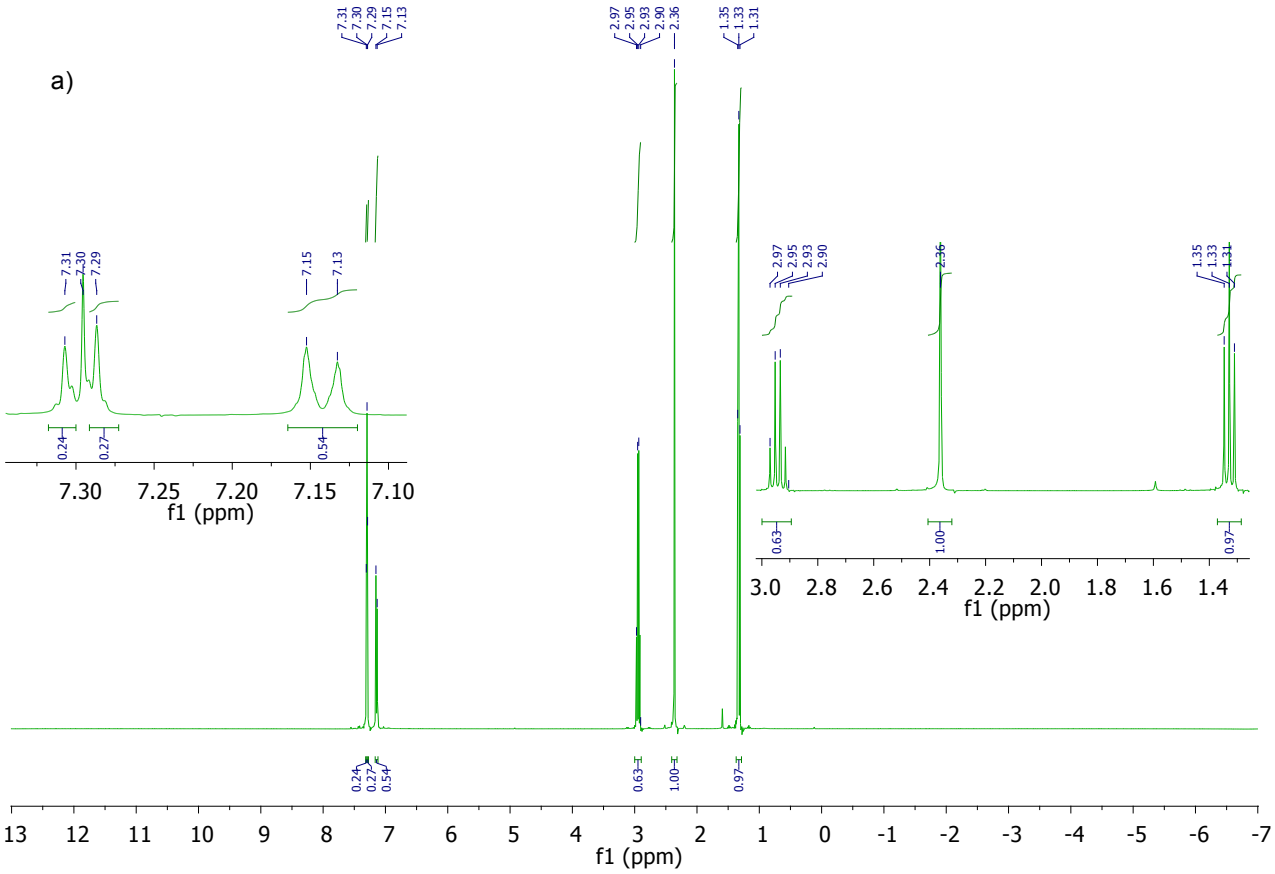


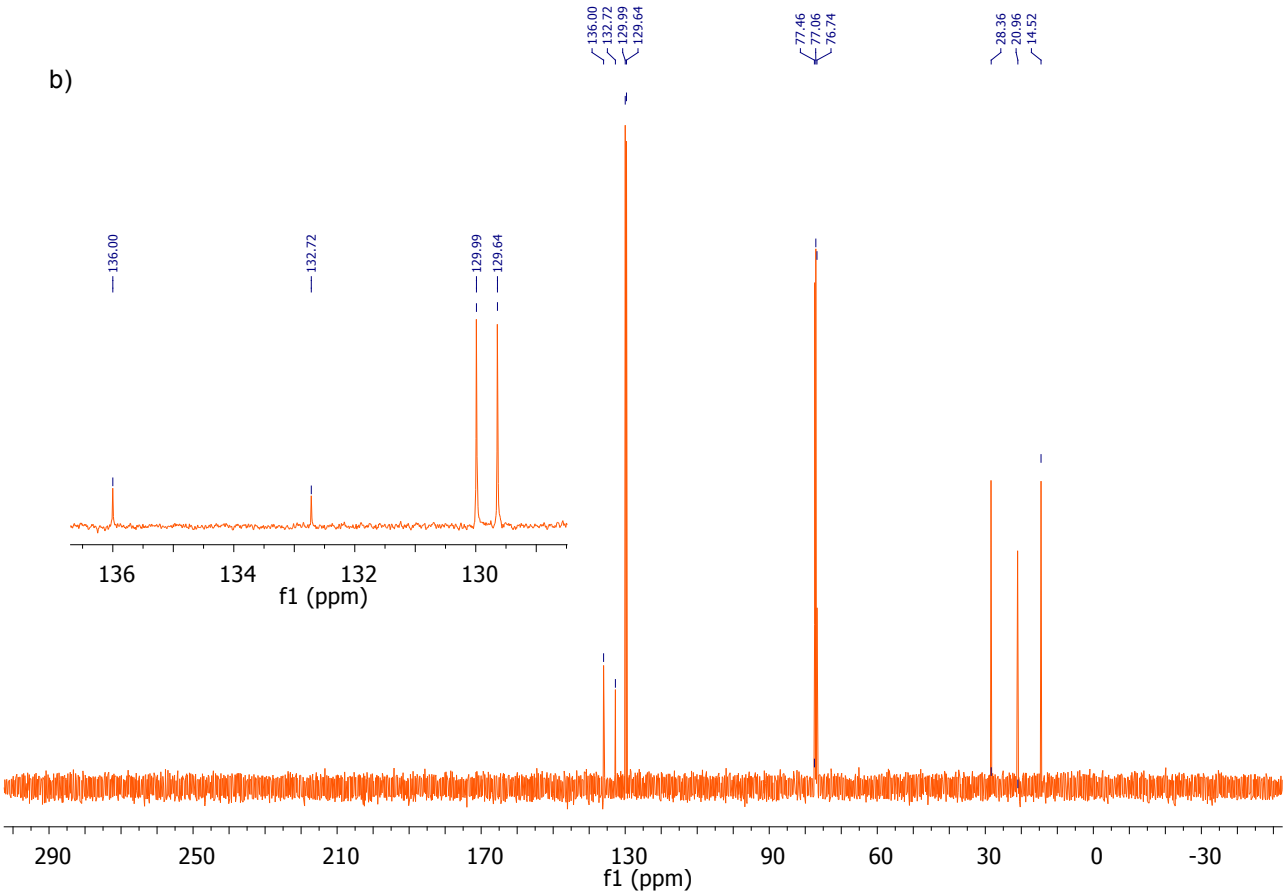
S12 (a,b): ^{1}H NMR, ^{13}C NMR spectra for Methyl(p-tolyl)sulfane **(5a)**.



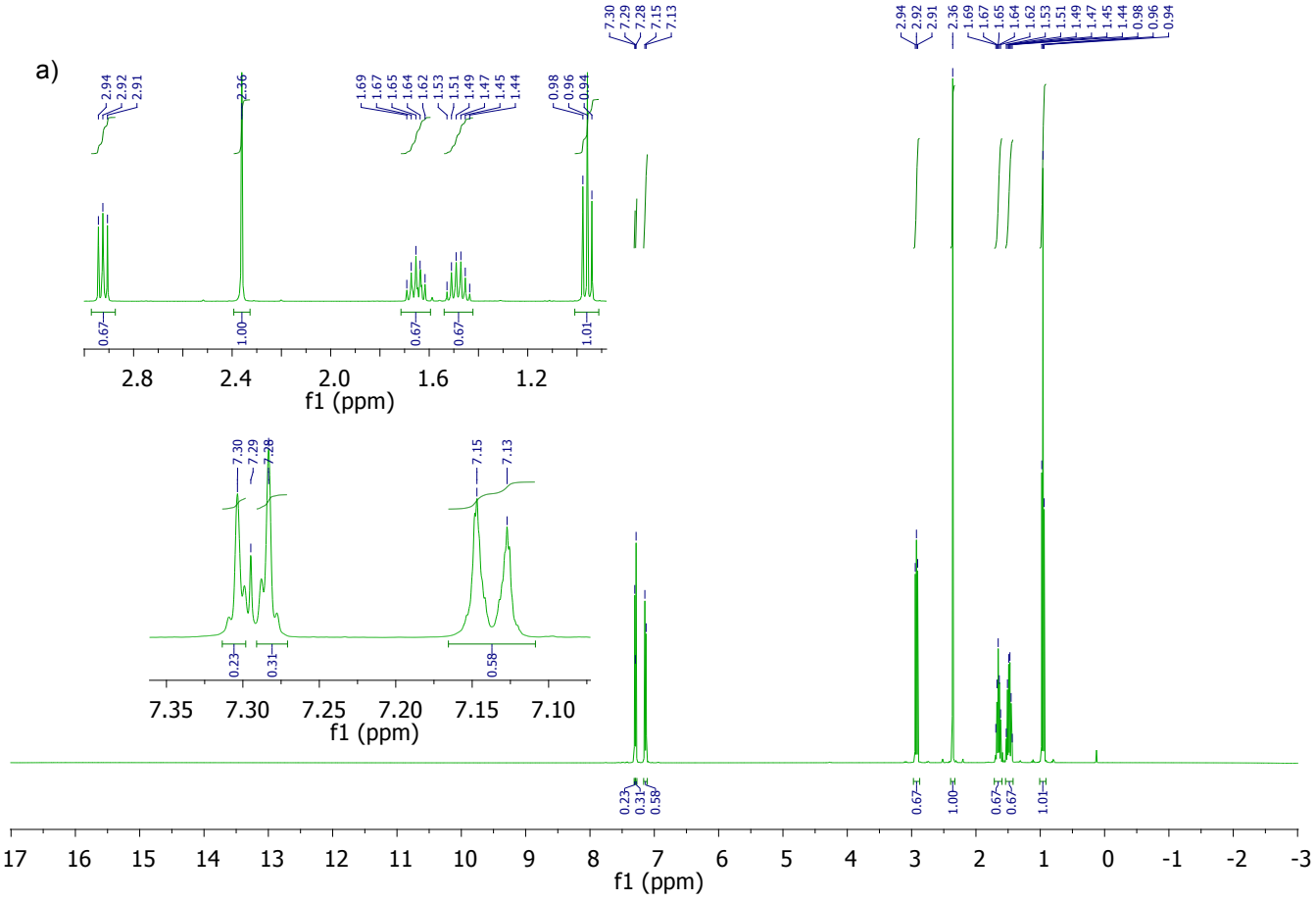


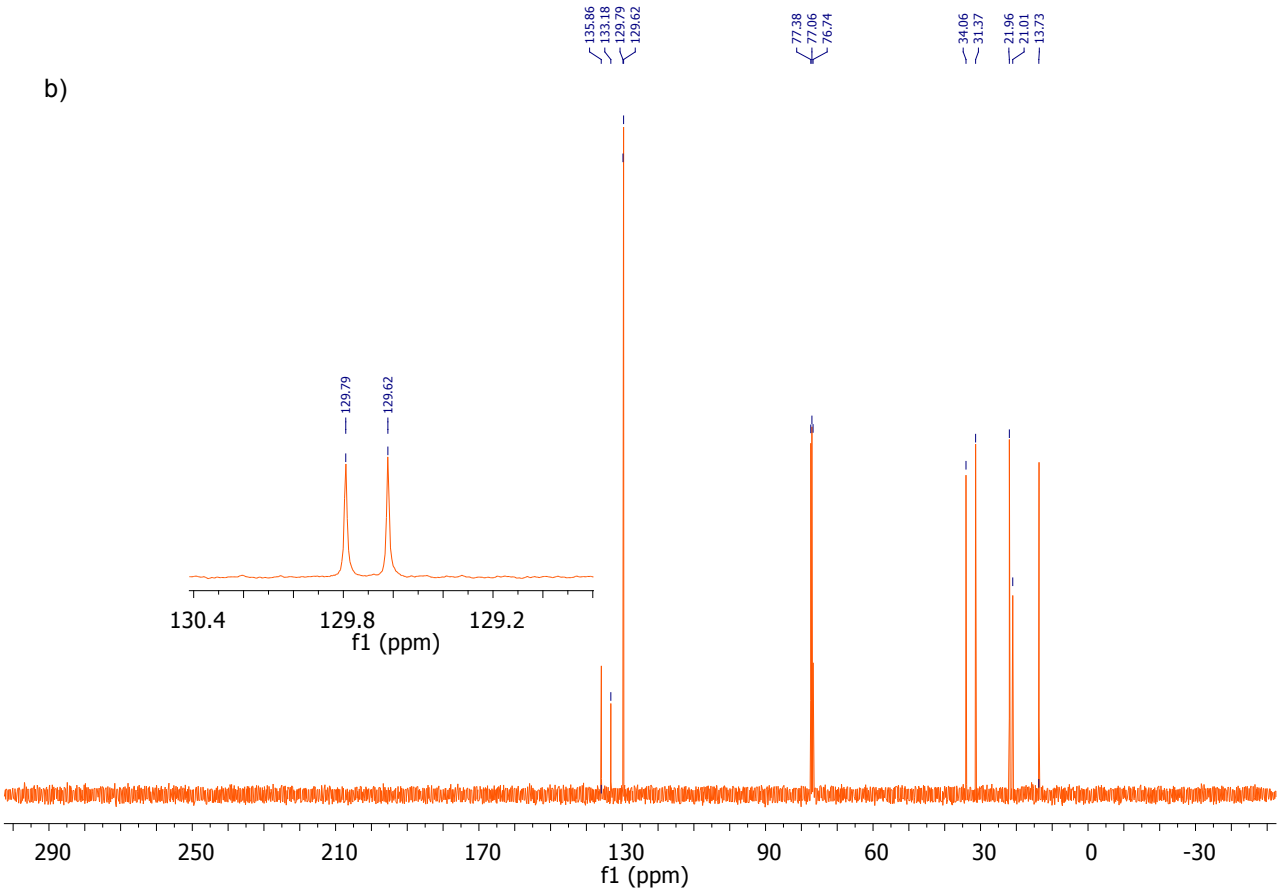
S13 (a,b): ^{1}H NMR, ^{13}C NMR spectra for Ethyl(p-tolyl)sulfane **(6a)**.





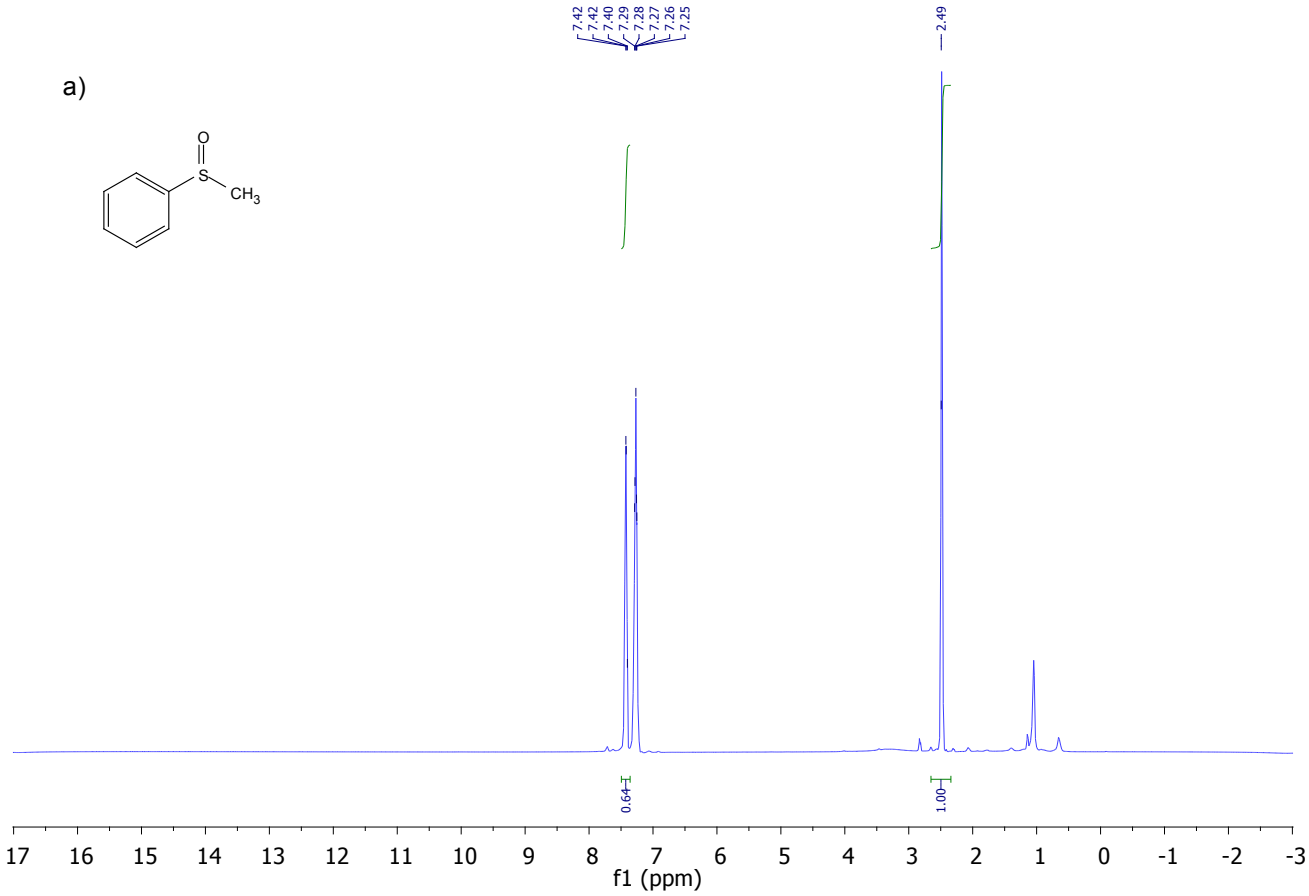
S14 (a,b): ^{1}H NMR, ^{13}C NMR spectra for Butyl(p-tolyl)sulfane **(7a)**.

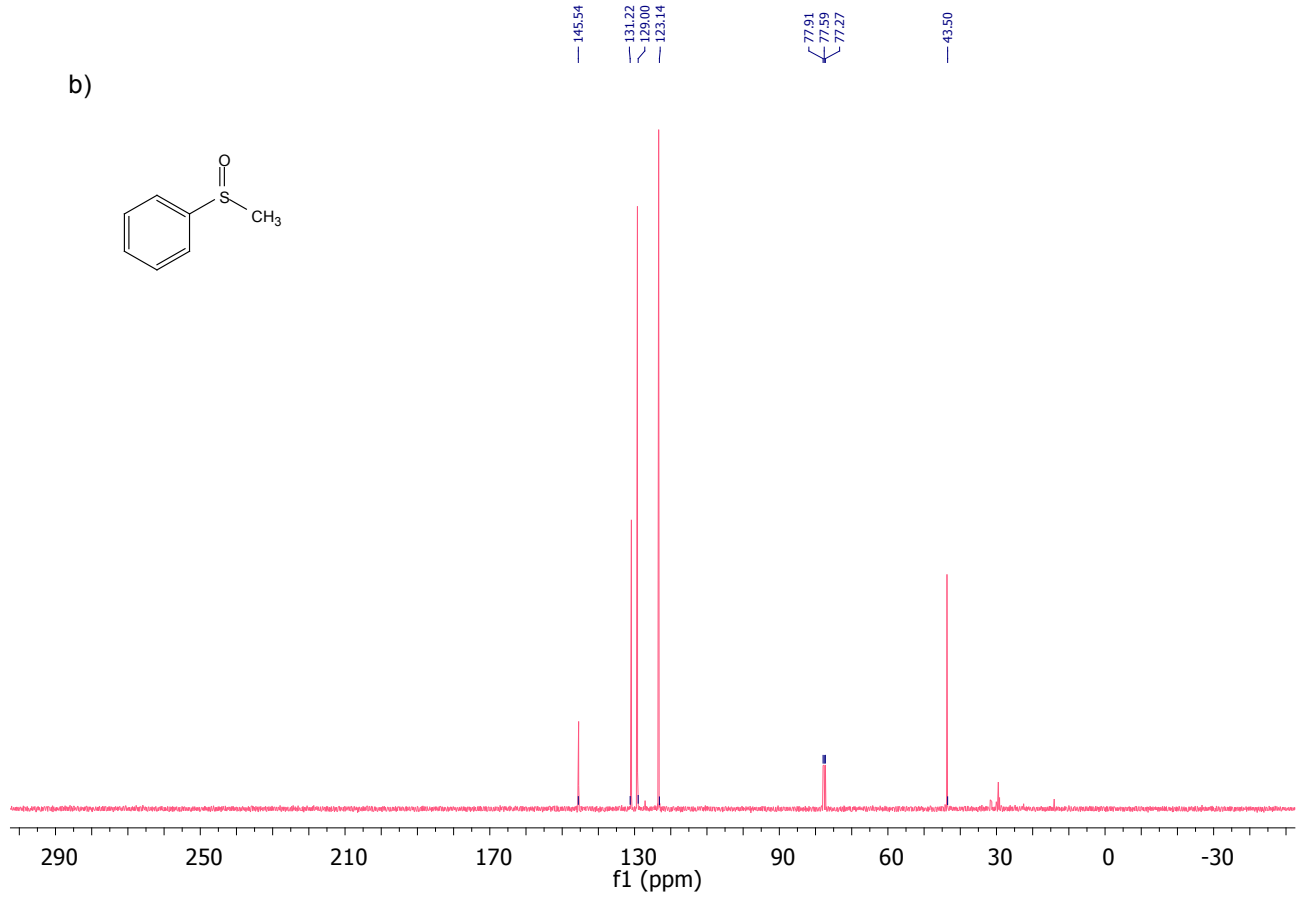




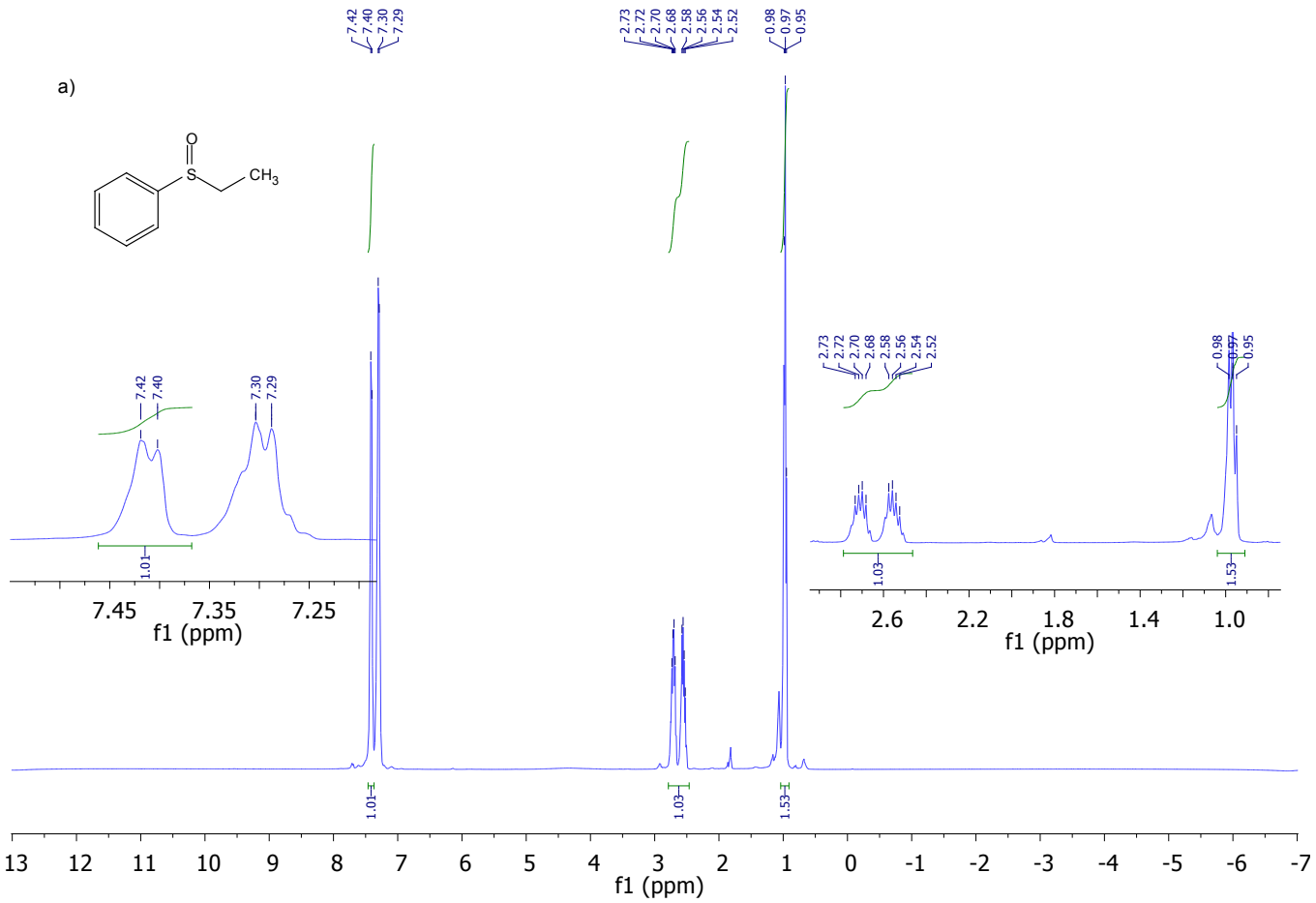
S15: Experimental setup for the photooxidation reactions performed under sunlight irradiation.

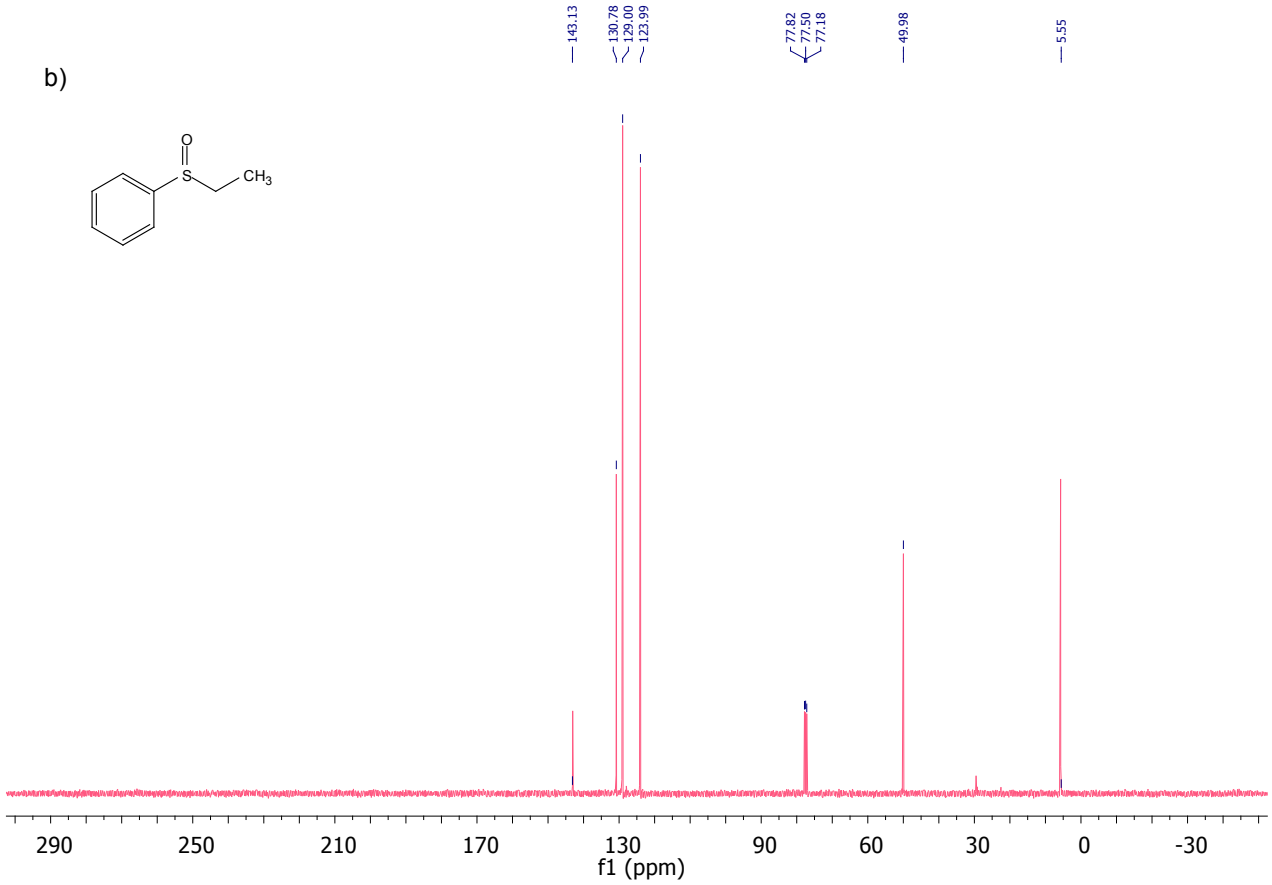
S16 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Methylsulfinyl)benzene **(1b)**.



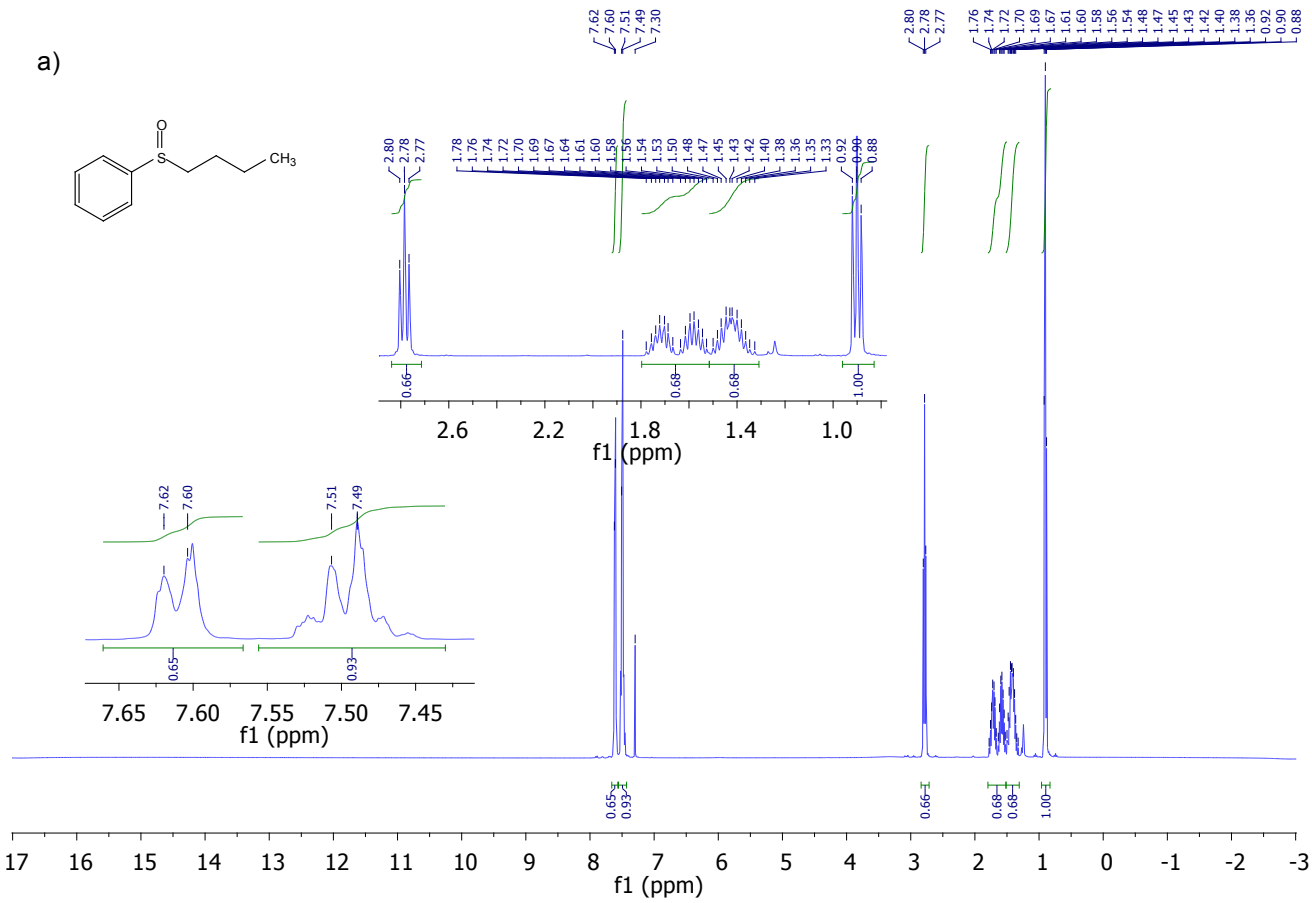


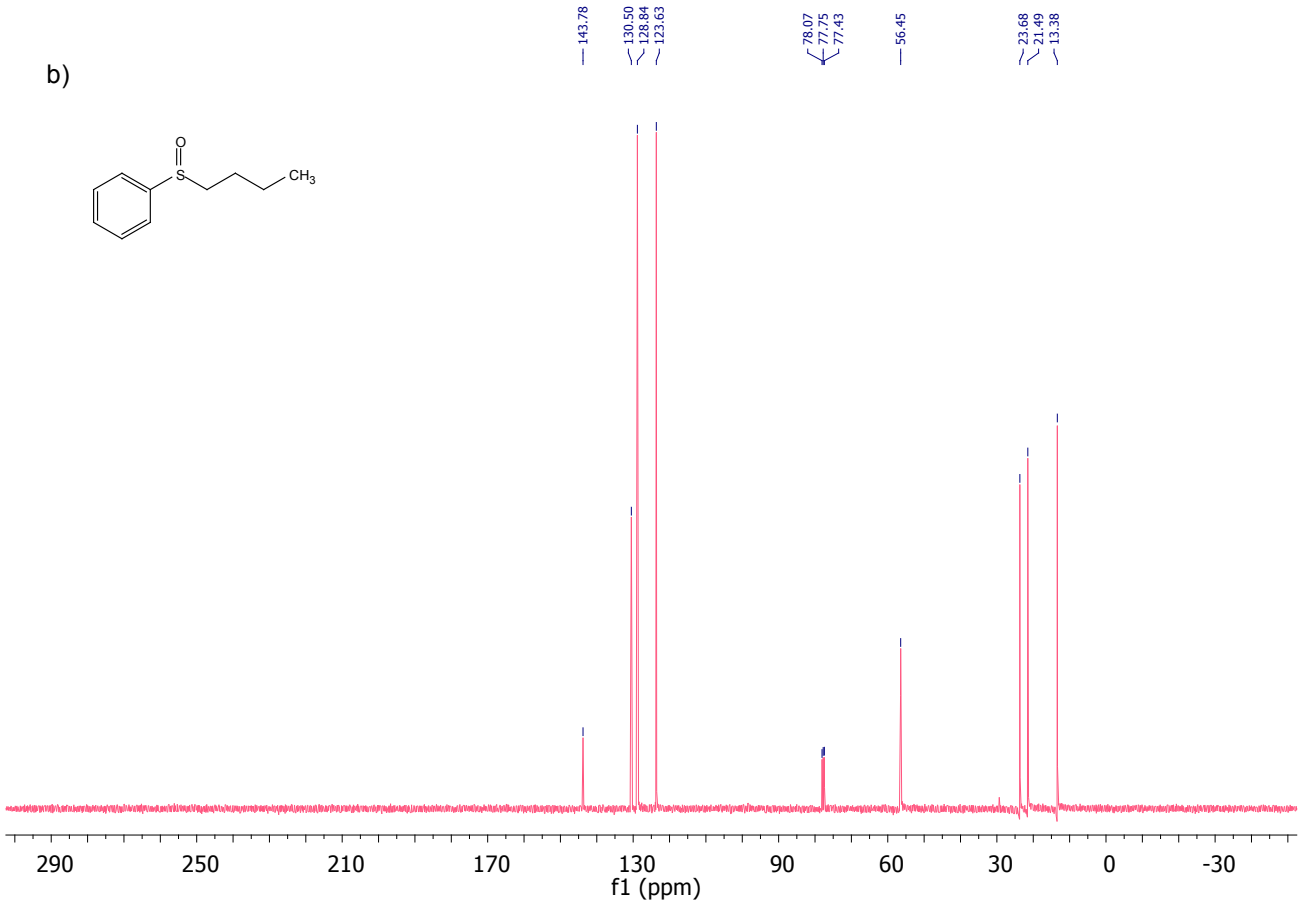
S17 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Ethylsulfinyl)benzene **(2b)**.



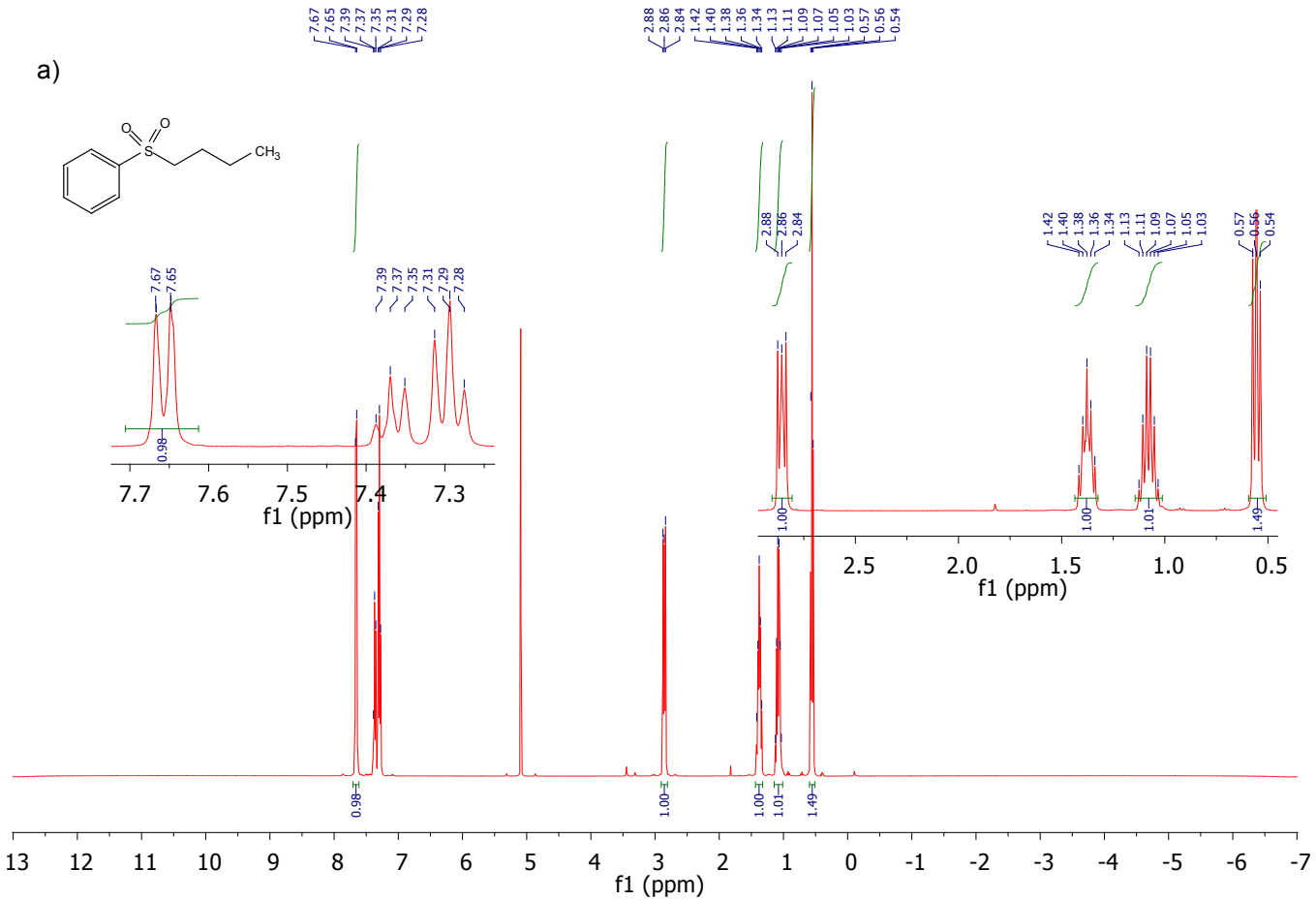


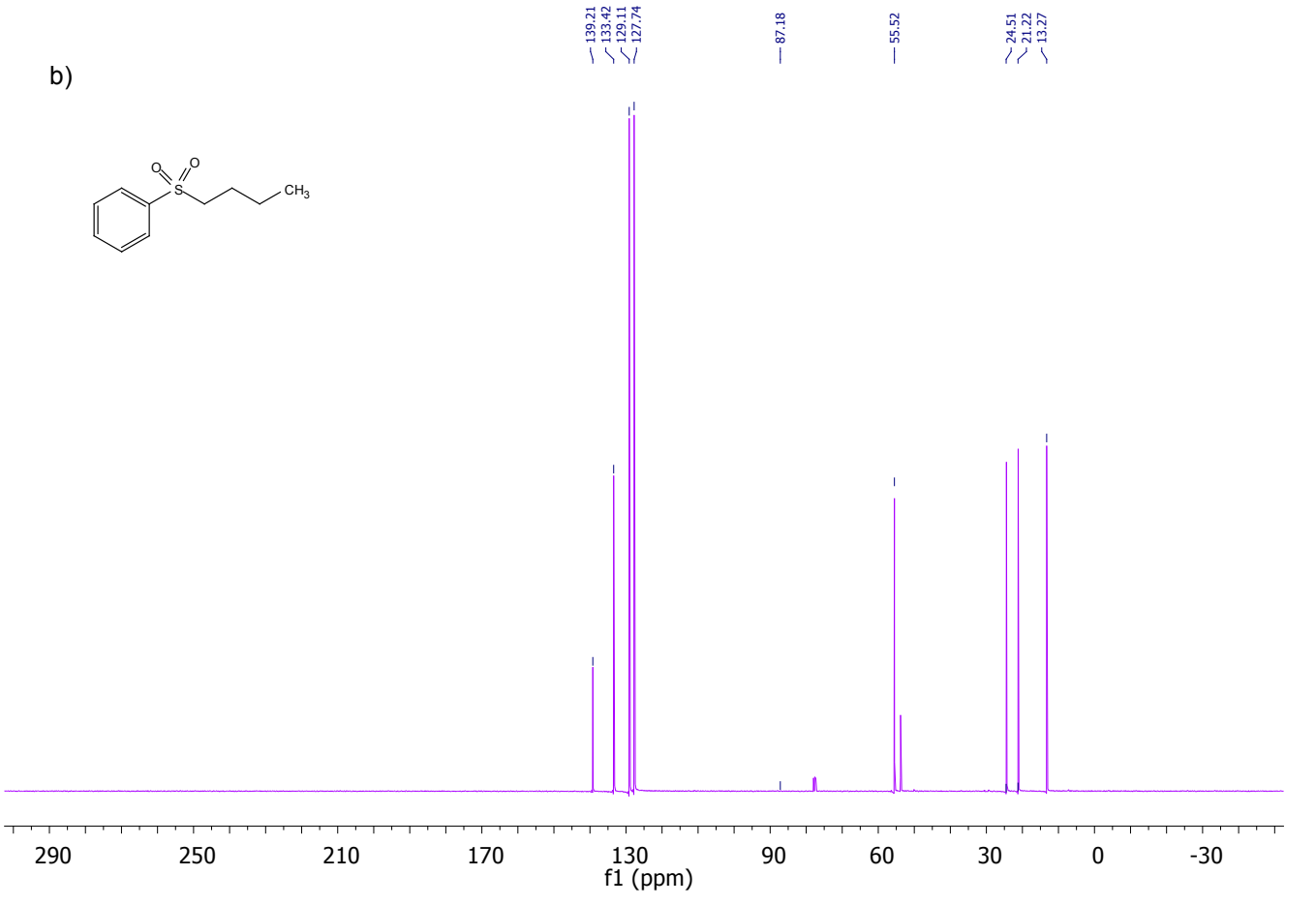
S18 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Butylsulfinyl)benzene **(3b)**.



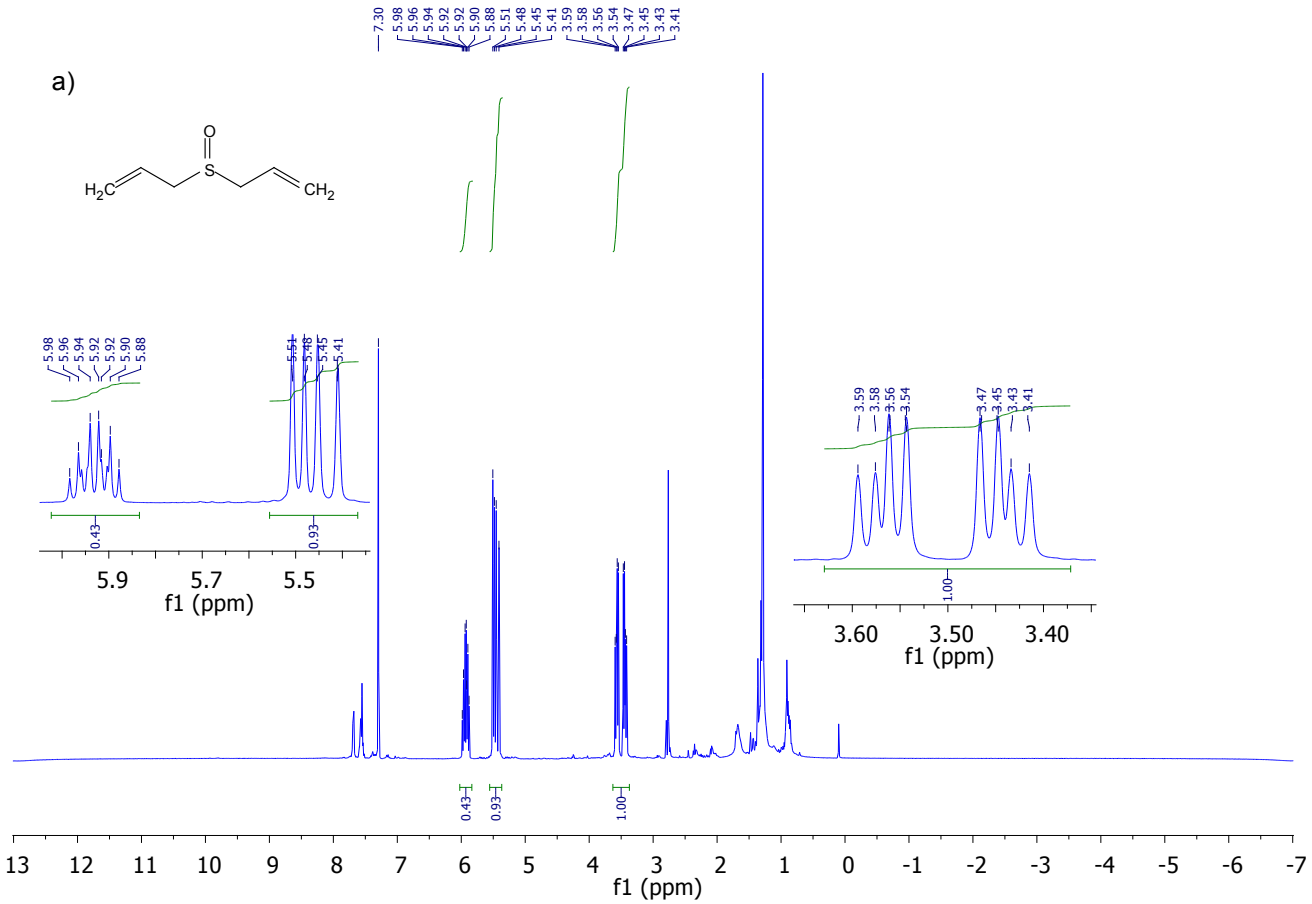


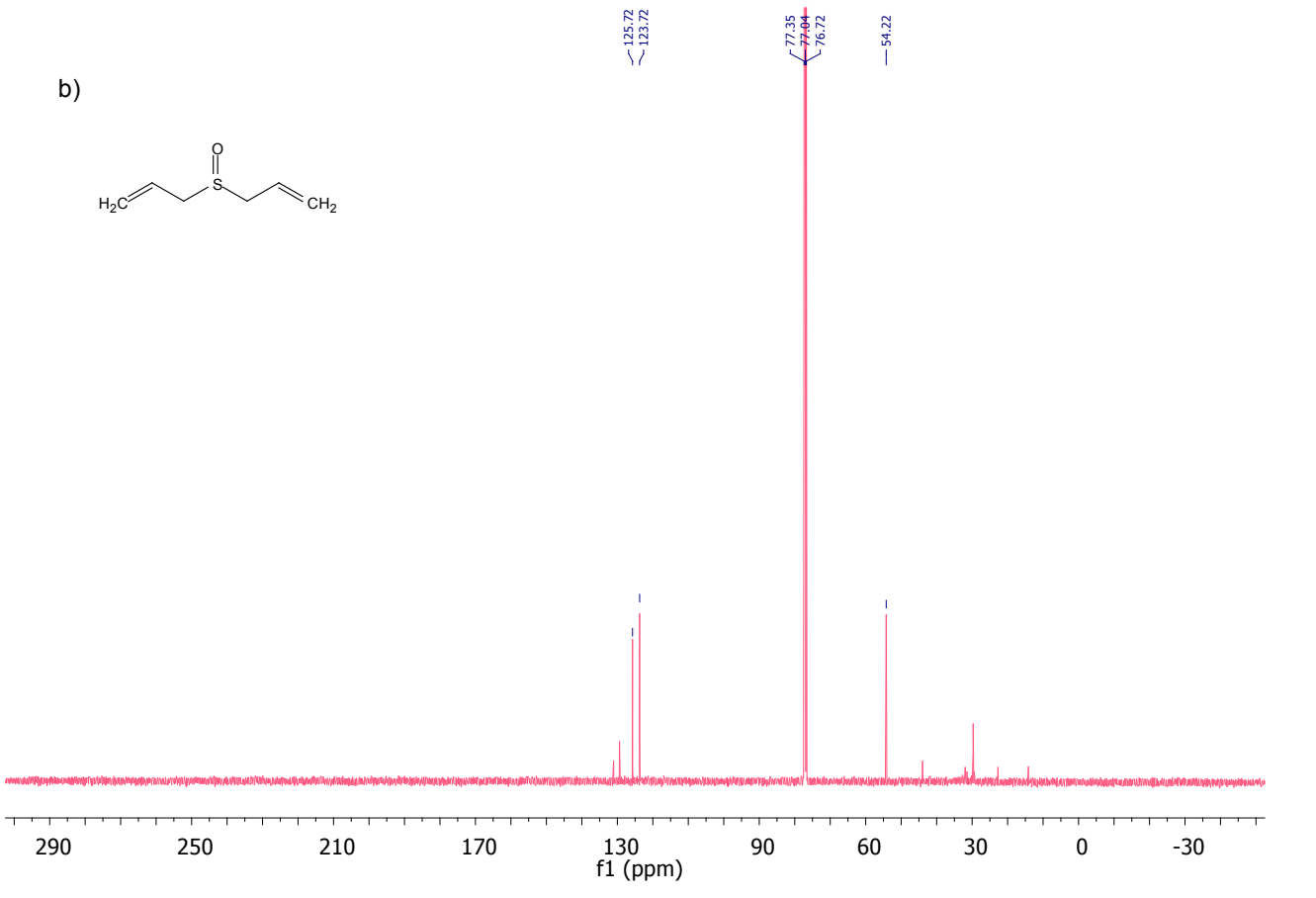
S19 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Butylsulfonyl)benzene **(3c)**.



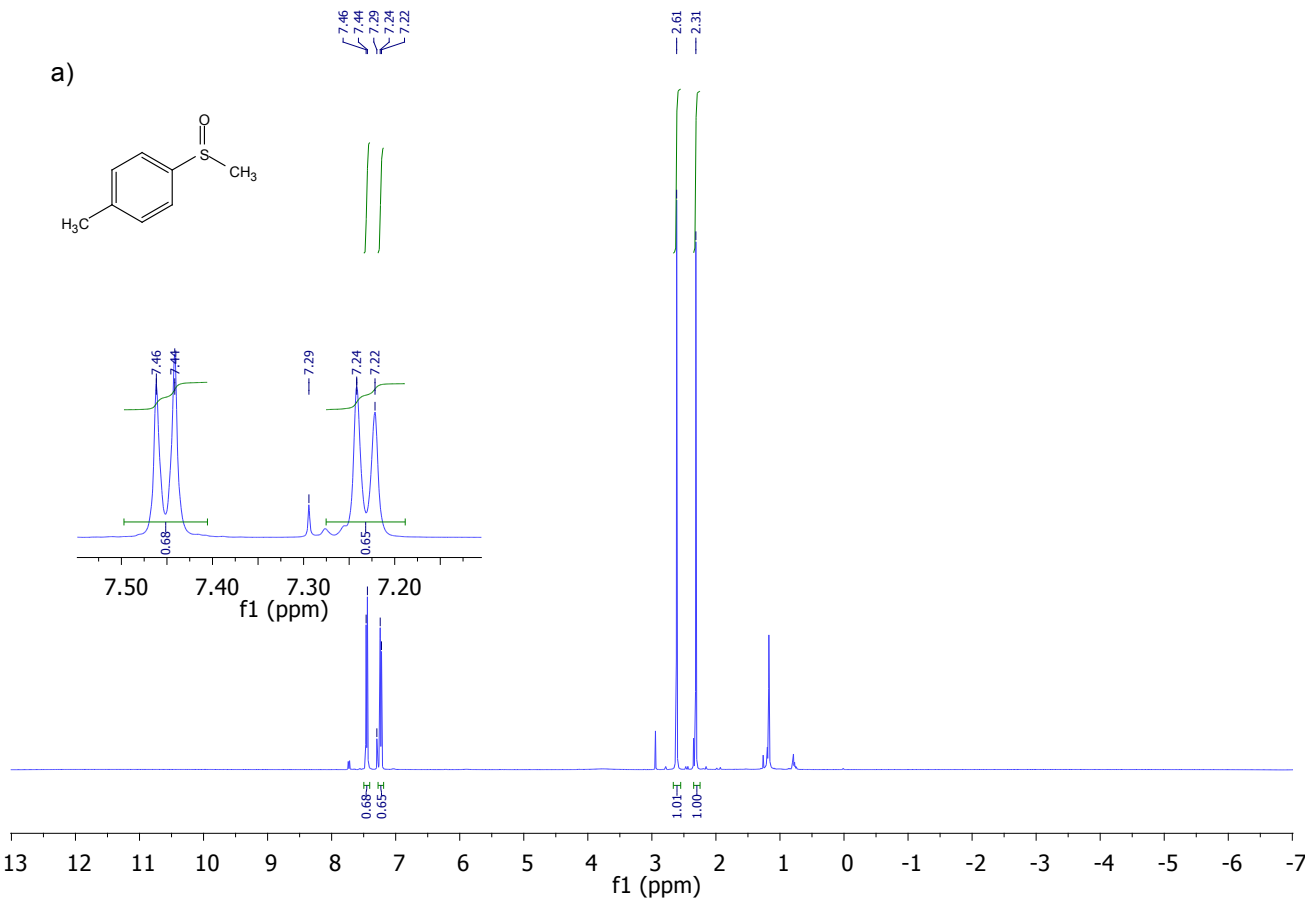


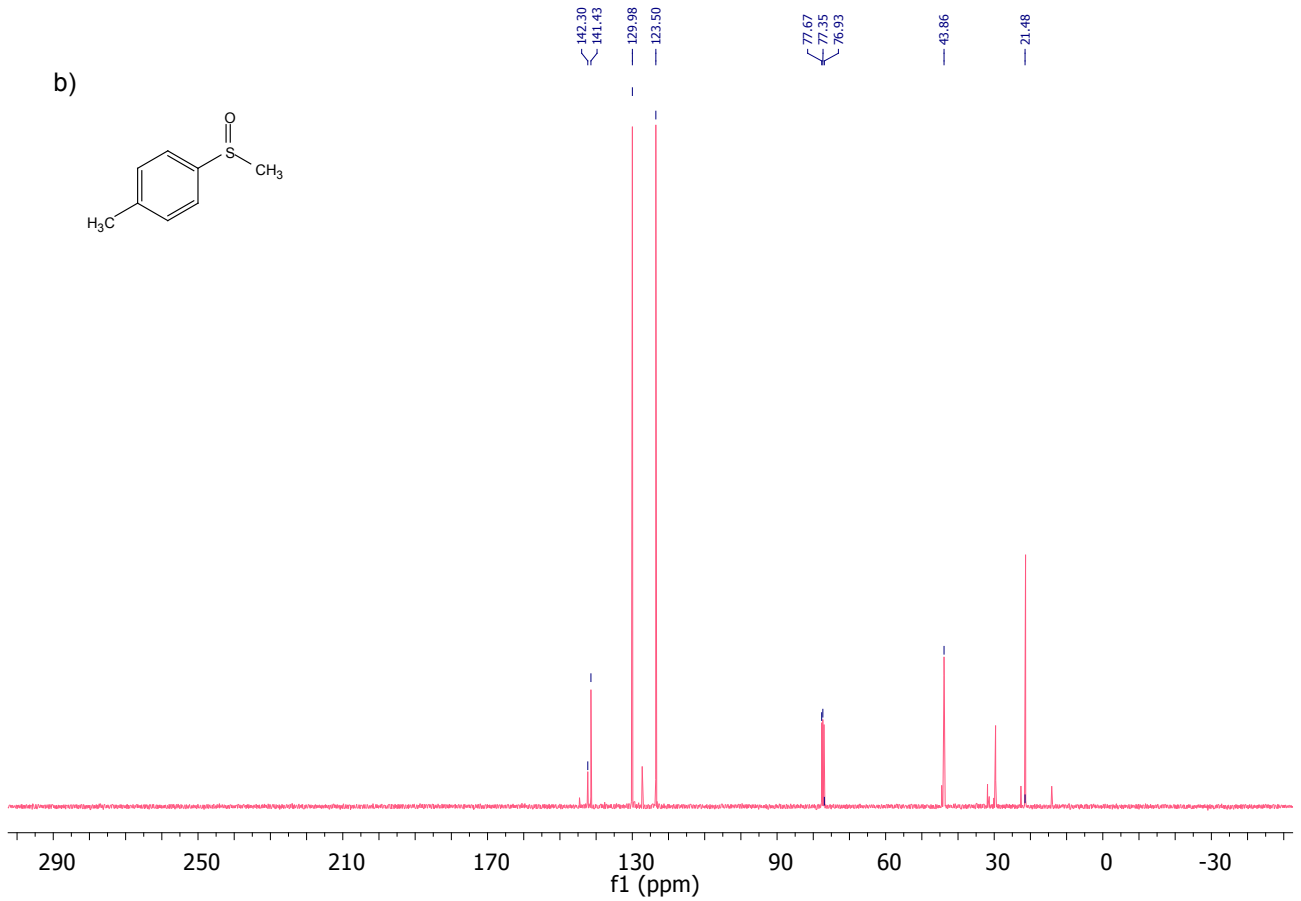
S20 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 3-(Allylsulfinyl)prop-1-ene **(4b)**.



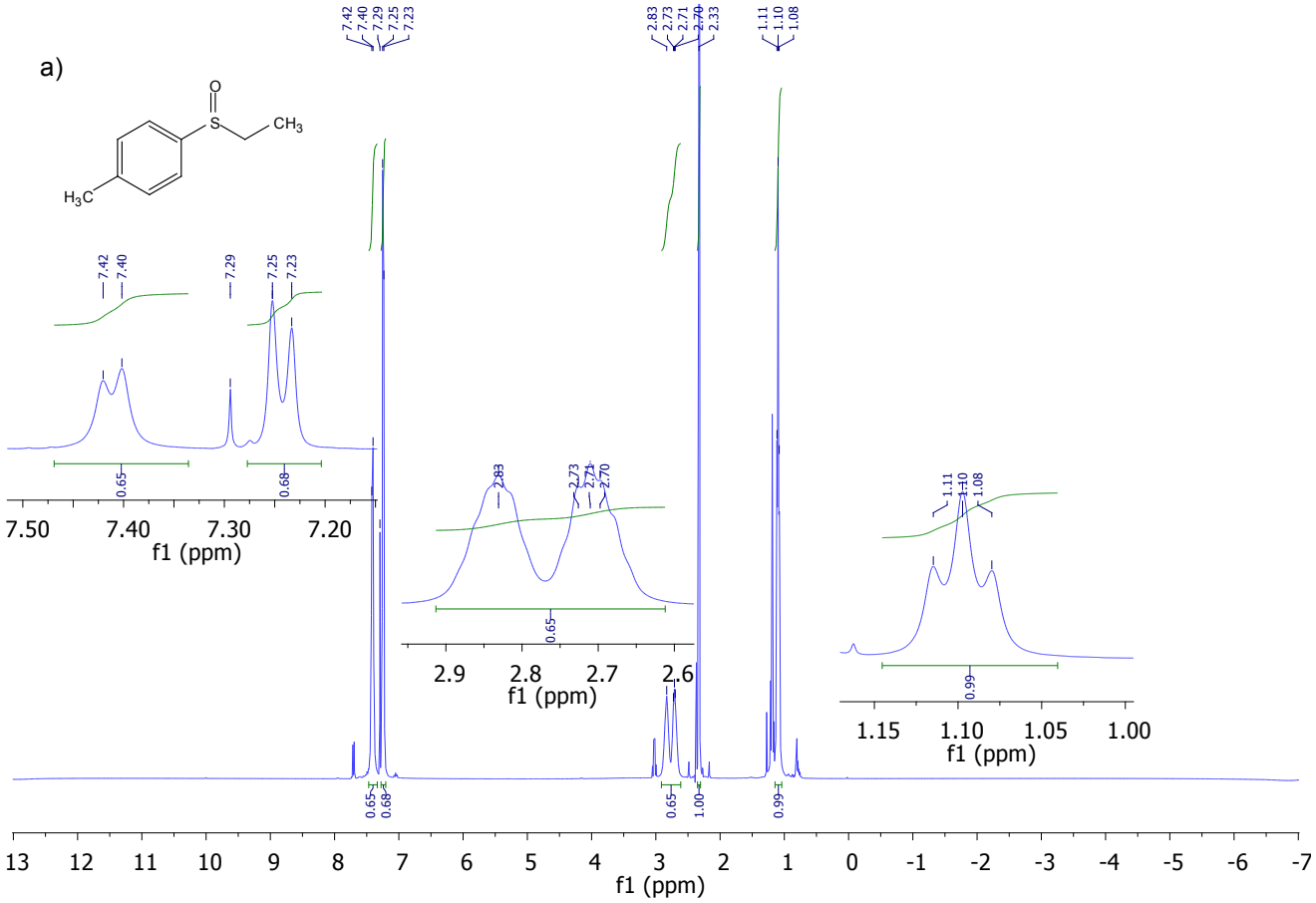


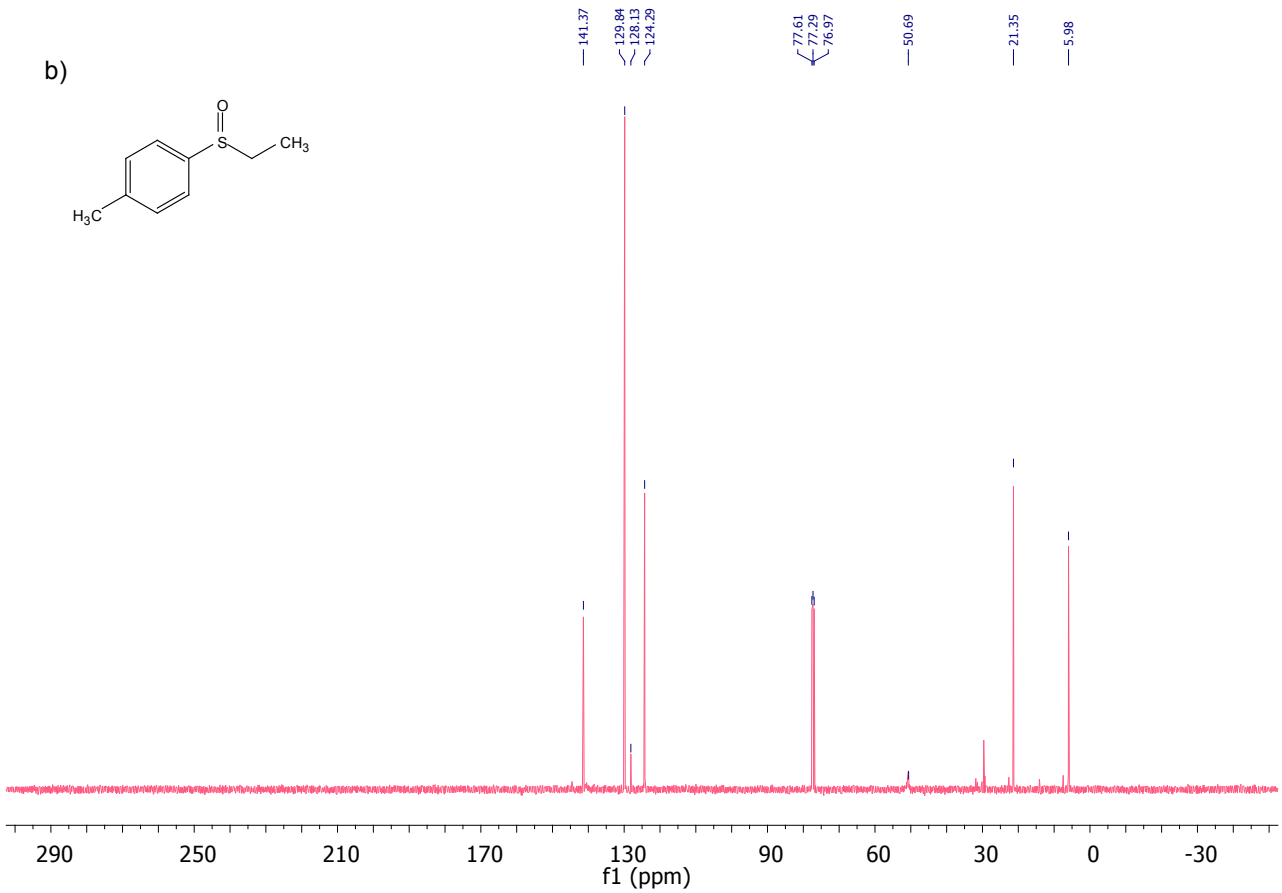
S21 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-methyl-4-(Methylsulfinyl)benzene **(5b)**.



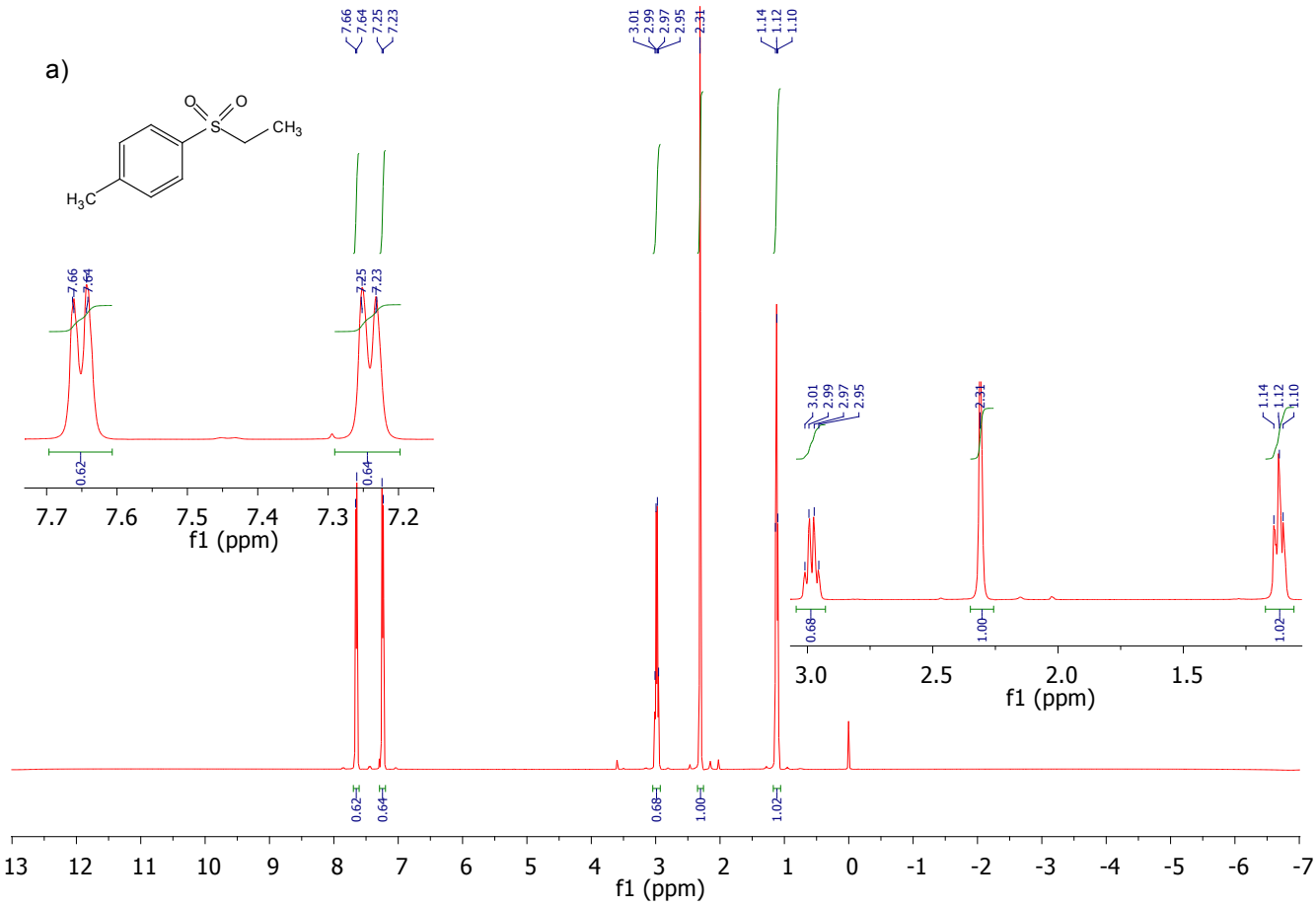


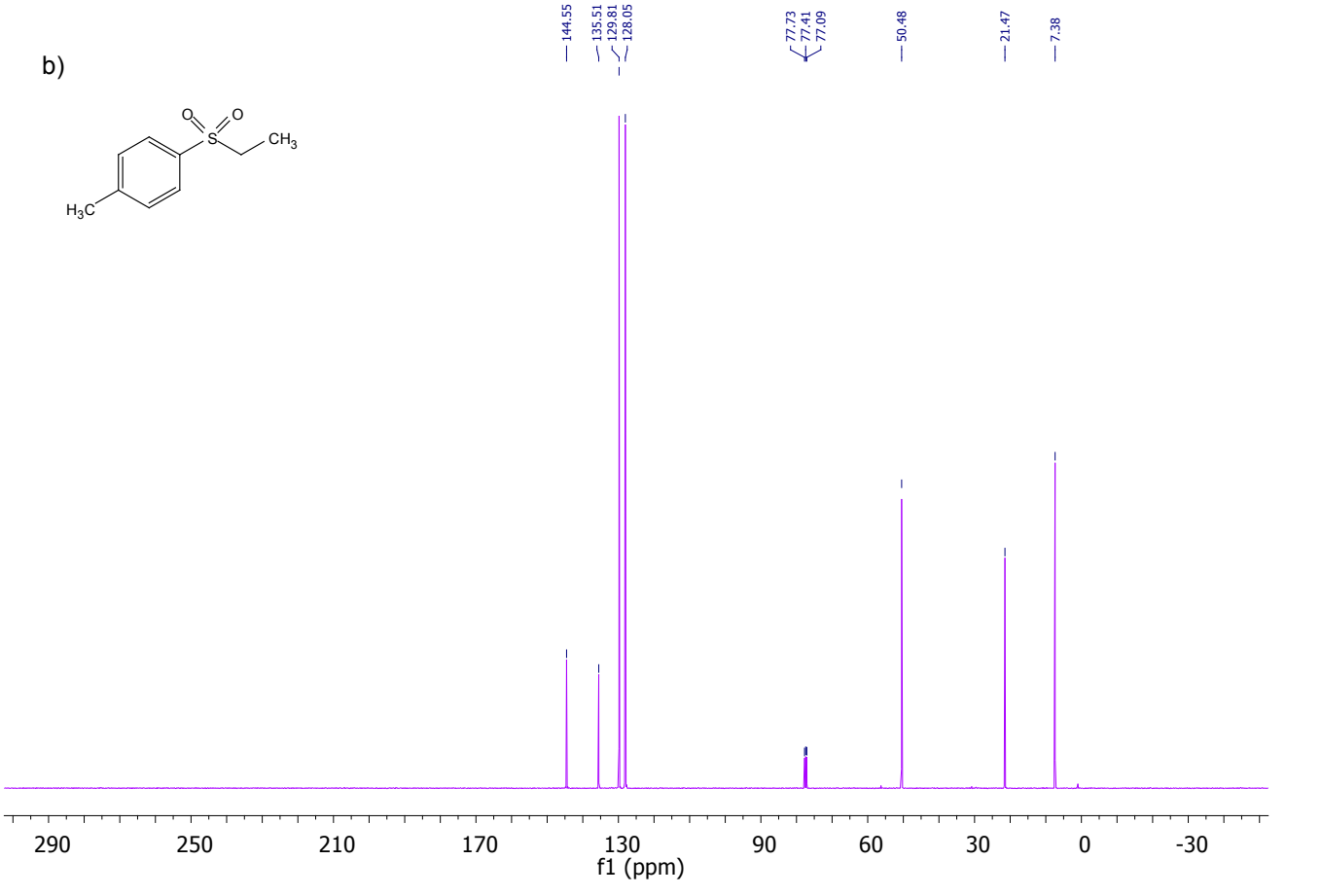
S22 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Ethylsulfinyl)-4-methylbenzene **(6b)**.



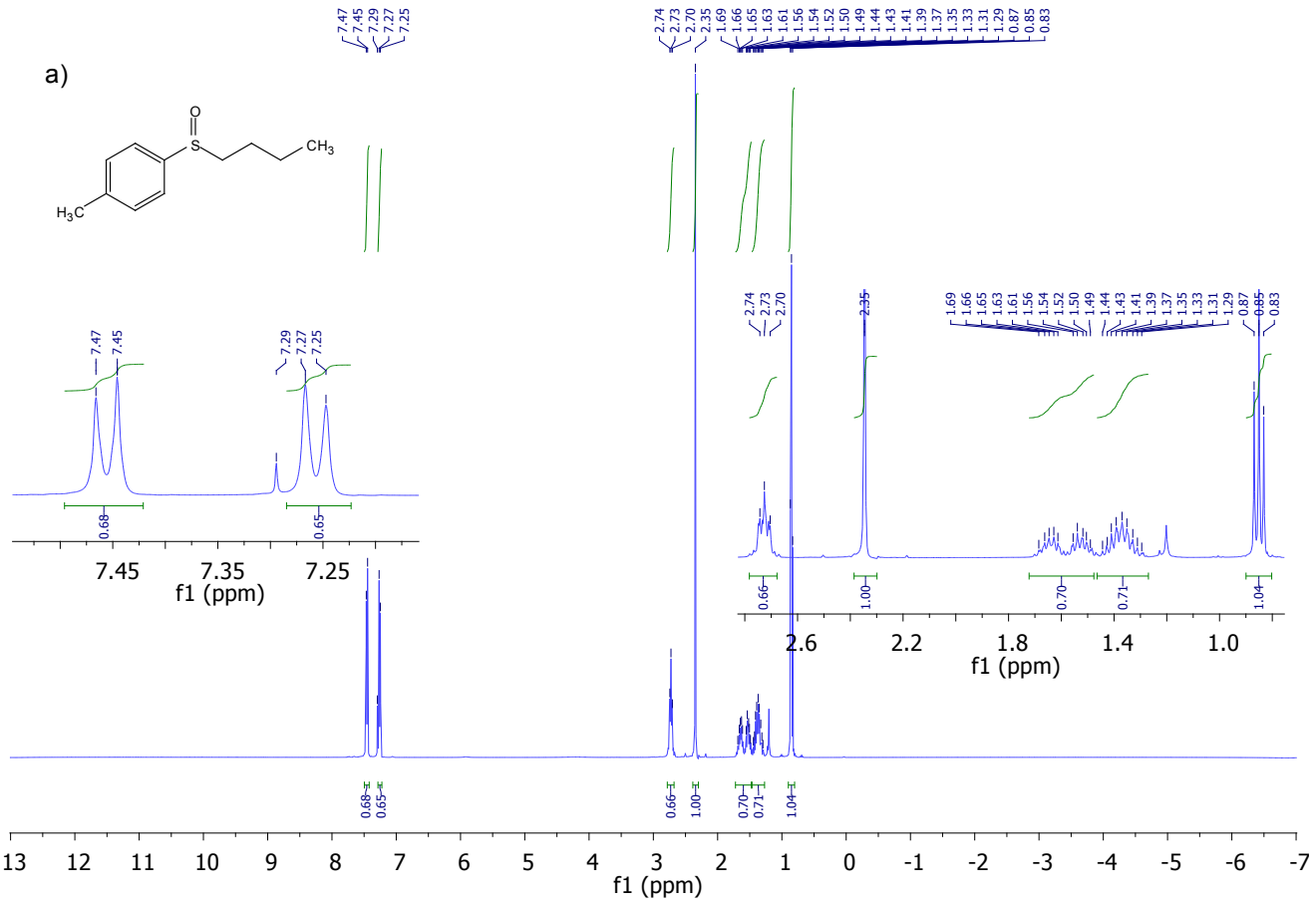


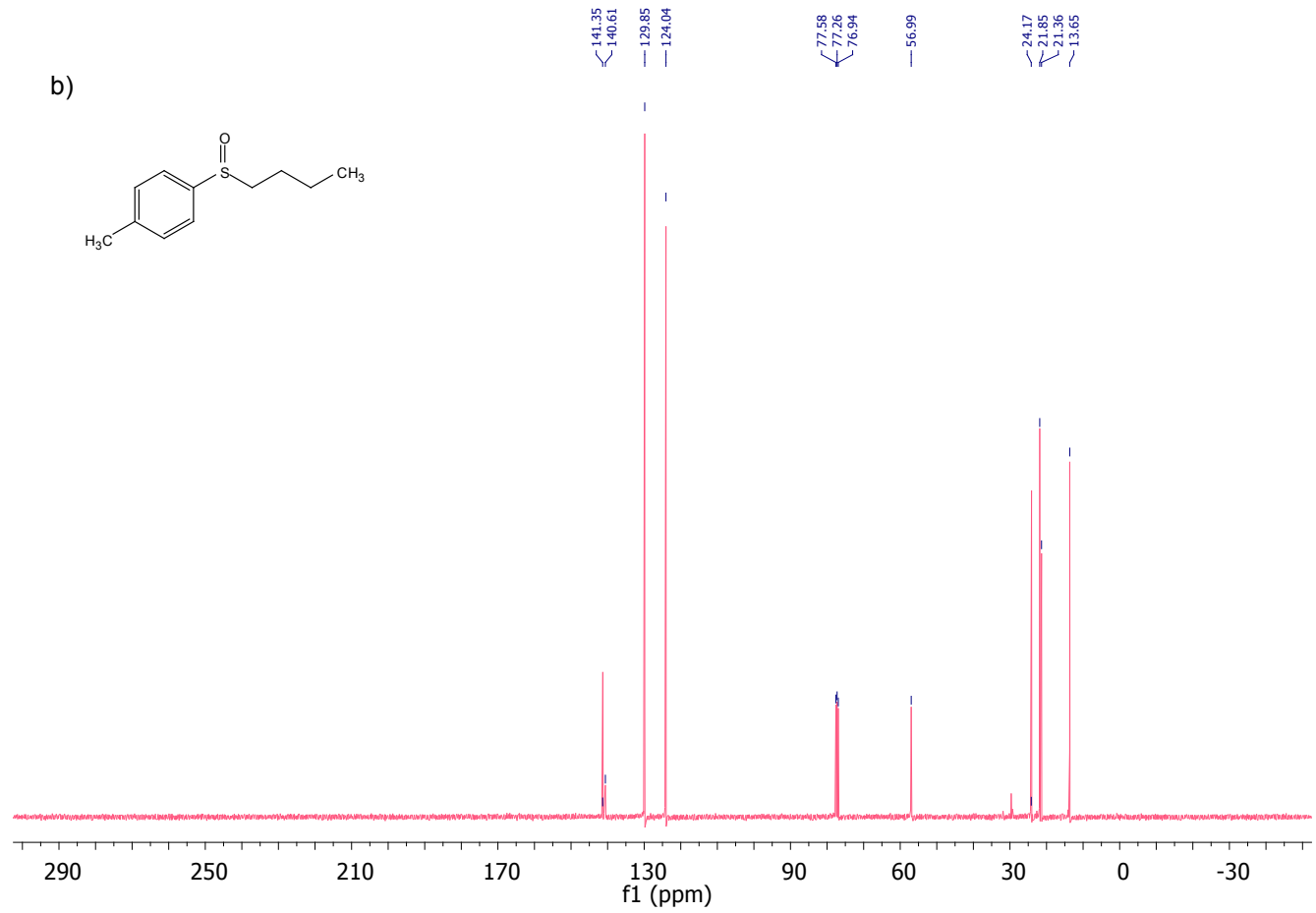
S23 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Ethylsulfonyl)-4-methylbenzene **(6c)**.



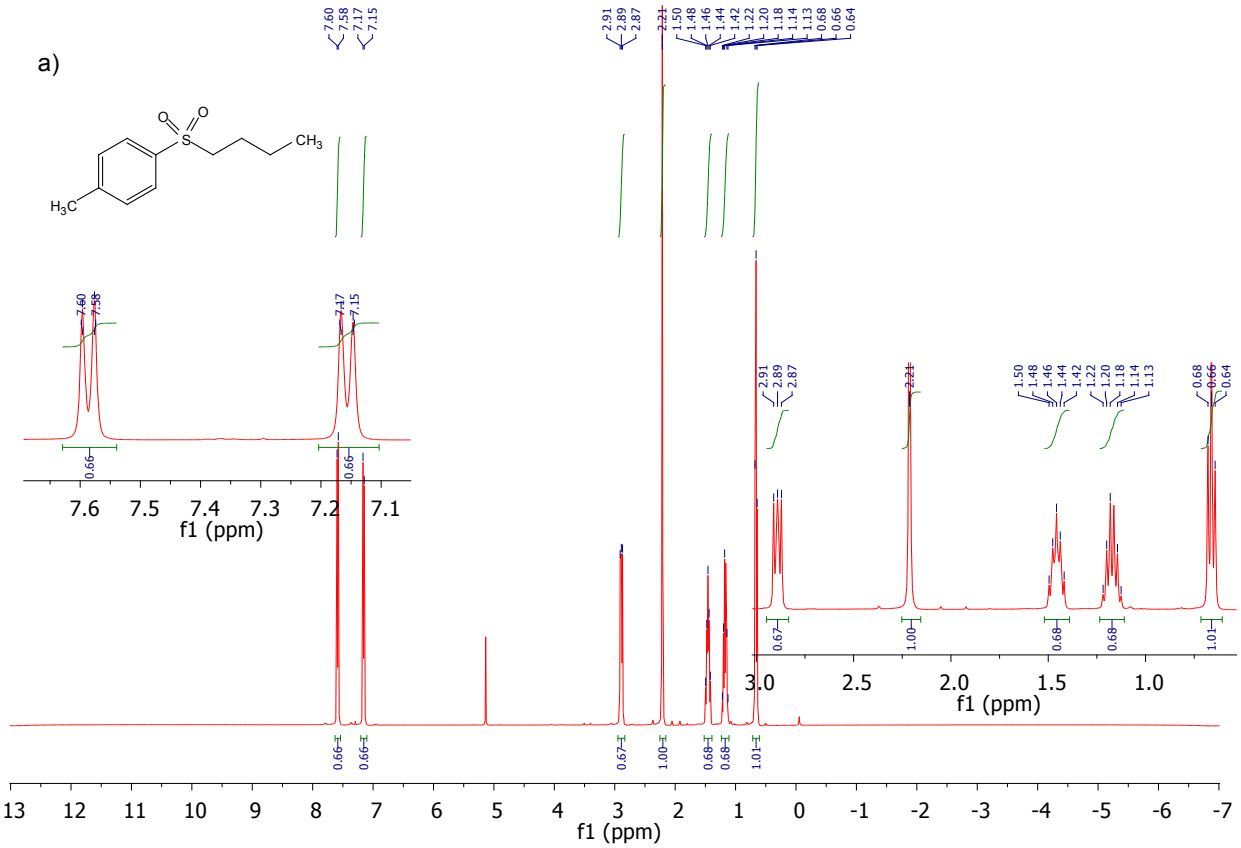


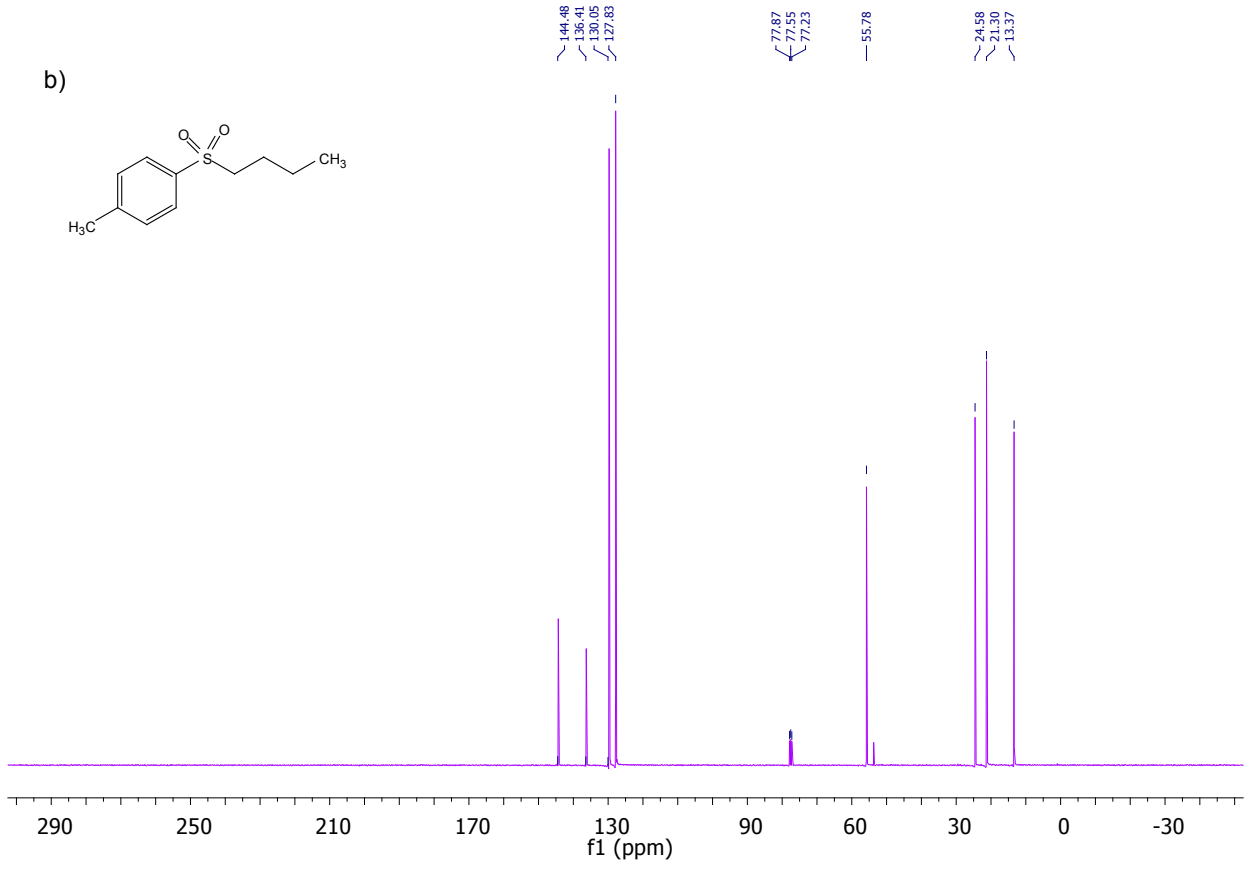
S24 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Butylsulfinyl)-4-methylbenzene **(7b)**.



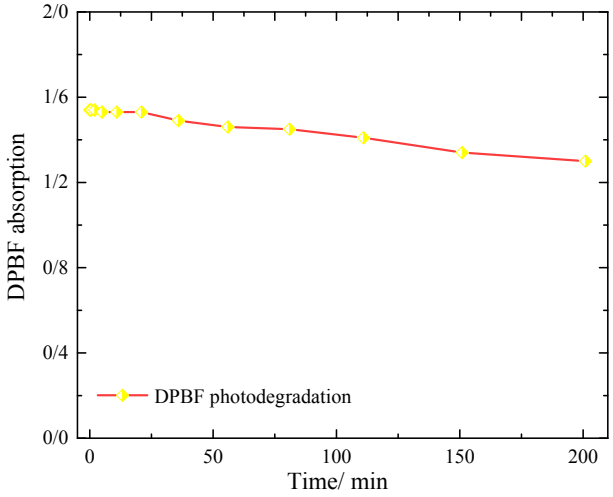


S25 (a,b): ^{1}H NMR, ^{13}C NMR spectra for 1-(Butylsulfonyl)-4-methylbenzene **(7c)**.

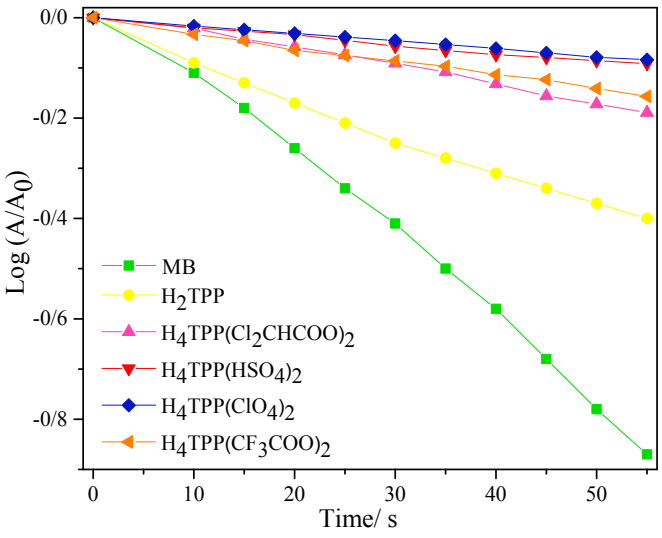




S26: The photostability of DPBF in the absence of $^1O_2$ under irradiation of a 10 W red LED lamp.



S27: Kinetic curves of DPBF decay upon oxidation with $^1O_2$ in the presence of H_2TPP and the corresponding diacids.



S28: The absorption spectrum of DPBF decay upon oxidation with $^1O_2$ in the presence of H_2TPP and the corresponding diacids.