Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information for

New insights on the influence of weak and strong acids on the oxidative stability and photocatalytic activity of porphyrins

Saeed Zakavi*, Saiedeh Hoseini and Aida G. Mojarrad

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

Contents:

S1a: Synthesis and spectral data (^{1}H NMR, ^{13}C NMR and UV-Vis) of the free base porphyrins

The *para* and *ortho* substituted meso-tetra(phenyl)porphyrins were synthesized and purified according to the Adler et al. method.[1] In a typical reaction, the solution of pyrrole (5.6 ml, 0.08 mol) and benzaldehyde (8 ml, 0.08 mol) were added to 300 ml refluxing propionic acid in a 1 l round bottom flask equipped with a water condenser. In order to prevent the aldehye and pyrrole from pouring or squirting out after addition to the refluxing propionic acid, pyrrole and benzaldehyde were separately dissolved in 5 ml propionic acid and then were added to the refluxing propionic acid (290 ml). The mixture was refluxed for 30 min. After cooling the reaction mixture to the room temperature, the solution was filtered and the filter cake was washed thoroughly with methanol and hot water, respectively. The product was chromatographed once on a neutral alumina column with dichloromethane to obtain purple crystals of H_2TPP. The spectral data (^{1}H NMR, ^{13}C NMR and UV-Vis) of the free base porphyrins are as follows. Also, the ^{1}H NMR and ^{13}C NMR spectra of the used porphyrins are shown in S2 to S7. The NMR data were in accordance with those reported in the literature.[2-6]

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 ($8H_\beta$, s); ^{13}C NMR (~100 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).

H_2T(4-OMe)PP. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: -2.72 (2H, br, s, NH), 7.29-7.32 ($8H_m$, d), 8.15-8.17 ($8H_o$, d), 8.89 ($8H_\beta$, s), 4.13 ($12H_{Me}$, s); ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 119.75 (C_{meso}), 134.67 (C_1), 135.62 (C_2, C_6), 112.20 (C_3, C_5), 159.39 (C_4), 131.34 (C_β), 55.61 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε)= 421 (5.61), 517 (4.32), 555 (4.22), 593 (4.06), 651 (4.11).

H_2T(2-Me)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.59 (2H, br, s, NH), 7.54-7.74 ($8H_m$ and $4H_p$, m, meta and para-position relative to C atom attached to meso position), 7.99-8.11 ($4H_o$, m, ortho-position relative to C atom attached to meso position), 8.70 ($8H_\beta$, s), 2.01-2.11 ($12H_{Me}$, m);); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 118.82 (C_{meso}), 139.54 (C_1), 139.63 (C_2), 128.38 (C_3), 129.22 (C_4), 124.21 (C_5), 133.90 (C_6), 141.48 (C_α), 129.22 (C_β), 21.37 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 416 (6.04), 512 (4.74), 545 (4.34), 589 (4.34), 645 (4.25).

H_2T(4-Me)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.76 (2H, br, s, NH), 7.55-7.58 ($8H_m$, d), 8.09-8.12 ($8H_o$, d), 8.86 ($8H_\beta$, s), 2.65 ($12H_{Me}$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 120.47 (C_{meso}), 139.73 (C_1), 134.92 (C_2, C_6), 127.81 (C_3, C_5), 137.71 (C_4), 131.37 (C_β), 21.57 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 418 (5.89), 516 (4.54), 551 (4.34), 590 (4.18), 647 (4.20).

H_2T(2-Cl)PP. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: -2.62 (2H, br, s, NH), 7.66-7.87 ($8H_m$ and $4H_p$, m, meta and para-position relative to C atom attached to meso position), 8.10-8.26 ($4H_o$, m, ortho-position relative to C atom attached to meso position), 8.72 ($8H_\beta$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 116.76 (C_{meso}), 137.10 (C_1), 136.94 (C_2), 129.01 (C_3), 129.93 (C_4), 125.32 (C_5), 135.52 (C_6), 140.50 (C_α), 135.39 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 416 (5.64), 512 (4.47), 543 (4.07), 587 (4.15), 643 (3.96).

H_2T(4-Cl)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.83 (2H, br, s, NH), 7.77-7.79 ($8H_m$, d), 8.15-8.17 ($8H_o$, d), 8.87 ($8H_\beta$, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 119.01 (C_{meso}), 140.37 (C_1), 135.52 (C_2, C_6), 127.07 (C_3, C_5), 134.41 (C_4), 131.64 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 418 (5.79), 513 (4.52), 547 (4.25), 590 (4.16), 647 (4.10).

S1b: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrin dications with CF_3COOH

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 ($8H_\beta$, m); ^{13}C NMR (~100MHz, $CDCl_3$, 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).

H_4T(4-OMe)PP(CF_3COO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 0.425 (4H, br, s, NH), 7.553-8.573 (8H_m, d), 8.527-8.562 (8H_β, 8H_o, br), 4.195 (12H_{Me}, s); ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 122.09 (C_{meso}), 133.44 (C_1), 140.01 (C_2, C_6), 114.01 (C_3, C_5), 161.49 (C_4), 146.11 (C_α), 127.75 (C_β), 55.84 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 449 (5.77), 686 (5.07).

H_4T(2-Me)PP(CF_3COO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -0.954 (4H, br, s, NH), 7.721-7.895 (8H_m and 4H_p, br, meta and para-positions relative to C atom attached to the meso position), 8.181-8.216 (4H_o, br, ortho-position relative to the C atom attached to the meso position), 8.651-8.682 (8H_β, s), 2.208-2.285 (H_{Me}, m); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 121.47 (C_{meso}), 138.33 (C_1), 140.86 (C_2), 128.41 (C_3), 129.08 (C_4), 125.39 (C_5), 136.62 (C_6), 145.51 (C_α), 130.54 (C_β), 21.87 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 432 (5.99), 583 (6.46), 633 (4.89).

H_4T(4-Me)PP(CF_3COO)$_2$. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 0.42 (4H, br, s, NH), 7.79-7.82 (8H_m, d), 8.46-8.49 (8H_o, d), 8.55 (8H_β, s), 2.67 (12H_{Me}, s); ^{13}C NMR (~100MHz,$CDCl_3$, TMS), δ/ppm: 122.60 (C_{meso}), 137.56 (C_1), 138.62 (C_2, C_6), 129.12 (C_3, C_5), 140.31 (C_4), 145.85 (C_α), 127.95 (C_β), 21.68 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 442 (5.85), 666 (5.01).

H_4T(2-Cl)PP(CF_3COO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 1.5 (4H, br, s, NH), 7.77-7.938 (8H_m and 4H_p, m, meta and para-positions relative to the C atom attached to the meso position), 8.29 (4H_o, br, ortho-position relative to C atom attached to the meso position), 8.681 (8H_β, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 117.99 (C_{meso}), 137.39 (C_1), 137.72 (C_2), 129.58 (C_3, C_4), 125.88 (C_5), 136.75 (C_6), 146.16 (C_α), 131.04 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 431 (5.76), 580 (4.69), 632 (4.75).

H_4T(4-Cl)PP(CF_3COO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 0.392 (4H, br, s, NH), 8.026-8.046 (8H_m, d), 8.518-8.539 (8H_o, d), 8.635 (8H_β, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 121.73 (C_{meso}), 138.11 (C_1), 139.22 (C_2, C_6), 128.81 (C_3, C_5), 137.50 (C_4), 145.67 (C_α), 128.38 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 439 (6.06), 656 (5.16).

S1c: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrin dications with $HClO_4$

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 (~100MHz, $CDCl_3$, 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).

H_4T(2-Cl)PP(ClO_4)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 1.3(4H, br, s, NH), 7.84-8.03 (8H_m and 4H_p, m, meta and para-positions relative to the C atom attached to the meso position), 8.38-8.42 (4H_o, br, ortho-position relative to C atom attached to the meso position), 8.79-8.26 (8H_β, m); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 119.46 (C_{meso}), 137.80 (C_1), 138.32(C_2), 129.87 (C_3, C_4), 126.52(C_5), 137.29 (C_6), 146.20 (C_α), 132.17 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 435 (4.60), 583 (3.41), 631 (3.50).

S1d: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrin dications with HCl

H_4TPP(Cl)$_2$. ^{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_β, m), no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100MHz, $CDCl_3$, 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).

H_4T(2-Cl)PP(Cl)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 1.497(4H, br, s, NH), 7.84-8.01 (8H_m and 4H_p, m, meta and para-positions relative to the C atom attached to the meso position), 8.37 (4H_o, br, ortho-position relative to C atom attached to the meso position), 8.53 (8H_β, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 118.72 (C_{meso}), 138.21 (C_1), 138.63 (C_2), 127.97 (C_3), 130.08 (C_4), 126.39 (C_5), 137.75 (C_6), 146.13 (C_α), 131.79 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 444 (4.48), 591 (3.39), 641 (3.49).

S1e: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrin dications with $CHCl_2COOH$

H_4TPP($CHCl_2COO$)$_2$. ^{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); ^{13}C NMR (~100 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).

H_4T(2-Cl)PP($CHCl_2COO$)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 1.3(4H, br, s, NH), 7.85-8.02 (8H_m and 4H_p, br, meta and para-positions relative to the C atom attached to the meso position), 8.34-8.47(4H_o, br, ortho-position relative to C atom attached to meso position), 8.65-8.71 (8H_β, br); ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 119.20 (C_{meso}), 137.76 (C_1), 138.52 (C_2), 129.07 (C_3, C_4), 126.73 (C_5), 137.53 (C_6), 145.58(C_α), 130.09 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 435 (4.47), 582 (3.36), 632 (3.45).

S1f: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrins dication with $CH_2ClCOOH$

H_4TPP(CH_2ClCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 8.009-8.078 (8H_m and 4H_p, m), 8.7 (8H_o, m), 8.78 (8H_β, s); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 122.63 (C_{meso}), 140.26 (C_1), 138.19 (C_2, C_6), 128.81 (C_3, C_5), 129.82 (C_4), 145.93 (C_α), 128.22 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm: 440 , 608, 659.

H_4T(4-OMe)PP(CH_2ClCOO)$_2$. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 7.57-7.59 (8H_m and 8H_o, d), 8.58 (8H_β, s), 4.19 (12H_{Me}, s); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 122.18 (C_{meso}), 133.44 (C_1), 139.95 (C_2, C_6), 114.05 (C_3, C_5), 161.52 (C_4), 146.13 (C_α), 128.13 (C_β), 56.28 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm: 452, 693.

H_4T(2-Me)PP(CH_2ClCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.72-7.8 (8H_m and 4H_p, br, meta and para-position relative to C atom attached to meso position), 8.21-8.28 (4H_o, br, ortho-position relative to C atom attached to meso position), 8.73-8.75 (8H_β, br), 2.24-2.32 (H_{Me}, m); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 120.3 (C_{meso}), 140.3 (C_1, C_2), 129.8 (C_3), 129.5 (C_4), 124.8 (C_5), 135.5 (C_6), 145.15 (C_α), 129.8 (C_β), 21.93 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm: 434, 584, 635.

H_4T(4-Me)PP(CH_2ClCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.85-7.87 (8H_m, d), 8.5334-8.56 (8H_o, d), 8.64 (8H_β, s), 2.71 (12H_{Me}, s); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 122.8 (C_{meso}), 137.43 (C_1), 138.64 (C_2, C_6), 129.22 (C_3, C_5), 140.5 (C_4), 145.8 (C_α), 128.22 (C_β), 21.48 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm: 445, 670.

H_4T(2-Cl)PP(CH_2ClCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.8-7.99 (8H_m and 4H_p, br, meta and para-positions relative to the C atom attached to the meso position), 8.3-8.5 (4H_o, br, ortho-position relative to C atom attached to meso position), 8.70-8.72 (8H_β, br); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 118.72 (C_{meso}), 137.7 (C_1), 137.83 (C_2), 128.28 (C_3, C_4), 126.46 (C_5), 137.53 (C_6), 145.7 (C_α), 131.81 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm: 434, 581, 632.

H_4T(4-Cl)PP(CH_2ClCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.98 (8H_m, d), 8.49 (8H_o, d), 8.74 (8H_β, s); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 121.8 (C_{meso}), 138.44 (C_1), 139.3 (C_2, C_6), 128.9 (C_3, C_5), 137.4 (C_4), 145.78 (C_α), 128.6 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm: 443, 660.

S1g: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the porphyrin dications with HCOOH

H_4TPP($HCOO$)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.777 (8H_m and 4H_p, d), 8.174 (8H_o, d), 8.828 (8H_β, s); no signal was observed for the NH protons at 20 ^{0}C, but at -60 ^{0}C, the NH resonance was observed at δ 0.49 ppm[1].; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 123.26 (C_{meso}), 139.23 (C_1), 138.85 (C_2, C_6), 129 (C_3, C_5), 130.70 (C_4), 145.67 (C_α), 128.78 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 439 (5.75), 604 (4.42), 657 (4.89).

H_4T(4-OMe)PP($HCOO$)$_2$. ^{1}H NMR (400MHz, $CDCl_3$, TMS), δ/ppm: 7.532 (8H_m, d), 8.547 (8H_o, d), 8.56 (8H_β, s), 4.162 (12H_{Me}, s); no signal was observed for the NH protons at 20 ^{0}C, but at -60 ^{0}C, the NH resonance was observed at δ

0.42 ppm[1].; ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 122.59 (C_{meso}), 132.67 (C_1), 140.31 (C_2, C_6), 114.62 (C_3, C_5), 162.13 (C_4), 145.99 (C_α), 128.46 (C_β), 55.89 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 452 (5.36), 695 (4.73).

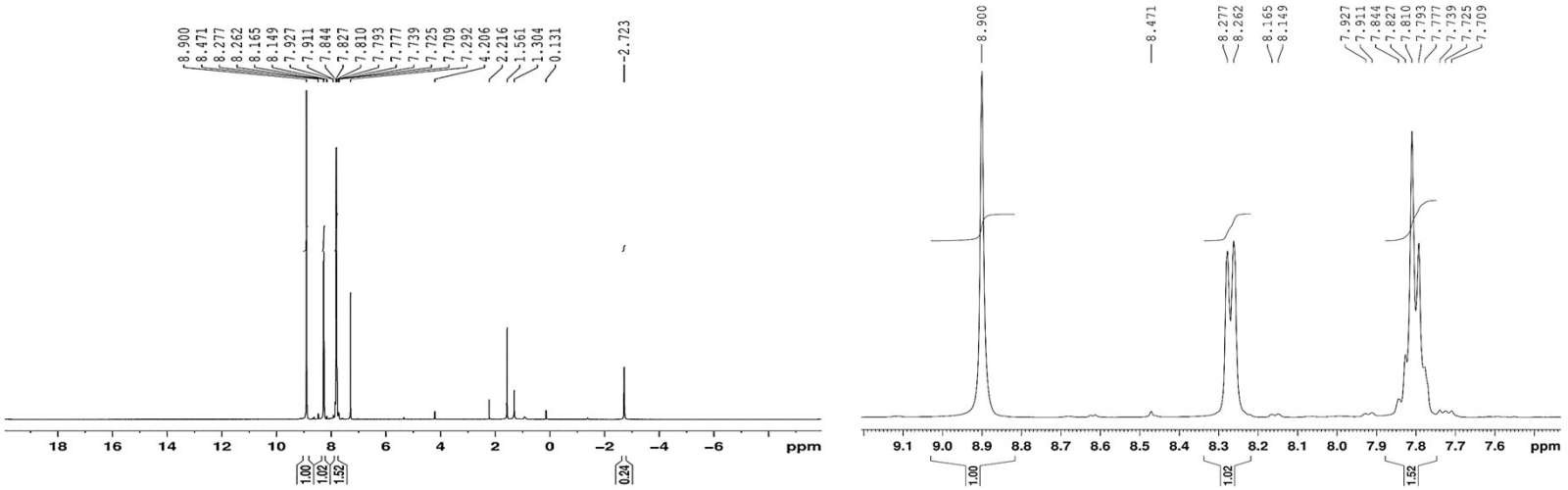
H_4T(2-Me)PP(HCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.863-7.9 (8H_m and 4H_p, br, meta and para-position relative to C atom attached to meso position), 8.254-8.332 (4H_o, br, ortho-position relative to C atom attached to meso position), 8.73-8.76 (8H_β, br), 2.144-2.203 (H_{Me}, m); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 121.69 (C_{meso}), 138.12 (C_1), 140.86 (C_2), 129.53 (C_3), 129.56 (C_4), 125.62 (C_5), 136.54 (C_6), 145.63 (C_α), 130.60 (C_β), 21.03 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 433 (5.79), 582 (4.49), 635 (4.69).

H_4T(4-Me)PP(HCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.88-7.91 (8H_m, d), 8.533-8.553 (8H_o, d), 8.7 (8H_β, s), 2.767 (12H_{Me}, s); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 123.1 (C_{meso}), 136.87 (C_1), 138.86 (C_2, C_6), 129.63 (C_3, C_5), 141.34 (C_4), 145.75 (C_α), 128.68 (C_β), 21.62 (C_{Me}); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 443 (5.88), 672 (5.09).

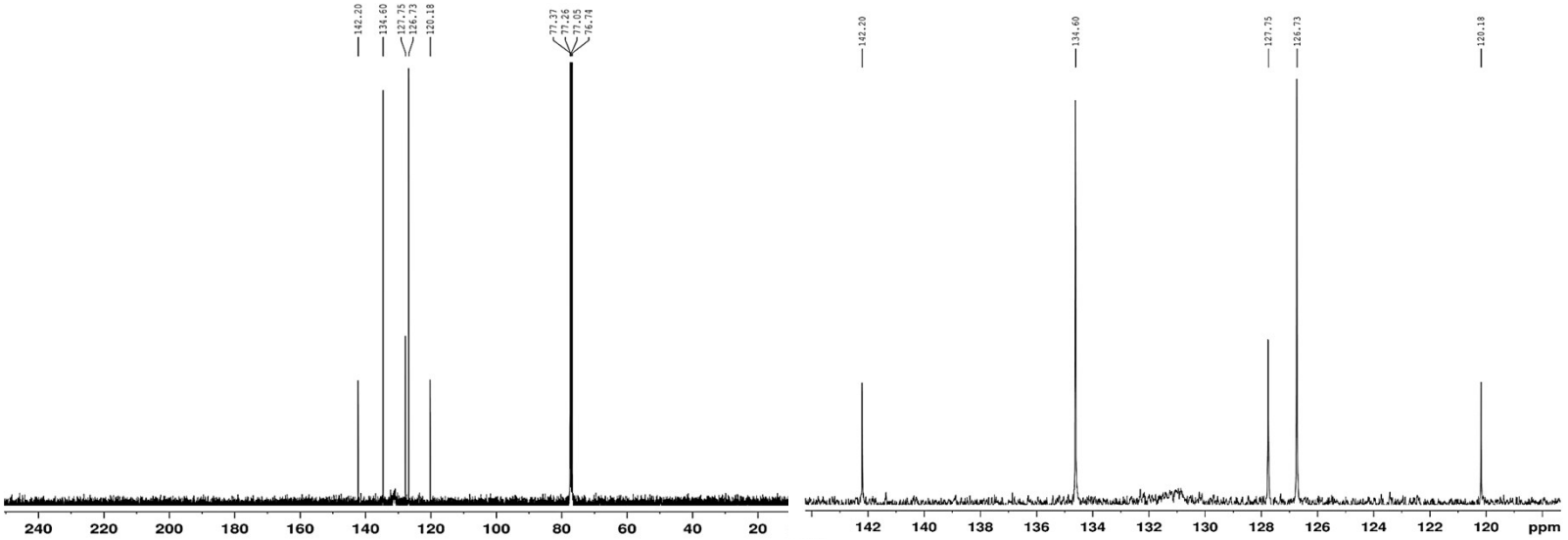
H_4T(2-Cl)PP(HCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.92-7.95 (8H_m and 4H_p, br, meta and para-positions relative to the C atom attached to the meso position), 8.4-8.5 (4H_o, br, ortho-position relative to C atom attached to meso position), 8.78-8.826 (8H_β, br); no signal was observed for the NH protons at 20 ^{0}C.; ^{13}C NMR (~100MHz, $CDCl_3$, TMS), δ/ppm: 119.24 (C_{meso}), 137.83 (C_1), 138.02 (C_2), 129.87 (C_3, C_4), 126.62 (C_5), 136.84 (C_6), 145.57 (C_α), 132.55 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 432 (5.65), 580 (4.41), 631 (4.52).

H_4T(4-Cl)PP(HCOO)$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 7.746 (8H_m, d), 8.4 (8H_o, d), 8.674 (8H_β, s); no signal was observed for the NH protons at 20 ^{0}C, but at -60 ^{0}C, the NH resonance was observed at δ 0.19 ppm[1].; ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 122.17 (C_{meso}), 138.09 (C_1), 139.59 (C_2, C_6), 129.19 (C_3, C_5), 137.54 (C_4), 145.66 (C_α), 128.94 (C_β); UV-vis in CH_2Cl_2, λ_{max}/nm (logε): 442 (5.65), 662 (4.91).

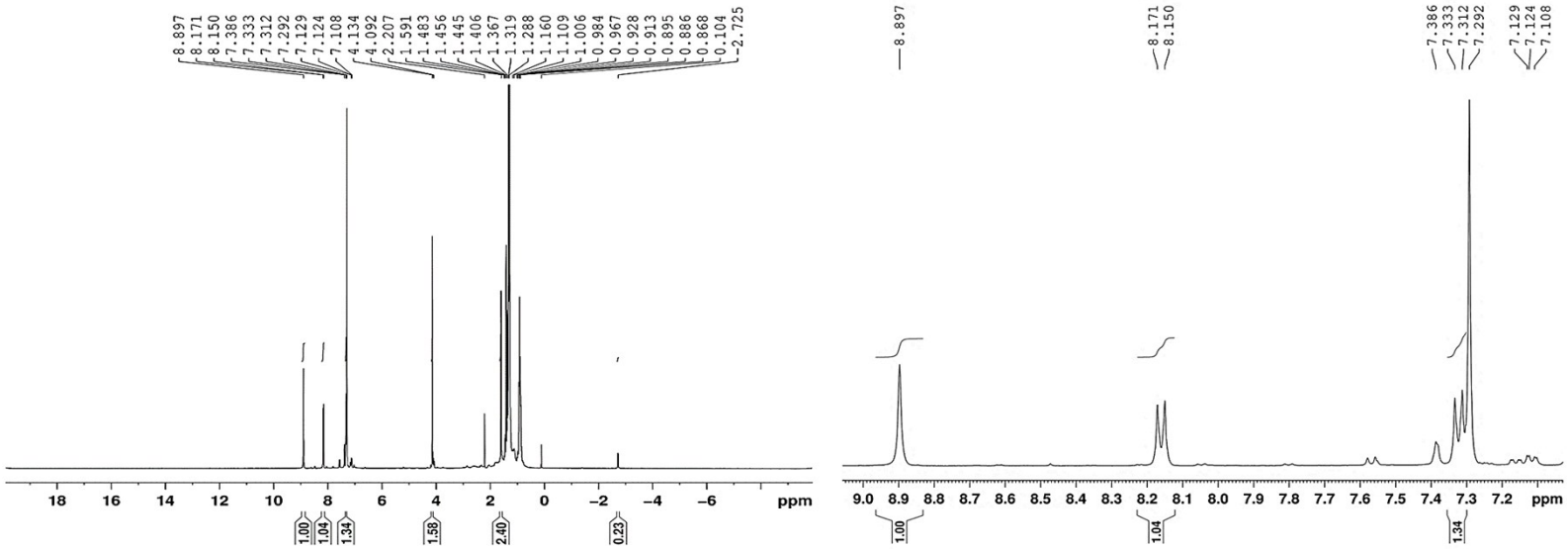
S2(a,b): ^{1}H NMR spectra of H_2TPP and the expansion of aromatic region



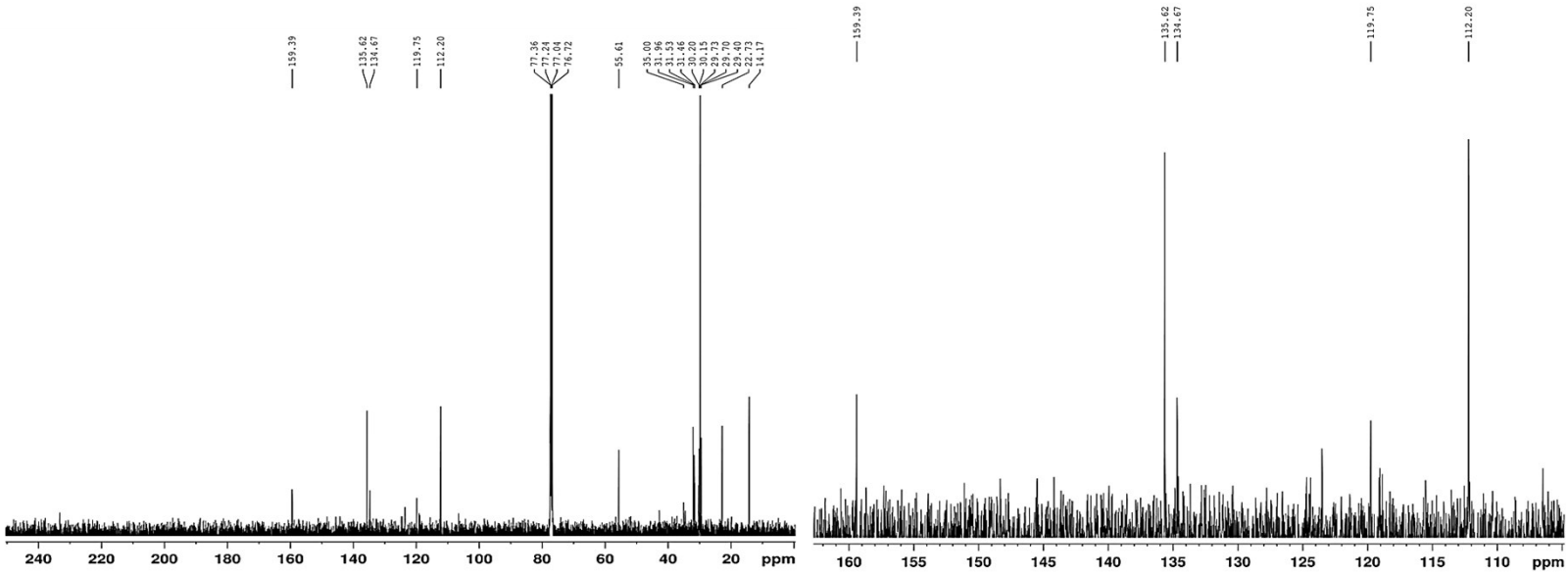
S2(c,d): ^{13}C NMR spectra of H_2TPP and the expansion of aromatic region



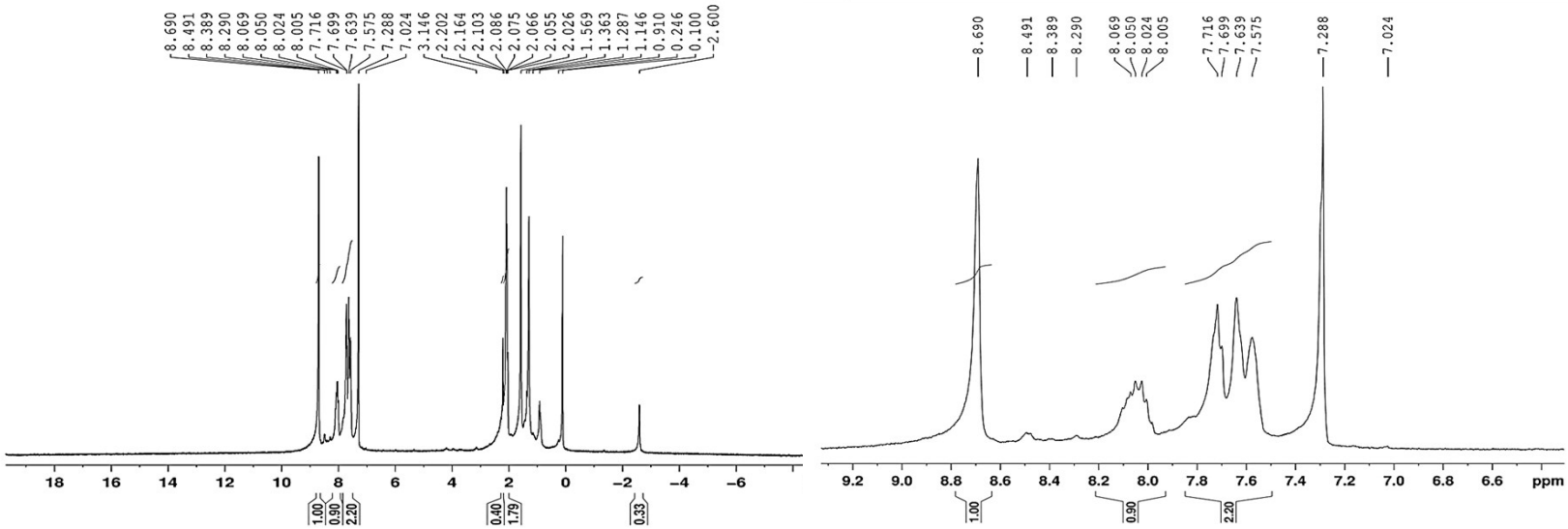
S3(a,b): ^{1}H NMR spectra of $H_2T(4\text{-}OMe)PP$ and the expansion of aromatic region



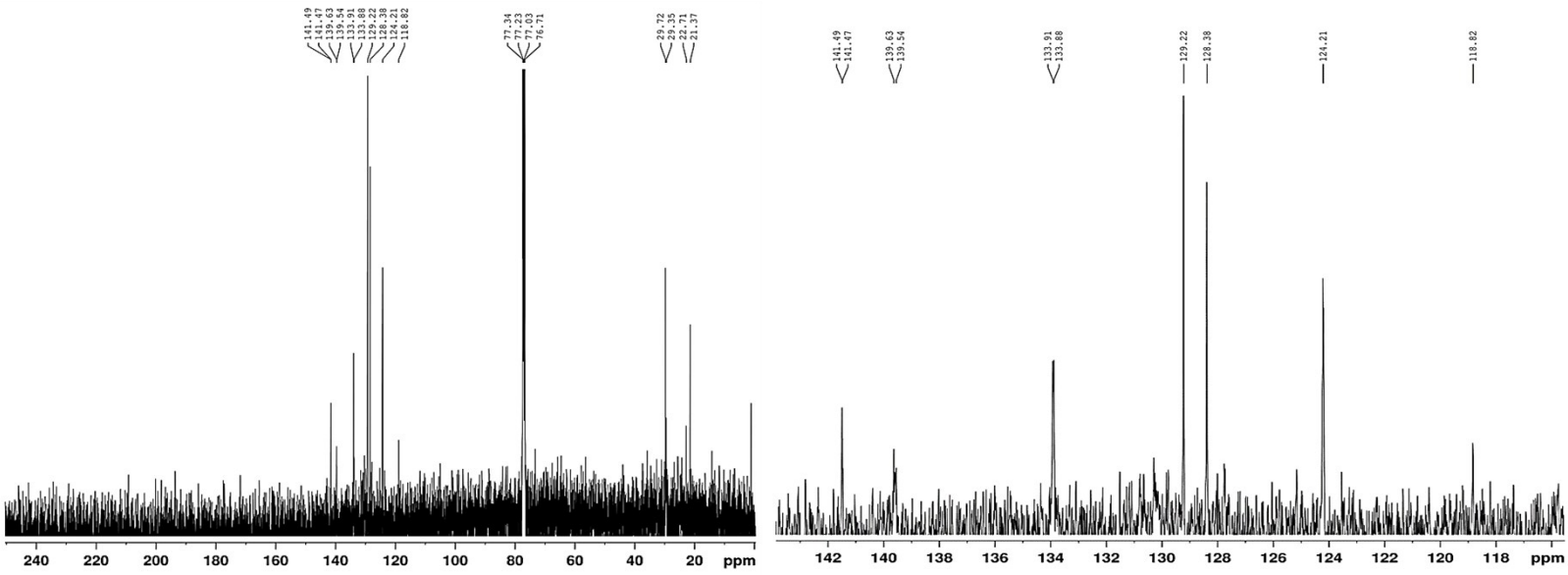
S3(c,d): ^{13}C NMR spectra of $H_2T(4\text{-}OMe)PP$ and the expansion of aromatic region



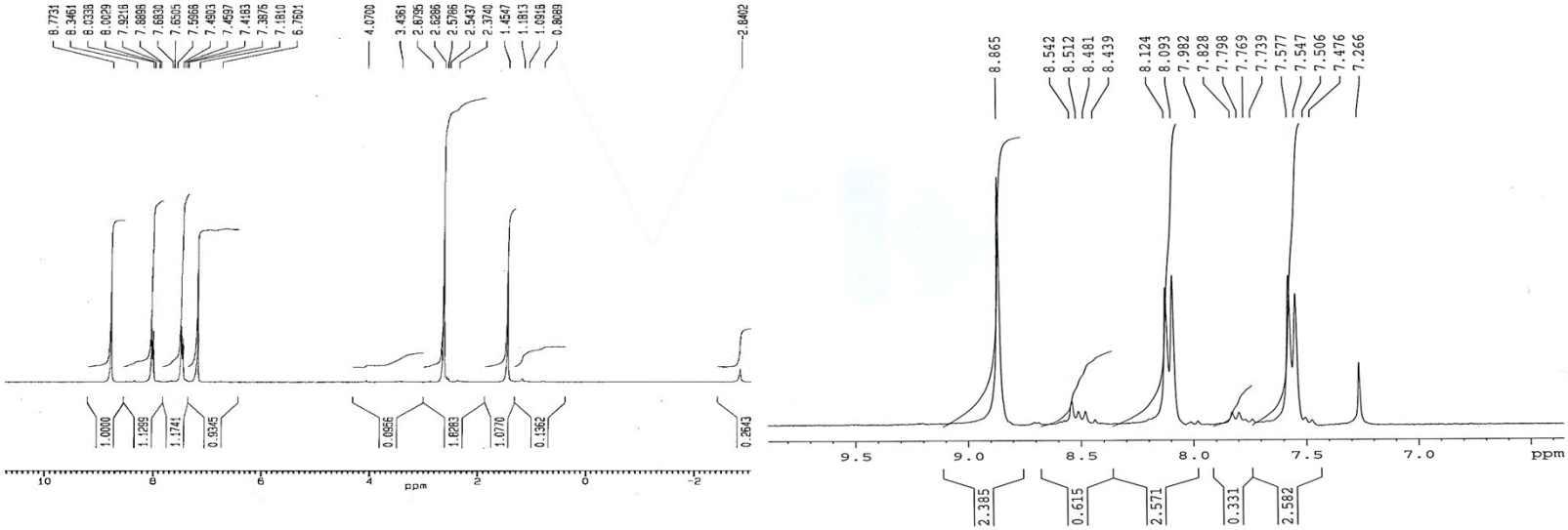
S4(a,b): ^{1}H NMR spectra of $H_2T(2\text{-}Me)PP$ and the expansion of aromatic region



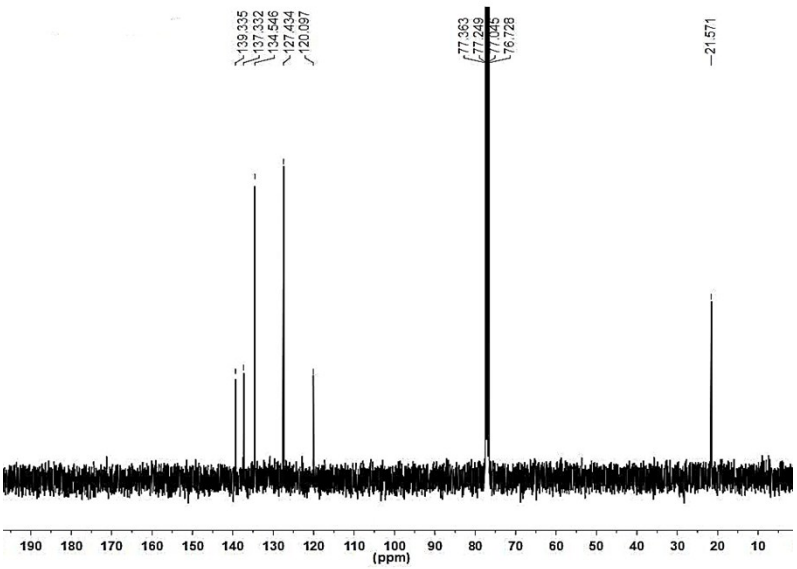
S4(c,d): ^{13}C NMR spectra of $H_2T(2\text{-Me})PP$ and the expansion of aromatic region

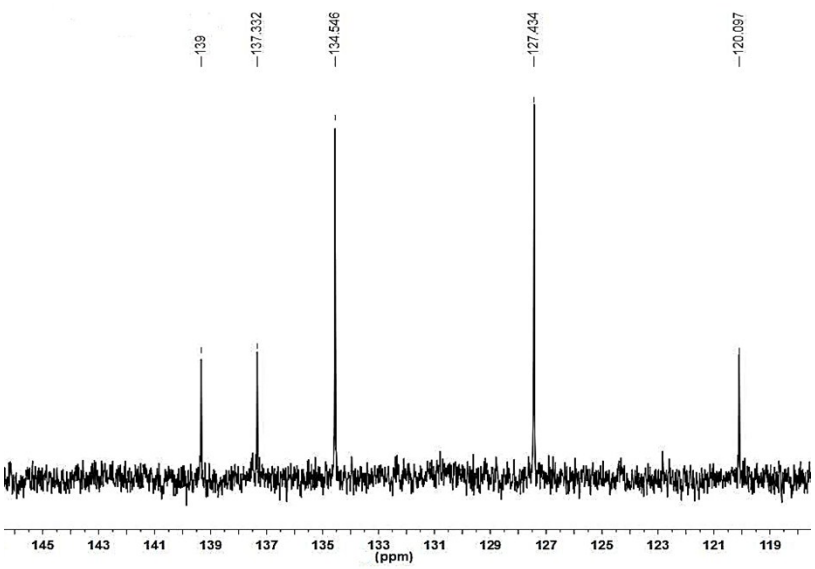


S5(a,b): ^{1}H NMR spectra of $H_2T(4\text{-Me})PP$ and the expansion of aromatic region

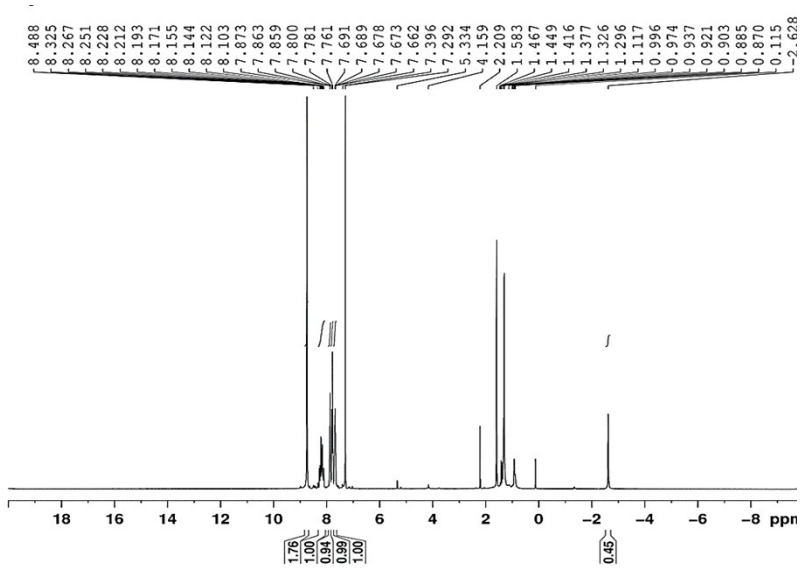


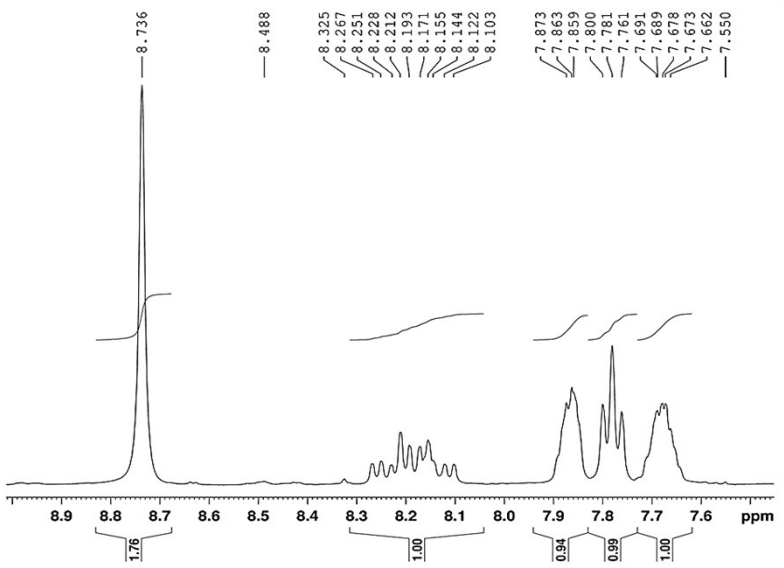
S5(c,d): ^{13}C NMR spectra of $H_2T(4\text{-Me})PP$ and the expansion of aromatic region



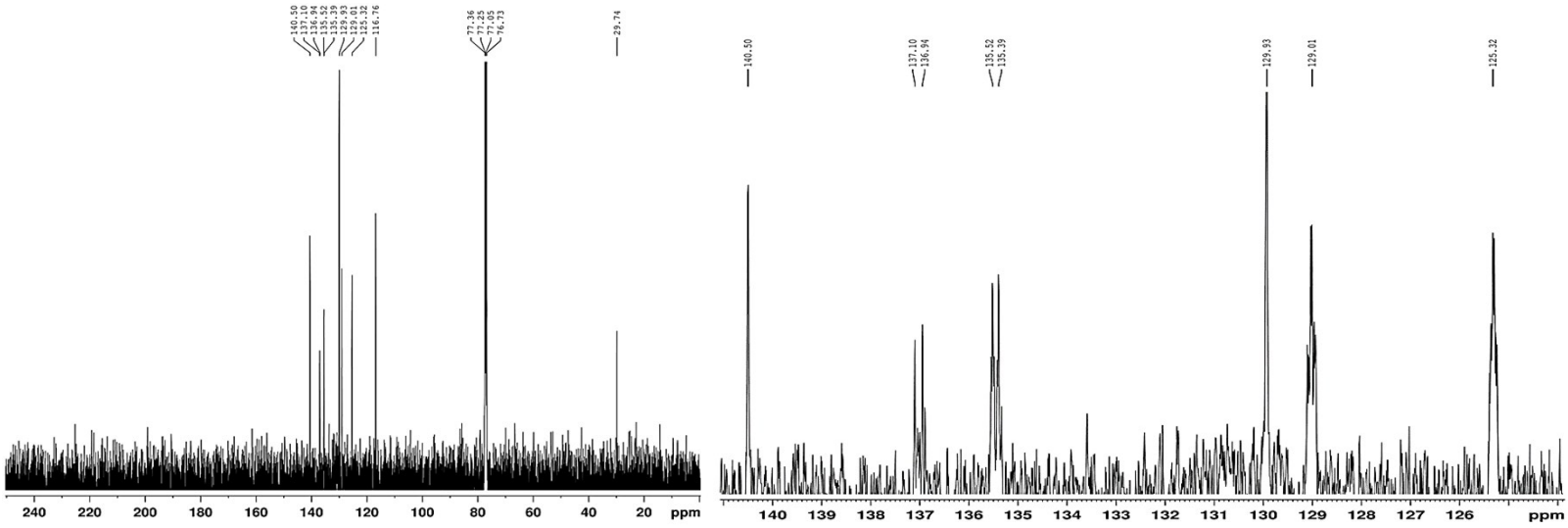


S6(a,b): ^{1}H NMR spectra of $H_2T(2\text{-Cl})PP$ and the expansion of aromatic region

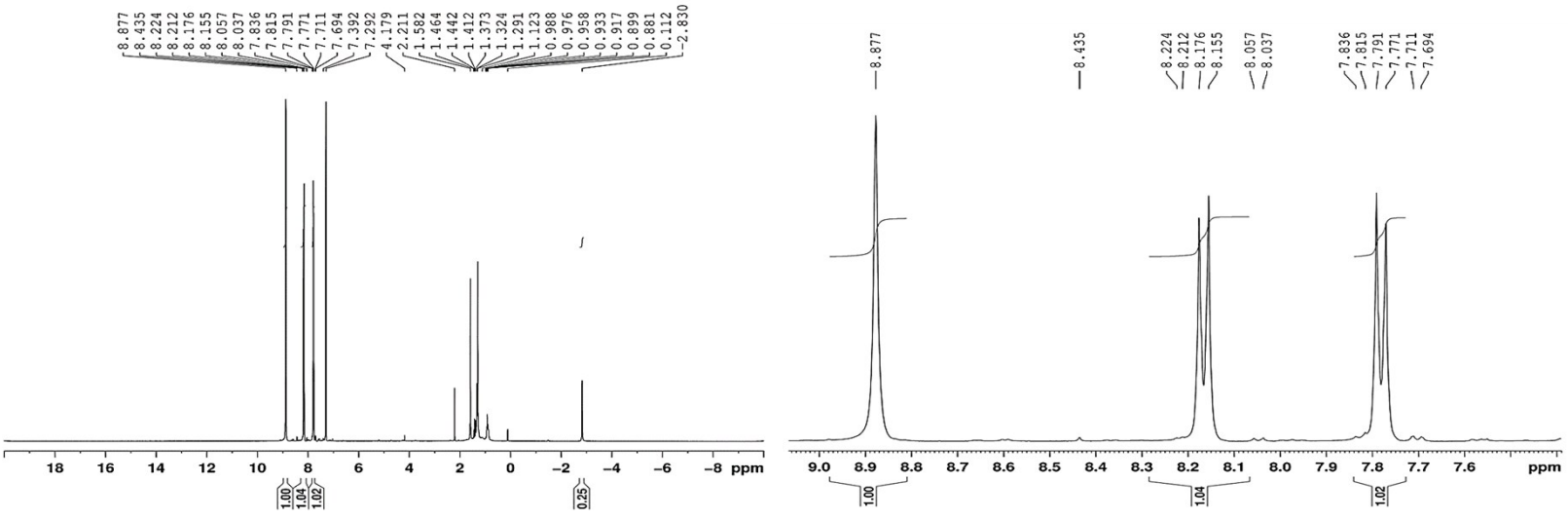




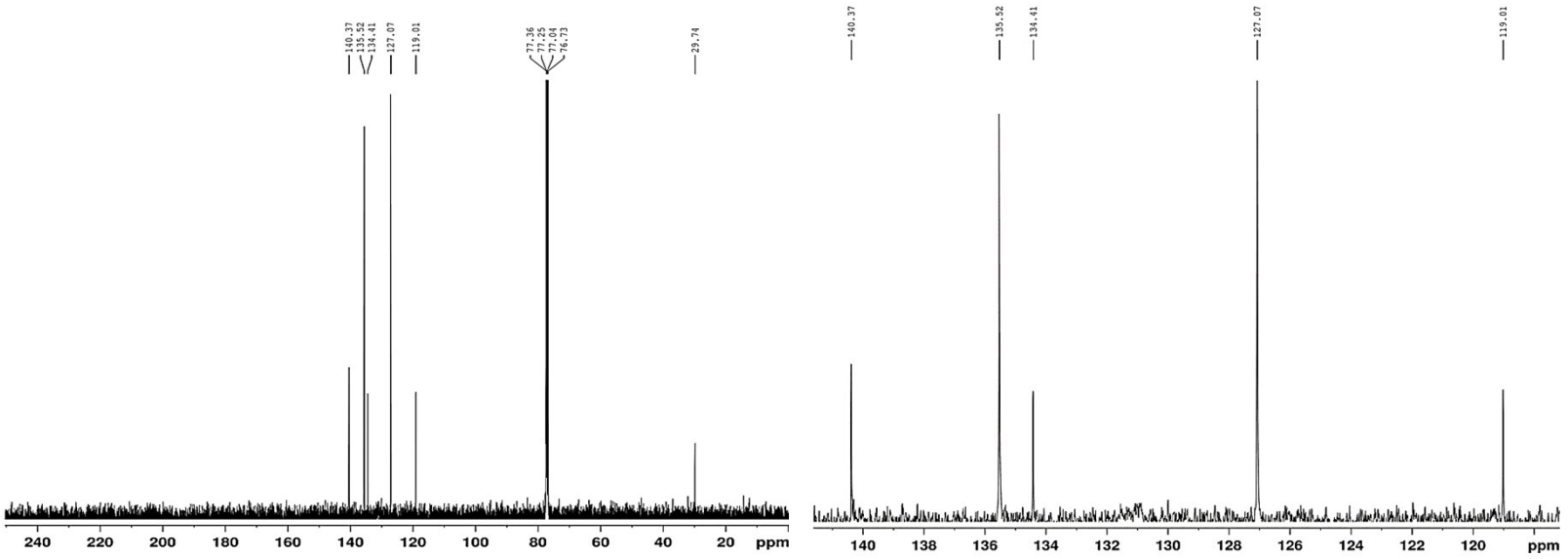
S6(c,d): ^{13}C NMR spectra of $H_2T(2\text{-Cl})PP$ and the expansion of aromatic region



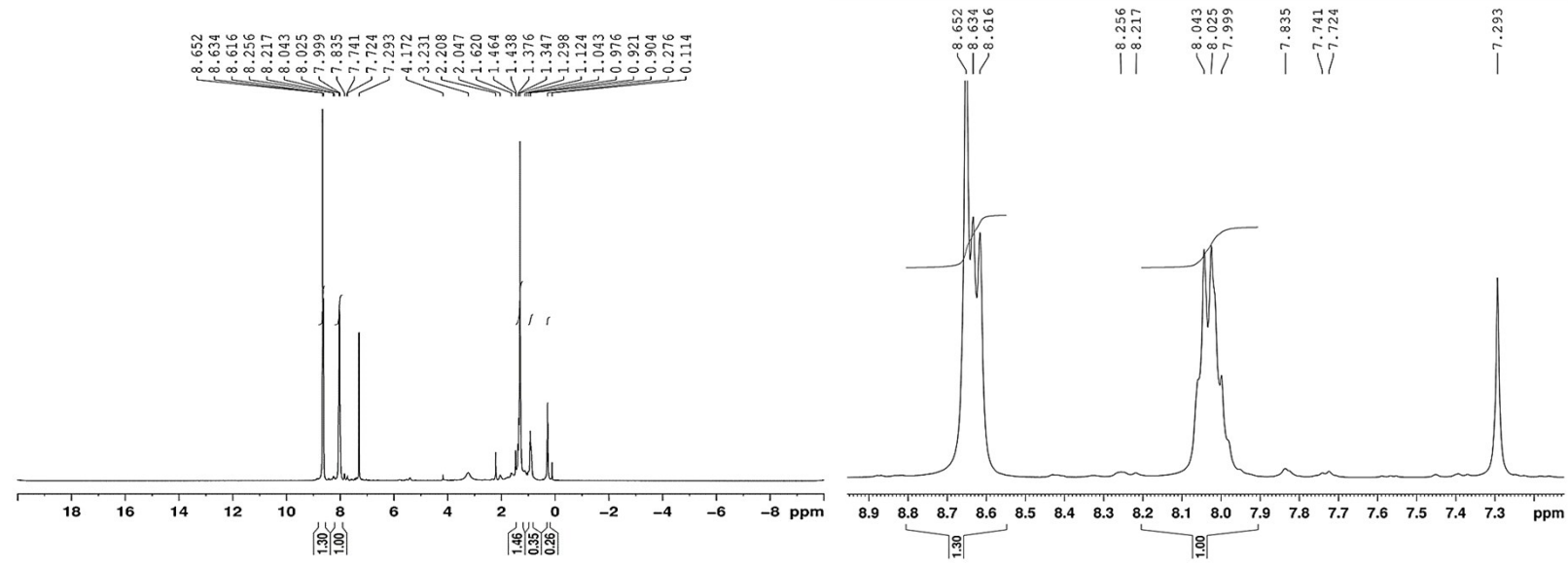
S7(a,b): ^{1}H NMR spectra of $H_2T(4\text{-Cl})PP$ and the expansion of aromatic region



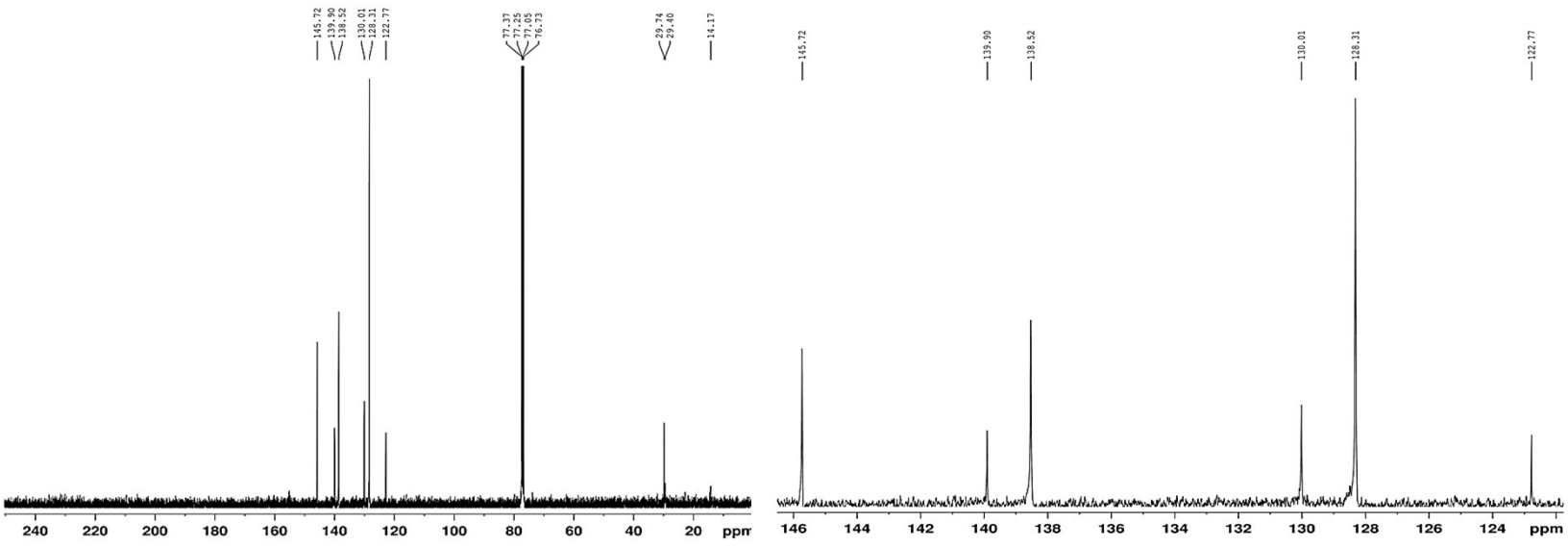
S7(c,d): ^{13}C NMR spectra of $H_2T(4\text{-}Cl)PP$ and the expansion of aromatic region



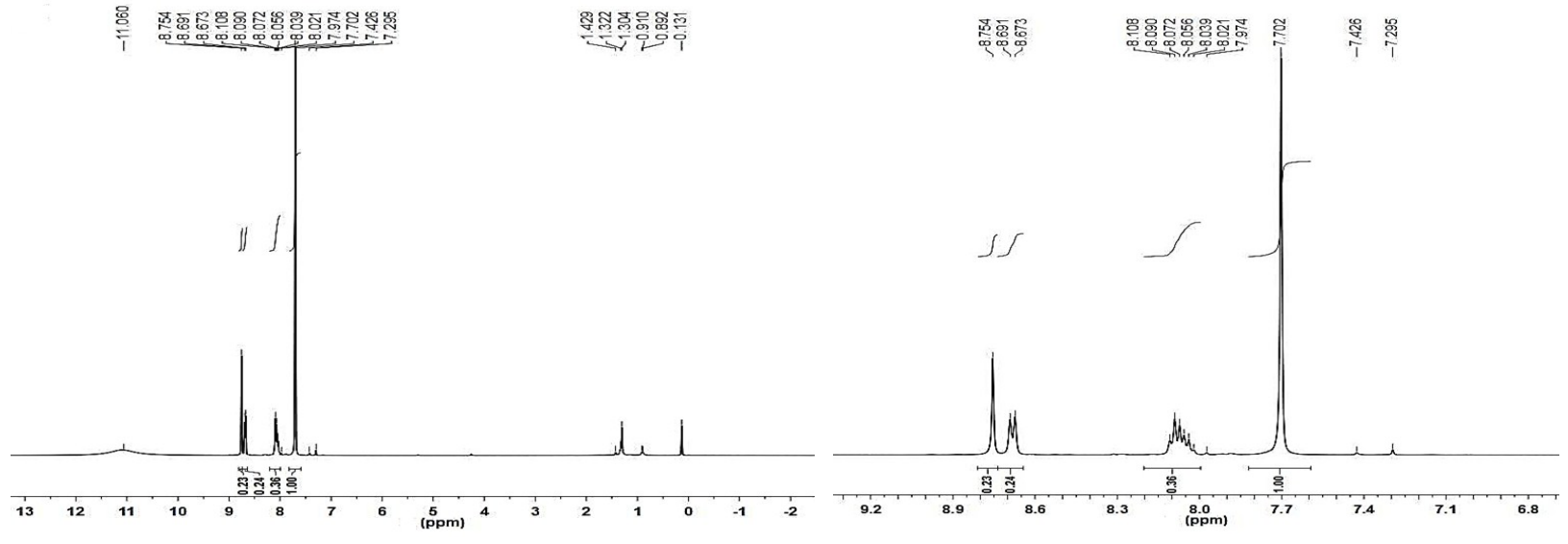
S8(a,b): ^{1}H NMR spectra of $H_4TPP(CF_3COO)_2$ and the expansion of aromatic region

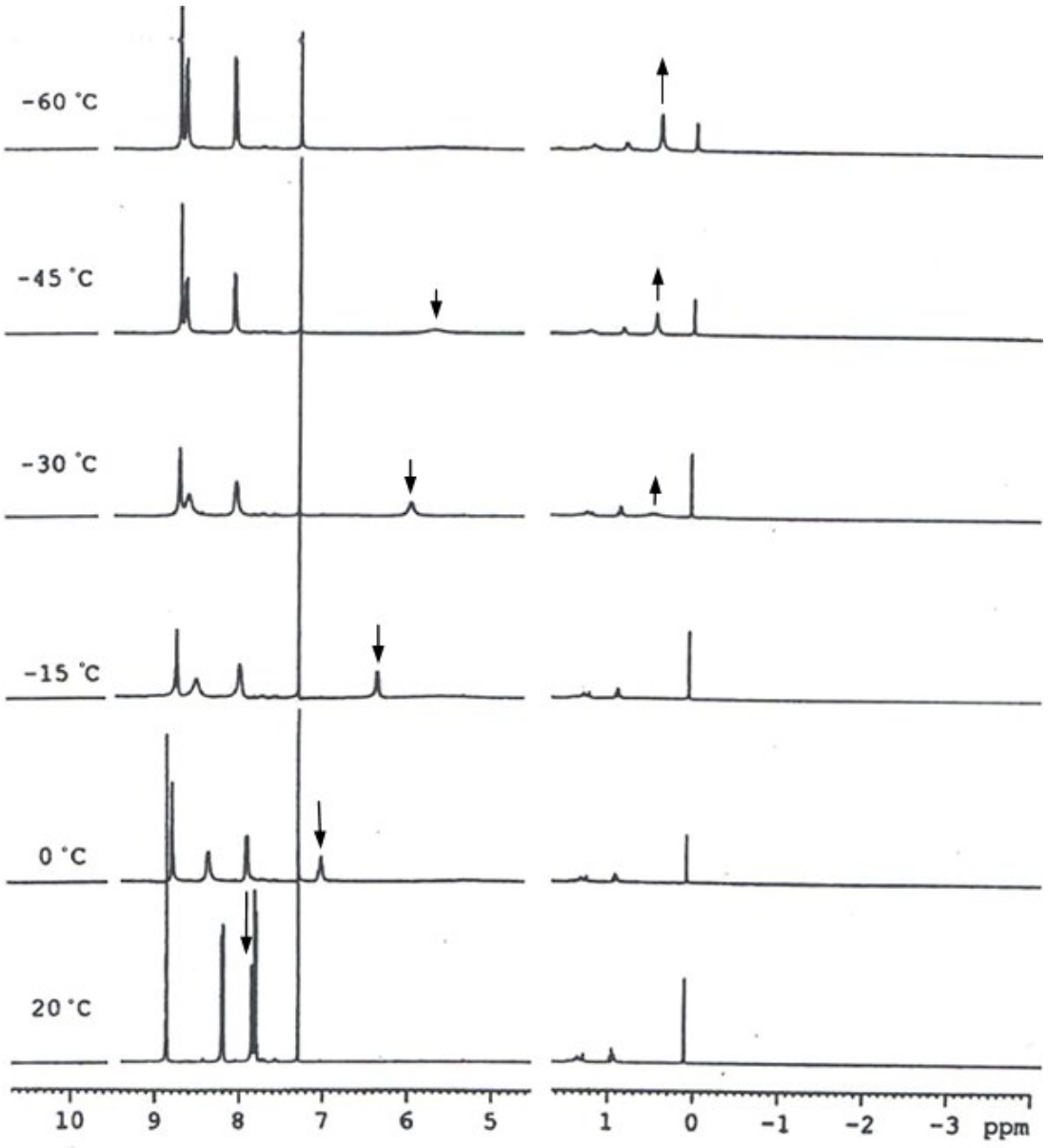


S8(c,d): ^{13}C NMR spectra of $H_4TPP(CF_3COO)_2$ and the expansion of aromatic region



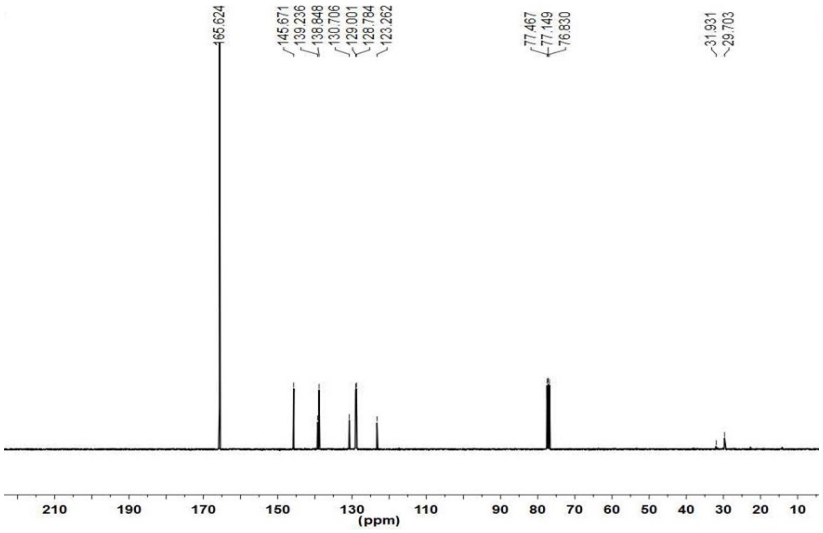
S9(a,b,c): ^1H NMR spectra of $H_4TPP(HCOO)_2$, the expansion of aromatic region and fffect of temperature on the chemical shifts of the protons of $H_4TPP(HCOO)_2$ in $CDCl_3$[7]

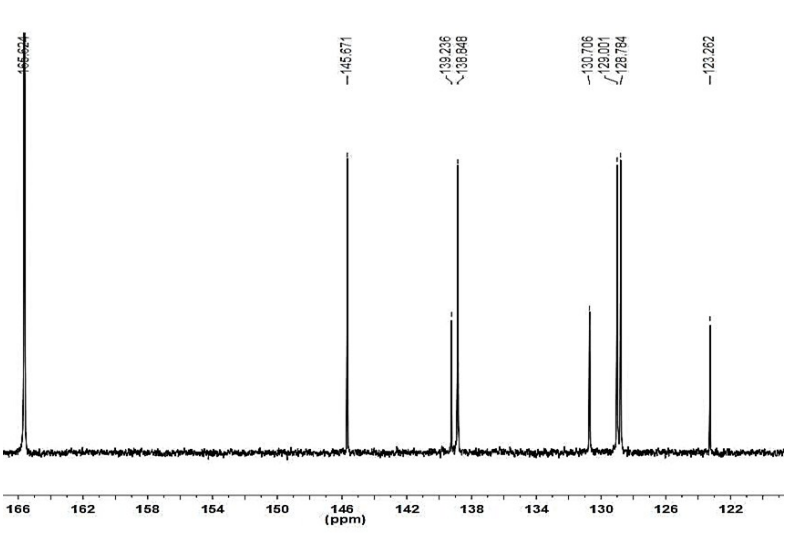




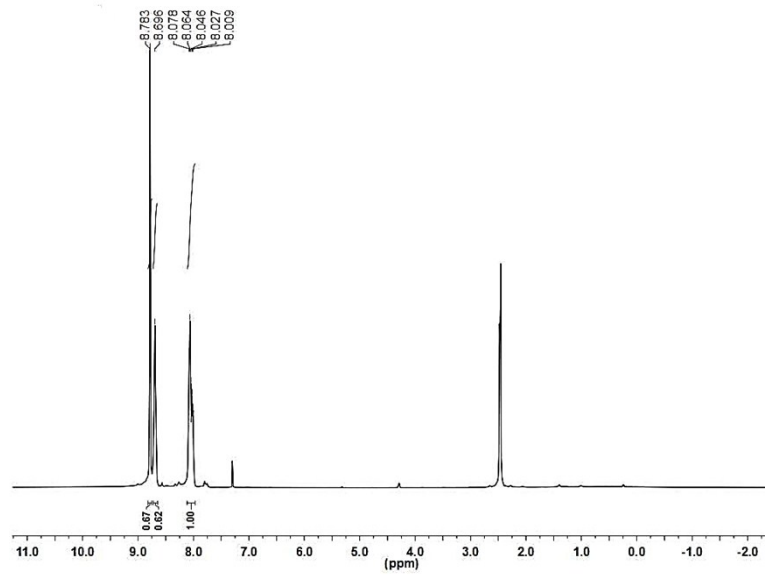
See Ref. 7 for more details

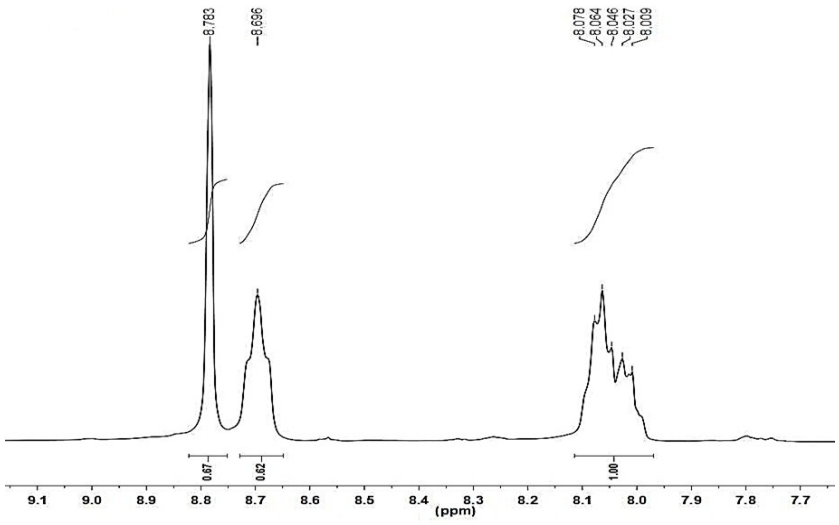
S9(d,e): ^{13}C NMR spectra of $H_4TPP(HCOO)_2$ and the expansion of aromatic region



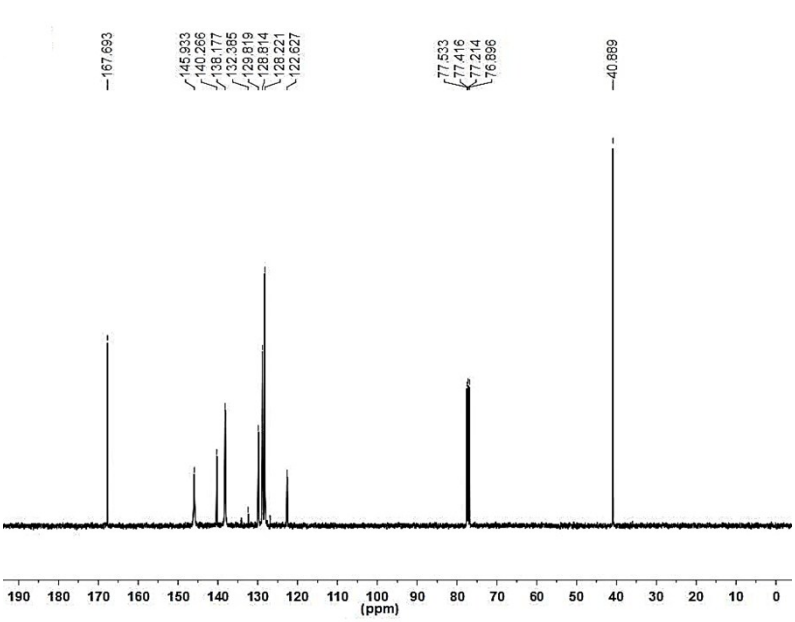


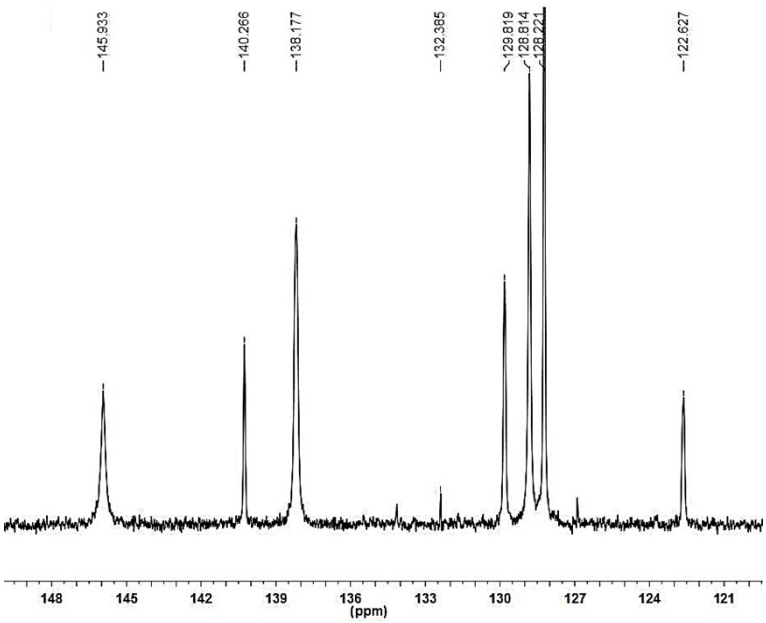
S10(a,b): ^{1}H NMR spectra of $H_4TPP(CH_2ClCOO)_2$ and the expansion of aromatic region



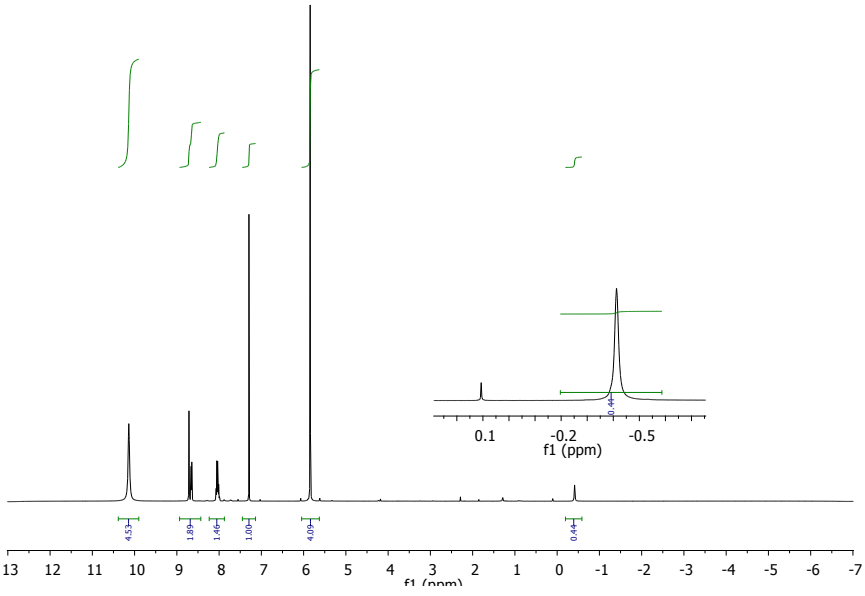


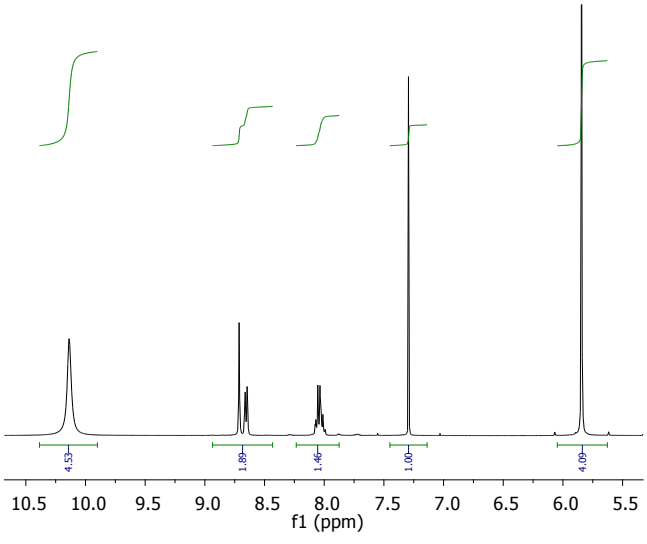
S10(c,d): ^{13}C NMR spectra of $H_4TPP(CH_2ClCOO)_2$ and the expansion of aromatic region



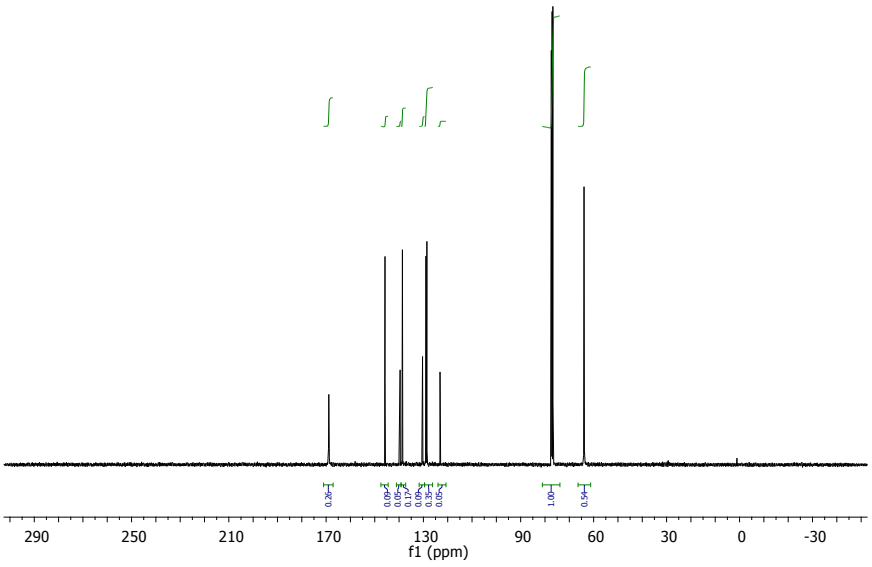


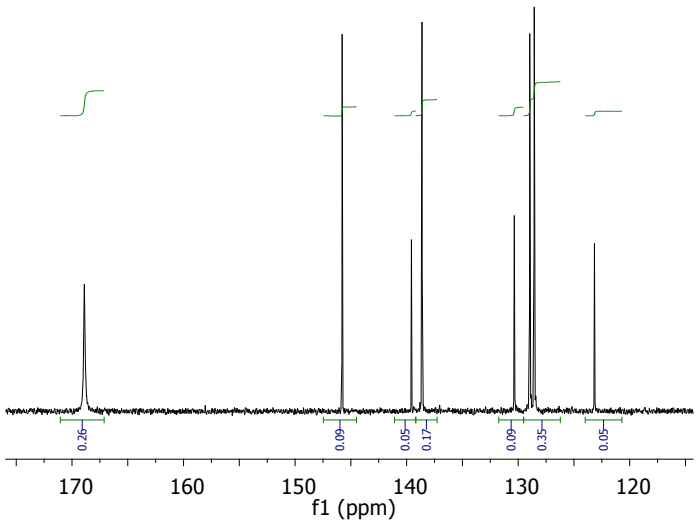
S11(a,b): ^{1}H NMR spectra of $H_4TPP(CHCl_2COO)_2$ and the expansion of aromatic region



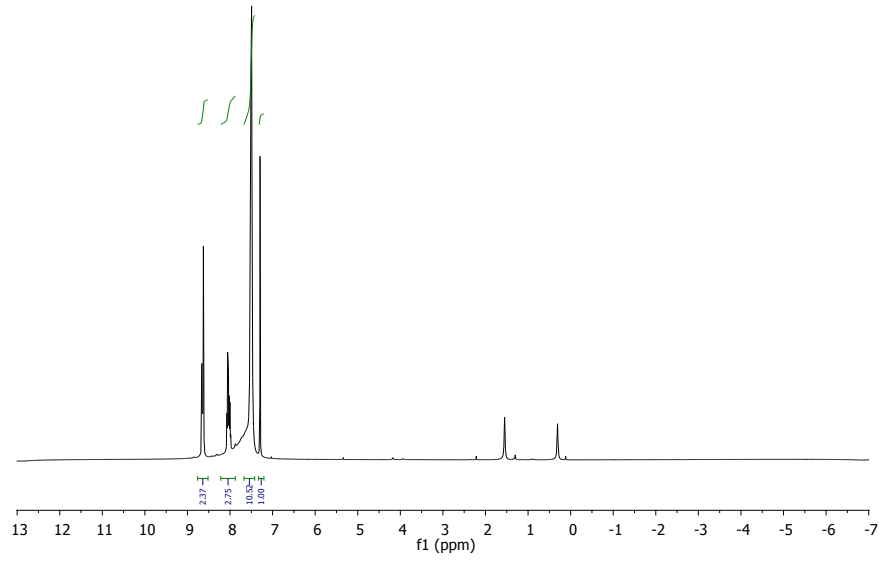


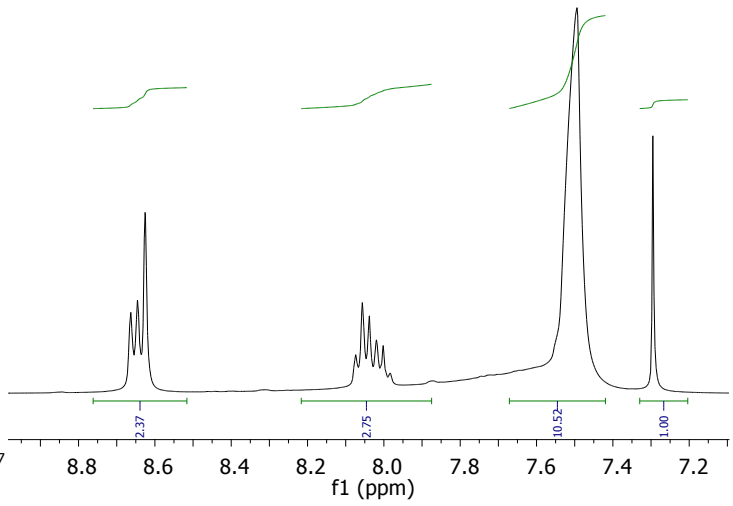
S11(c,d): ^{13}C NMR spectra of $H_4TPP(CHCl_2COO)_2$ and the expansion of aromatic region



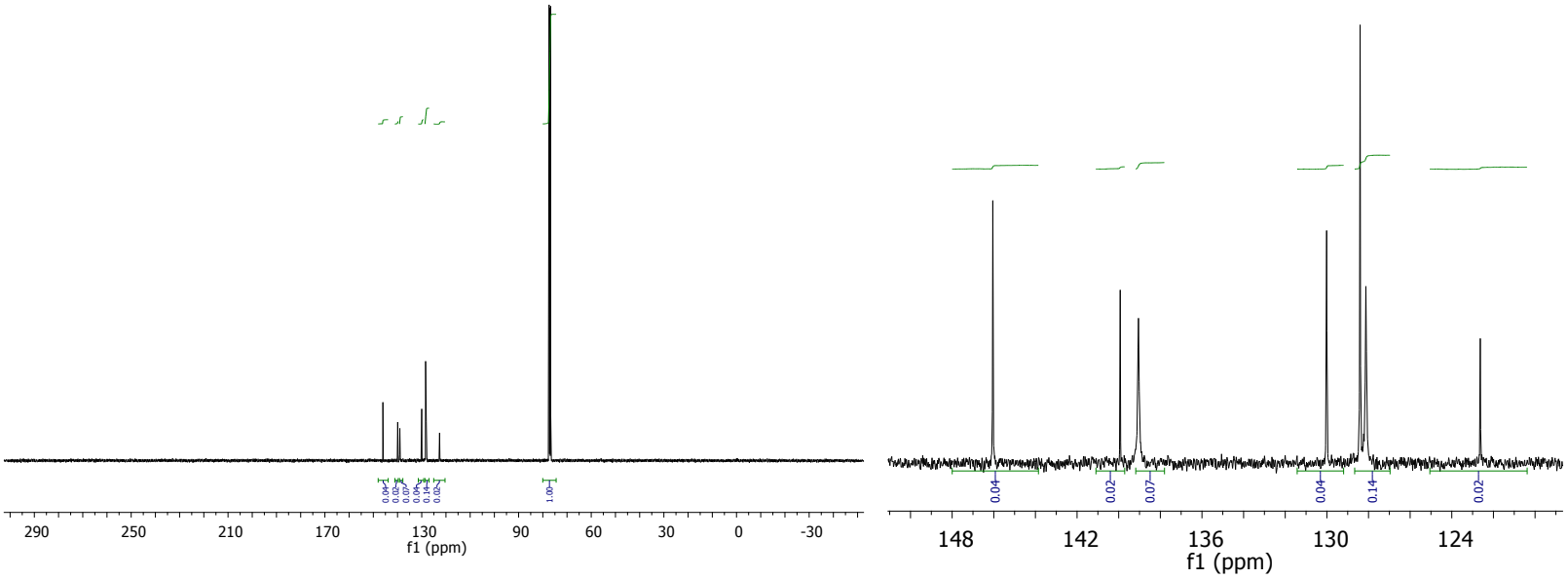


S12(a,b): ^{1}H NMR spectra of $H_4TPP(Cl)_2$ and the expansion of aromatic region

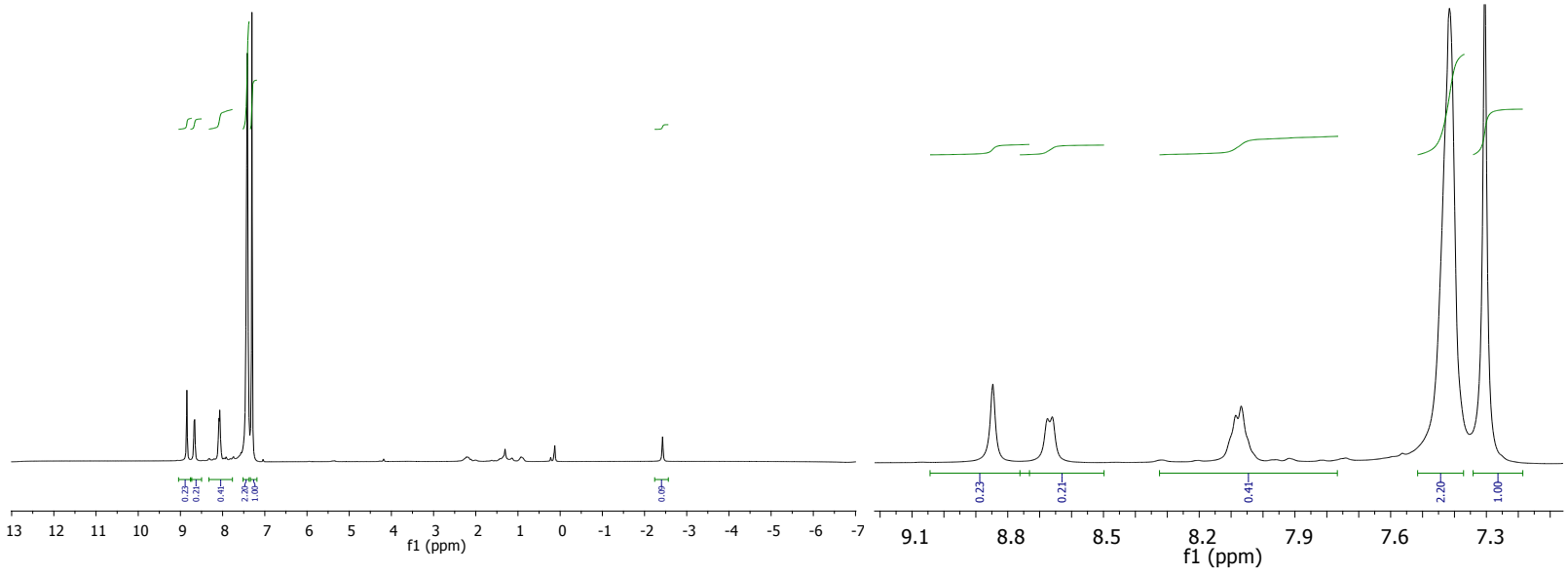




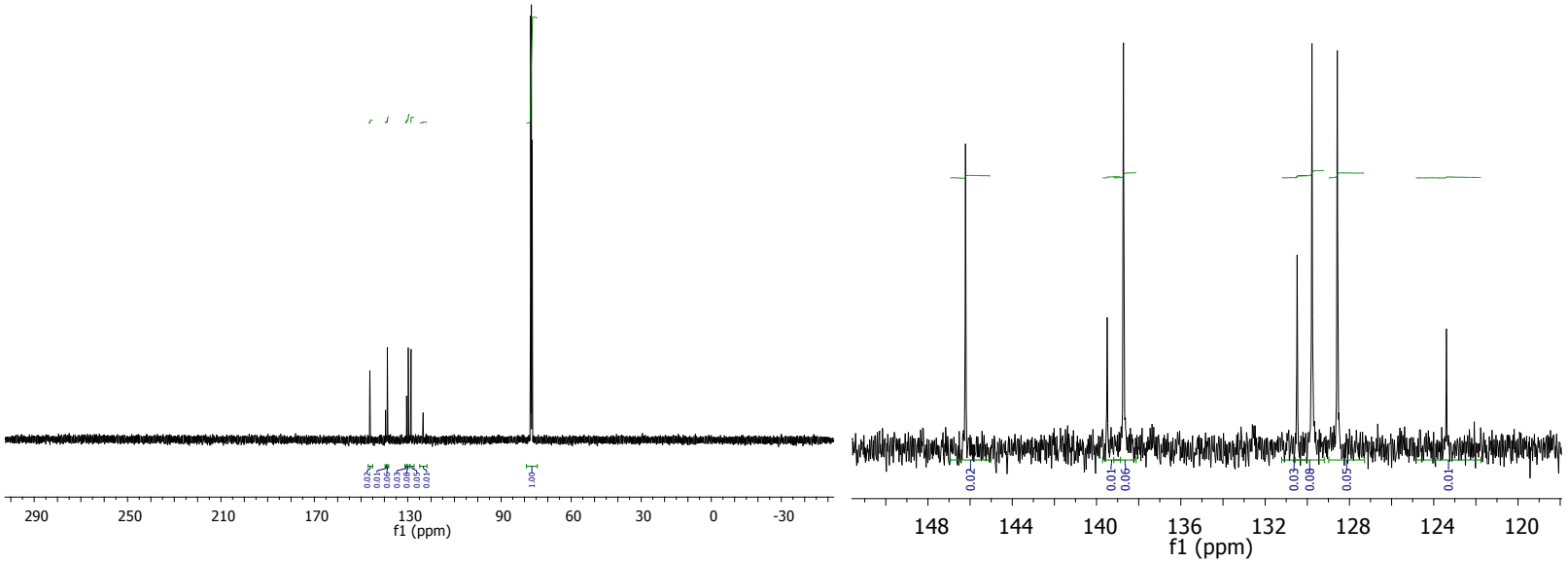
S12(c,d): ^{13}C NMR spectra of $H_4TPP(Cl)_2$ and the expansion of aromatic region



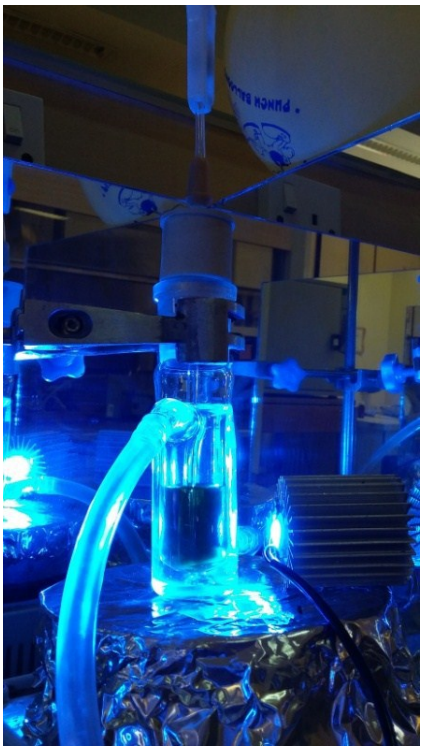
S13(a,b): ^{1}H NMR spectra of $H_4TPP(ClO_4)_2$ and the expansion of aromatic region



S13(c,d): ^{13}C NMR spectra of $H_4TPP(ClO_4)_2$ and the expansion of aromatic region



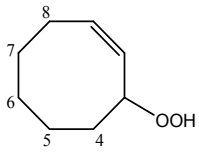
S14: Double walled cylindrical glass vessel equipped with water circulation used for the photooxidation reactions (10 W red or blue LED lamps or a 200 W white mercury compact fluorescent lamp (CFL) were used as the light source).



S15: ^{13}C NMR data of Cyclooct-1-en-3-yl hydroperoxide

Cyclooct-1-en-3-yl hydroperoxide. ^{13}C NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: 32.85 (C_4), 26.20 (C_5), 26.41 (C_6), 23.76 (C_7) , 28.90 (C_8), , 129.75 (C_{unsat}), 131.88 (C_{unsat}), 82.88 (COOH).

The ^{13}C NMR data of Cyclooct-1-en-3-yl hydroperoxide as the sole product is consistent with the previously reported data.[8,9]



1 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
2 R. J. Abraham, G. E. Hawkes, M. F. Hudson, and Kevin M. Smith*, J. Chem. Soc., Perkin Trans.* 2, 1975, 204-211.
3 A. Gradillas, C. del Campo, J. V. Sinisterra and E. F. Llama, *J. Chem. Soc., Perkin Trans. 1,* 1995, 2611.
4 S. S. Eaton and G. R. Eaton, Inorg. Chem., 1976, **15**, 134.
5 D. Mohajer, S. Zakavi, S. Rayati, M. Zahedi, N. Safari, H. R. Khavasi and S. Shahbazian, *New J. Chem*. 2004, **28**, 1600.
6 R.W.A. Johnstone, M.L.P.G. Nanes, M.M. Pereira, R.W.A. Johnstone, A.M.de.A.R. Gonsalves, A.C. Serra, *Heterocycles*, 1996, **43**, 1425.
7. S. Zakavi, M. Najafi Ragheb, *Inorg. Che. Commun.*, 2013, **36**, 113.
8 R. D. Chambed, G. Sandford, A. Shah, *Synth. Commun.,* 1996*,* **26***,* 1861.
9 R. W. Denny, A. Nikon, *Org. React*., 1973, **20**, 133.