Electronic Supplementary Information

for

Kinetic and mechanistic aspects of solid state, nanostructured porphyrin diacid photosensitizers in photooxidation of sulfides

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S1: ^{1}H NMR, ^{13}C NMR and UV-Vis spectral data of the used porphyrins

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(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 (4Ho, 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(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 (4Ho, 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, λmax/nm (logε): 416 (5.64), 512 (4.47), 543(4.07), 587 (4.15), 643 (3.96).

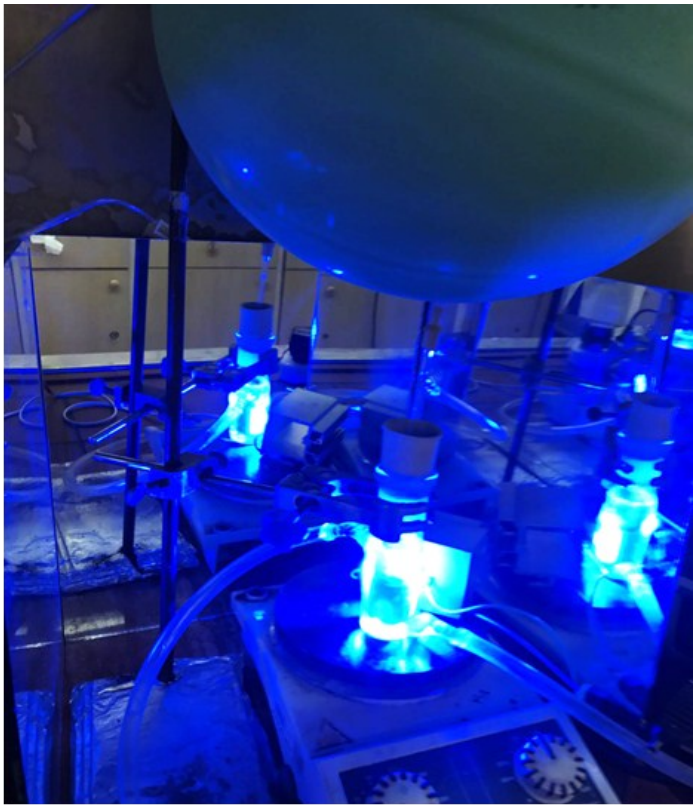
H_2T(4-Cl)PP. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ/ppm: -2.83 (2H, br, s, NH), 7.77-7.79 (8Hm, d), 8.15-8.17 (8Ho, d), 8.87(8Hβ, s); ^{13}C NMR (~100 MHz, $CDCl_3$, TMS), δ/ppm: 119.01 (Cmeso), 140.37 (C1), 135.52 (C2, C6), 127.07 (C3, C5), 134.41(C4), 131.64 (Cβ); UV-vis in CH_2Cl_2, λmax/nm (logε): 418 (5.79), 513 (4.52), 547 (4.25), 590 (4.16), 647 (4.10).

H_2T(4-OMe)PP. ^{1}H NMR (400 Hz, $CDCl_3$, 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 (Cβ), 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(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(8Hβ, 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_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 ($8H_β$, 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, C6), 128.12 (C_3, C5), 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).

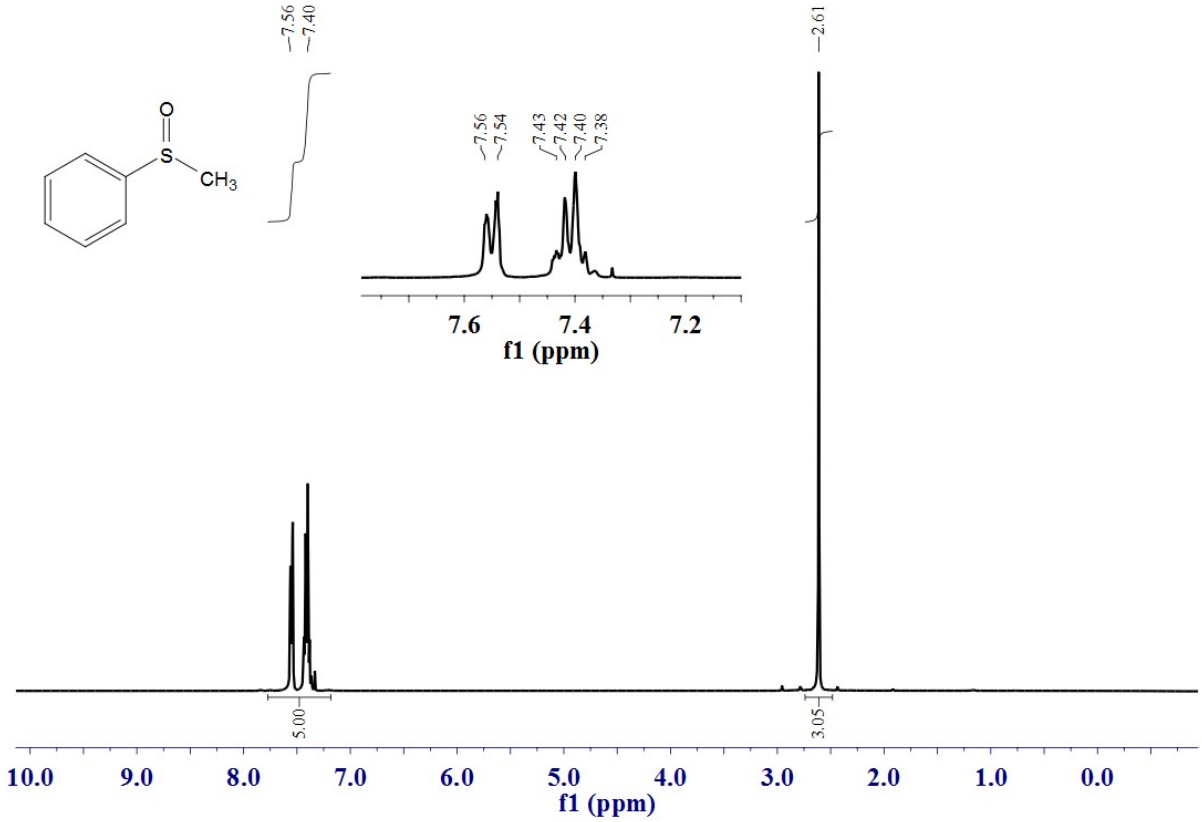
S2. Experimental setup for the photooxidation reactions



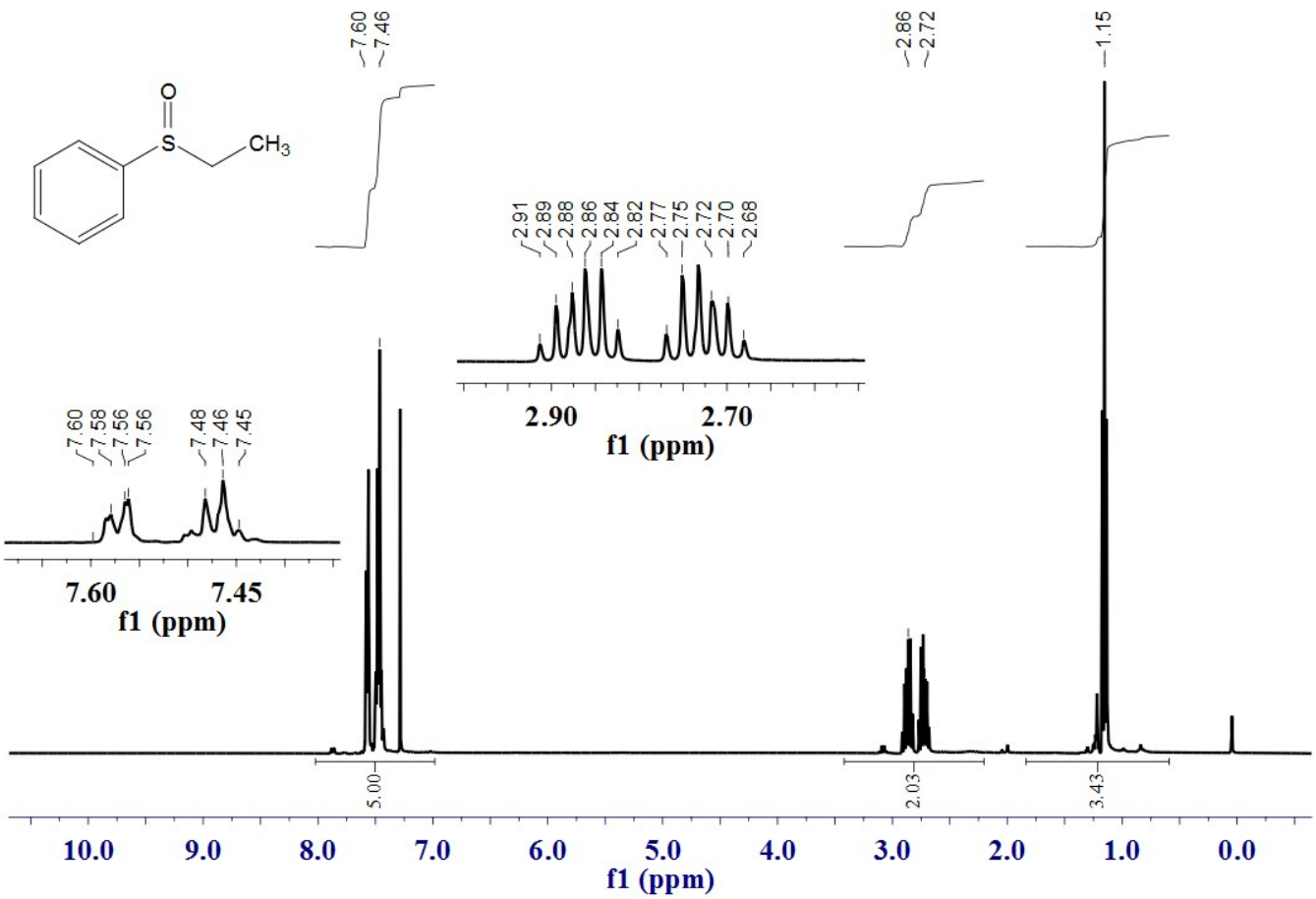
S3: Procedures for the oxidation of different sulfides and characterization of the oxidation products

Methyl phenyl sulfoxide: Methyl phenyl sulfide (409.20 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material

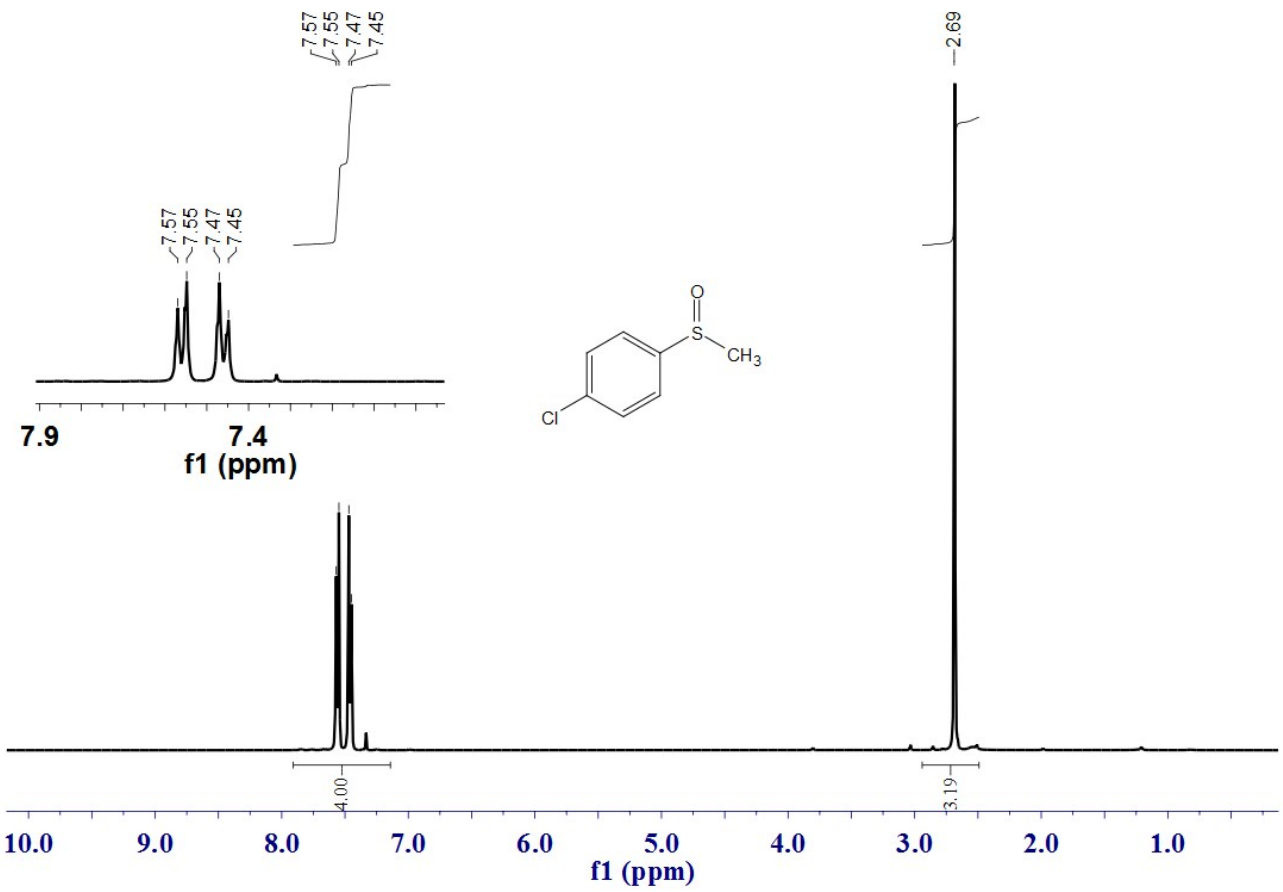
was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Methyl phenyl sulfoxide; yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.56–7.38 (m, 5H), 2.61 (s, 3H).



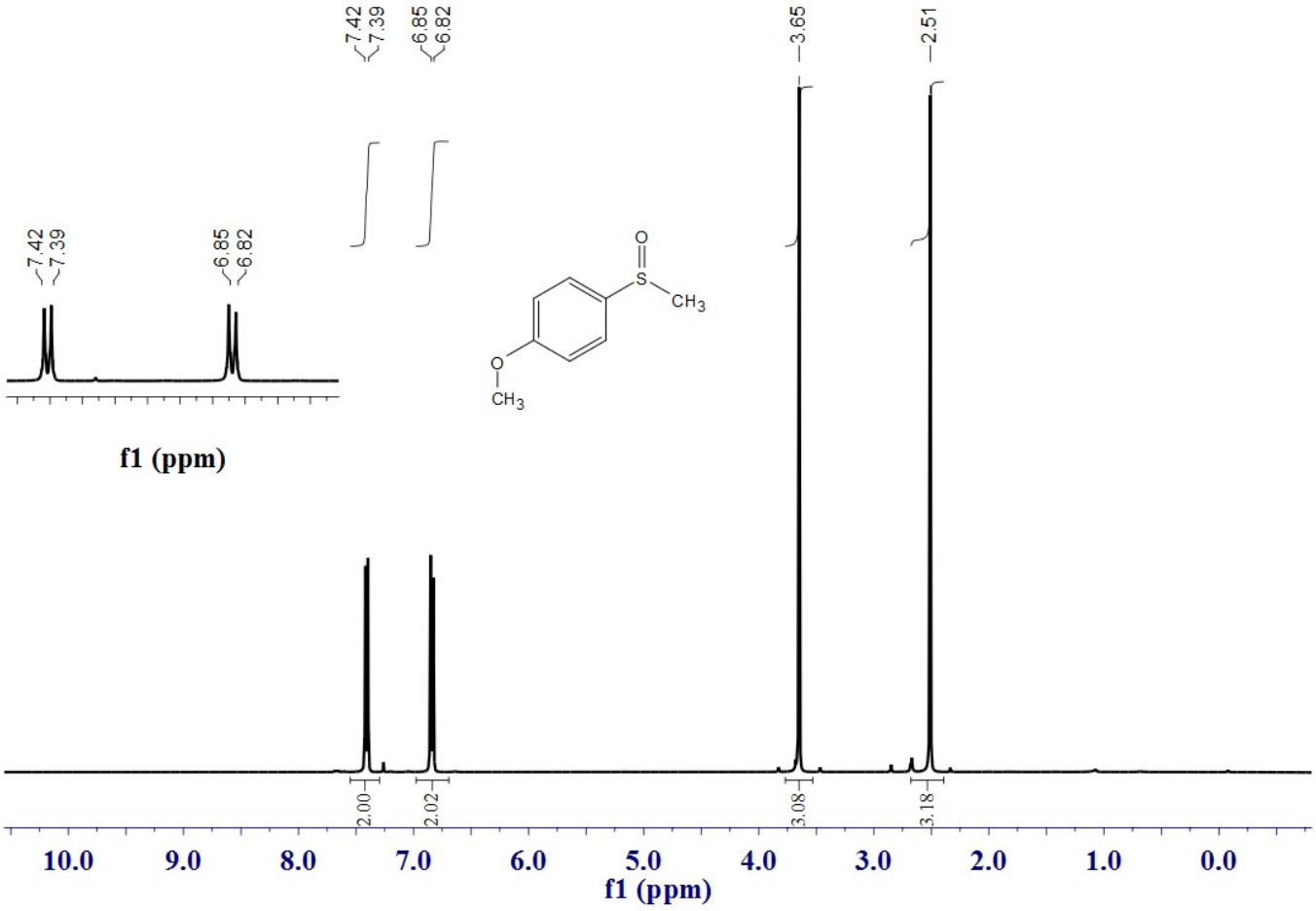
Ethyl phenyl sulfoxide: Ethyl phenyl sulfide (465.18 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Ethyl phenyl sulfoxide; yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.60–7.45 (m, 4H), 2.91-2.82 (m, 1H), 2.77-2.68 (m, 1H), 1.15 (t ,3H).



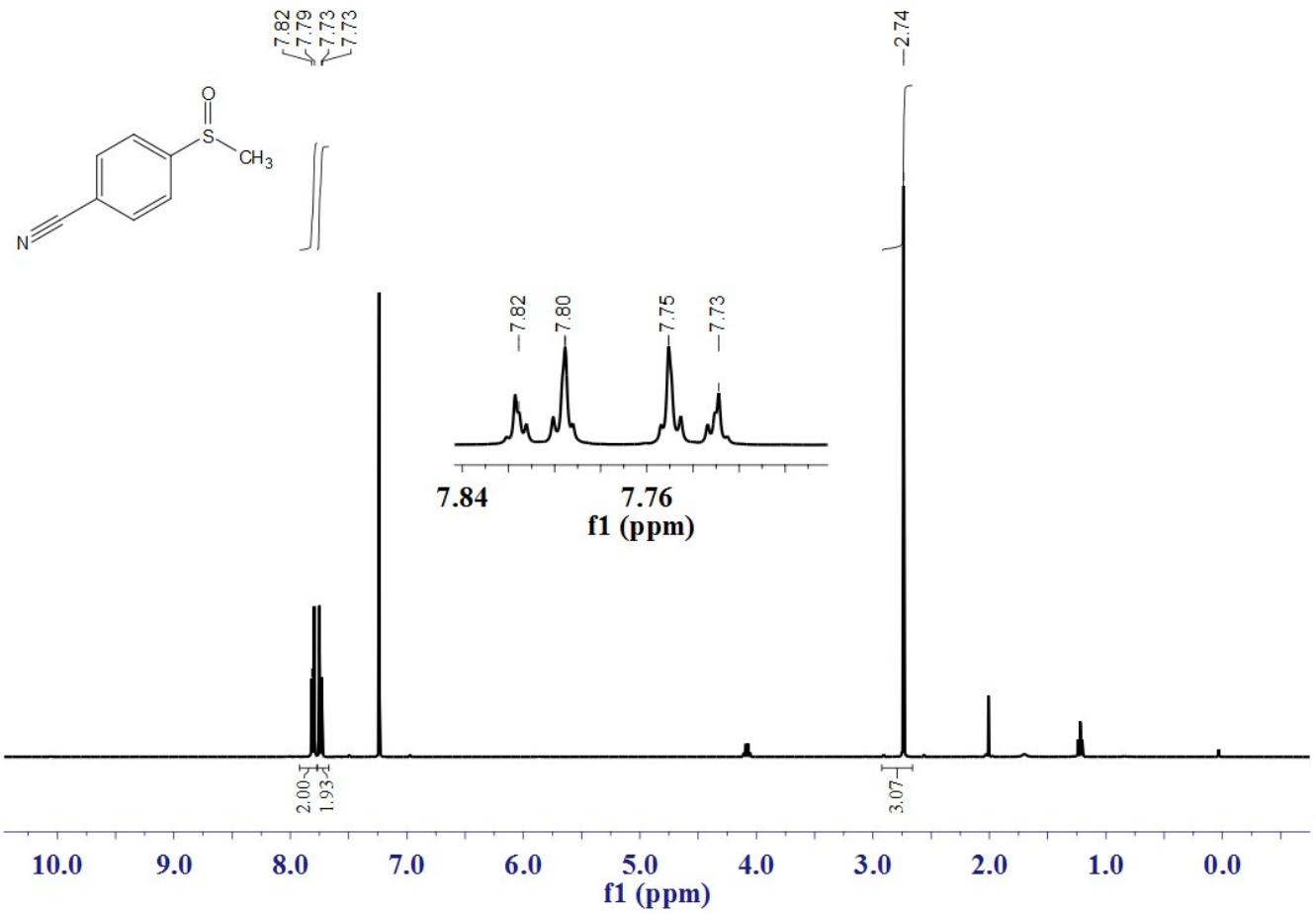
4-Chlorophenyl methyl sulfoxide: 4-Chlorophenyl methyl sulfide (675.16 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Chlorophenyl methyl sulfoxide; yield: 99%. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.57-7.55 (m, 2H), 7.47-7.45 (m, 2H), 2.69 (s, 3H).



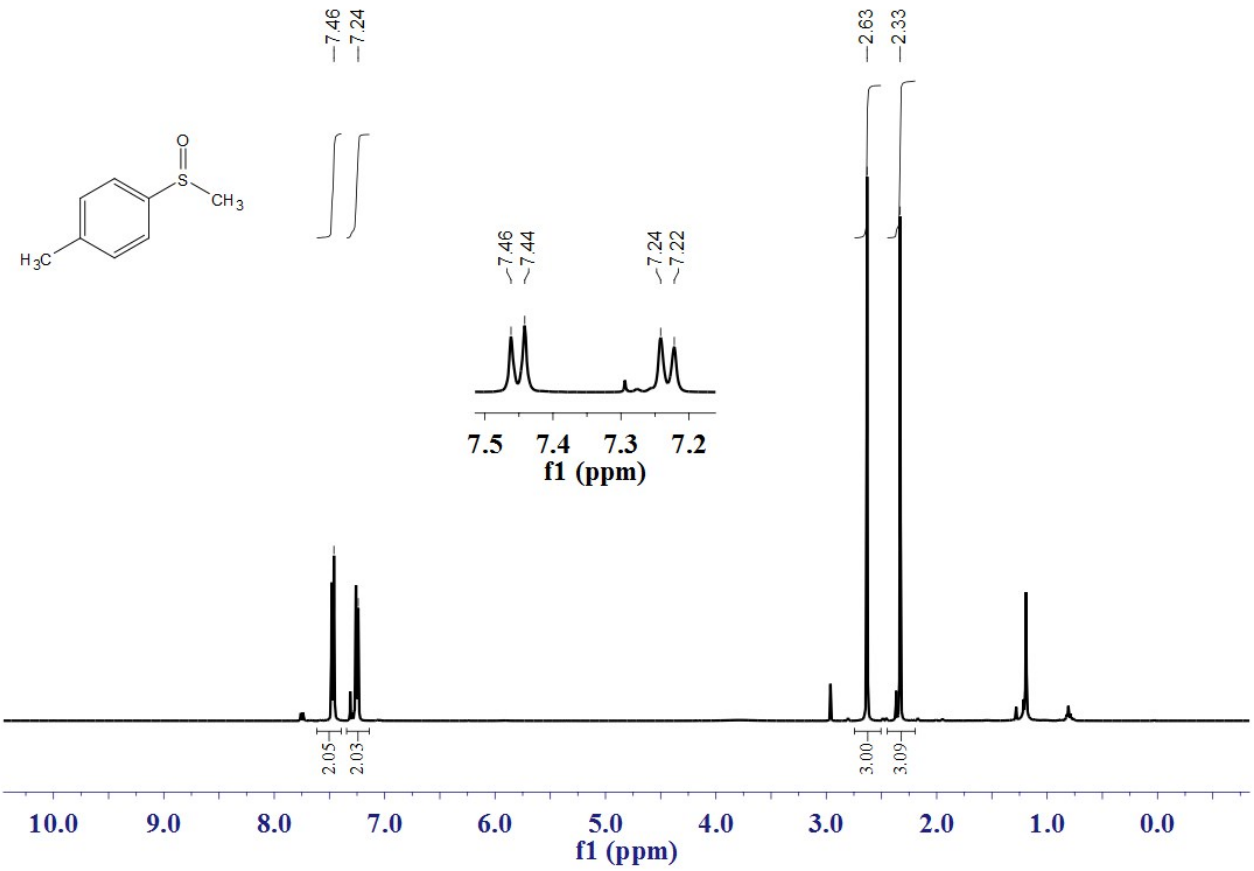
4-Methoxyphenyl methyl sulfoxide: 4-Methoxyphenyl methyl sulfide (564.83 mg, 3.3mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Methoxy phenyl sulfoxide; yield: 95%. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.42 (d, 2H), 6.85 (d, 2H), 3.65 (s,3H), 2.51 (s,3H).



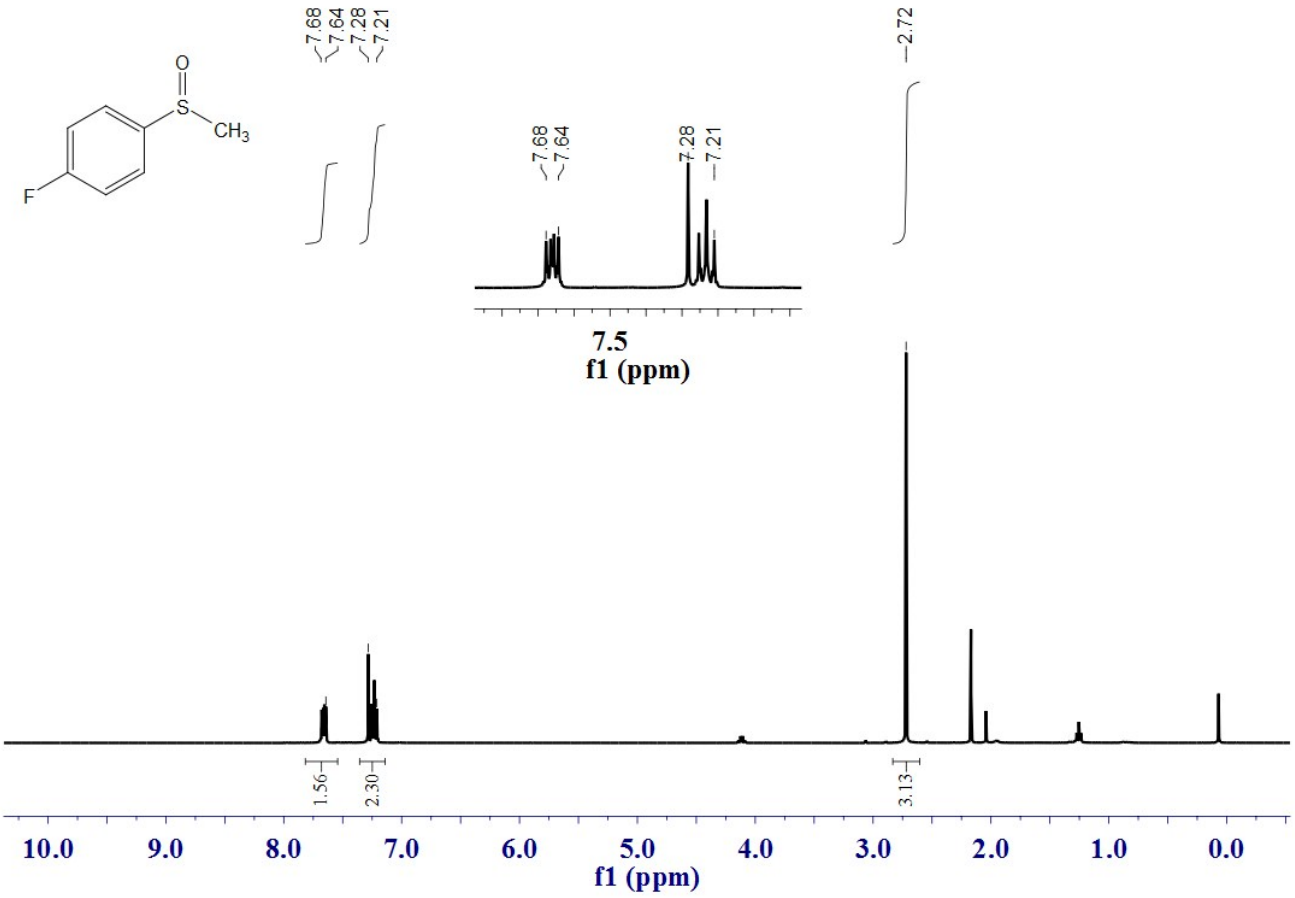
4-Cyanophenyl methyl sulfoxide: 4-Cyano phenyl methyl sulfide (492.36 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Cyanophenyl methyl sulfoxide; yield: 93%. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.82-7.80 (m, 2H), 7.75-7.73 (m, 2H), 2.74 (s, 3H).



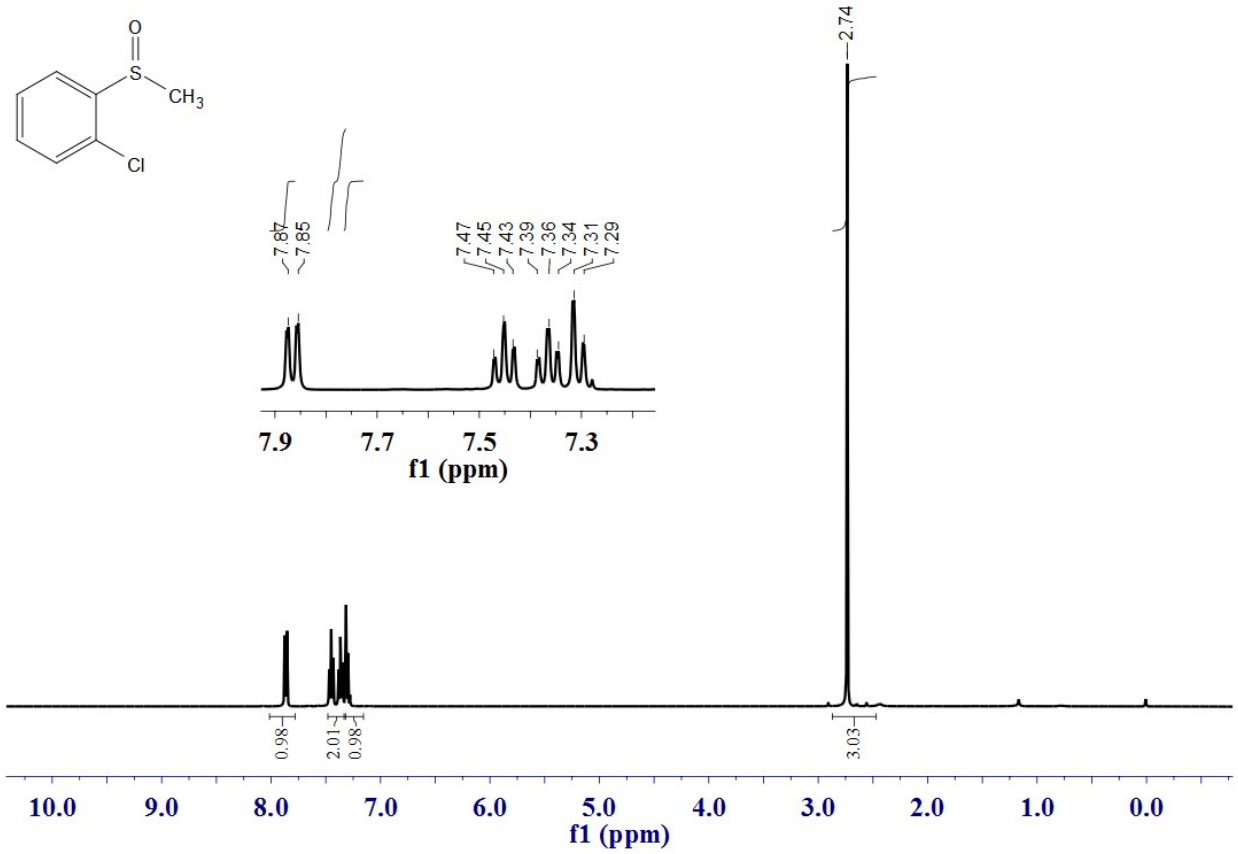
1-methyl 4- methyl phenyl sulfoxide: 1-methyl 4- methyl phenyl sulfide (468.47 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 1-methyl 4- methyl phenyl sulfoxide; yield: 99%. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.46-7.44 (d, 2H), 7.24-7.22 (d, 2H), 2.63 (s, 3H), 2.33 (s,3H).



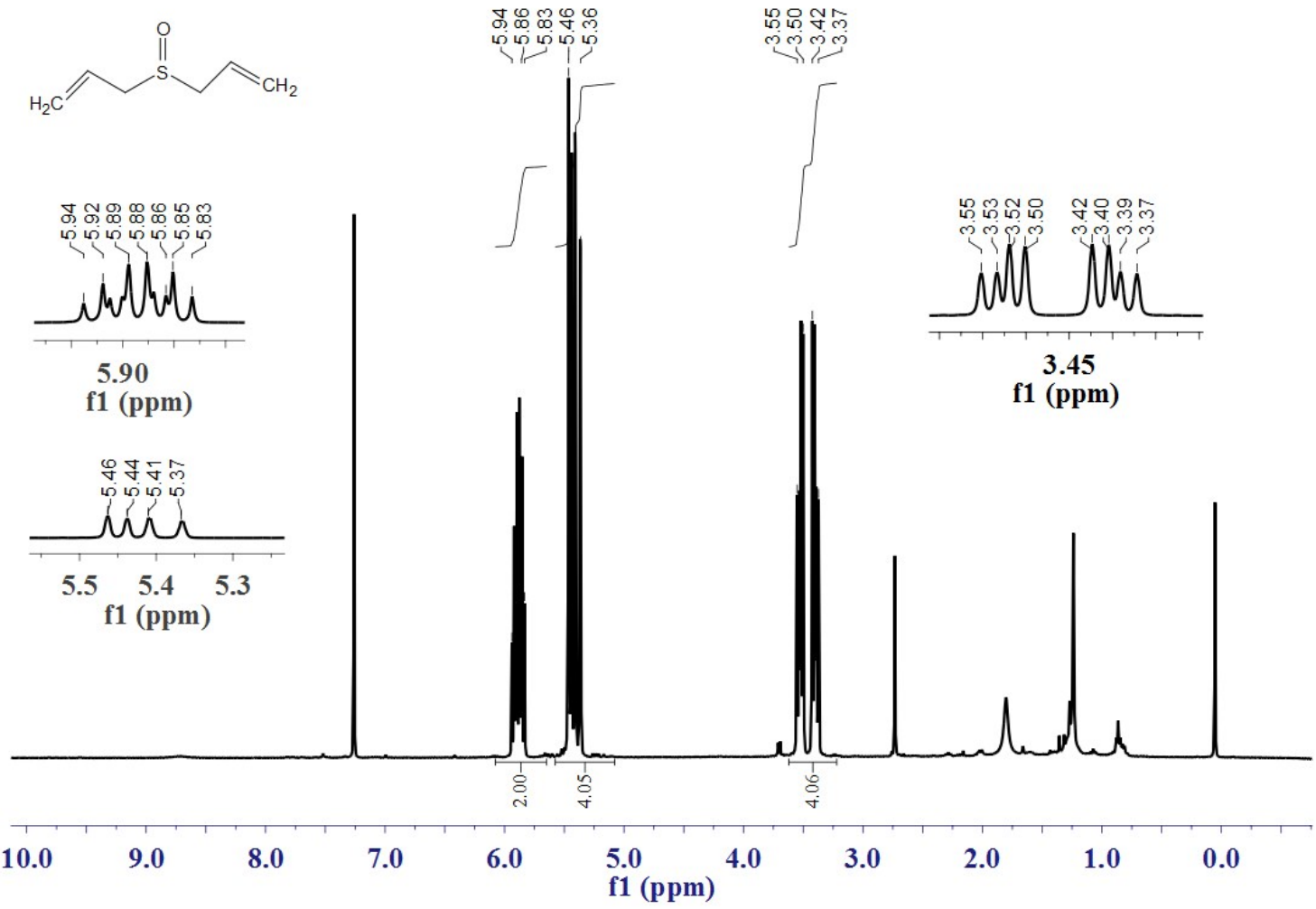
4-Flourophenyl methyl sulfoxide: 4-Flourophenyl methyl sulfide (797.74 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 4-Flourophenyl methyl sulfoxide; yield: 99%. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.68-7.64 (m, 2H), 7.28-7.21 (m, 2H), 2.72 (s, 3H).



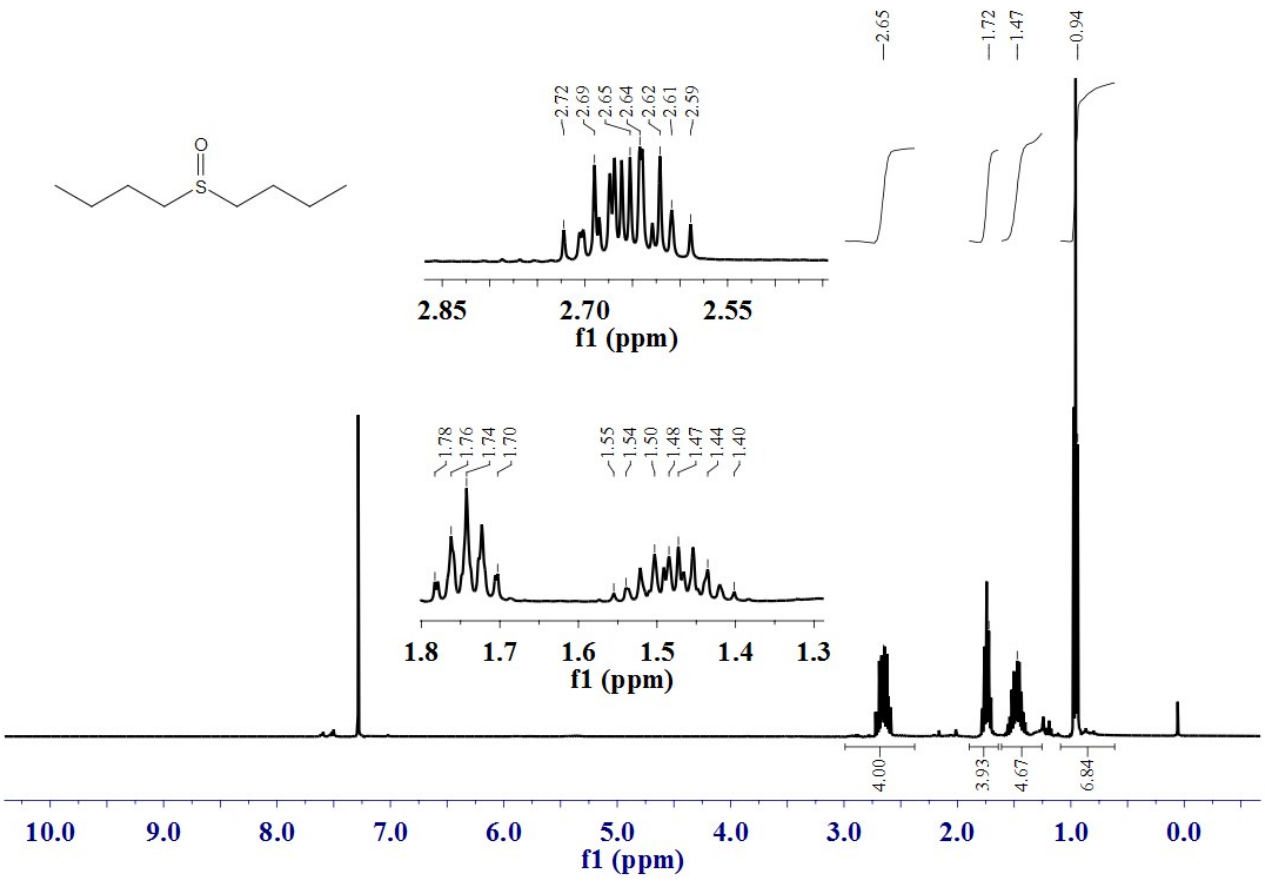
2-Chlorophenyl methyl sulfoxide: 2-Chlorophenyl methyl sulfide (675.16 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give 2-Chlorophenyl methyl sulfoxide; yield: 99%. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.87-7.88 (d, 1H), 7.47-7.34 (m, 2H), 7.31-7.29 (m, 1H), 2.74 (s, 3H).


O
S
CH3
Cl
7.87
7.85
7.47
7.45
7.43
7.39
7.36
7.34
7.31
7.29
7.9
7.7
7.5
7.3
f1 (ppm)
2.74
0.98
2.01
0.98
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

Diallyl sulfoxide: Dibutyl sulfide (335.40 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Diallyl sulfoxide; yield: 97%. ^1H NMR (400 MHz, $CDCl_3$): δ= 5.94-5.83 (m, 2H), 5.46-5.35 (m, 4H), 3.55-3.37 (d, 4H).

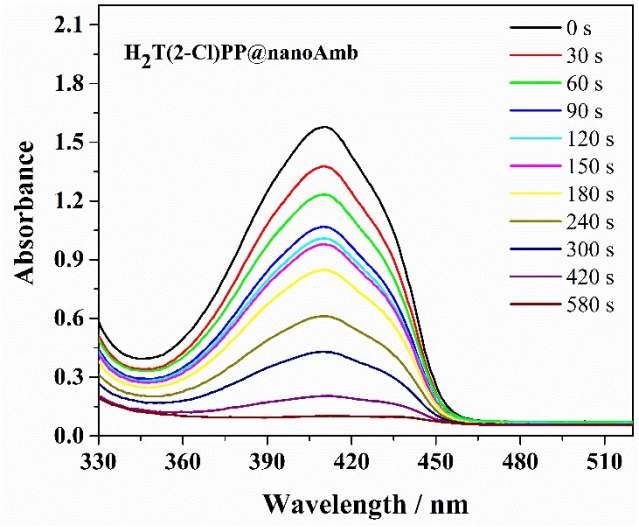


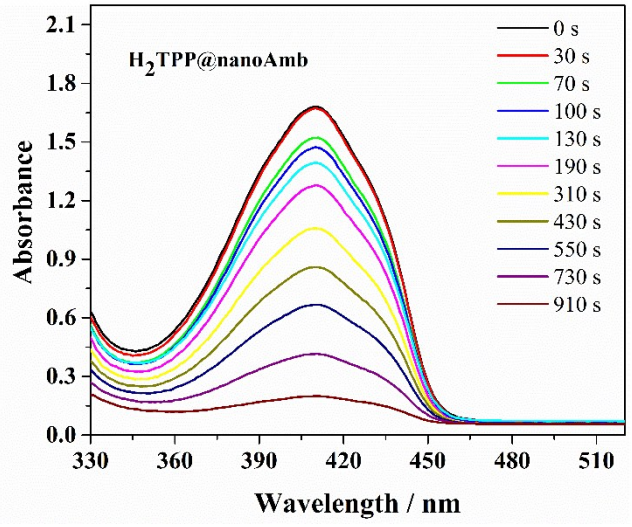
Dibutyl sulfoxide: Dibutyl sulfide (405.54 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Dibutyl sulfoxide; yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.72-2.59 (m, 4H), 1.78- 1.70 (m, 4H), 1.55-1.40 (m, 4H), 0.94 (t,6H).

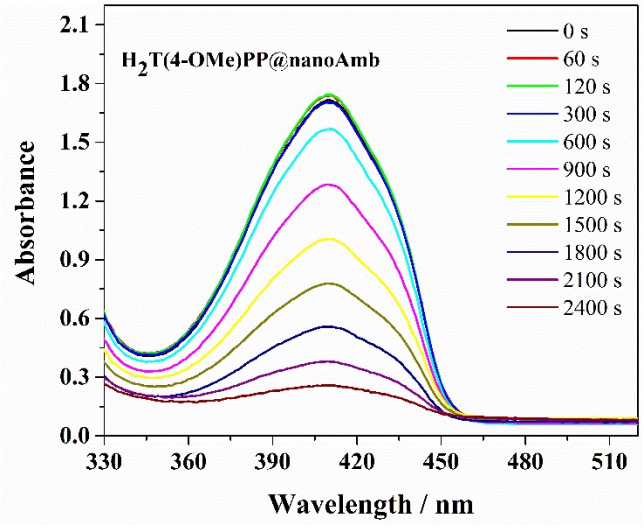


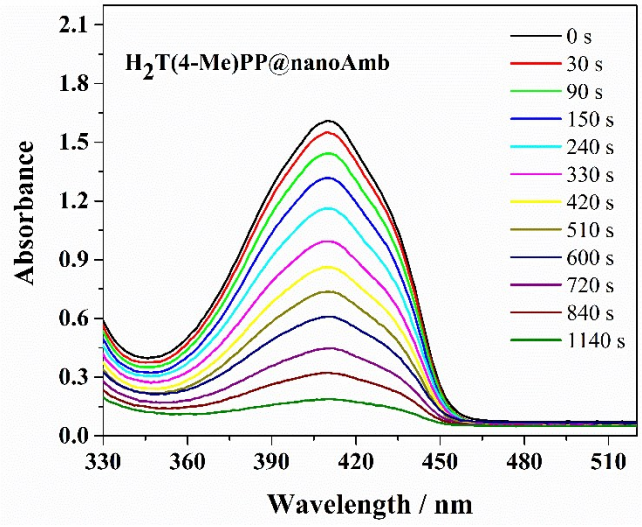
Benzyl phenyl sulfoxide: Benzyl phenyl sulfide (660.99 mg, 3.3 mmol) was performed according to the general procedure using H_2TPP@nanoAmb (0.66×10^{-3} mmol). Crude material was separated by TLC on silica gel plates (ethyl acetate and n-hexane in a 1:4 volume ratio) to give Benzyl phenyl sulfoxide; yield: 75%. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.437-7.7.22 (m, 8H), 6.97 (d, 2H), 4.07-4.04 (d, 1H), 3.99-3.96 (d, 1H).

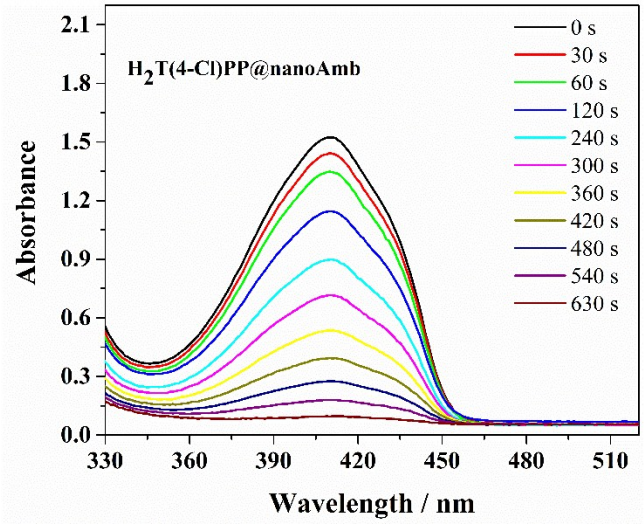
S5. The change in the UV–vis spectrum of DPBF upon irradiation with a 10W red LED lamp in the presence of the immobilized porphyrins.

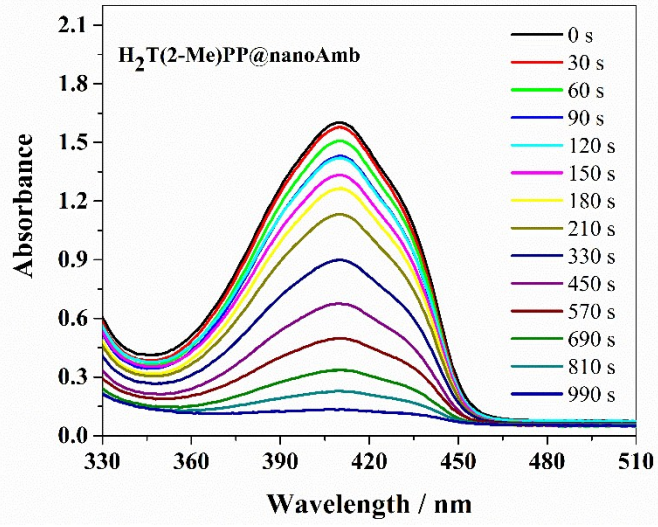


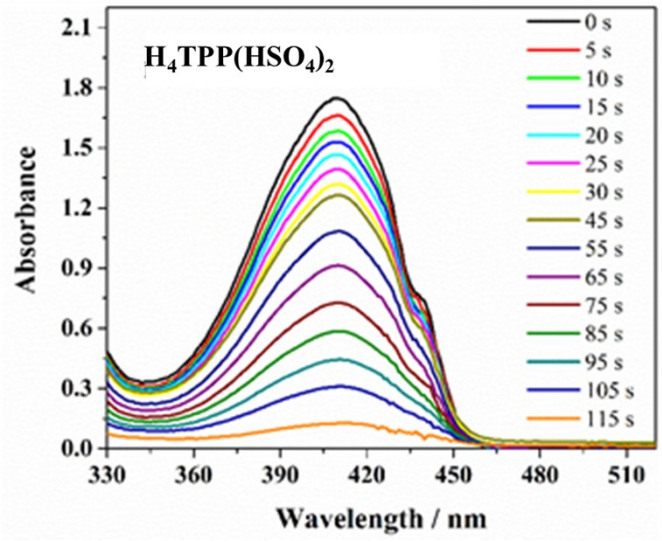




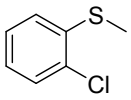
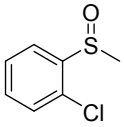
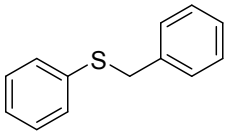
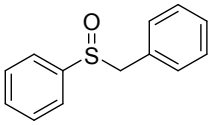
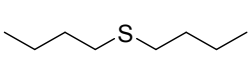
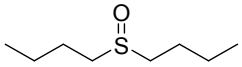
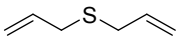
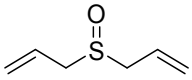








S6. Photooxidation of different sulfides by H_2TPP@nanoAmb.[a]

Substrate	Product	Conversion[b] [Selectivity](%)	TON [TOF(h^{-1})]
		99 [100]	4950 [1650]
		75 [100]	3750 [1250]
		70 [100]	3500 [1166]
		97 [100]	4850 [1616]

[a] The catalyst and substrate were used in 1:5000 molar ratio. A 20 W white LED lamp was used as the light source. [b] For a reaction time of 3 h in 1:1 acetonitrile (5 mL)/ water (5 mL) solvent mixture.