

Supplementary Information for:

**Lewis acid induced spectral changes of sterically hindered and unhindered
meso-tetra(aryl)porphyrins: Fluorescence emission spectra**

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S1: ^1H NMR, ^{13}C NMR and UV-Vis spectral data of *meso*-tetra(aryl)porphyrins:

H_2TPP . ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.77 (2H, br, s, NH), 7.77-7.84 (8 H_m and 4 H_p , m), 8.26-8.27 (8 H_o , d), 8.90 (8 H_B , 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_B); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 417 (5.79), 513 (4.58), 548 (4.38), 590 (4.30), 647 (4.29).

$\text{H}_2\text{T(4-OCH}_3\text{)PP}$. ^1H NMR (400MHz, CDCl_3 , TMS), δ/ppm : -2.72 (2H, br, s, NH), 7.29-7.32 (8 H_m , d), 8.15-8.17 (8 H_o , d), 8.89 (8 H_B , s), 4.13 (12 H_{Me} , s); ^{13}C NMR (400 MHz, 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_B), 55.61 (C_{Me}); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 421 (5.61), 517 (4.32), 555 (4.22), 593 (4.06), 651 (4.11).

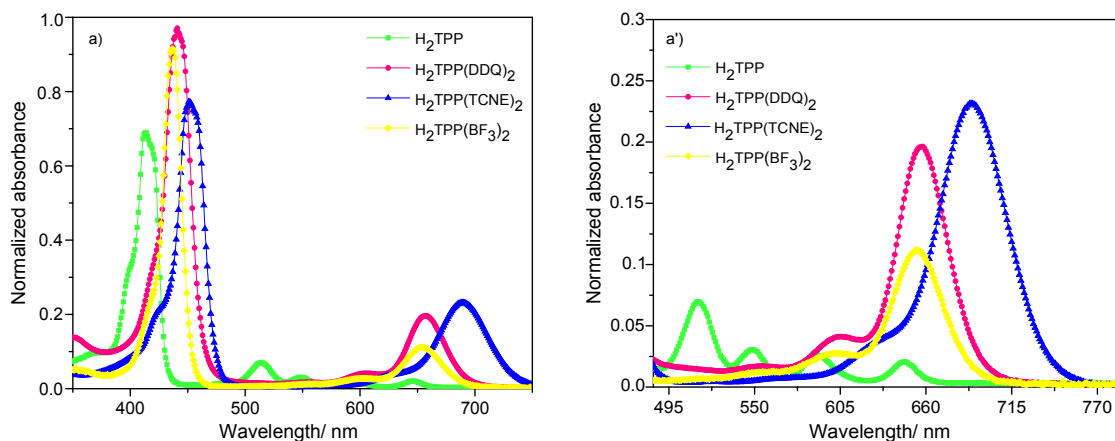
$\text{H}_2\text{T(4-CH}_3\text{)PP}$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.76 (2H, br, s, NH), 7.55-7.58 (8 H_m , d), 8.09-8.12 (8 H_o , d), 8.86 (8 H_B , s), 2.65 (12 H_{Me} , s); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 120.47 (C_{meso}), 139.73 (C_1), 134.92 (C_2 , C_6), 127.81 (C_3 , C_5), 137.71 (C_4), 131.37 (C_B), 21.57 (C_{Me}); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 418 (5.89), 516 (4.54), 551 (4.34), 590 (4.18), 647 (4.20).

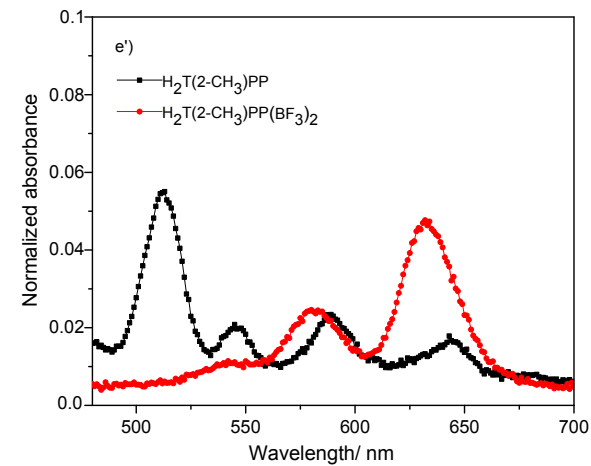
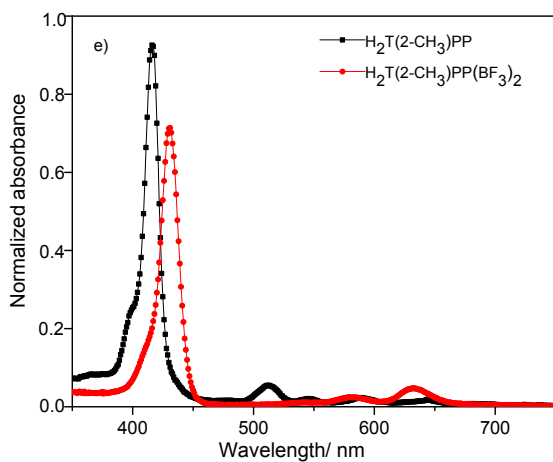
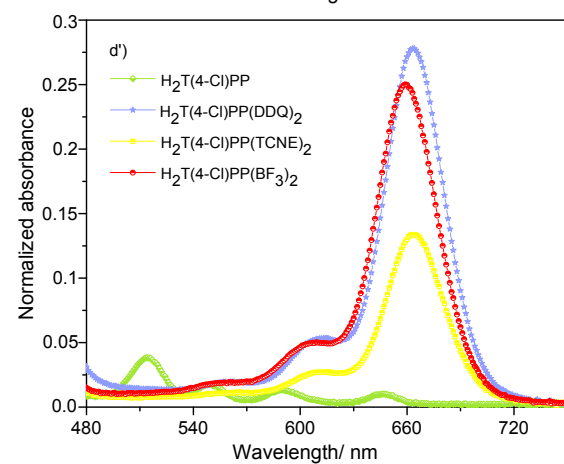
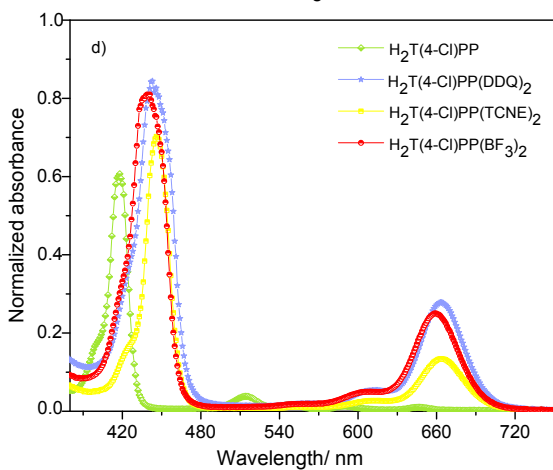
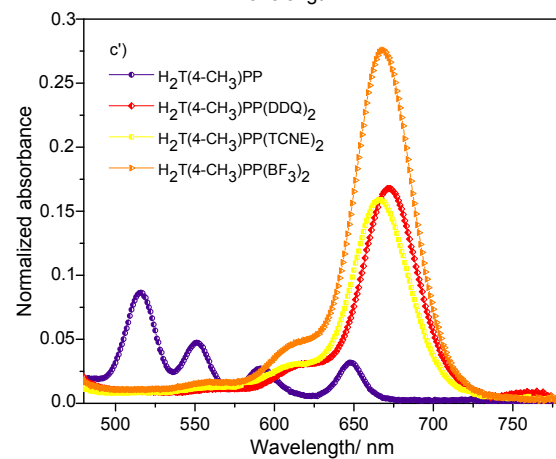
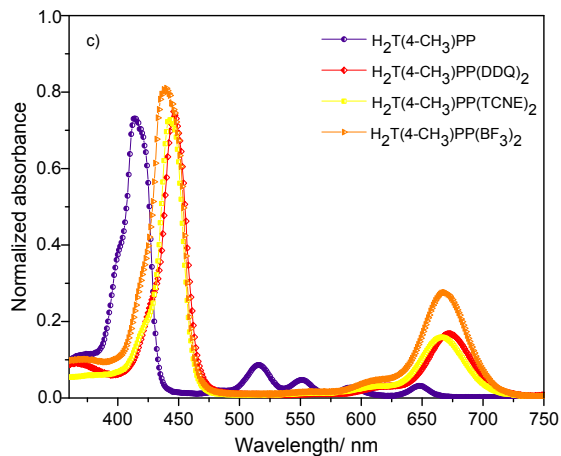
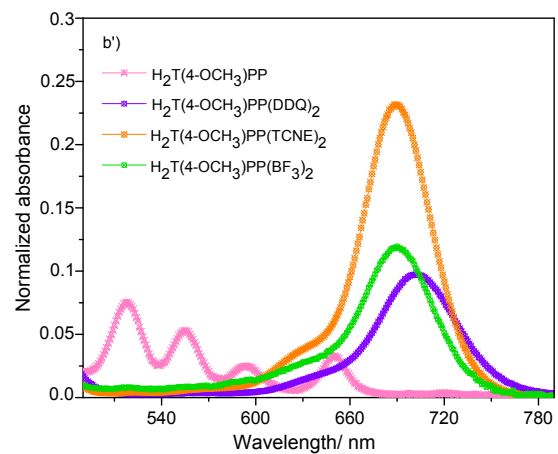
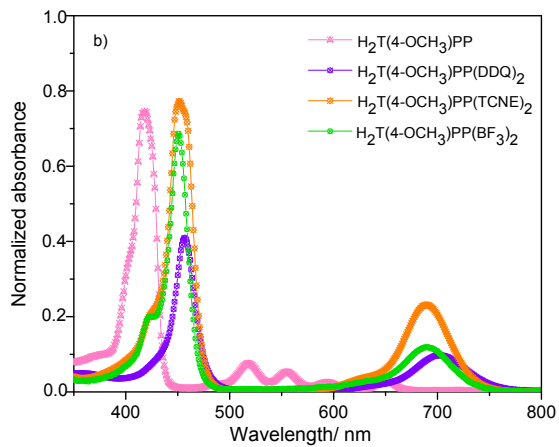
$\text{H}_2\text{T(4-Cl)PP}$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.83 (2H, br, s, NH), 7.77-7.79 (8 H_m , d), 8.15-8.17 (8 H_o , d), 8.87 (8 H_B , s); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 119.01 (C_{meso}), 140.37 (C_1), 135.52 (C_2 , C_6), 127.07 (C_3 , C_5), 134.41 (C_4), 131.64 (C_B); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 418 (5.79), 513 (4.52), 547 (4.25), 590 (4.16), 647 (4.10).

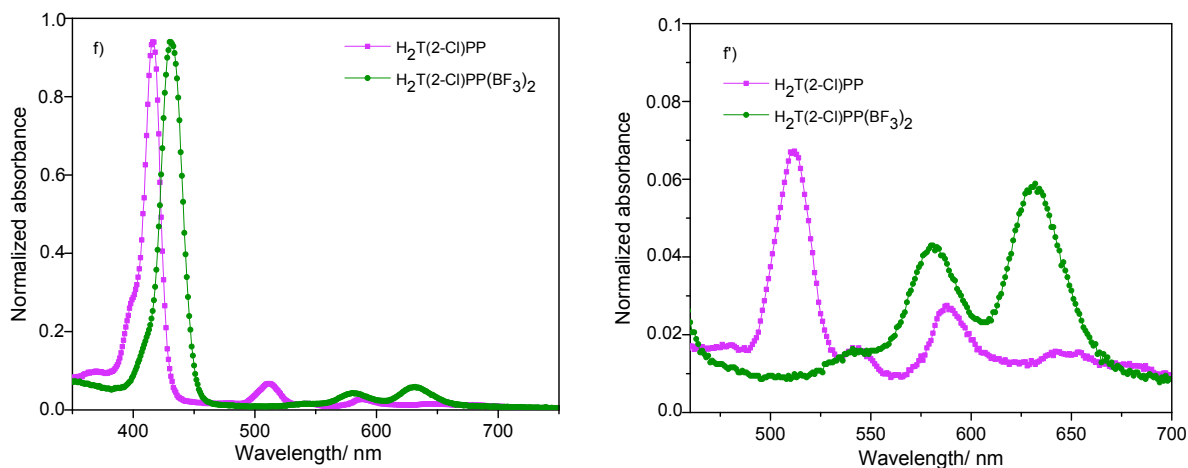
$\text{H}_2\text{T(2-CH}_3\text{)PP}$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.59 (2H, br, s, NH), 7.54-7.74 (8 H_m and 4 H_p , m, *meta* and *para* position relative to C atom attached to the *meso* position), 7.99-8.11 (4 H_o , m, *ortho* position relative to C atom attached to the *meso* position), 8.70 (8 H_B , s), 2.01-2.11 (12 H_{Me} , m); ^{13}C NMR (400 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_B), 21.37 (C_{Me}); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 416 (6.04), 512 (4.74), 545 (4.34), 589 (4.34), 645 (4.25).

$\text{H}_2\text{T(2-Cl)PP}$. ^1H NMR (400MHz, CDCl_3 , TMS), δ/ppm : -2.62 (2H, br, s, NH), 7.66-7.87 (8 H_m and 4 H_p , m), 8.10-8.26 (4 H_o , m), 8.72 (8 H_B , s); ^{13}C NMR (400 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_B); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 416 (5.64), 512 (4.47), 543 (4.07), 587 (4.15), 643 (3.96).

S2: (a-f) UV-Vis spectra of *meso*-tetra(aryl)porphyrins and their molecular complexes with DDQ, TCNE and BF_3 , (a'-f') The expanded region of Q-bands in UV-Vis spectra.







S3: ^1H NMR, ^{13}C NMR, ^{11}B NMR, ^{19}F NMR and UV-Vis spectral data of 1:2 molecular complexes of *meso*-tetra(aryl)porphyrins with BF_3 .

$\text{H}_2\text{TTPP}(\text{BF}_3)_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.87 (2H, br, s, NH), 8.83 (8H $_{\beta}$, s), 8.65-8.67 (8H $_o$, m), 8.02-8.10 (8H $_m$ and 4H $_p$, m); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 146.03 (C $_{\alpha}$), 129.77 (C $_{\beta}$), 123.43 (C $_{meso}$), 139.35 (C $_1$), 138.73 (C $_2$), 128.60 (C $_3$), 130.55 (C $_4$). ^{11}B NMR (400 MHz, CDCl_3 , $\text{BF}_3\cdot\text{OEt}_2$), δ/ppm : -6.40, (The ^{11}B signal of the free $\text{BF}_3\cdot\text{OEt}_2$ was observed at 0.14 ppm); ^{19}F NMR (400 MHz, CDCl_3 , CFCl_3), δ/ppm : -155.52, (The ^{19}F signal of the free $\text{BF}_3\cdot\text{OEt}_2$ was observed at -152.85 ppm); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 437 (5.64), 605 (4.03), 654 (4.67).

$\text{H}_2\text{T(4-OCH}_3\text{)PP}(\text{BF}_3)_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.37 (2H, br, s, NH), 8.68 (8H $_{\beta}$, s), 8.59-8.60 (8H $_o$, br), 7.57-7.61 (8H $_m$, m), 4.06-4.22 (12 H $_{Me}$, m); ^{13}C NMR spectra of $\text{H}_2\text{T(4-OCH}_3\text{)PP}(\text{BF}_3)_2$ was not obtained due to the low solubility of the adduct in CDCl_3 at the concentration needed for ^{13}C NMR study; ^{11}B NMR (400 MHz, CDCl_3 , $\text{BF}_3\cdot\text{OEt}_2$), δ/ppm : -5.95; ^{19}F NMR (400 MHz, CDCl_3 , CFCl_3), δ/ppm : -155.39; UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 451 (4.73), 690 (4.08).

$\text{H}_2\text{T(4-CH}_3\text{)PP}(\text{BF}_3)_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.69 (2H, br, s, NH), 8.77 (8H $_{\beta}$, s), 8.53, 8.55 (8H $_o$, d), 7.86, 7.88 (8H $_m$, d), 2.82 (12 H $_{Me}$, s); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 146.10 (C $_{\alpha}$), 129.48 (C $_{\beta}$), 123.28 (C $_{meso}$), 136.96 (C $_1$), 138.80 (C $_2$), 129.44 (C $_3$), 141.07 (C $_4$), 21.70 (C $_{Me}$); ^{11}B NMR (400 MHz, CDCl_3 , $\text{BF}_3\cdot\text{OEt}_2$), δ/ppm : -6.30; ^{19}F NMR (400 MHz, CDCl_3 , CFCl_3), δ/ppm : -155.73, -155.68; UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 441 (5.44), 668 (4.73).

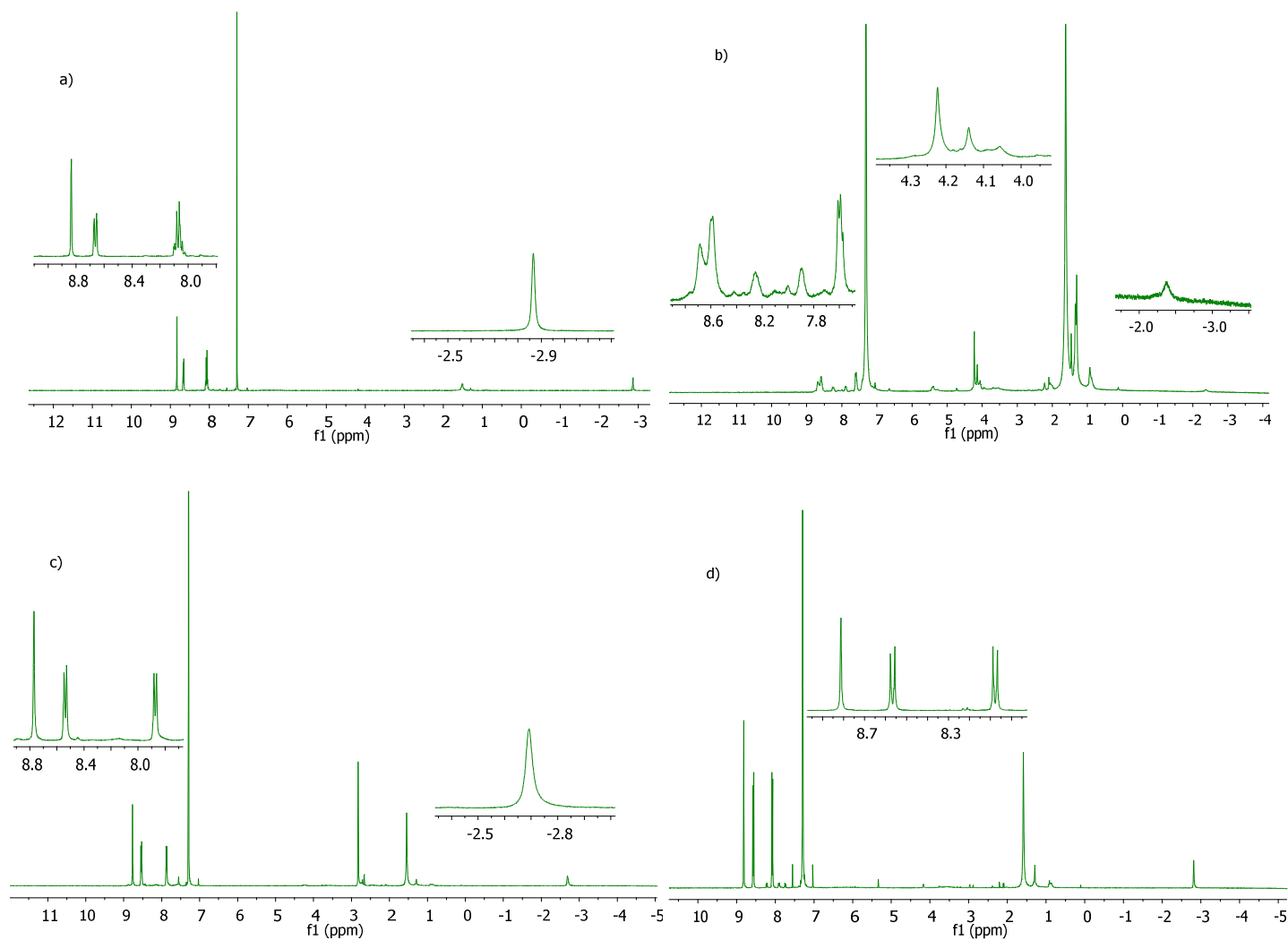
$\text{H}_2\text{T(4-Cl)PP}(\text{BF}_3)_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -2.81 (2H, br, s, NH), 8.81 (8H $_{\beta}$, s), 8.56, 8.58 (8H $_o$, d), 8.07, 8.09 (8H $_m$, d); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 146.03 (C $_{\alpha}$), 128.86 (C $_{\beta}$), 122.42 (C $_{meso}$), 138.10 (C $_1$), 139.31 (C $_2$), 129.11 (C $_3$), 137.60 (C $_4$); ^{11}B NMR (400 MHz, CDCl_3 , $\text{BF}_3\cdot\text{OEt}_2$), δ/ppm : -6.33; ^{19}F NMR (400 MHz, CDCl_3 , CFCl_3), δ/ppm : -155.14; UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 440 (5.99), 600 (4.52), 658 (5.29).

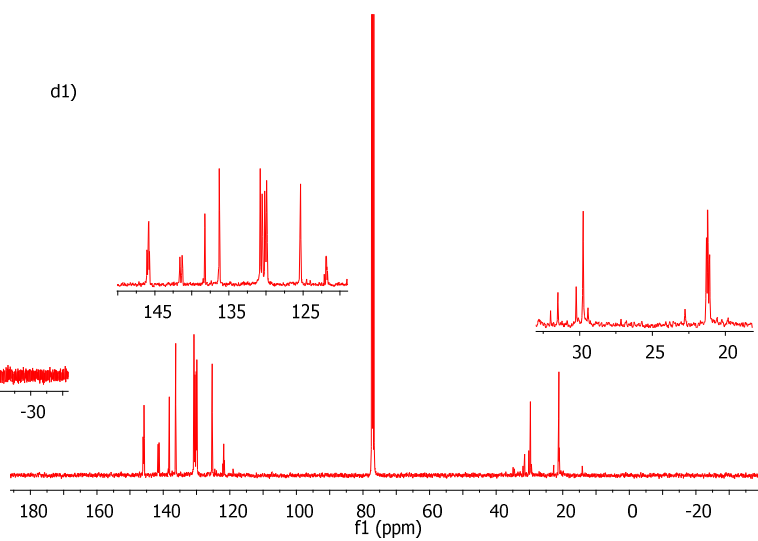
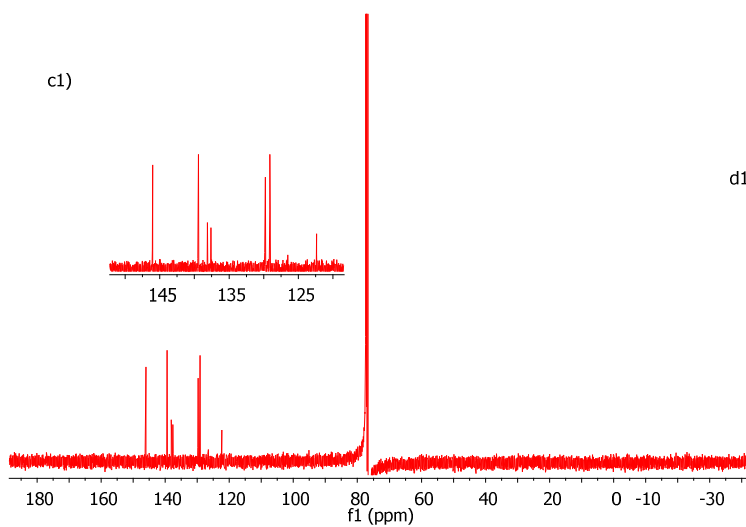
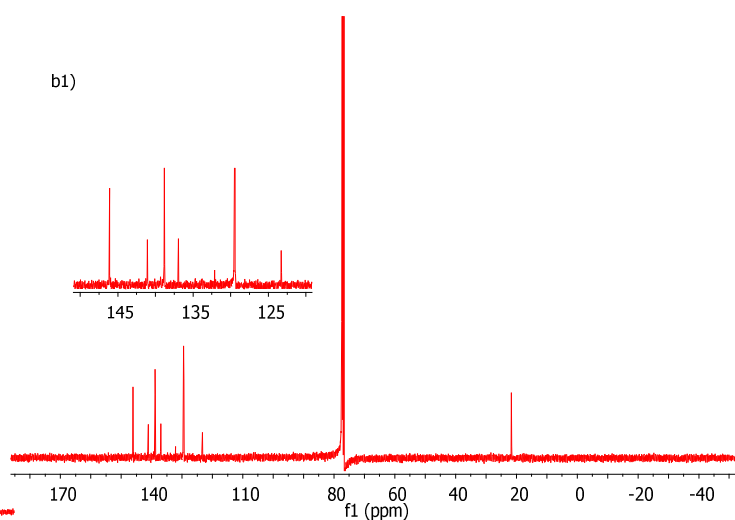
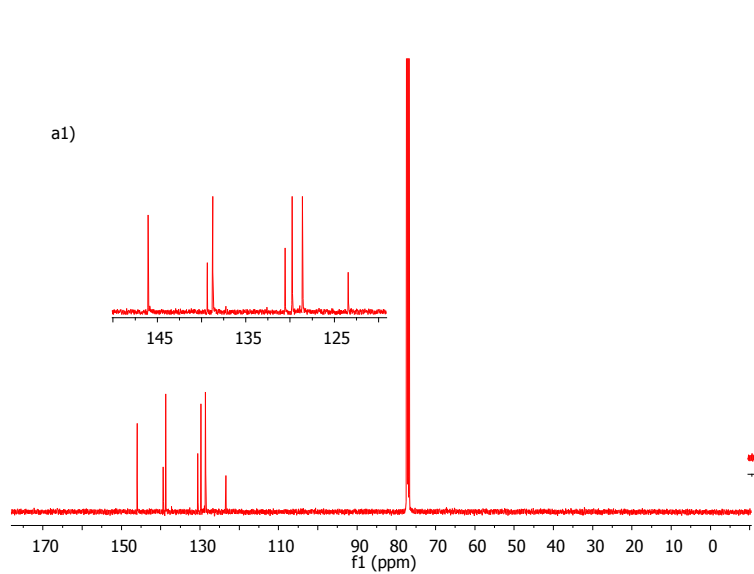
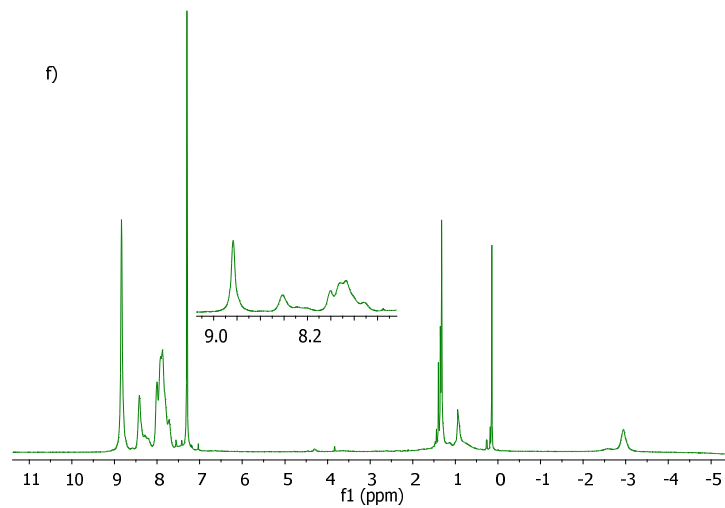
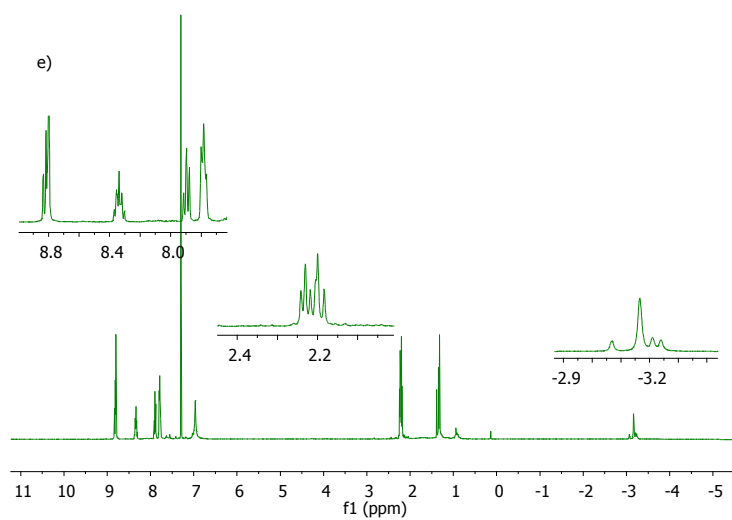
$\text{H}_2\text{T(2-CH}_3\text{)PP}(\text{BF}_3)_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -3.24, -3.21, -3.17, -3.07 (2H, br, s, NH), 8.80-8.84 (8H $_{\beta}$, m), 8.30-8.37 (4H $_o$, m), 7.77-7.92 (8H $_m$, 8H $_p$, m), 2.18-2.24 (12H $_{Me}$, m); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 145.72, 145.89, 146.01, 146.07 (C $_{\alpha}$), 130.44, 130.78 (C $_{\beta}$), 121.79, 121.90 (C $_{meso}$), 141.23, 141.36 (C $_1$), 141.56, 141.65 (C $_2$),

129.86, 129.91 (C₃), 130.05, 130.15 (C₄), 125.33 (C₅), 136.30 (C₆), 21.07-21.30, 29.43, 29.76, 30.23 (C_{Me}); ¹¹B NMR (400 MHz, CDCl₃, BF₃·OEt₂), δ/ppm: -6.28; ¹⁹F NMR (400 MHz, CDCl₃, CFCl₃), δ/ppm: -155.12, -149.70, -149.66, -148.39, -147.63, -147.57; UV-vis in CH₂Cl₂, λ_{max}/nm: 431 (5.87), 583 (4.18), 634 (4.50).

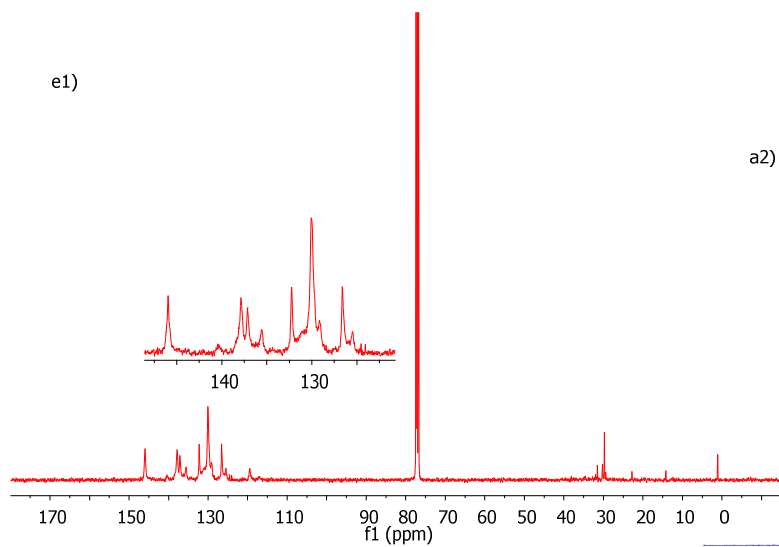
H₂T(2-Cl)PP(BF₃)₂. ¹H NMR (400 MHz, CDCl₃, TMS), δ/ppm: -2.94 (2H, br, s, NH), 8.83 (8H_β, s), 8.20-8.41 (4H_o, m), 7.72-8.00 (8H_m and 4H_p, m); ¹³C NMR (400 MHz, CDCl₃, TMS), δ/ppm: 145.96 (C_α), 132.24 (C_β), 119.51 (C_{meso}), 137.87 (C₁), 137.13 (C₂), 129.10 (C₃), 130.0 (C₄), 126.61 (C₅), 135.60 (C₆); ¹¹B NMR (400 MHz, CDCl₃, BF₃·OEt₂), δ/ppm: -5.94; ¹⁹F NMR (400 MHz, CDCl₃, CFCl₃), δ/ppm: -155.07; UV-vis in CH₂Cl₂, λ_{max}/nm: 430 (5.79), 581 (4.15), 632 (4.47).

S6: ¹H NMR spectra of a) H₂TPP(BF₃)₂, b) H₂T(4-OCH₃)PP(BF₃)₂, c) H₂T(4-CH₃)PP(BF₃)₂, d) H₂T(4-Cl)PP(BF₃)₂, e) H₂T(2-CH₃)PP(BF₃)₂ and f) H₂T(2-Cl)PP(BF₃)₂; ¹³C NMR spectra of a₁) H₂TPP(BF₃)₂, b₁) H₂T(4-CH₃)PP(BF₃)₂, c₁) H₂T(4-Cl)PP(BF₃)₂, d₁) H₂T(2-CH₃)PP(BF₃)₂ and e₁) H₂T(2-Cl)PP(BF₃)₂; ¹¹B NMR spectra of a₂) BF₃·OEt₂ (The inset shows ¹¹B background signals of the NMR tube), b₂) H₂TPP(BF₃)₂, c₂) H₂T(4-OCH₃)PP(BF₃)₂, d₂) H₂T(4-CH₃)PP(BF₃)₂, e₂) H₂T(4-Cl)PP(BF₃)₂, f₂) H₂T(2-CH₃)PP(BF₃)₂, g₂) H₂T(2-Cl)PP(BF₃)₂ and ¹⁹F NMR spectra of a₃) BF₃·OEt₂, b₃) H₂TPP(BF₃)₂, c₃) H₂T(4-OCH₃)PP(BF₃)₂, d₃) H₂T(4-CH₃)PP(BF₃)₂, e₃) H₂T(4-Cl)PP(BF₃)₂, f₃) H₂T(2-CH₃)PP(BF₃)₂, g₃) H₂T(2-Cl)PP(BF₃)₂.

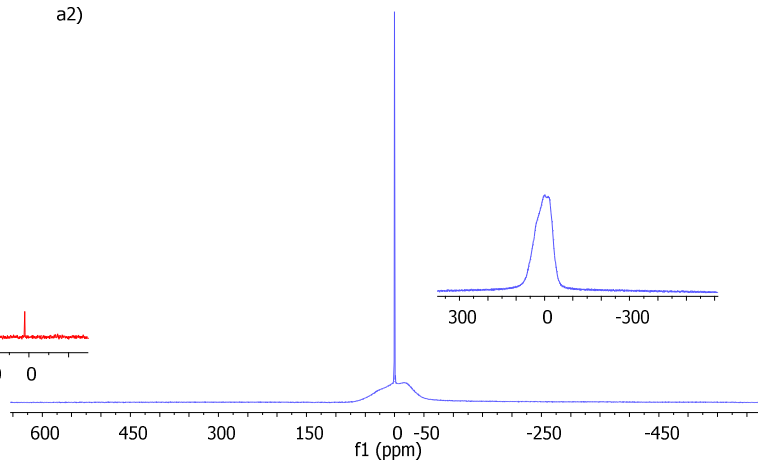




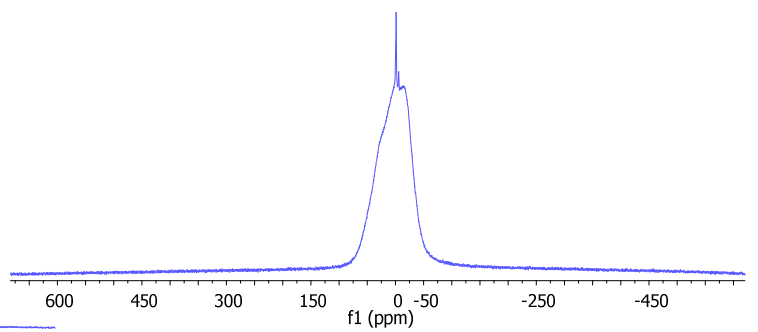
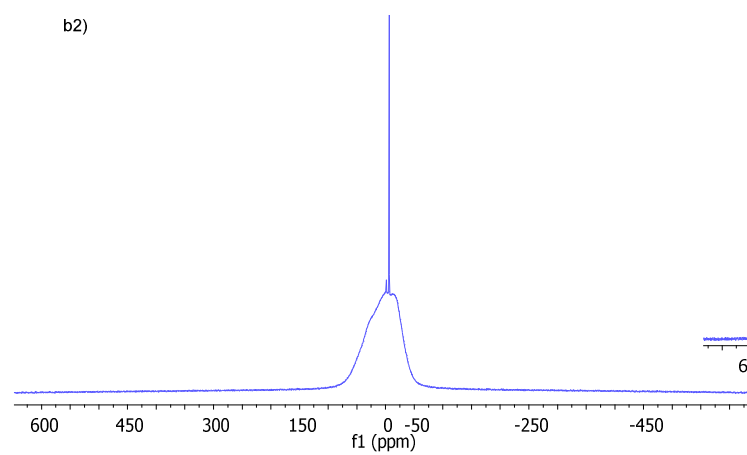
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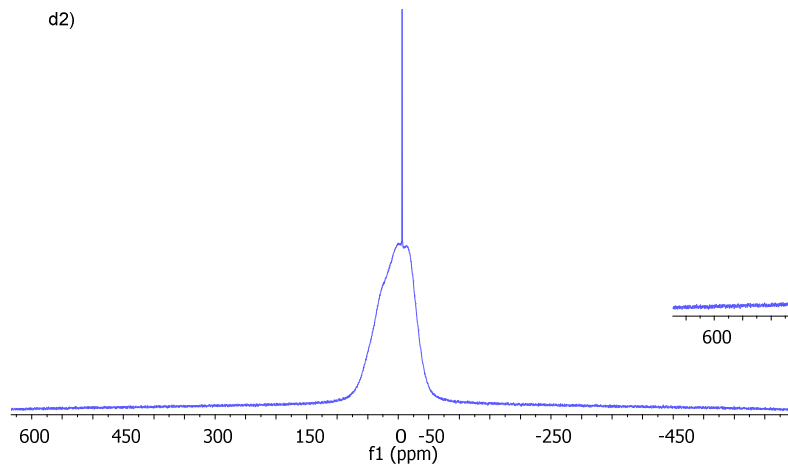
a2)



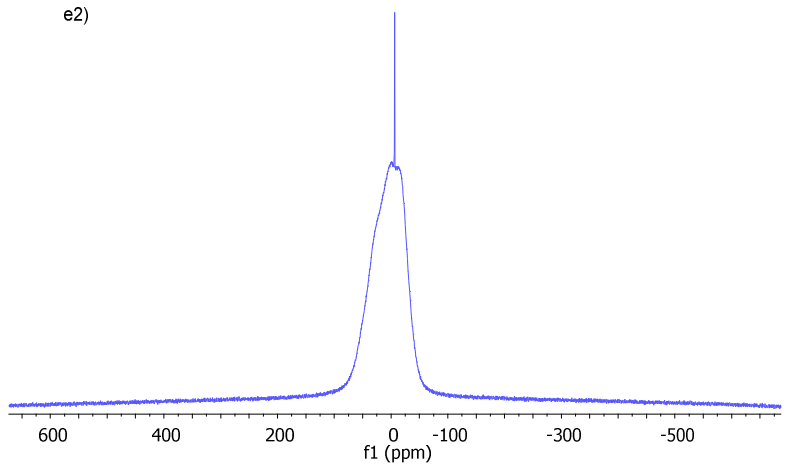
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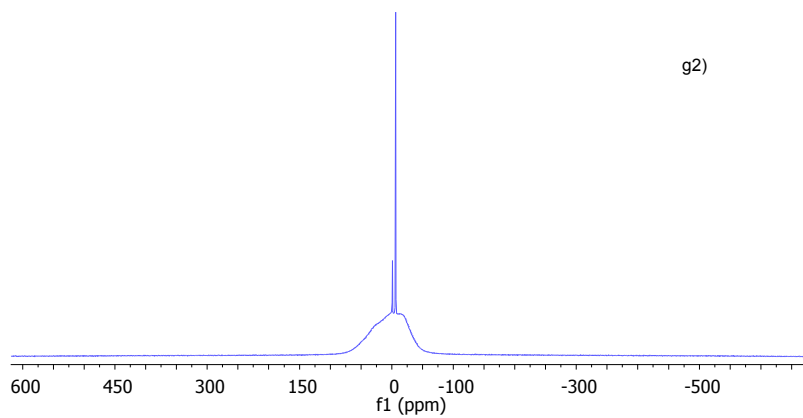
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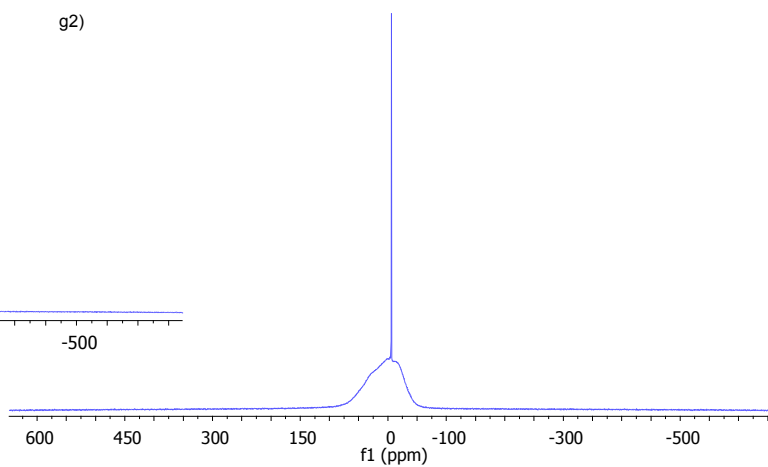
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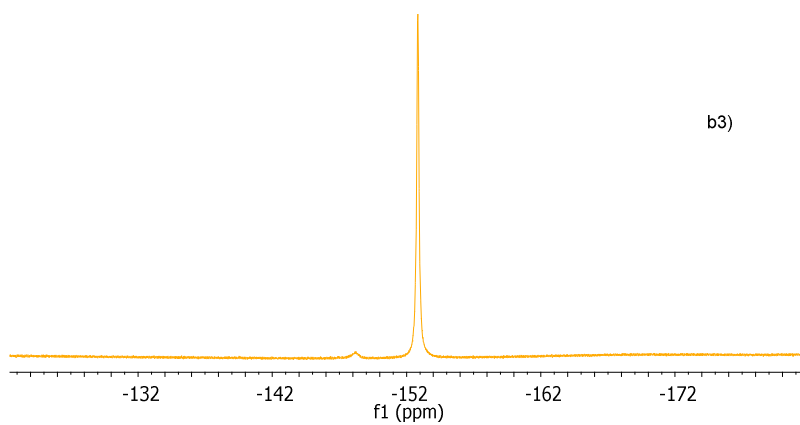
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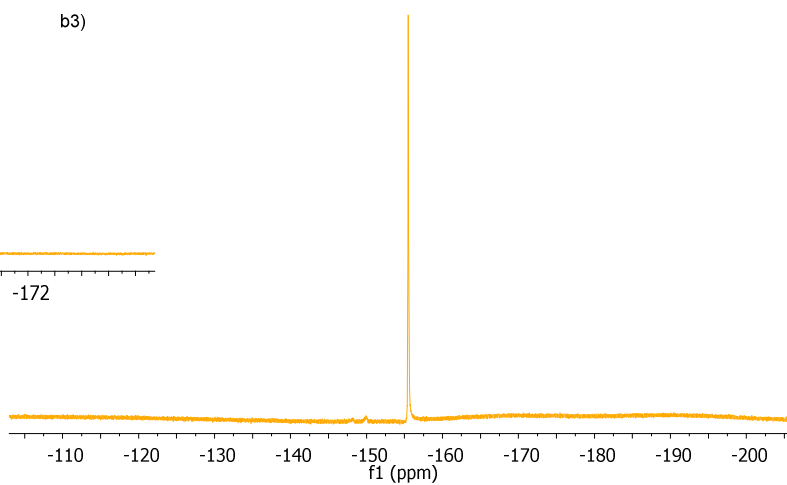
g2)



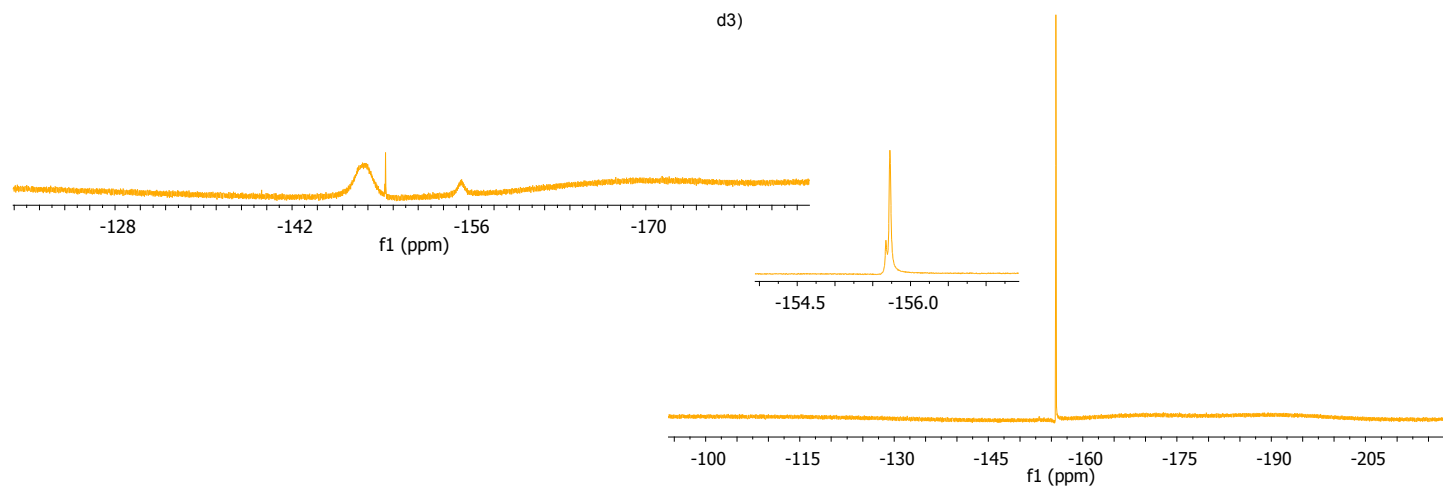
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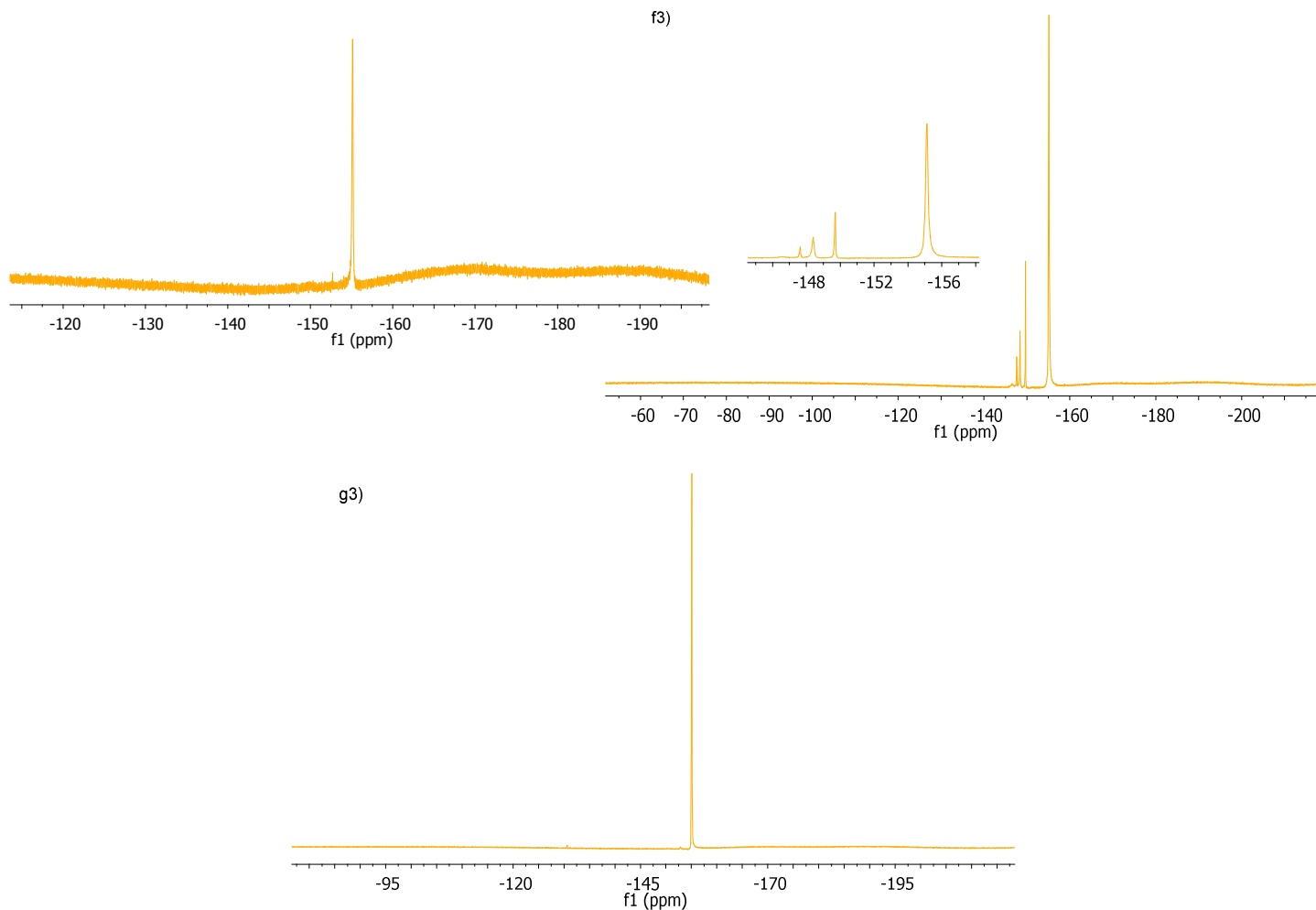
b3)



c3)



e3)



S7: ^1H NMR, ^{13}C NMR and UV-Vis spectral data of the 1:2 molecular complexes of *meso*-tetra(aryl)porphyrins with DDQ.

$\text{H}_2\text{TPP}(\text{DDQ})_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -0.36 (2H, br, s, NH), 8.61 (8 H_β , s), 8.68 (8 H_α , d), 7.99 (8 H_m and 4 H_p , m); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 145.96 (C_α), 128.95 (C_β), 123.44 (C_{meso}), 139.89 (C_1'), 138.87 (C_2'), 128.73 (C_3'), 130.51 (C_4'). The DDQ molecules of $\text{H}_2\text{TPP}(\text{DDQ})_2$, 171.81 (C_1), 172.07 (C_4), 143.33 (C_2 , C_3), 135.39 (C_5), 87.99 (C_6), 165.43 (C_7), 112.23 (C_8); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 441 (4.78), 606 (3.69), 655 (4.23).

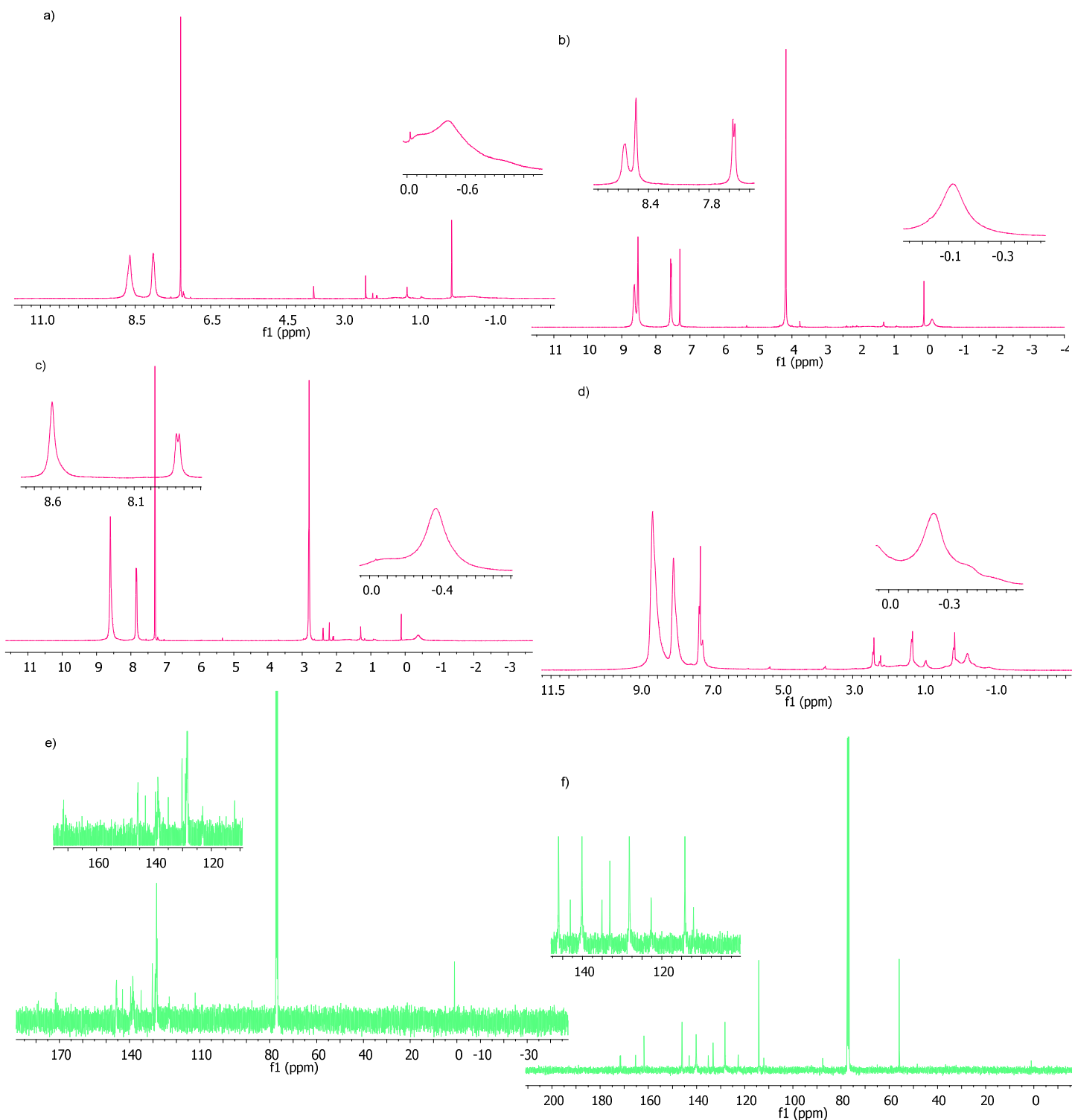
$\text{H}_2\text{T}(4\text{-OCH}_3)\text{PP}(\text{DDQ})_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -0.13 (2H, br, s, NH), 8.48 (8 H_β , s), 8.59, 8.62 (8 H_α , d), 7.50, 7.54 (8 H_m , d), 4.15 (12 H_{Me} , s); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 146.36 (C_α), 128.53 (C_β), 123.01 (C_{meso}), 133.44 (C_1'), 140.46 (C_2'), 114.50 (C_3'), 162.11 (C_4'); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 454 (5.58), 690 (4.84).

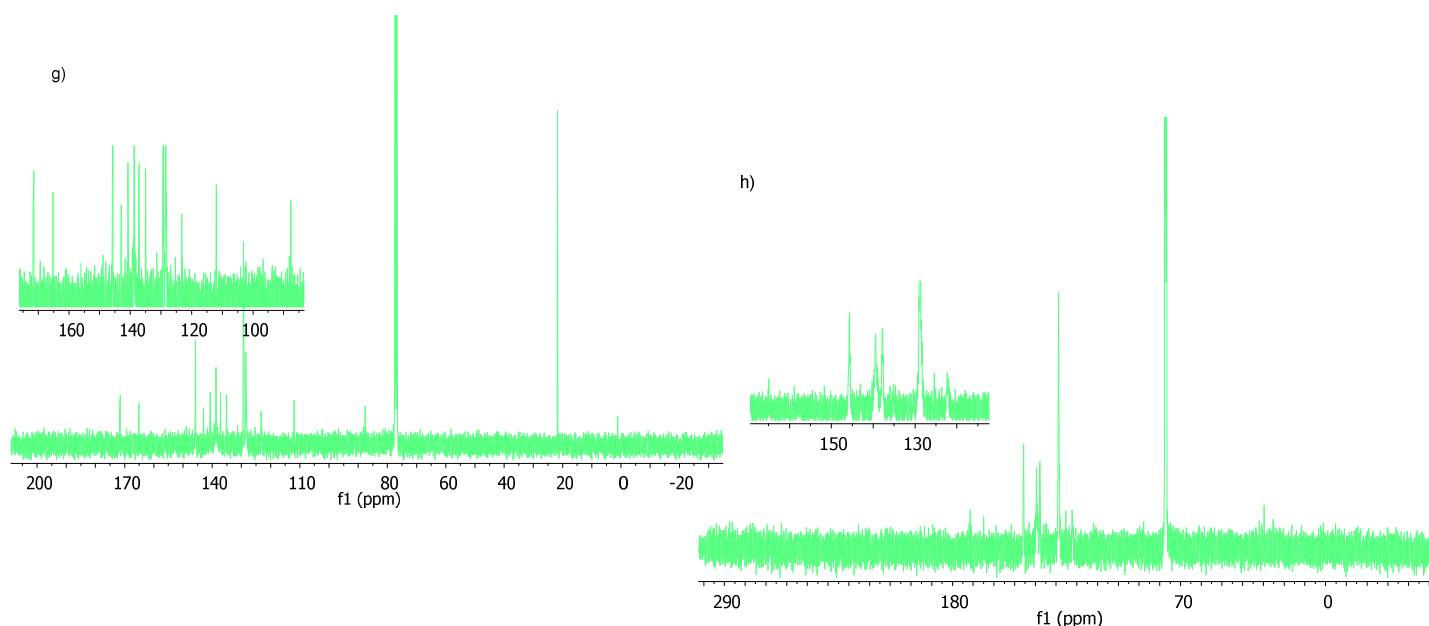
$\text{H}_2\text{T}(4\text{-CH}_3)\text{PP}(\text{DDQ})_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -0.38 (2H, br, s, NH), 8.55 (8 H_β , s), 8.55 (8 H_α , d), 7.78, 7.81 (8 H_m , d), 2.77 (12 H_{Me} , s); ^{13}C NMR (400 MHz, CDCl_3 ,

TMS), δ /ppm: 146.05 (C_α), 128.68 (C_β), 121.82 (C_{meso}), 137.47 (C_1'), 138.94 (C_2'), 129.35 (C_3'), 140.93 (C_4'); UV-vis in CH_2Cl_2 , λ_{max} /nm (log ϵ): 446 (5.65), 669 (4.85).

H₂T(4-Cl)PP(DDQ)₂. ¹H NMR (400 MHz, CDCl₃, TMS), δ /ppm: -0.29 (2H, br, s, NH), 8.59 (8H _{β} , s), 8.59 (8H _{α} , d), 7.98, 8.01 (8H _{m} , d); ¹³C NMR (400 MHz, CDCl₃, TMS), δ /ppm: 145.87 (C_α), 128.91 (C_β), 122.39 (C_{meso}), 137.87 (C_1'), 139.66 (C_2'), 129.11 (C_3'), 137.12 (C_4'); UV-vis in CH_2Cl_2 , λ_{max} /nm (log ϵ): 446 (5.46), 662 (4.95).

S4: ¹H NMR spectra of a) H₂TPP(DDQ)₂, b) H₂T(4-OCH₃)PP(DDQ)₂, c) H₂T(4-CH₃)PP(DDQ)₂ and d) H₂T(4-Cl)PP(DDQ)₂; ¹³C NMR spectra of e) H₂TPP(DDQ)₂, f) H₂T(4-OCH₃)PP(DDQ)₂, g) H₂T(4-CH₃)PP(DDQ)₂ and h) H₂T(4-Cl)PP(DDQ)₂.





S5: ^1H NMR, ^{13}C NMR and UV-Vis spectral data of the 1:2 molecular complexes of *meso*-tetra(aryl)porphyrins with TCNE.

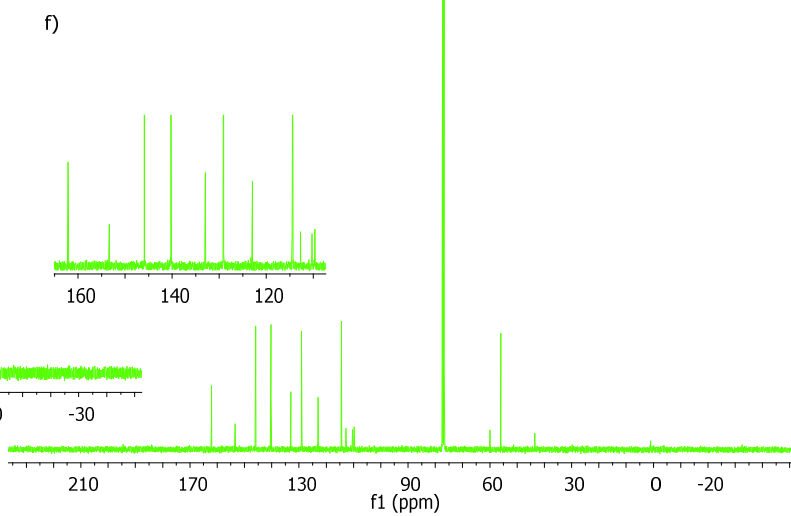
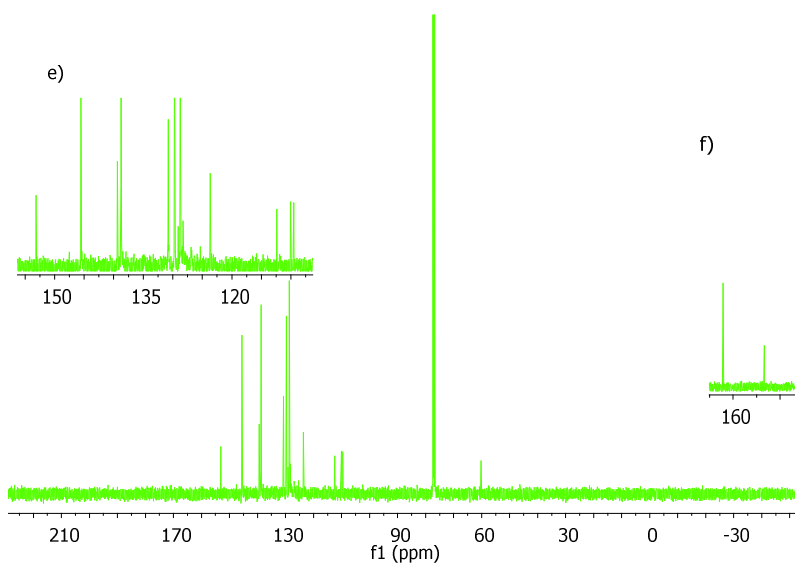
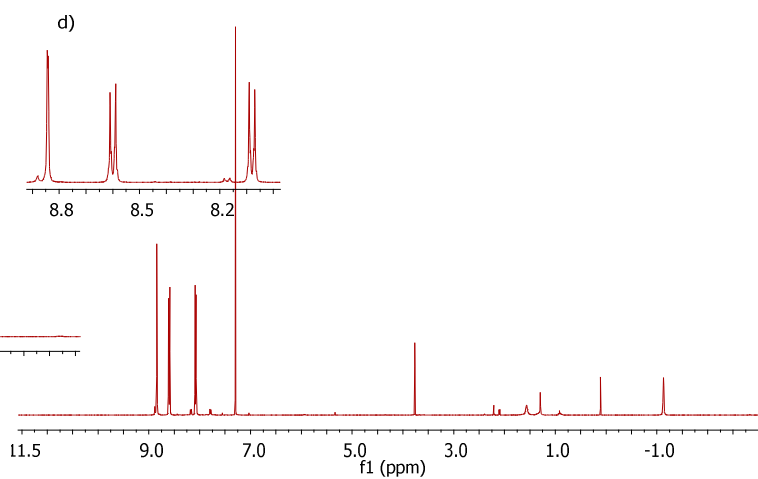
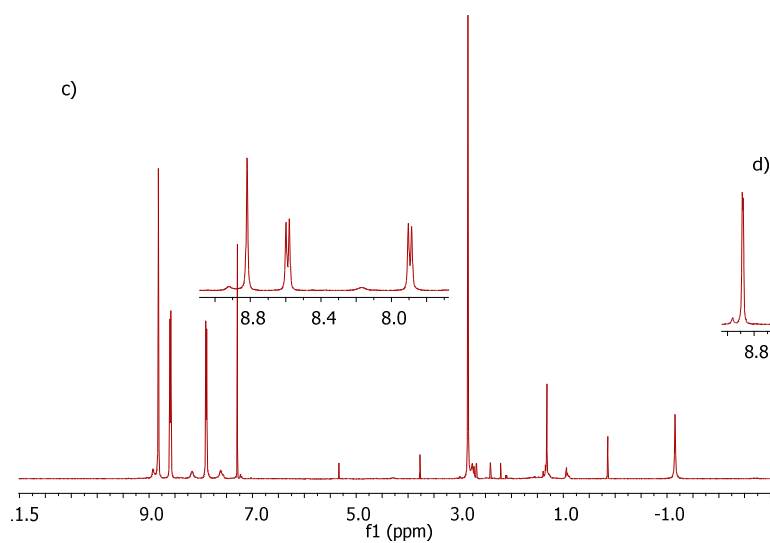
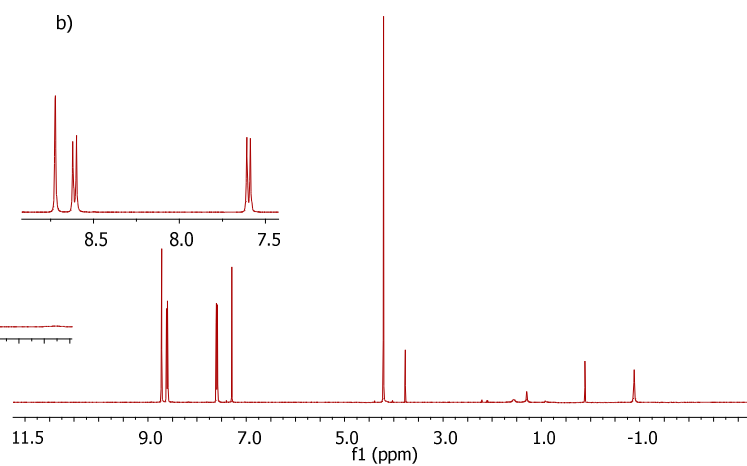
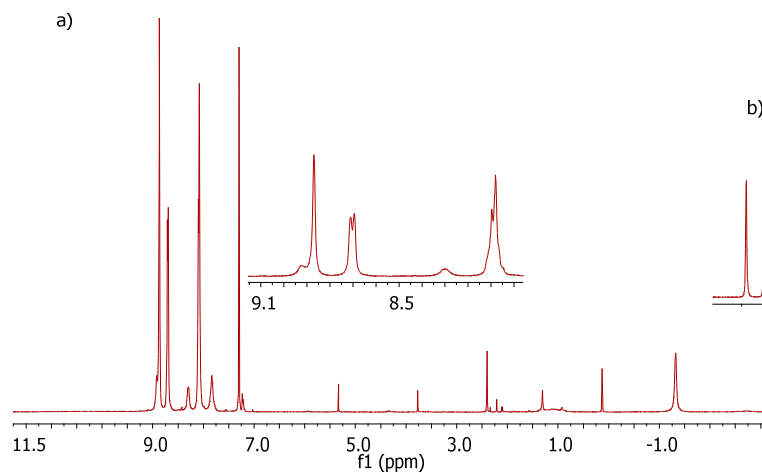
$\text{H}_2\text{TPP}(\text{TCNE})_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -1.26 (2H, br, s, NH), 8.81 (8 H_β , s), 8.64, 8.67 (8 H_α , d), 8.03, 8.07 (8 H_m and 4 H_p , m); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 145.84 (C_α), 129.98 (C_β), 123.95 (C_{meso}), 139.70 (C_1'), 139.07 (C_2'), 129 (C_3'), 131.03 (C_4'). The TCNE molecules of $\text{H}_2\text{TPP}(\text{TCNE})_2$, 108.25 (C_1 , C_2), 112.31 (C_3 , C_4 , C_5 , C_6); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 439 (5.79), 605 (3.85), 655 (4.83).

$\text{H}_2\text{T}(4\text{-OCH}_3)\text{PP}(\text{TCNE})_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -0.92 (2H, br, s, NH), 8.68 (8 H_β , s), 8.55, 8.59 (8 H_α , d), 7.54, 7.58 (8 H_m , d), 4.18 (12 H_{Me} , s); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 146.30 (C_α), 129.45 (C_β), 123.33 (C_{meso}), 133.35 (C_1'), 140.60 (C_2'), 114.81 (C_3'), 162.52 (C_4'); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 454 (5.66), 691 (4.85).

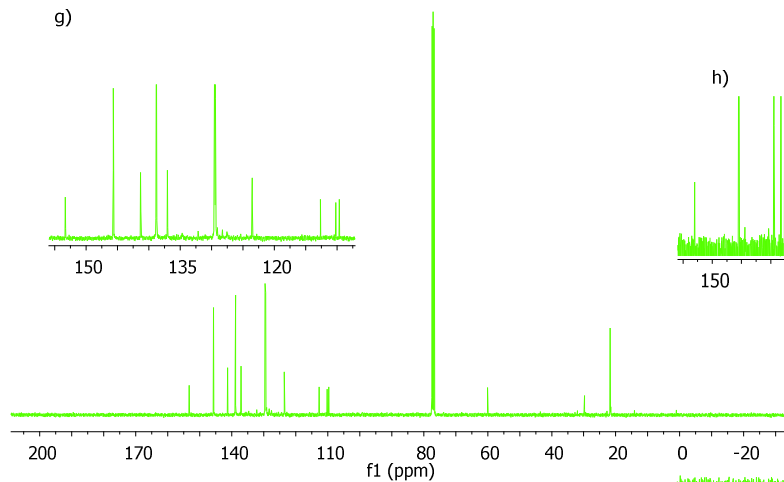
$\text{H}_2\text{T}(4\text{-CH}_3)\text{PP}(\text{TCNE})_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -1.20 (2H, br, s, NH), 8.76 (8 H_β , s), 8.51, 8.54 (8 H_α , d), 7.82, 7.85 (8 H_m , d), 2.80 (12 H_{Me} , s); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 145.96 (C_α), 129.69 (C_β), 123.83 (C_{meso}), 137.36 (C_1'), 139.11 (C_2'), 129.82 (C_3'), 141.59 (C_4'); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 445(5.69), 667(4.69).

$\text{H}_2\text{T}(4\text{-Cl})\text{PP}(\text{TCNE})_2$. ^1H NMR (400 MHz, CDCl_3 , TMS), δ/ppm : -1.16 (2H, br, s, NH), 8.81 (8 H_β , s), 8.55, 8.58 (8 H_α , d), 8.03, 8.06 (8 H_m , d); ^{13}C NMR (400 MHz, CDCl_3 , TMS), δ/ppm : 145.89 (C_α), 130.01 (C_β), 122.95 (C_{meso}), 138.66 (C_1'), 139.81 (C_2'), 129.52 (C_3'), 138.01 (C_4'); UV-vis in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ (log ϵ): 444 (5.42), 659 (4.57).

S8: ^1H NMR spectra of a) $\text{H}_2\text{TPP}(\text{TCNE})_2$, b) $\text{H}_2\text{T}(4\text{-OCH}_3)\text{PP}(\text{TCNE})_2$, c) $\text{H}_2\text{T}(4\text{-CH}_3)\text{PP}(\text{TCNE})_2$ and d) $\text{H}_2\text{T}(4\text{-Cl})\text{PP}(\text{TCNE})_2$; ^{13}C NMR spectra of e) $\text{H}_2\text{TPP}(\text{TCNE})_2$, f) $\text{H}_2\text{T}(4\text{-OCH}_3)\text{PP}(\text{TCNE})_2$, g) $\text{H}_2\text{T}(4\text{-CH}_3)\text{PP}(\text{TCNE})_2$ and h) $\text{H}_2\text{T}(4\text{-Cl})\text{PP}(\text{TCNE})_2$.



g)



h)

