**Supporting Information**

# Synthesis, crystallographic characterization and homogeneous catalytic activity of novel unsymmetric porphyrins

*A. R. Antonangelo,[a] K. C. M. Westrup,[a] L. A. Burt,[b] C. Grazia Bezzu,[b] T. Malewschik,[a] G. S. Machado,[c] F. S. Nunes,[a] N. B. McKeown,[b#] and S. Nakagaki[a*].*

[a]Laboratório de Bioinorgânica e Catálise, Departamento de Química, Universidade Federal do Paraná, Curitiba, Brazil, 81531-990.

[b]EastChem School of Chemistry, The University of Edinburgh, Edinburgh, Scotland, UK, EH9 3FJ.

[c]Centro de Estudos do Mar, Pontal do Paraná - PR, Universidade Federal do Paraná (UFPR), Brazil

[#*] Corresponding author: e-mail address: neil.mckeown@ed.ac.uk, shirleyn@ufpr.br

## Table of Contents

## 1. NMR

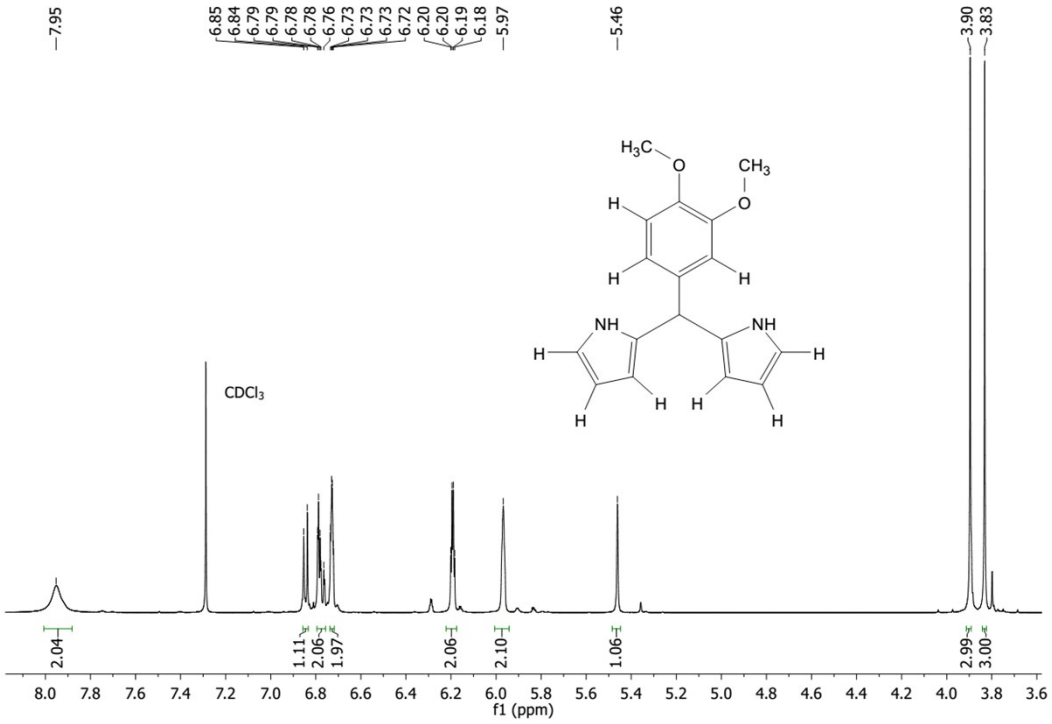



**Figure S1.** $^{1}$H NMR spectra of 5-(3,4-dimethoxyphenyl)dipyrromethane ($CDCl_3$).

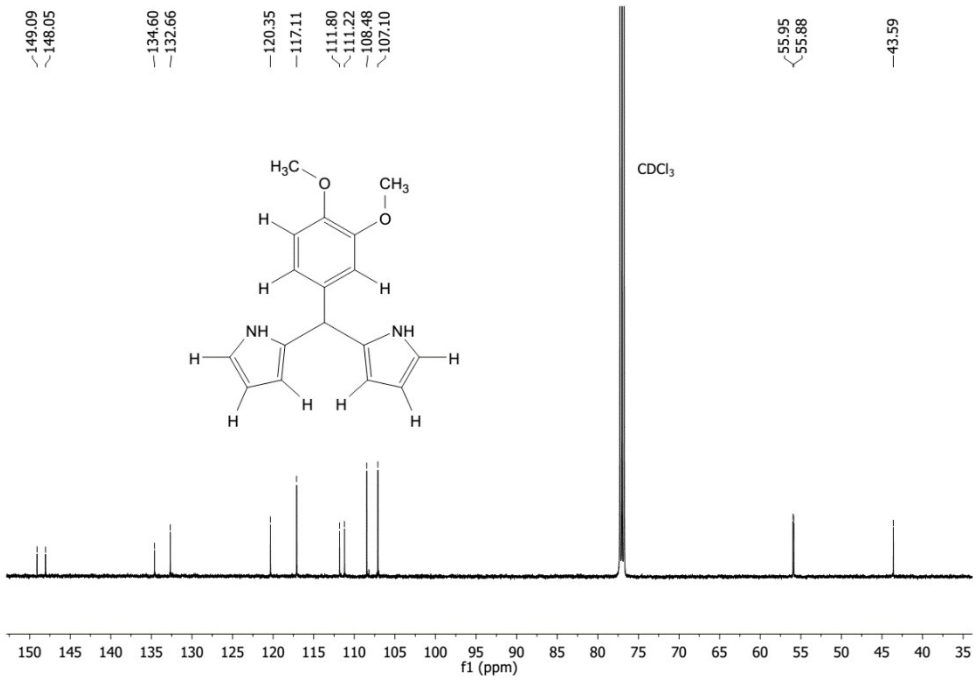



**Figure S2.** $^{13}$C NMR spectra of 5-(3,4-dimethoxyphenyl)dipyrromethane ($CDCl_3$).

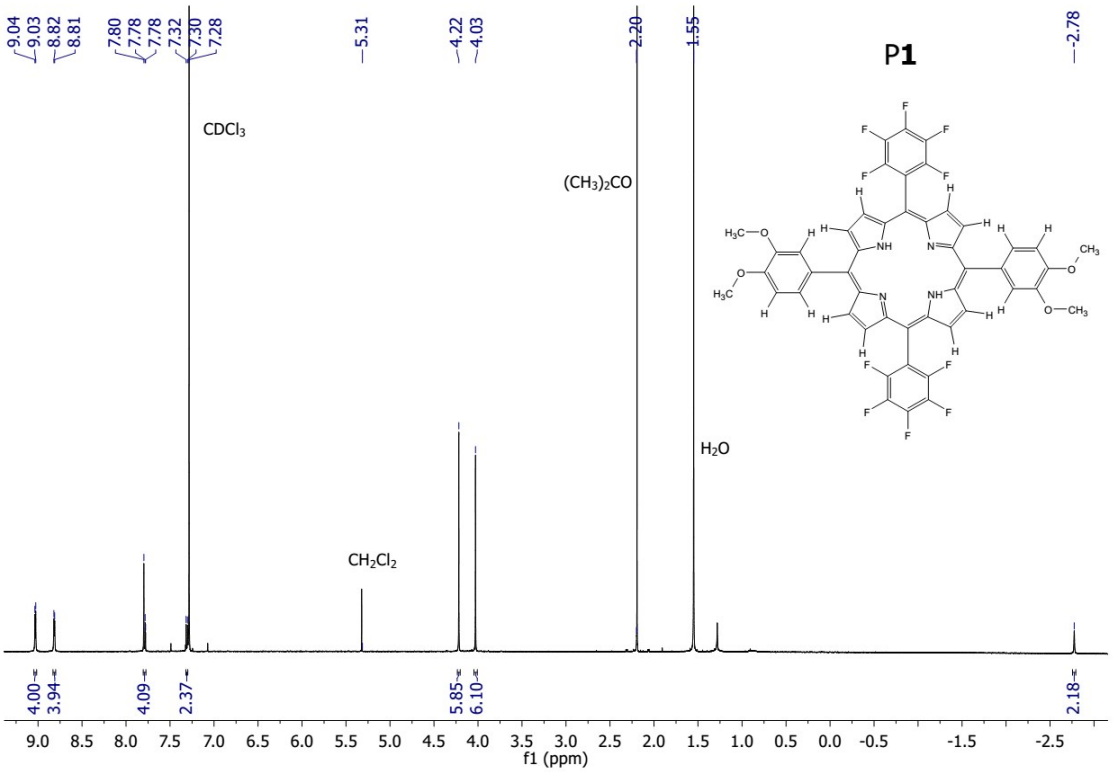



**Figure S3**. $^{1}$H NMR spectra of *trans*-5,15-bis-(pentafluorophenyl)-10,20-bis-(3,4-dimethoxyphenyl)porphyrin (P**1**) ($CDCl_3$).

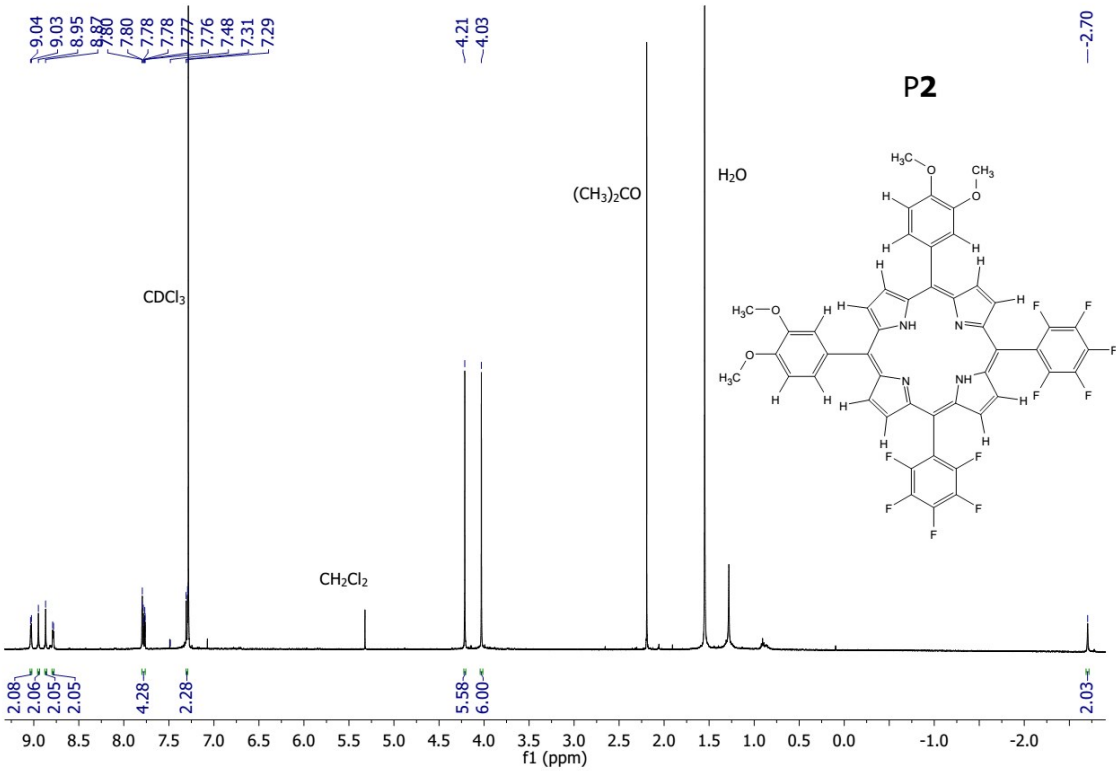



**Figure S4.** $^{1}$H NMR spectra of *cis*-5,15-bis-(pentafluorophenyl)-10,20-bis-(3,4-dimethoxyphenyl)porphyrin (P**2**) ($CDCl_3$).

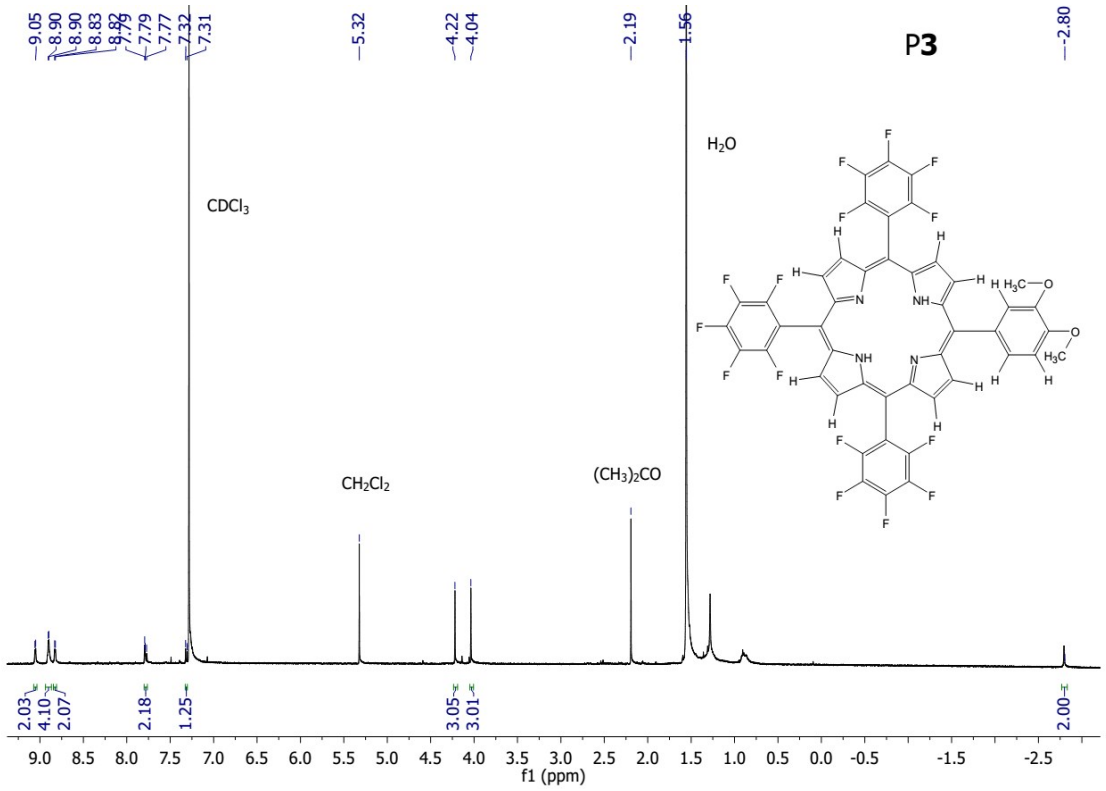



**Figure S5.** $^{1}H$ NMR spectra of 5,10,15-tris-(pentafluorophenyl)-20-(3,4-dimethoxyphenyl)porphyrin (P**3**) ($CDCl_3$).

## 2. UV-VIS

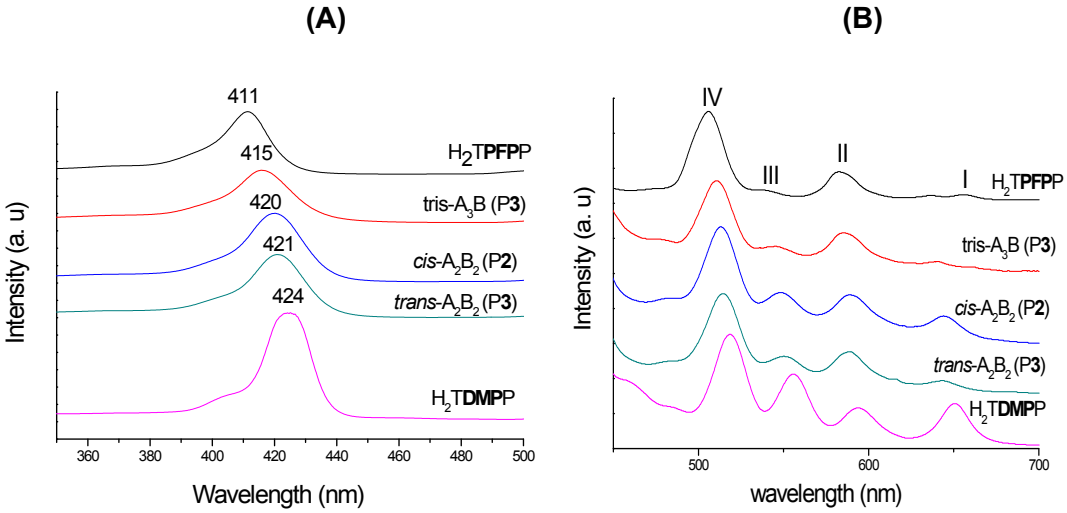



**Figure S6.** UV-VIS spectra of the free base porphyrins, $H_2$T**PFP**P, *tris*-$A_3$B (P**3**), *cis*-$A_2B_2$ (P**2**), *trans*-$A_2B_2$ (P**1**) and $H_2$T**DMP**P in $CH_2Cl_2$, **(A)** Soret band and **(B)** Q bands (IV, III, II, I).

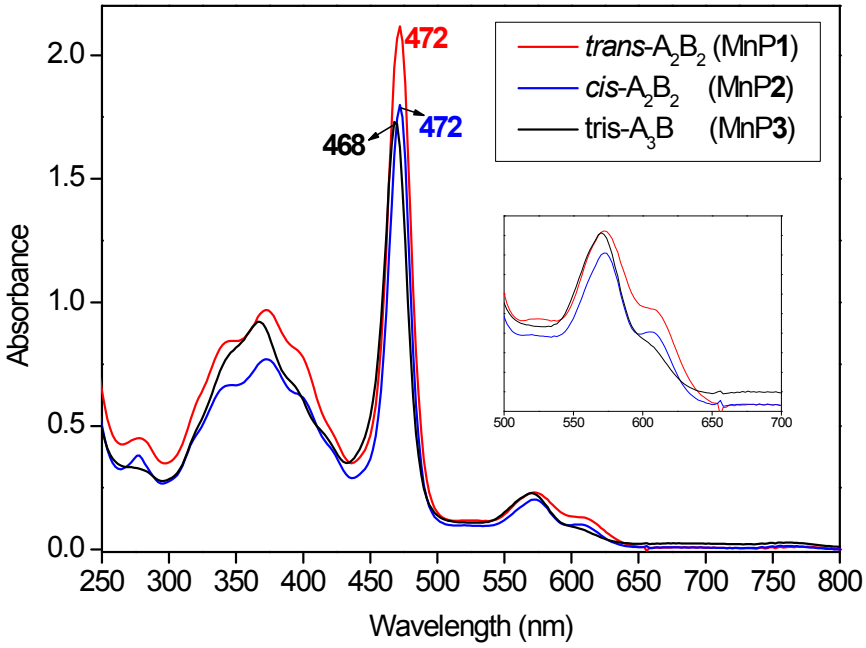



**Figure S7.** UV-VIS spectra of the *trans*-$A_2B_2$ (MnP**1**), *cis*-$A_2B_2$ (MnP**2**) and tris-$A_3B$ (MnP**3**)-porphyrins in $CH_2Cl_2$.

**3. EPR**

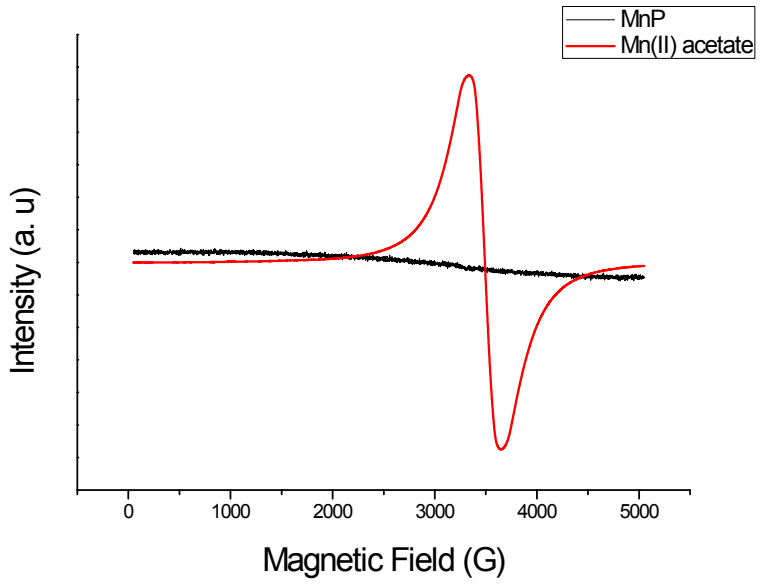



**Figure S8.** EPR spectra of the new metalloporphyrins MnP (black) and Mn(II) acetate (red).

## 4. Mass spectroscopy (MALDI)

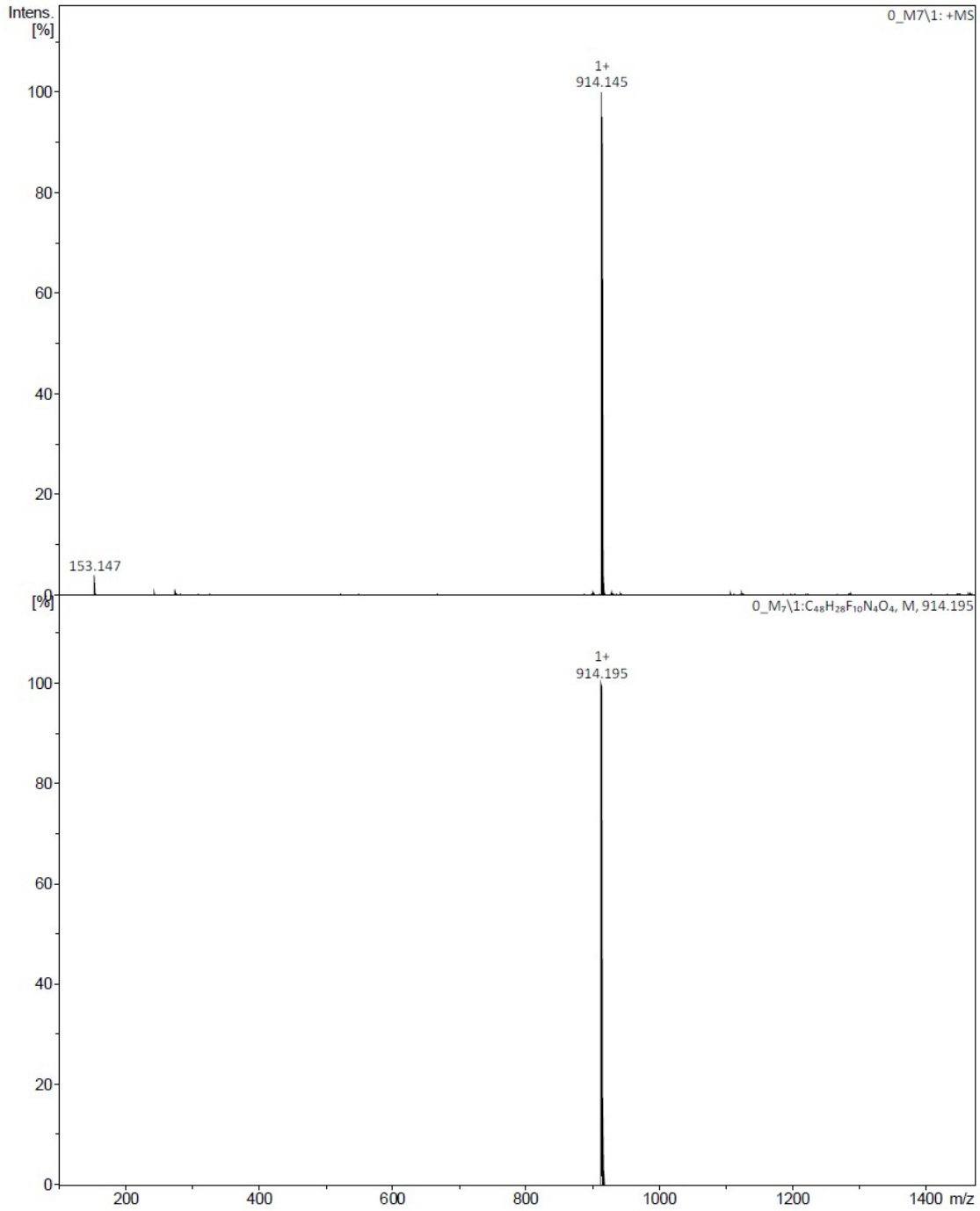



**Figure S9**. MALDI of *trans*-5,15-bis-(pentafluorophenyl)-10,20-bis-(3,4-dimethoxyphenyl)porphyrin (P**1**).

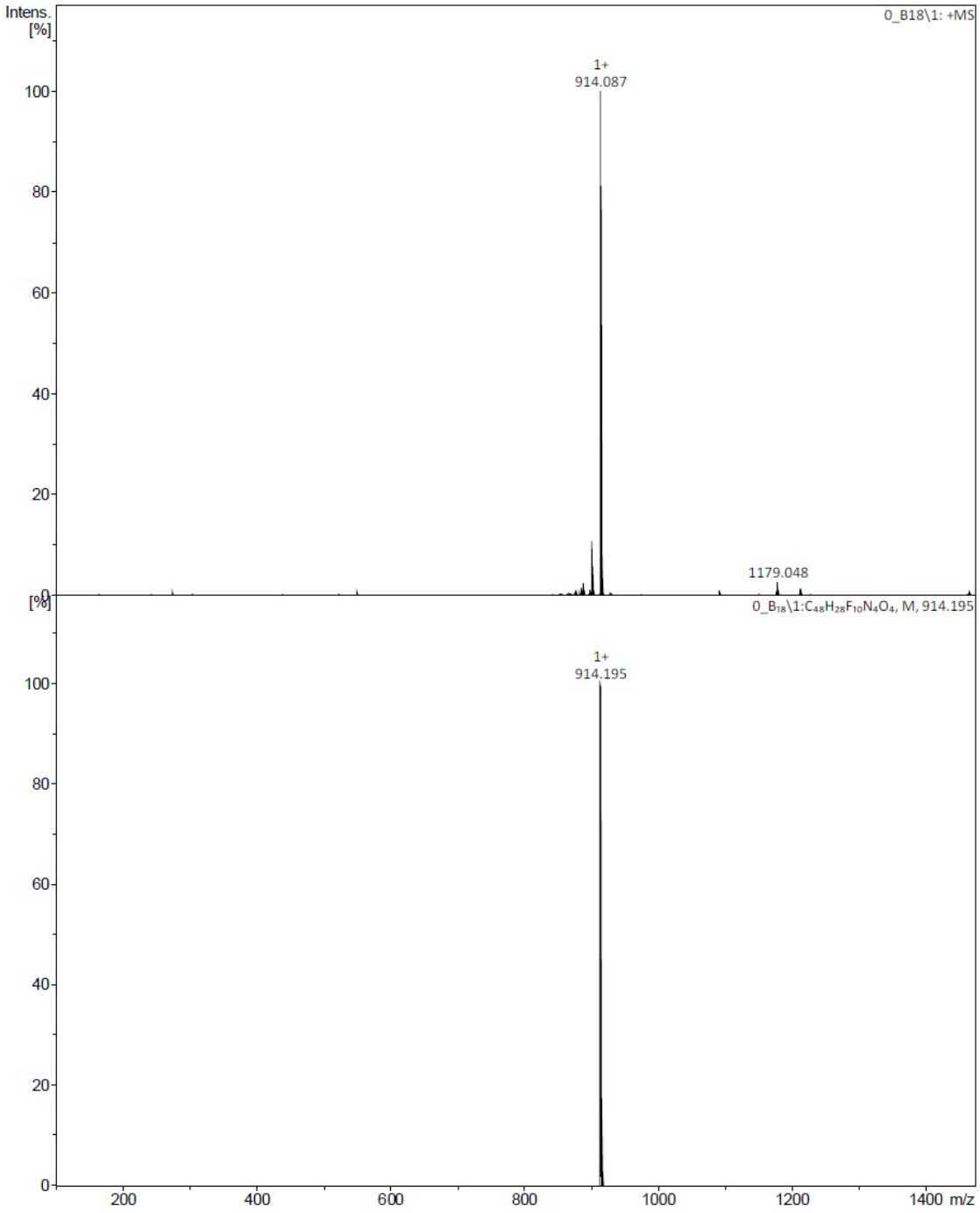



**Figure S10.** MALDI of *cis*-5,15-bis-(pentafluorophenyl)-10,20-bis-(3,4-dimethoxyphenyl)porphyrin (P**2**).

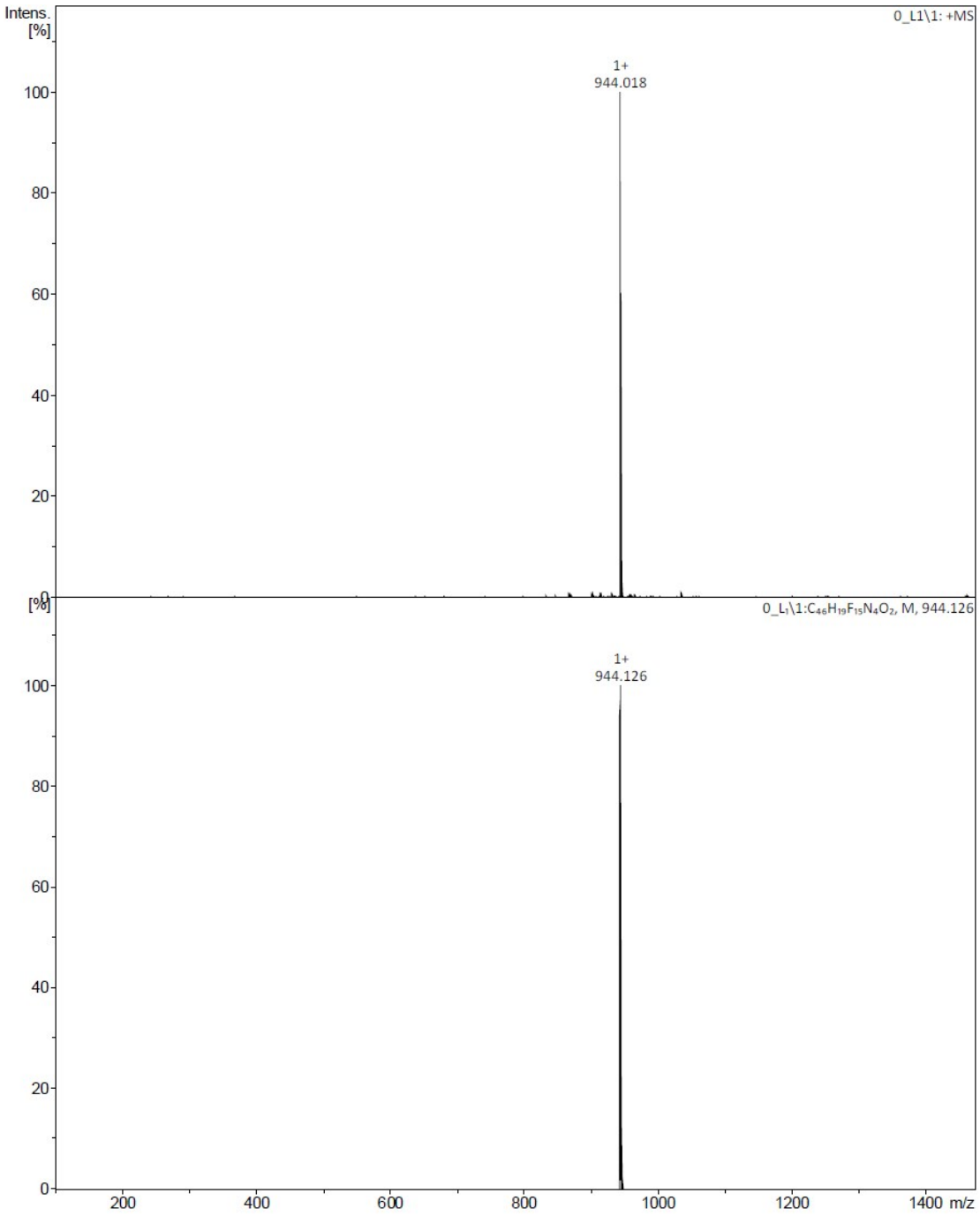



**Figure S11.** MALDI of 5,10,15-tris-(pentafluorophenyl)-20-(3,4-dimethoxyphenyl)porphyrin (P**3**).

## 5. Single-crystal X-ray data

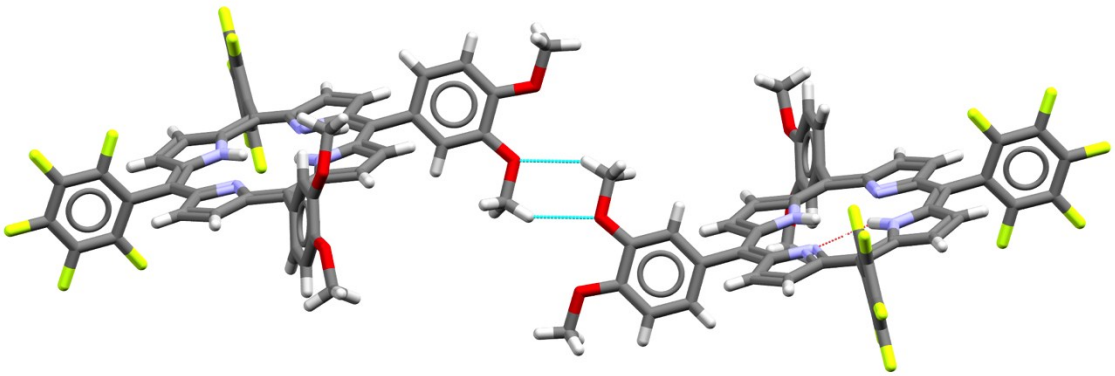
### *trans*-5,15-bis-(pentafluorophenyl)-10,20-bis-(3,4-dimethoxyphenyl)porphyrin (P1).

**Experimental.** Red plate shaped single crystals of P**1** were crystallized from a mixture of chloroform and methanol by slow vapour diffusion. A suitable crystal was selected and mounted on a MITIGEN holder in paratone oil on i19-FFD-air (fixed Chi) Pilatus M2 diffractometer using synchrotron radiation (λ = 0.6889Å) in i19-1 at the diamond light source facility equipped with a Dectris Pilatus M2 hybrid pixel detector. The crystal was kept at 100 K during the collection. A multiscan absorption correction was applied (the minimum and maximum apparent transmissions are 0.471 and 1.000). Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Direct Methods and refined with the ShelXL[3] refinement package using Least Squares minimisation. All hydrogens atoms were refined as riding with appropriate geometric restraints and constraints. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre. Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 1483009. **Crystal Data.** $C_{50}H_{30}Cl_6F_{10}N_4O_4$ ($M$ =1153.48 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 13.948(3) Å, $b$ = 15.6771(17) Å, $c$ = 11.2006(16) Å, $\beta$ = 109.177(18)°, $V$ = 2313.2(7) Å$^3$, $Z$ = 2, $T$ = 100 K, μ(Zr$K_\alpha$) = 0.430 mm$^{-1}$, $D_{calc}$ = 1.656 g/cm$^3$, 8341 reflections measured (2.996° ≤ 2Θ ≤ 40.268°), 2340 unique ($R_{int}$ = 0.0857, $R_{sigma}$ = 0.0726) which were used in all calculations. The final $R_1$ was 0.0725 (I > 2σ(I)), $wR_2$ was 0.2565 (all data) and GooF = 1.039.

### *cis*-5,10-bis-(pentafluorophenyl)-15,20-bis-(3,4-dimethoxyphenyl)porphyrin (P2).

**Experimental:** Single crystals of P**2** were recrystallized from a mixture of chloroform and methanol by vapour diffusion. A suitable crystal was selected and mounted on a MITIGEN holder with paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer using Cu-$K_\alpha$ radiation (λ = 1.5418Å) equipped with an Atlas CCD detector. The crystal was kept at 200 K during data collection due to sample instability at lower temperatures. A Gaussian absorption correction was applied (the minimum and maximum apparent transmissions are 0.874 and 1.000). Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation. Hydrogens atoms were refined as riding with appropriate geometric restraints and constraints. Hydrogens were placed on the pyrrolic nitrogens from a Fourier difference map and the nitrogen hydrogen distance constrained to 0.88 Å. Full

crystallographic details have been deposited at the Cambridge Crystallographic Data Centre. Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 1536642. **Crystal Data.** $C_{50}H_{30}Cl_6F_{10}N_4O_4$ (*M* =1153.48 g/mol): monoclinic, space group I2/a (no. 15), *a* = 12.0821(2) Å, *b* = 17.9808(2) Å, *c* = 22.7546(3) Å, *β* = 96.0320(10)°, *V* = 4915.97(12) Å$^3$, *Z* = 4, *T* = 199.97(14) K, μ(CuKα) = 3.974 mm$^{-1}$, $D_{calc}$ = 1.559 g/cm$^3$, 39378 reflections measured (6.278° ≤ 2Θ ≤ 152.246°), 5127 unique ($R_{int}$ = 0.0661, $R_{sigma}$ = 0.0289) which were used in all calculations. The final $R_1$ was 0.0659 (I > 2σ(I)), $wR_2$ was 0.1943 (all data) and GooF = 1.034.



**S12.** Demonstration of the hydrogen bonding interactions between two molecules of P**2**.

**5,10,15-tris-(pentafluorophenyl)-20-(3,4-dimethoxyphenyl)porphyrin (P3).** **Experimental**: Single crystals of P**3** were recrystallized by slow vapour diffusion of methanol into a solution of chloroform. A suitable crystal was selected and mounted on a MITIGEN holder paratone on a Rigaku Oxford Diffraction SuperNova diffractometer using Cu-$K_\alpha$ radiation (λ = 1.5418 Å) equipped with an Atlas CCD detector. The crystal was kept at 120 K during data collection. A Gaussian absorption correction was applied (the minimum and maximum apparent transmissions are 0.626 and 1.000). Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation. Hydrogens atoms were refined as riding with appropriate geometric restraints and constraints. Hydrogens were placed on the pyrrolic nitrogens from a Fourier difference map and the nitrogen hydrogen distance constrained to 0.84 Å. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre. Any request to the CCDC for these materials should quote the full

literature citation and reference number CCDC 1536643. **Crystal Data.** $C_{47}H_{22}F_{15}N_4O_3$ (M =975.68 g/mol): monoclinic, space group Cc (no. 9), a = 11.5360(2) Å, b = 26.8989(6) Å, c = 15.0809(3) Å, β = 109.961(2)°, V = 4398.56(16) $Å^3$, Z = 4, T = 120.01(10) K, μ(CuKα) = 1.211 $mm^{-1}$, $D_{calc}$ = 1.473 $g/cm^3$, 35344 reflections measured (8.792° ≤ 2Θ ≤ 152.168°), 7617 unique ($R_{int}$ = 0.0660, $R_{sigma}$ = 0.0402) which were used in all calculations. The final $R_1$ was 0.1043 (I > 2σ(I)), $wR_2$ was 0.3001 (all data) and GooF = 1.497.

**Table S1.** Selected crystal data, data collection and structure refinement parameters for the data of P**1**, P**2** and P**3**.

| | **P1** | **P2** | **P3** |
|---|---|---|---|
| Crystal data | | | |
| Sum formula | $C_{50}H_{30}Cl_6F_{10}N_4O_4$ | $C_{50}H_{30}Cl_6F_{10}N_4O_4$ | $C_{47}H_{22}F_{15}N_4O_3$ |
| Formula weight | 1153.48 | 1153.48 | 975.68 |
| Temperature/K | 100 | 200 | 120 |
| Crystal system | monoclinic | monoclinic | Monoclinic |
| Space group` | $P2_1/c$ | $I2/a$ | $Cc$ |
| a/Å | 13.948(3) | 12.0821(2) | 11.5360(2) |
| b/Å | 15.6771(17) | 17.9808(2) | 26.8989(6) |
| c/Å | 11.2006(16) | 22.7546(3) | 15.0809(3) |
| β/° | 109.177(18) | 96.0320(10) | 109.961(2) |
| Volume/Å$^3$ | 2313.2(7) | 4915.97(12) | 4398.56(16) |
| Z | 2 | 4 | 4 |
| Radiation | Zr- Kα (λ = 0.6889) | CuKα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| $\rho_{calc}$g/cm$^3$ | 1.656 | 1.559 | 1.473 |
| μ/mm$^{-1}$ | 0.43 | 3.974 | 1.211 |
| Crystal size/mm$^3$ | 0.1 × 0.01 × 0.01 | 0.188 × 0.091 × 0.085 | 0.514 × 0.224 × 0.055 |
| Data collection | | | |
| Tmin, Tmax | 0.471, 1.000 | 0.874, 1.000 | 0.626, 1.000 |
| 2Θ range for data collection/° | 2.996 to 40.268 | 6.278 to 152.246 | 6.240 to 152.168 |
| Reflections collected | 8341 | 39378 | 35755 |
| Independent reflections | 2340 [$R_{int}$ = 0.0857, $R_{sigma}$ = 0.0726] | 5127 [$R_{int}$ = 0.0661, $R_{sigma}$ = 0.0289] | 7617 [$R_{int}$ = 0.0660, $R_{sigma}$ = 0.0400] |
| Rint | 0.086 | 0.066 | 0.066 |
| Refinement | | | |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0725, $wR_2$ = 0.1897 | $R_1$ = 0.0659, $wR_2$ = 0.1874 | $R_1$ = 0.1043, $wR_2$ = 0.2897 |
| Final R indexes [all data] | $R_1$ = 0.1160, $wR_2$ = 0.2565 | $R_1$ = 0.0708, $wR_2$ = 0.1943 | $R_1$ = 0.1079, $wR_2$ = 0.3001 |
| Goodness-of-fit on F$^2$ | 1.040 | 1.034 | 1.392 |
| Data/restraints/parameters | 2340/84/336 | 5127/38/378 | 7617/397/767 |
| H-atom treatment | H-atom parameters constrained | H-atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.85/-0.82 | 0.47/-0.52 | 0.73/-0.51 |
| CCDC depostion number | 1483009 | 1536642 | 1536643 |

## 6. REFERENCES

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339-341.

[2] G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **A71**, 3-8.

[3] G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **A71(Pt1)**, 3-8.