Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 4373–4377

TETRAHEDRON LETTERS

Nucleophilic substitution of hydrogen in *meso*-nitroaryl-substituted porphyrins—unprotected at the NH-centers in the core ring

Stanisław Ostrowski,[a,b,*] Natalia Urbańska[a] and Agnieszka Mikus[a]

[a]*Institute of Chemistry, University of Podlasie, ul. 3 Maja 54, 08-110 Siedlce, Poland*
[b]*Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warszawa, Poland*

Received 28 February 2003; revised 1 April 2003; accepted 10 April 2003

Abstract—Unprotected 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin and 5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrin react in the presence of a base at low temperature with carbanions (which bear a leaving group X at the carbanionic center) affording vicarious nucleophilic substitution of hydrogen (VNS) products in good yields (50–89%). The reactivity is explained in terms of the predominance of the porphyrin *N*-anion resonance forms at this temperature.

Many porphyrin derivatives are widely used as photosensitizers in photodynamic theraphy (PDT).[1] Recent clinical trials involving this simple technique have yielded promising results,[2] and the mode of action of photosensitizers was found to be dependent upon their chemical structure. Therefore, new methods for the synthesis of hydrophilic, lipophilic and amphiphilic porphyrins (especially unsymmetrical ones) are being sought.

Previously, we have presented a method for the selective functionalization of nitro-*meso*-tetraphenylporphyrin derivatives[3] using the vicarious nucleophilic substitution of hydrogen (VNS).[4] In this reaction, free NH-acidic groups in the core ring of the above electrophilic porphyrins were 'blocked', and we found that very labile protection of NH functions can be achieved by simple complexation with copper and zinc cations.[3] This reaction proceeded smoothly and with high yields. Conversely, multiple attempts of the VNS reaction utilizing unprotected 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin with carbanions of chloro- and bromomethyl *para*-tolyl sulphones (the standard nucleophiles for this reaction) were unsuccessful.

The vicarious nucleophilic substitution of hydrogen (VNS)[4] involves the addition of a carbanion, which bears a leaving group **X** (**X** = Cl, Br, OPh, SPh, etc.) at the carbanionic center, to a nitroarene (or other electrophilic aromatic or heteroaromatic compound; see Scheme 1), followed by base induced β-elimination of HX, and protonation as the final step. This leads to the substitution of hydrogen.

Porphyrins behave as very weak acids, with two NH groups capable of losing protons. Alkali metal alkoxides allow spectroscopic observation even of the di-*N*-anion in these systems. Both pK_a values for these compounds have been estimated to be ca. 16.[5] Hence, under the strongly basic conditions of the VNS reaction (*t*-BuOK/DMSO, rt[3]), the porphyrin macrocycle should exist in the *N*-anionic form (see Fig. 1). On the

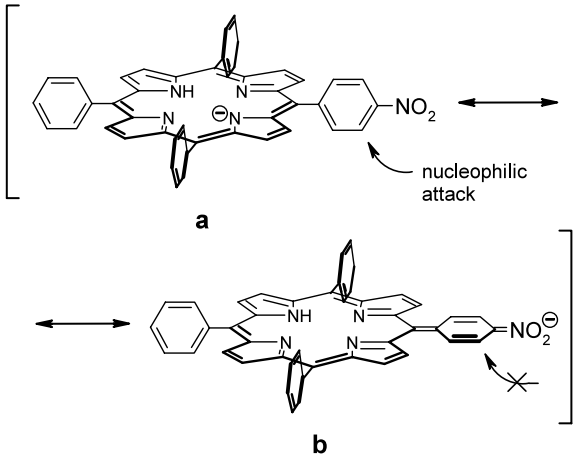


Figure 1. Resonance structures of the 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin anion.

* Corresponding author. Tel.: (+48)-25-643-1113, fax: (+48)-25-644-2045; e-mail: stan@ap.siedlce.pl

0040-4039/03/$ - see front matter
doi:10.1016/S0040-4039(03)00933-X

other hand, it is well-known that the VNS substitution takes place in the electron-impoverished *ortho*- or *para*-position to an NO_2 group in the nitroaryl moiety. However, in the discussed 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin anion (**a**), the electronic nature of the nitrophenyl ring can be greatly affected by conjugation with a neighboring negatively charged porphyrin core ring.

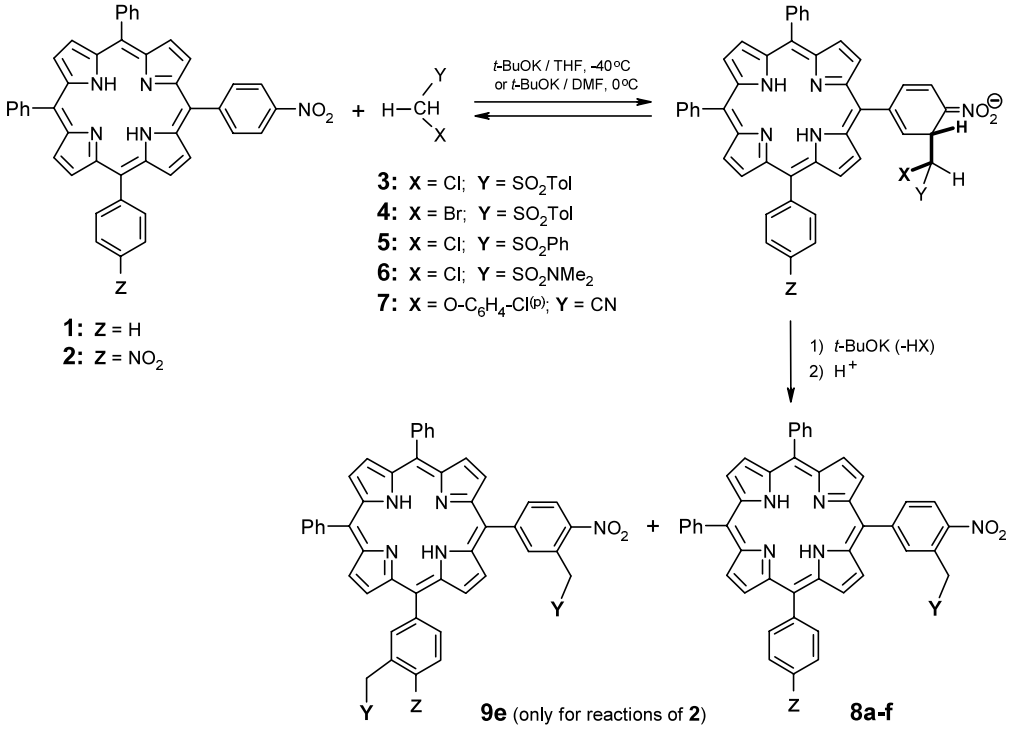
Usually, the [18π]-electron aromatic porphyrin system and *meso*-substituted aryl rings remain in mutually orthogonal planes, thus impeding conjugation. Nevertheless, the lack of success when attempting the VNS reaction in unprotected 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**1**) might be explained simply by the possibility of conjugation due to the free-rotation around the *meso*- C–C bond. This should result in coplanarity of these rings. Consequently, the negative charge could be delocalized onto the six-membered ring, as well as the NO_2 group (resonance structure **b**), thus increasing the electron density therein and deactivating the ring toward carbanion addition.

At low temperatures, this free rotation should be suppressed, and all four *meso*-aryl rings should still remain in vertical planes to the central core ring, thus limiting the conjugation. This gives an opportunity for the VNS reaction, as the negative charge is localized mainly in the porphyrin core ring. The resonance structure **a** may predominate; hence, the nitroaryl moiety can be regarded as an isolated system, so allowing the nucleophilic addition in the position *ortho*- to the NO_2 group.

This could indeed be the case, as, in *t*-BuOK/THF at −30°C to −40°C or *t*-BuOK/DMF at 0°C, the unprotected nitroporphyrins[6] **1** and **2** react according to the VNS scheme to give the desired products in good yield (50–89%). This was achieved by reactions with carbanions of α-halomethyl aryl sulphones (**3**–**5**),[7,8] α-chloromethyl *N*,*N*-dialkyl sulphonamide (**6**),[9] and *para*-chlorophenoxyacetonitrile (**7**).[10] By this route, the introduction of arylsulphonylmethyl, *N*,*N*-dimethyl sulphonamidomethyl and cyanomethyl substituents was realized (Scheme 1, Table 1). The products obtained allow opportunities for further transformations, and might be easily converted into other porphyrin derivatives. For applications involving total porphyrin system synthesis, this procedure conveniently avoids both complexation and decomplexation steps.

Table 1. Products and the yields (see Scheme 1 and experimental details[12])

Substituents Z	Y	Porphyrin	Carbanion precursor and procedure		Products and yields	
H	SO_2Tol	**1**	**3**,	A	**8a**,	83%
H	SO_2Tol	**1**	**4**,	A	**8a**,	74%
H	SO_2Ph	**1**	**5**,	A	**8b**,	88%
H	SO_2NMe_2	**1**	**6**,	A	**8c**,	89%
H	CN	**1**	**7**,	B	**8d**,	51%
NO_2	SO_2Tol	**2**	**3**,	C	**8e**,	15%
					9e,	42%
NO_2	CN	**2**	**7**,	D	**8f**,	30%
					10,	~20%



Scheme 1. Reactions of *meso*-nitroaryl-substituted porphyrins with carbanions bearing a leaving group at the carbanionic center.

The reaction yields with α-halomethyl aryl sulphones and α-chloromethyl *N*,*N*-dialkyl sulphonamide (in THF at −40°C) were high (74–89%; in DMF at this temperature the yields were lower due to problems with the homogenity of the reaction mixture). The reaction with the *para*-chlorophenoxyacetonitrile anion at −20°C to −40°C in THF and in DMF gave no desired product, probably due to difficulties in the elimination step at this temperature (OAr is a rather poor leaving group[11]). The intended reaction was finally achieved at 0°C in DMF. However, at this higher temperature, the conjugation effect may partially operate; hence the yield is relatively lower (51%).

In the reactions of 5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrin (**2**, $Z=NO_2$), the substitution takes place in one or two of the *meso*-nitrophenyl rings to give a mixture of products with reasonable yields (**8e**/**9e** or **8f**/**10**), ca. 50–57%. In the case of *para*-chlorophenoxyacetonitrile (**7**), the reaction proceeded according to the VNS mechanism in one nitrophenyl ring, whereas in the other one, it stopped at the addition stage of the carbanion to the electrophilic ring. Thus, the product of the oxidative substitution **10** was formed (Fig. 2). Prolonging the reaction time, as well as the use of a larger excess of the base, failed to induce the elimination; it also led to the partial degradation of the products, decreasing the overall yield. Product **10**, despite several attempts, could not be separated from the contaminants via chromatography. For one of the additional products found in this mixture, on the basis of MS spectra, structure **11** was assigned. This compound was possibly formed via the substitution of hydrogen in one aryl ring and S_NAr replacement of an NO_2 group in a different aryl ring by a carbanion moiety.

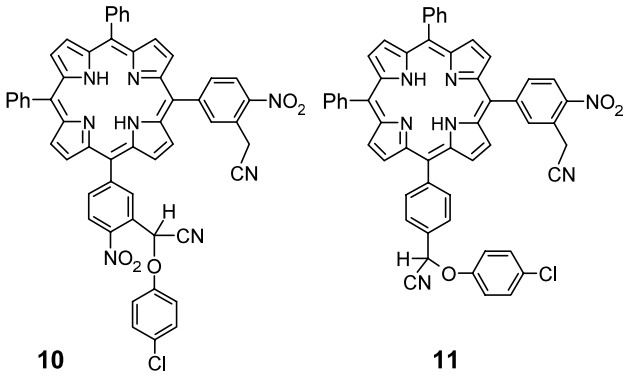


Figure 2. Products of the reaction of **2** with **7**.

We present herein a method for the selective nucleophilic derivatization of *meso*-tetraarylporphyrins, nitro-substituted in an aryl ring or in multiple rings. These nitroporphyrins react at low temperatures with carbanions which bear a leaving group **X** at the carbanionic center, according to the VNS mechanism to give the desired products in good yield (50–89%). Some of the products obtained give opportunities for further transformations and might be easily converted into other porphyrin derivatives.

The reaction conditions found for VNS in 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (without protection of the acidic NH centers in the core ring) allow in this type of nucleophilic reaction the avoidance of two synthetic steps (complexation/decomplexation). The control of this process by the reaction conditions is probably general in nature, and can be applied for other similar nucleophilic reactions in porphyrin systems. These observations (regarding the influence of the predominant participation of the mesomeric forms in porphyrin anions on their reactions with nucleophiles) may well receive future attention in the area of nucleophilic porphyrin skeleton modifications.

References

1. (a) Sternberg, E. D.; Dolphin, D.; Brückner, Ch. *Tetrahedron* **1998**, *54*, 4151; (b) Hsi, R. A.; Rosenthal, D. I.; Glatstein, E. *Drugs* **1999**, *57*, 725.
2. (a) Dougherty, T. J.; Kaufman, J. E.; Goldfarb, A. *Cancer Res*. **1985**, *38*, 2628; (b) Delaney, T. F.; Glatstein, E. *Compr. Ther*. **1988**, *14*, 43; (c) Schweitzer, V. G. *Otolaryngol. Head Neck Surg*. **1990**, *102*, 225.
3. (a) Ostrowski, S.; Shim, Y. K. *Bull. Korean Chem. Soc*. **2001**, *22*, 9; (b) Ostrowski, S.; Mikus, A.; Shim, Y. K.; Lee, J.-Ch.; Seo, E.-Y.; Lee, K.-I.; Olejnik, M. *Heterocycles* **2002**, *49*, 1615.
4. Mąkosza, M.; Wojciechowski, K. *Liebigs Ann./Recueil* **1997**, 1805.
5. Phillips, J. N. *Rev. Pure Appl. Chem*. **1960**, *10*, 35.
6. (a) Kruper, W. J., Jr.; Chamberlin, T. A.; Kochanny, M. *J. Org. Chem*. **1989**, *54*, 2753; (b) Ostrowski, S.; Łopuszyńska, B. *Synth. Commun*., submitted.
7. Mąkosza, M.; Danikiewicz, W.; Wojciechowski, K. *Liebigs Ann. Chem*. **1987**, 711.
8. Mąkosza, M.; Goliński, J.; Baran, J. *J. Org. Chem*. **1984**, *49*, 1488.
9. Jacobsen, H. J.; Senning, A.; Kaae, S. *Acta Chem. Scand*. **1971**, *25*, 3031.
10. Grochowski, E.; Eckstein, Z. *Bull. Acad. Pol. Sci., Ser. Sci. Chim*. **1963**, *11*, 443.
11. Stirling, Ch. J. M. *Acc. Chem. Res*. **1979**, *12*, 198.
12. The porphyrins used, and the starting carbanion precursors, were obtained according to methods described in earlier literature: 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**1**)[6a] (with 66% yield), 5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrin (**2**)[6] (with 42% yield), α-chloromethyl *para*-tolyl sulphone (**3**),[7] α-bromomethyl *para*-tolyl sulphone (**4**),[8] α-chloromethyl phenyl sulphone (**5**),[8] *N*,*N*-dimethyl-(chloromethane)sulphonamide (**6**),[9] *para*-chlorophenoxyacetonitrile (**7**).[10]

    Procedure A. To a stirred solution of *t*-BuOK (112 mg, 1.0 mmol) in anhydrous THF (3.5 mL, under argon) a solution of 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**1**; 132 mg, 0.20 mmol) and a carbanion precursor (**3**–**6**; 0.30 mmol) in THF (1.5 mL) was added dropwise via syringe at −30°C to −40°C during ca. 5 min. After an additional 30–40 min of stirring at this temperature the mixture was poured into a 3% aqueous solution of NH_4Cl (50 mL), and the products were extracted with $CHCl_3$ (3×10 mL). After drying with anhydrous Na_2SO_4 and evaporation of the solvent, the residue was chro-

matographed (silica gel, 230–400 mesh, Merck AG; eluent: $CHCl_3$/*n*-hexane, 2:1 or $CHCl_3$), to give respectively: **8a**—137 mg, 83% (from **3**) or 123 mg, 74% (from **4**); **8b**—143 mg, 88%; **8c**—139 mg, 89%.

Procedure B. To a stirred solution of *t*-BuOK (151 mg, 1.35 mmol) in anhydrous DMF (1.5 mL, under argon), a solution of 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**1**; 30 mg, 0.046 mmol) and *para*-chlorophenoxyacetonitrile (30 mg, 0.18 mmol) in DMF (1 mL) was added dropwise via syringe at 0°C during ca. 10 min. After an additional 5.5 h of stirring at this temperature the mixture was poured into 3% HCl containing ice (30 mL). The precipitate was filtered, washed with water, and then dissolved in $CHCl_3$ (40 mL). After drying with anhydrous Na_2SO_4 and evaporation of the solvent, the product **8d** was isolated by column chromatography (eluent: $CHCl_3$/*n*-hexane, 3:1), yield: 16 mg (51%).

Procedure C. *t*-BuOK (13 mg, 0.12 mmol) was dissolved in anhydrous THF (1 mL). The solution was stirred under argon and cooled to −30°C. To this mixture, a solution of 5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrin (**2**; 16 mg, 0.023 mmol) and chloromethyl *para*-tolyl sulphone (15 mg, 0.073 mmol) in THF (0.5 mL) was added via syringe (ca. 5 min). The reaction was continued at this temperatue until completion (ca. 25 min; TLC monitoring in $CHCl_3$). It was then poured into a 3% aqueous solution of NH_4Cl (20 mL). The product was extracted with $CHCl_3$ (2×10 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography using $CHCl_3$ as the eluent. The yield of the pure product **8e** was 3 mg (15%); of product **9e**—10 mg (42%).

Procedure D. To a stirred solution of *t*-BuOK (376 mg, 3.36 mmol) in anhydrous DMF (4 mL), a solution of 5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrin (**2**; 40 mg, 0.057 mmol) and *para*-chlorophenoxyacetonitrile (94 mg, 0.56 mmol) in DMF (3 mL) was added dropwise via syringe at 0°C during ca. 10 min. After an additional 4.5 h of stirring at this temperature, the mixture was poured into 3% HCl containing ice (70 mL). The products were extracted with $CHCl_3$ (3×10 mL), and the combined organic layers were washed with water (3×20 mL). After drying over $MgSO_4$ and evaporation of the solvent, the residue was chromatographed ($CHCl_3$/*n*-hexane, 2:1) to give: **8f**—13 mg (30%) and **10**—10.5 mg (20%).

Data for the products:

5-[4-Nitro-3-(toluene-4-sulphonylmethyl)-phenyl]-10,15,20-triphenylporphyrin (8a). Data: see Ref. 3b.

5-[4-Nitro-3-(phenylsulphonylmethyl)-phenyl]-10,15,20-triphenylporphyrin (8b). Mp >300°C; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 8.93 (2 H, d, J=4.8, H$^\beta$-pyrrole), 8.87 (4 H, s, H$^\beta$-pyrrole), 8.79 (2 H, d, J=4.8, H$^\beta$-pyrrole), 8.41 (1 H, part of AB, J=8.8, H-Ar(NO_2)), 8.37 (1 H, part of AB coupled with another proton, J=8.8 and 1.6, H-Ar(NO_2)), 8.35 (1 H, d, J=1.6, H-Ar(NO_2)), 8.26–8.17 (6 H, m, H-Ph), 7.95–7.88 (2 H, m, H-SO_2Ph), 7.83–7.70 (9 H, m, H-Ph), 7.61–7.47 (3 H, m, H-SO_2Ph), 5.25 (2 H, s, CH_2), −2.80 (2 H, s, 2×NH); UV–vis λ_{max} ($CHCl_3$)/nm 645 (log ε 3.75) 591 (3.91), 553 (4.10), 516.5 (4.40), 414 (5.42, Soret), 327 (4.25); MS (EI) m/z 816 (1%), 815 (4), 814 (9) and 813 (14) [isotopic M$^+$], 675 (3), 673 (6), 629 (3), 628 (4), 627 (2), 616 (7), 615 (14), 614 (3), 551 (3), 539 (1), 538 (2), 537 (2), 536 (3), 307 (3), 306 (2), 208 (3), 207 (3), 141 (16), 89 (17), 78 (48), 77 (100), 65 (13), 64 (38), 51 (48), 44 (48); HRMS (ESI) m/z 814.2568 (M+H, $C_{51}H_{36}N_5O_4S$ requires 814.2488).

***N,N*-Dimethyl-*C*-[2-nitro-5-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-methanesulphonamide (8c)**. Data: see Ref. 3b

[2-Nitro-5-(10,15,20-triphenylporphyrin-5-yl)-phenyl]-acetonitrile (8d). Mp >300°C; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 8.91 (2 H, d, J=4.8, H$^\beta$-pyrrole), 8.86 (4 H, s, H$^\beta$-pyrrole), 8.71 (2 H, d, J=4.8, H$^\beta$-pyrrole), 8.61 (1 H, part of AB, J=8.3, H-Ar(NO_2)), 8.57 (1 H, br s, H-Ar(NO_2)), 8.43 (1 H, part of AB coupled with another proton, J=8.3 and 1.7, H-Ar(NO_2)), 8.30–8.15 (6 H, m, H-Ph), 7.88–7.69 (9 H, m, H-Ph), 4.51 (2 H, s, CH_2CN), −2.79 (2 H, s, 2×NH); UV–vis λ_{max} ($CHCl_3$)/nm 647 (log ε 3.62), 591 (3.79), 555 (3.96), 516 (4.19), 419 (5.42, Soret); MS (EI) m/z 701 (3%), 700 (13), 699 (53) and 698 (100) [isotopic M$^+$], 682 (9), 681 (14), 669 (4), 668 (8), 659 (9), 658 (18, M–CH_2CN), 614 (5), 575 (5), 574 (5), 536 (2), 349 (6, doubly charged ion M^{2+}), 326 (5), 207 (5), 44 (28); HRMS (ESI) m/z 699.2513 (M+H, $C_{46}H_{31}N_6O_2$ requires 699.2508).

5-(4-Nitrophenyl)-10-[4-nitro-3-(toluene-4-sulphonylmethyl)-phenyl]-15,20-diphenylporphyrin (8e). Mp >300°C; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 8.97–8.70 (8 H, m, H$^\beta$-pyrrole), 8.65 (1 H, part of AB, J=8.5, H-Ar(NO_2)), 8.45–8.31 (6 H, m, H-Ar(NO_2)), 8.26–8.15 (4 H, m, H-Ph), 7.83–7.70 (8 H, m, 6 H of H-Ph and 2 H of H-Tol), 7.33 (2 H, apparent d, J=8.3, H-Tol), 5.22 (2 H, s, CH_2), 2.35 (3 H, s, CH_3), −2.82 (2 H, s, 2×NH); UV–vis λ_{max} ($CHCl_3$)/nm 646 (log ε 3.48), 590.5 (3.63), 555.5 (3.78), 518 (3.99), 420.5 (5.14, Soret); MS (EI) m/z 875 (<1%), 874 (1), 873 (3) and 872 (5) [isotopic M$^+$], 795 (1), 735 (1), 690 (1), 734 (1), 673 (1), 355 (2), 207 (13), 107 (67), 91 (81), 77 (23), 65 (18), 64 (29), 44 (100); HRMS (ESI) m/z 873.2501 (M+H, $C_{52}H_{37}N_6O_6S$ requires 873.2495).

5,10-Bis[4-nitro-3-(toluene-4-sulphonylmethyl)-phenyl]-15,20-diphenylporphyrin (9e). Mp >300°C; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 8.99–8.75 (8 H, m, H$^\beta$-pyrrole), 8.40 (2 H, part of AB coupled with another proton, J=8.6 and 1.7, H-Ar(NO_2)), 8.39–8.28 (4 H, m, H-Ar(NO_2)), 8.27–8.16 (4 H, m, H-Ph), 7.85–7.71 (10 H, m, 6 H of H-Ph and 4 H of H-Tol), 7.34 (4 H, apparent d, J=7.5, H-Tol), 5.22 (4 H, br s, 2×CH_2), 2.34 (6 H, s, 2×CH_3), −2.86 (2 H, s, 2×NH); UV–vis λ_{max} ($CHCl_3$)/nm 646 (log ε 3.68), 591 (3.91), 555.5 (4.10), 518 (4.38), 422 (5.56, Soret); MS (LSIMS) m/z 1064 (2%, M+H+Na), 1042 (3) and 1041 (2) [isotopic M+H], 855 (1), 794 (1), 713 (1), 550 (3), 207 (24), 91 (64); HRMS (ESI) m/z 1041.2708 (M+H, $C_{60}H_{45}N_6O_8S_2$ requires 1041.2740).

{2-Nitro-5-[10-(4-nitrophenyl)-15,20-diphenylporphyrin-5-yl]-phenyl}-acetonitrile (8f). Mp >300°C; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 9.10–8.40 (15 H, m, H$^\beta$-pyrrole and H-Ar(NO_2)), 8.30–8.15 (4 H, m, H-Ph), 7.90–7.70 (6 H, m, H-Ph), 4.54 (2 H, s, CH_2CN), −2.79 (2 H, s, 2×NH); UV–vis λ_{max} ($CHCl_3$)/nm 646.5 (log ε 3.59), 590.5 (3.89), 556 (4.11), 517.5 (4.25), 421 (5.43, Soret); MS (EI) m/z 745 (<1%), 744 (<1) and 743 (1) [isotopic M$^+$], 702 (<1, M–H–CH_2CN), 533 (5), 281 (10), 221 (17), 207 (45), 44 (100), 40 (56); HRMS (ESI) m/z 744.2447 (M+H, $C_{46}H_{30}N_7O_4$ requires 744.2359).

(4-Chlorophenoxy)-{5-[10-(3-cyanomethyl-4-nitrophenyl)-15,20-diphenylporphyrin-5-yl]-2-nitrophenyl}-acetonitrile (10). Main product in the mixture (>95% purity); for contaminated product ^{1}H NMR, UV–vis and MS spectra were recorded; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 9.08–8.38 (14 H, m, H^{β}-pyrrole and H-Ar(NO_2)), 8.27–8.16 (4 H, m, H-Ph), 7.84–7.72 (6 H, m, H-Ph), 7.33 (2 H, apparent d, $J=8.7$, H-Ar(Cl)), 7.07 (2 H, apparent d, $J=8.7$, H-Ar(Cl)), 6.98 (1 H, s, CH), 4.54 (2 H, s, CH_2CN), −2.79 (2 H, s, 2×NH); UV–vis λ_{max} ($CHCl_3$)/nm 646, 592, 553.5, 518, 421.5 (Soret)—as the product was not pure the log ε values are not given herein; HRMS (LSIMS) m/z 909.2501 (M+H, $C_{54}H_{34}N_8O_5{}^{35}Cl$ requires 909.2341), 908 (M^+).

(4-Chlorophenoxy)-{4-[10-(3-cyanomethyl-4-nitrophenyl)-15,20-diphenylporphyrin-5-yl]-phenyl}-acetonitrile (11). This was not isolated; the structure was proposed on the basis of MS (the molecular ion and two characteristic fragmentation ions were detected in the mixture, in which compound **10** was the main product); $m/z=863$ (M^+), 754 (M–C_6H_4-Cl), 738 (M–O-C_6H_4-$Cl^{(p)}$).