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SYNTHESIS OF (ALKYNYL)PHENYL PORPHYRINS BY PALLADIUM CATALYSED CROSS COUPLING REACTIONS

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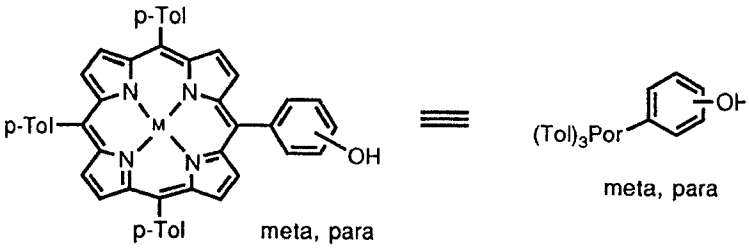
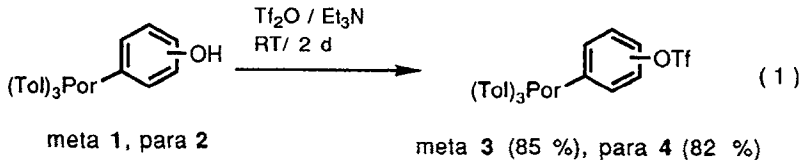
Abstract: meso-para and meso-meta-(phenyltriflate)tritolyl porphyrins and the zinc complexes are coupled with alkynyl stannanes or terminal alkynes with palladium catalyst to give the meso-para and meta(m-alkynylphenyl)tritolylylkphenyl porphyrins as well as the zinc complex in good yields.

Porphyrins have been used as biomimetic model for the cytochrome P_{450} oxidation of hydrocarbons. Alkynyl porphyrins have been used as the intermediates for the construction of trimeric porphyrins[1] as well as building blocks for porphyrin-based advanced materials.[2] The syntheses depend on the use of alkynyl aldehydes or equivalents through the acid-catalysed condensation with pyrrole.[3] Our apporach to the synthesis of unsymmetrical alkynyl(phenyl) porphyrins takes advantage of the mildness and neutral conditions of the palladium-catalysed cross-coupling reactions of aryl triflates with organostannes developed by Stille.[4] In this paper, we report our success on the cross-coupling reactions of meso-para and meta-(phenyltriflato)tritolyl porphyrin, **5a**, **6a** and the zinc complexes **7a** with alkynyl stannanes or terminal alkynes with palladium

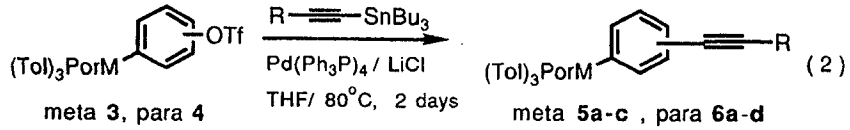
Table 1 Cross coupling reaction of porphyrin triflate with alkynyl stannanes

Entry	Substituent	M	R	Yield	Compound
1	meta	H_2	TMS	74 %	**5b**
2	meta	H_2	Ph	72 %	**5c**
3	meta	H_2	n-Bu	76 %	**5d**
4	meta	H_2	TMS	76%	**6b**
5	para	H_2	Ph	73 %	**6c**
6	para	H_2	n-Bu	76 %	**6d**
7	para	Zn	TMS	75 %	**7b**





(1)

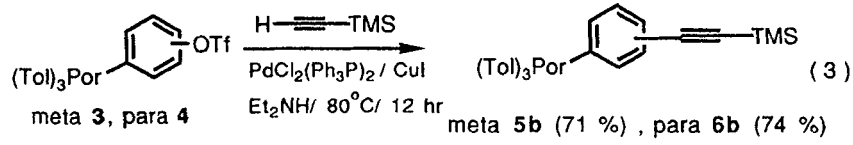


(2)

catalysts to give the meso-para and meso(p-alkynyl-phenyl)tritolyl porphyrins as well as the zinc complex in good yields.

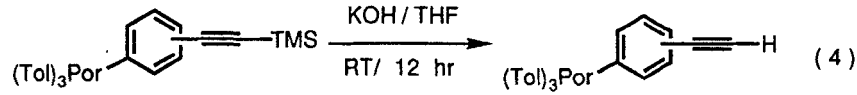
The easily accessible p and m -(hydroxylphenyl)tritolyl-porphyrins **1**, **2** [5] were firstly converted to the triflates **3** (85 %) and **4** (82 %) by treatment with Tf_2O/ Et_3N [7] [Eqn 1]. Subsequent Stille's coupling with the alkynyl stannanes produced the unsymmetrical porphyrins in excellent yields [Eqn. 2, Table 1]. The three alkynyl stannanes used all gave high yields of the alkynyl(phenyl) porpyrins. Using the $Pd(Ph_3P)_2Cl$ catalyst in Et_2NH with (trimethylsilyl)acetylene, the porphyrin **5b**, **6b** could be effectively obtained in high yield [Eqn 3]. The (trimethylsilyl)ethynyl porphyrins **5b**, **6b** were easily desilylated by treatment of KOH in THF/H_2O to form the porphyrins **8** and **9** [Eqn 4].

In summary , we have found a mild method for the preparation of (alkynyl)phenyl porphyrins from the porphyrin aryl triflates in good yields. Work is continuing on the palladium-catalysed cross coupling reactions of porphyrin triflates.



meta **3**, para **4**

meta **5b** (71 %) , para **6b** (74 %) (3)



meta **5b**, para **6b**

meta **8** (85 %) , para **9** (86 %) (4)

Experimental

^{1}HNMR spectra were recorded with a Bruker WM 250MHz NMR spectrometer in $CDCl_3$ using TMS as internal standard. UV spectra were recorded with a Hitachi U-2000 Spectrophotometer in CH_2Cl_2. FAB Mass spectra were recorded with a J EOL J MS-HX 110 Mass Spectrometer using m-nitrobenzyl alcohol (NBA) as matrix in National Tsing

Hua University in Taiwan. THF was freshly distilled from sodium benzophenone ketyl before use. Hexane was distilled over $CaCl_2$. Et_2NH and pyridine were distilled from KOH. Other reagents were used as supplied.

General procedure for the preparation of porphyrin triflates 3 and 4

Monohydroxyphenyl tritolylporphyrin **1** or **2**[5] (0.269 g, 0.4 mmol) in dry pyridine (15 ml) was cooled down to 0 °C, triflic anhydride (0.34 ml, 2 mmol) was thus added via the syringe.[6] The resulting mixture was stirred at 0 °C for 5 min. and then allowed to warm up to room temperature and stirred continuously for 1-2 days until all starting porphyrins were reacted completely. The mixture was worked up by adding cooled water (80 ml), the purple solid formed was filtered, washed with cooled water (30 ml) and collected. The collected porphyrin triflates were redissolved in minimum amount of methylene chloride, and purified by column chromatography using methylene chloride as an eluent.

Porphyrin 3 (82%) : ^{1}HNMR ∂ 8.86 (m, 8H), 8.24 (d, J = 7.5 Hz, 1 H), 8.16 (d, J =2.0 Hz, 1 H), 8.08 (d, J = 7.8 Hz, 6 H), 7.82 (t, J = 7.9 Hz, 1H), 7.71 (d, J = 6.4 Hz, 1 H), 7.54 (d, J = 7.8 Hz, 6 H), 2.69 (s, 9 H), -2.81 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 416.5 (29.41), 514.5 (3.21), 550.0 (1.48), 589.5 (0.94), 645.5 (0.74) ; R_f = 0.68 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 805 $(M+1)^+$, 804 $(M)^+$. Anal. Calcd for $C_{48}H_{35}F_3N_4O_3S$: C, 71.59; H, 4.35; N, 6.97. Found : C, 71.19; H, 4.46; N, 6.79.

Porphyrin 4 (85%) : ^{1}HNMR ∂ 8.85 (m, 8 H), 8.28 (d, J = 8.5 Hz, 2 H), 8.07 (d, J = 7.8 Hz, 6 H), 7.66 (d, J = 8.5 Hz, 2 H), 7.54 (d, J = 7.8 Hz, 6 H), 2.69 (s, 9 H), -2.81 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 418.0 (27.41), 514.5 (1.29), 550.0 (0.63), 589.5 (0.39) ; R_f = 0.67 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 805 $(M+1)^+$, 804 $(M)^+$. Anal. Calcd for $C_{48}H_{35}F_3N_4O_3S$: C, 71.59; H, 4.35; N, 6.97. Found : C, 71.55; H, 4.45; N, 6.92.

Zinc porphyrin 7a[6] (79%) : ^{1}HNMR ∂ 8.92 (m, 8H), 8.29 (d, J = 8.5 Hz, 2 H), 8.10 (d, J = 7.8 Hz, 6 H), 7.68 (d, J = 8.5 Hz, 2 H), 7.57 (d, J = 7.8 Hz, 6 H), 2.71 (s, 9 H). UV/vis

(wave-length max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 420.0 (27.41), 475.0 (0.55), 512.5 (0.65), 548.0 (3.54), 589.5 (0.96) ; R_f = 0.61 (CH_2Cl_2 : hexane= 1:1).

General procedure for the palladium-catalysed cross-coupling of porphyrin aryl triflates 3 and 4 with alkynyl stannanes.[7]

Unsymmetrical porphyrin aryl triflate (0.065 mmol), alkynyl stannanes (0.096 mmol), anhydrous LiCl (0.52 mmol) and $Pd(Ph_3P)_4$ (0.009 mmol) were added into a 25 ml telfon-stoppered flask, and dry THF (10ml) was added. The purple suspension was degassed by Freeze-Pump-Thaw method (three times) and then the mixture was heated at 90 °C under N_2 for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, the crude product was purified by column chromatography on silica gel using 1:3 mixture of methylene chloride:hexane as an eluent. The purple band was collected and evaporated to dryness to give purple solid which was further recrystallised by using the solvent mixture of chloroform-methanol to give pure alkynyl porphyrins.

General procedure for the preparation of porphyrins 5b and 6b from the Pd-catalysed cross coupling of porphyrin triflates 3 and 4 with trimethylsilyl acetylene.

Porphyrin aryl triflate **3** or **4** (0.065 mmol), and $Pd(Ph_3P)_2Cl_2$ (0.009 mmol) were added into 25ml telfon-stoppered flask, and then ethynyl trimethylsilane (0.13 mmol) in dry diethylamine (10ml) was added. The purple suspension was degassed by Freeze-Pump-Thaw method (3 cycles) and then the mixture was heated at 90 °C under N_2 for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, the crude product was purified by column chromatography on silica gel using 1:3 mixture of methylene chloride : hexane as an eluent. The purple band was collected and evaporated to dryness to give purple solid which was further recrystallised by using the solvent mixture of chloroform-methanol to give pure alkynyl porphyrins.

Porphyrin 5b (74%): ^{1}HNMR : ∂ 8.85 (m, 8 H), 8.33 (s,1 H), 8.14 (d, *J* = 7.6Hz, 1 H), 8.08 (d, *J* = 7.9 Hz, 6 H), 7.88 (d,*J* = 7.8 Hz, 1 H), 7.67 (t,*J* = 7.7 Hz, 1 H), 7.54 (d, *J* = 7.9 Hz, 6 H), 2.69 (s, 9 H), 0.26 (s, 9 H), -2.81 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, cm^{-1} M^{-1}): 418.0 (28.83), 515.5 (1.71), 551.0 (0.83), 590.0 (0.50) 646.0 (0.42) ; R_f = 0.65 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 753 $(M+1)^+$, 752 $(M)^+$. Anal. Calcd for $C_{52}H_{44}N_4Si$: C, 82.97; H, 5.85; N, 7.44. Found : C, 82.92; H, 5.84; N, 7.26.

Porphyrin 5c (72%): ^{1}HNMR : ∂ 8.85 (m, 8H), 8.39 (s, 1 H), 8.17 (d, *J* = 7.9 Hz, 1 H), 8.08 (d, *J* = 7.8 Hz, 6 H), 7.94 (d, *J*= 7.8 Hz, 1 H), 7.72 (t, *J* = 7.8 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 8 H), 7.32 (m, 3 H), 2.69 (s, 9 H), -2.80 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 419.0 (29.12), 485.5 (0.44), 515.0 (2.21), 550.5 (1.08), 590.0 (0.65), 645.5 (0.54) ; R_f = 0.69 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 757 $(M+1)^+$, 756 $(M)^+$. Anal. Calcd for $C_{55}H_{40}N_4$: C, 87.26; H, 5.34; N, 7.40. Found : C, 86.64; H, 5.42; N, 7.26.

Porphyrin 5d (76%): ^{1}HNMR : ∂ 8.85 (m, 8H), 8.25 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 7H), 7.80 (d, *J* = 7.8 Hz, 1 H), 7.64 (t, *J* = 7.7 Hz, 1 H), 7.54 (d, *J* = 7.8 Hz, 6 H), 2.69 (s, 9 H), 2.45 (t, *J* = 6.9 Hz, 2 H), 1.43-1.61 (m, 4 H), 0.92 (t, *J* = 7.2 Hz, 3 H), -2.81 (s, 2 H). UV/vis (wave-length max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 416.0 (29.82), 484.0 (1.07), 515.0 (5.33), 591.0 (1.58), 645.5 (1.33) ; R_f =0.68 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 737 $(M+1)^+$, 736 $(M)^+$. Anal. Calcd for $C_{53}H_{44}N_4$: C, 86.41; H, 5.98; N, 7.61. Found : C, 85.84; H, 6.05; N, 7.38.

Porphyrin 6b (76%): ^{1}HNMR : ∂ 8.84 (m, 8 H), 8.14 (d, *J* = 8.2 Hz, 2 H), 8.07 (d, *J* = 7.9 Hz, 6 H), 7.85 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J*= 7.9 Hz, 6 H), 2.69 (s,9 H), 0.36 (s, 9 H), -2.81 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4,$cm^{-1}M^{-1}$): 420.0 (30.24), 485.0 (1.47), 515.5 (7.04), 551.0 (3.94), 591.0 (2.11) ; R_f = 0.69 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 753 $(M+1)^+$, 752 $(M)^+$. Anal. Calcd for $C_{52}H_{44}N_4Si$: C, 82.97; H, 5.85; N, 7.44. Found : C, 82.64; H, 5.85; N, 7.26.

Porphyrin 6c (73%): ^{1}HNMR : ∂ 8.85 (m, 8 H), 8.20 (d, *J* = 7.9 Hz, 2 H), 8.08 (d, *J* = 7.8 Hz, 6 H), 7.92 (d, *J* = 7.9 Hz, 2 H), 7.67 (d, *J* = 5.3 Hz, 2 H), 7.54 (d, *J* = 7.9 Hz, 6 H), 7.42 (m,3 H), 2.69 (s, 9 H), -2.80 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 418.5 (29.51), 485.0 (0.67), 515.5 (3.04), 551.5 (1.79), 591.0 (0.92) ; R_f = 0.66 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 757 $(M+1)^+$, 756 $(M)^+$. Anal. Calcd for $C_{55}H_{40}N_4$: C, 7.26; H, 5.34; N, 7.40. Found : C, 86.75; H, 5.40; N, 7.27.

Porphyrin 6d (76%): ^{1}HNMR : ∂ 8.81 (m, 8 H), 8.12 (d, *J* = 8.2 Hz, 2 H), 8.07 (d, *J* = 7.8 Hz, 6 H), 7.77 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 7.9 Hz, 6 H), 2.69 (s, 9 H), 2.57 (t, *J* = 6.9 Hz, 2 H), 1.64 (m, 4 H), 1.03 (t, *J* = 7.2 Hz, 3 H), -2.80 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 417.5 (29.38), 515.5 (2.24), 551.5 (1.26), 591.0 (0.69) ; R_f = 0.69 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 737 $(M+1)^+$, 736 $(M)^+$. Anal. Calcd for $C_{53}H_{44}N_4$: C, 86.41; H, 5.98; N, 7.61. Found : C, 85.96; H, 12; N, 7.44.

Zinc porphyrin 7b (75%): ^{1}HNMR : ∂ 8.91 (m, 8 H), 8.14 (d, *J* = 8.2 Hz, 2 H), 8.07 (d, *J* = 7.9 Hz, 6 H), 7.85 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 7.9 Hz, 6 H), 2.69 (s, 9 H), 0.36 (s, 9 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 420.0 (29.80), 475.0 (0.55), 512.0 (0.65), 548.5 (3.54), 587.5 (0.96) ; R_f = 0.62 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 816 $(M+1)^+$, 815 $(M)^+$. Anal. Calcd for $C_{52}H_{44}N_4SiZn$: C, 76.56; H, 5.15; N, 6.87. Found : C, 75.93; H, 5.30; N, 6.54.

General procedure for the desilylation of porphyrin 5b and 6b

5-Trimethylsilylethynylphenyl]-10,15,20-tritolylporphyrin (0.065mmol) was dissolved in 15 ml THF and potassium hydroxide (6.5 mmol) aqueous solution was added, the whole mixture was stirred at room temperature for 12 hr, then it was worked up by washing the organic layer with water and saturated NaCl solution, then the organic layer was dried ($MgSO_4$) and evaporated to dryness. It was purified by column chromatography on silica gel using 1:3 of methylene chloride: hexane as an eluent. The purple band was collected and evaporated to dryness to give purple solid, it was recrystallised by using the solvent mixture of chloroform-methanol to give pure ethynylphenyl porphyrins.

Porphyrin 8 (85%): ^{1}HNMR : ∂ 8.84 (m, 8 H), 8.34 (s, 1 H), 8.18 (d, J = 7.4 Hz, 1 H), 8.08 (d, J = 7.9 Hz, 6 H), 7.89 (d, J = 7.5 Hz, 1 H), 7.69 (t, J = 7.8 Hz), 7.54 (d, J = 7.7 Hz, 6 H), 3.15 (s, 1 H), 2.69 (s, 9 H), -2.82 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, cm^{-1} M^{-1}): 420.0 (28.83), 484.0 (0.81), 515.0 (4.10), 550.0 (1.98), 590.0 (1.22) 646.0 (1.01) ; R_f = 0.69 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 681 $(M+1)^+$, 680 $(M)^+$. Anal. Calcd for $C_{49}H_{36}N_4$: C, 86.47; H, 5.29; N, 8.24. Found : C, 84.29; H, 5.50; N, 7.74.

Porphyrin 9 (86%): ^{1}HNMR : ∂ 8.85 (m, 8 H), 8.17 (d, J =8.0 Hz, 2 H), 8.08 (d, J = 7.9 Hz, 6 H), 7.87 (d, J = 8.0 Hz, 2 H), 7.54 (d, J =7.8 Hz, 6 H), 3.30 (s, 1 H), 2.69 (s, 9 H), -2.80 (s, 2 H). UV/vis (wavelength max , nm, CH_2Cl_2, X 10^4, $cm^{-1}M^{-1}$): 417.0 (29.37), 515.5 (2.32), 551.0 (1.25), 591.0 (0.70) ; R_f = 0.67 (CH_2Cl_2 : hexane= 1:1). FABMS : *m/z* 681 $(M+1)^+$, 680 $(M)^+$. Anal. Calcd for $C_{49}H_{36}N_4$: C, 86.47; H, 5.29; N, 8.24. Found : C, 84.11; H, 5.43; N, 7.93.

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