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# PtCl<sub>2</sub>-catalyzed benzannulation of nickel(II) 2,3-dialkynylporphyrins to form unusual phenanthroporphyrins

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#### ABSTRACT

Reaction of Ni(II) 2,3-dibromo-5,10,15,20-tetraphenylporphyrin with substituted stannyl alkynes generates substituted 2,3-dialkynylporphyrins in good yields. Thermolysis of these motifs with stoichiometric or even catalytic equivalents of PtCl<sub>2</sub> yields unusual phenanthroporphyrins with only small amounts of the established picenoporphyrin or other side products.

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#### 1. Introduction

The synthesis of  $\pi$ -extended porphyrins and their corresponding electro-optical properties are pertinent to the development of novel hybrid organic-inorganic materials for applications such as photodynamic therapy and solar energy conversion [1-5]. Here, effective macrocycle periphery modification is paramount to the synthesis of unusual chromophores, and efficient organometallic strategies for such functionalization are only now emerging [6-10]. In general, the success of these synthetic methods requires incorporation of specific functionality at either the *meso-* or  $\beta$ ,  $\beta'$ -pyrrole positions. Like several established organometallic coupling strategies (e.g., Stille, Suzuki, Sonogashira), transformations of alkyne functionalities are extremely versatile for formation of cyclized hydrocarbon constructs [11], and thus can serve as an effective route to unusual  $\pi$ extended porphyrinic structures [12,13]. Within this theme, we report the preparation of Ni(II) 2,3-dialkynylporphyins and the PtCl<sub>2</sub>-catalyzed cyclization of the diyne-ene motif [14,15] to form unusual phenanthroporphyrin constructs [16].

#### 2. Results and discussion

Ni(II) 2,3-dialkynylporphyrins 2a-e are prepared by Stille crosscoupling [17–19] of the dibromoporphyrin [20] precursor with a series of substituted, trimethyl(ethynyl)tin reagents [21,22] (Scheme 1). In the case of **2a**, subsequent removal of the R = TMS protecting group with K<sub>2</sub>CO<sub>3</sub> in THF/MeOH, produces nickel(II) 2,3-diethynyl-5,10,15,20-tetraphenylporphyrin **2b** in 75% yield [23].

The thermal Bergman cyclization of compounds such as 2c occurs only at high temperatures (~190 °C) [17], but the thermal barrier can be reduced by decreasing the steric bulk of the R-group [24], introducing electron withdrawing functionality at the alkyne termini [25], or enhancing the formation of the final product through intermediate oxidation [23]. Although picenporphyrin product can be obtained in this manner by direct heating, lower temperature cyclization strategies that introduce new architectures would be advantageous.

Heating of **2b** at 130 °C in toluene for 8 h yields the fully cyclized picenoporphyrin **3b** product in 68% yield (Scheme 2). This product is proposed to be formed by 1,4-radical addition across the adjacent *meso*-phenyl rings [17]. In marked contrast, heating of **2b** (85–90 °C) in the presence of PtCl<sub>2</sub> (1 equiv) for 1 h, leads to 100% consumption of starting material and formation of the unusual phenanthroporphyrin **4b** (68%) and benzoporphyrin **5** (6%) (entry 1, Table 1). The absence of picenoporphyrin products suggests that initial  $\pi$ - and subsequent  $\sigma$ -bonding of Pt(II) to the alkyne carbons is operative in the mechanism as proposed for simple enediyne motifs [15]. Reaction of **2b** with 0.5 equiv of Pt(II) generates nearly identical results (entry 2, Table 1). Decreasing catalyst concentration to 0.1 equiv and subsequent reaction over 4 h still produces **4b** in 56% (entry 3, Table 1). Formation of **4b** is even competent with





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**Scheme 1.** Stille coupling of the Ni(II) 2,3-dibromoporphyrin with select stannyl alkynes produces the corresponding dialkynylporphyrins in good yields.

0.1 equiv of Pt(II) at 40  $^{\circ}$ C over 72 h, generating **4b** in 35% yield (entry 4, Table 1), albeit with considerable unreacted starting material.

In addition to catalytically decreasing the thermal barrier to alkyne cyclization, and generating the unusual phenanthroporphyrin skeleton for R = H, the reaction is even viable for the thermally very stable R = TMS (**2a**) [24], as well as R = Ph, Pr, *i*-Pr (**2c**-e) (Scheme 3).

For **2a**, stoichiometric reaction with PtCl<sub>2</sub> at 125 °C results in deprotection of one or both of the –TMS functional groups and subsequent cyclization to yield phenanthroporphyrins **6** (5%) and doubly deprotected **4b** (45%). This reaction is intriguing in that **2a** is extremely stable to cyclization, but can be activated via an in situ deprotection/cyclization step with the same reagent. Additionally, reaction of **2c**–**e** under analogous conditions affords **4c**–**e** with smaller amounts of the picenoporphyrin derivatives **3c**–**e**, as well as reduced alkyne and benzoporphyrin products **7** (10%) and **8** (5%), respectively, from reaction of **2e** (see Supplementary material). Although compounds **4d**–**e** and **3d**–**e** are formed in comparable



**Scheme 2.** Thermal Bergman and Pt(II)-catalyzed cyclization of 2,3diethynylporphyrin to form piceno- and phenanthroporphyrin products, respectively.

Table 1	
Yields for Pt(II)-catalyzed cycloaromatization	of 2b

Entry	Reaction conditions	Conversion <sup>a</sup>	<b>2b</b> <sup>b</sup> (%)	<b>3b</b> (%)	<b>4b</b> (%)	5 (%)
1	PtCl <sub>2</sub> (1 equiv), toluene, 85–90 °C, 1 h.	100%	_	_	68	6
2	PtCl <sub>2</sub> (0.5 equiv), toluene, 85–90 °C, 1 h.	100%	-	-	65	5
3	PtCl <sub>2</sub> (0.1 equiv), toluene, 85–90 °C, 4 h.	95%	5	5	56	5
4	PtCl <sub>2</sub> (0.1 equiv), toluene, 40 °C, 72 h.	80%	20	-	35	2
5	Toluene, 130 °C, 8 h.	100%	_	68	-	-

<sup>a</sup> Conversion is based on consumption of **2b**.

<sup>b</sup> Recovered starting material.

yields to **4c** and **3c**, respectively, they could not be isolated in pure form despite multiple purification steps. However, their presence is clearly distinguishable by the NMR signatures of their  $\beta$ -pyrrolic protons and equally downfield-shifted *meso*-phenyl protons ( $\delta$ 8.5–9.7 ppm). Picenoporphyrins typically exhibit two downfield doublets ( $\delta \sim 9.65$  and 8.9 ppm) and one singlet ( $\delta \sim 8.5$  ppm) with small *J* ( $\sim 5.2$  Hz) for the  $\beta$ -pyrrolic protons, and one doublet ( $\delta$  $\sim 9.35$ ) with larger *J* ( $\sim 7.6$  Hz) for two *meso*-phenyl protons. In contrast, the asymmetric phenanthroporphyrins are characterized by six doublets with small *J* ( $\sim 4.8$  Hz) between 8.5–9.6 ppm and a single doublet ( $\delta \sim 8.7$  ppm) of larger *J* ( $\sim 7.2$  Hz) for one *meso*phenyl proton.

X-ray quality crystals of 2c-e, 3c, 4b, and 5-8 have all been obtained by slow diffusion, with a subset of structures shown in Fig. 1. The Ni(II) 2,3-dialkynylporphyrins 2c and 2e exhibit the typical ruffle distortion due to the relatively small size of the Ni(II) ion in the macrocycle core. In marked contrast, the picenoporphyrin derivative 3c has a planar piceno unit resulting from *meso*phenyl ring addition, that is oriented at ~38° relative to the ruffled porphyrin plane. Unlike these two types of structures, phenanthroporphyrin 4b is strongly saddled, with the phenanthro unit participating in the distortion analogously to the remaining *meso*phenyl groups. The structural deviation of 4b from 3c indicates that



**Scheme 3.** Pt(II)-catalyzed cyclization of substituted dialkynylporphyrins to yield phenanthroporphyrins.



Fig. 1. Representative X-ray structures of 2,3-dialkynylporphyrins 2c,e, as well as thermally cyclized picenoporphyrin 3c, and Pt(II)-cyclized phenanthroporphyrin 4b.

addition to both *meso*-phenyl rings is required to override the structural preference of base Ni(II) porphyrin scaffolds, within which ruffled and saddled conformations are common.

The electronic absorption spectra of **2b**–**4b**(Fig. 2) show sharp Soret features between  $\lambda \sim 420-450$  nm (**2b**: 430 nm; **3b**: 451 nm; **4b**: 443 nm), and a set of three weaker Q-bands (**2b**: 542, 582, 630 nm; **3b**: 539, 580, 629 nm; **4b**: 524, 561, 610 nm). The appearance of three Q-bands in the spectrum reflects reduction in the symmetry of the macrocycle core and lifting of the degeneracy of the traditional eg ( $\pi^*$ ) Goutermann LUMO [26]. The consequential bathochromic shift of the Soret and Q-bands, and hyperchromic shift of the low-energy Q-band, derive from the extended conjugation and intensity borrowing from the Soret band components due to the reduced symmetry [27–30]. These differences in electronic structure can be used to readily distinguish each compound via the red-shifted Soret and Q-region energy/intensity distribution.

#### 3. Conclusions

Thermal activation of Ni(II) 2,3-dialkynylporphyins in the presence of stoichiometric-to-catalytic quantities of PtCl<sub>2</sub> promotes cyclization of the enediyne unit to form fused phenanthro-(primary product) or picenoporphyrin (secondary product) scaf-folds at moderate temperatures and in good yields. Both the methodology for macrocycle periphery modification, and the extended aromatic porphyrinoids themselves, are intriguing

demonstrations of how organometallic strategies are coincident with the development of novel macrocyclic architectures possessing unusual chemical features.



**Fig. 2.** Electronic absorption spectra of dialkynylporphyrin **2b** (-), picenoporphyrin **3b**  $(\cdots)$ , and Pt-cyclized phenanthroporphyrin **4b** (-). Inset: Magnification of the Q-band region.

#### 4.1. Materials and general procedures

All of the chemicals and solvents were obtained from Aldrich and Fluka. Reactions were carried out under nitrogen atmosphere with the use of Schlenk and dry box techniques. Solvents used in the reactions were dried and degassed by standard procedures. The products were purified by flash chromatography using silica gel (200-400 mesh) or activated neutral aluminum oxide (~150 mesh). UV-visible spectra were obtained using Perkin Elmer Lamba 19 spectrophotometer using UV Winlab software. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Gem 300 MHz or VXR 400 MHz NMR spectrometer and referenced to the proton or carbon resonances resulting from incomplete deuteration of deuterated solvents. IR spectra were recorded from KBr pellets on a Nicolet 510P FT IR spectrometer. FD mass data were obtained from University of Illinois with a micro mass Quatto-I mass spectrometer and MALDI-TOF, FAB and EI-HRMS data were recorded on Bruker Biglex III MALDI-TOF and Thermo Finnigan MAT 95 XP high resolution mass spectrometer, respectively.

Trimethyl(trimethylsilylethynyl)tin, trimethyl(propylethynyl) tin and trimethyl-(isopropylethynyl)tin were synthesized by following the literature procedures [21,22]. Trimethyl(phenylethynyl)tin was used as received from Aldrich. Nickel(II) 2,3-bis(trimethylsilylethynyl)-5,10,15,20-tetraphenylporphyrin **2a** was prepared by cross-coupling reaction [17–19] of nickel(II) 2,3-dibromo-5,10,15,20-tetraphenylporphyrin **1** [20] with trimethyl(trimethylsilylethynyl)tin in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, which on subsequent deprotection of trimethylsilyl group with K<sub>2</sub>CO<sub>3</sub> in THF/ MeOH, produces nickel(II) 2,3-diethynyl-5,10,15,20-tetraphenylporphyrin **2b** in 75% yield [23].

#### 4.2. Nickel(II) 2,3-bis(phenylethynyl)-5,10,15,20tetraphenylporphyrin (**2c**)

2,3-dibromo-5,10,15,20-То mixture of nickel(II) а tetraphenylporphyrin (0.50 g, 0.60 mmol) and (Ph<sub>3</sub>P)<sub>4</sub>Pd (0.075 g, 0.065 mmol) in dry THF (50 mL), trimethyl(phenylethynyl)tin (0.42 g, 1.59 mmol) was added and reaction mixture was stirred under N<sub>2</sub> at 75 °C for 5 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure and crude product was purified by Si-gel column (40% CH<sub>2</sub>Cl<sub>2</sub> in hexane). Yield: 65%. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-4}$ ) = 592 (1.60), 547 (1.74), 438 (22.39); IR (cm<sup>-1</sup>): 3049, 2928, 2191, 1597, 1492, 1441, 1366, 1344, 1254, 1230, 1176, 1073, 1003, 914, 834, 798, 752, 718, 700; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.68 (d, J = 5.4 Hz, 4H, β-pyrrolic H), 8.64 (d, J = 5.1 Hz, 2H, βpyrrolic H), 8.02-7.97 (m, 8H, meso-ArH), 7.71-7.62 (m, 12H, meso-ArH), 7.34-7.31 (m, 4H, ArH), 7.28-7.25 (m, 6H, ArH); MALDI-TOF-MS m/z 871 (MH<sup>+</sup>), FAB-HRMS calcd. for C<sub>60</sub>H<sub>37</sub>N<sub>4</sub>Ni (MH<sup>+</sup>): 871.23712. Found: 871.23743.

#### 4.3. Nickel(II) 2,3-bis(propylethynyl)-5,10,15,20tetraphenylporphyrin (**2d**)

To a suspension of nickel(II) 2,3-dibromo-5,10,15,20tetraphenylporphyrin (0.30 g, 0.36 mmol) and (Ph<sub>3</sub>P)<sub>4</sub>Pd (0.045 g, 0.039 mmol) in dry THF (25 mL), a solution of trimethyl(propylethynyl)tin (0.25 g, 1.08 mmol) in THF (10 mL) was added. The reaction mixture was stirred at 70–75 °C for 6 h. After completion of the reaction, the mixture was cooled to 25 °C and solvent was evaporated off under reduced pressure. The residue was purified on Si-gel column by using 50% CH<sub>2</sub>Cl<sub>2</sub> in hexane as solvent. Yield: 75%. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon \times 10^{-4}$ ) = 578 (0.76), 542 (1.66), 430 (24.02); IR (cm<sup>-1</sup>): 3050, 2956, 2220, 1598, 1490, 1440, 1365, 1346, 1271, 1198, 1177, 1071, 1006, 967, 835, 793, 748, 716, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.68 (d, J = 5.1 Hz, 4H,  $\beta$ -pyrrolic H), 8.63 (d, J = 5.1 Hz, 2H,  $\beta$ -pyrrolic H), 7.99–7.96 (m, 4H, *meso*-ArH), 7.92–7.88 (m, 4H, *meso*-ArH), 7.68–7.64 (m, 6H, *meso*-ArH), 7.61–7.59 (m, 6H, *meso*-ArH), 2.19 (t, J = 7.2 Hz, 4H, 2CH<sub>2</sub>), 1.52–1.44 (m, 4H, 2CH<sub>2</sub>), 0.99 (t, J = 7.5 Hz, 6H, 2CH<sub>3</sub>); MALDI-TOF-MS m/z 802 (M<sup>+</sup>), EI-HRMS calcd. for C<sub>54</sub>H<sub>40</sub>N<sub>4</sub>Ni (M<sup>+</sup>): 802.2600. Found: 802.2586.

#### 4.4. Nickel(II) 2,3-bis(isopropylethynyl)-5,10,15,20tetraphenylporphyrin (**2e**)

To a mixture of nickel(II) 2,3-dibromo-5,10,15,20tetraphenylporphyrin (0.30 g, 0.36 mmol) and (Ph<sub>3</sub>P)<sub>4</sub>Pd (0.045 g, 0.04 mmol) in dry THF (25 mL), a solution of trimethyl(isopropylethynyl)tin (0.25 g, 1.08 mmol) in THF (10 mL) was added. The reaction mixture was stirred at 70-80 °C for 5 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and evaporated to dryness under reduced pressure. The crude compound was purified on Si-gel column by using CH<sub>2</sub>Cl<sub>2</sub>:hexane (1:4) as eluent. Yield: 80%. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ ) = 579 (0.87), 542 (1.86), 428 (25.09); IR (cm<sup>-1</sup>): 3047, 2967, 2215, 1598, 1576, 1481, 1440, 1365, 1346, 1310, 1190, 1178, 1147, 1073, 1005, 947, 836, 794, 749, 716, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.67 (s, 2H, β-pyrrolic H), 8.64 (d, J = 5.1 Hz, 2H,  $\beta$ -pyrrolic H), 8.62 (d, J = 5.1 Hz, 2H,  $\beta$ pyrrolic H), 7.99-7.96 (m, 4H, meso-ArH), 7.90-7.87 (m, 4H, meso-ArH), 7.69-7.58 (m, 12H, meso-ArH), 2.60-2.54 (m, 2H, 2CH), 1.13  $(d, I = 6.9 \text{ Hz}, 12\text{H}, 4\text{CH}_3)$ ; MALDI-TOF-MS m/z 802 (M<sup>+</sup>), FAB-HRMS calcd. for C<sub>54</sub>H<sub>41</sub>N<sub>4</sub>Ni (MH<sup>+</sup>): 803.2684. Found: 803.2721.

#### 4.5. Thermolysis of nickel(II) 2,3-diethynyl-5,10,15,20tetraphenylporphyrin (**2b**)

A mixture of **2b** (50 mg, 0.07 mmol) and toluene (1.0 mL) was heated at 130 °C in pressure tube for 8 h. After completion of the reaction, the mixture was cooled to 25 °C and then diluted with  $CH_2Cl_2$  (10 mL). The solvent was evaporated off, the crude solid was loaded on Si-gel column and eluted with  $CH_2Cl_2$ :hexane (1:1) as solvent. The major green band was collected and recrystallized with  $CH_2Cl_2$ /MeOH to afford nickel(II) 10,15-diphenyl-piceno [20,1,2,3,4,5-fghij]porphyrin **3b** [23] in 68% yield.

#### 4.6. Thermal cycloaromatization of nickel(II) 2,3-diethynyl-5,10,15,20-tetra-phenylporphyrin (**2b**) in the presence of PtCl<sub>2</sub> (entries 1–4 in Table 1)

A mixture of **2b** (50 mg, 0.07 mmol) and PtCl<sub>2</sub> (0.1–1.0 equiv) in toluene (1.0 mL) was heated under appropriate conditions (see Table 1). After completion of the reaction, the mixture was cooled to 25 °C and evaporated under reduced pressure. The crude product was loaded on activated neutral aluminum oxide column and eluted with 20% CH<sub>2</sub>Cl<sub>2</sub> in hexane as solvent to afford phenanthroporphyrin 4b and benzoporphyrin 5. Characterization data for **4b**: UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon \times 10^{-4}$ ) = 610 (1.28), 560 (0.90), 444 (16.79); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.51 (d, J=4.8 Hz, 1H), 8.98 (d, J = 8.8 Hz, 2H), 8.90 (d, J = 4.8 Hz, 1H), 8.88 (d, J = 8.8 Hz, 1H), 8.67 (dd, J = 5.6, 5.2 Hz, 2H), 8.61 (d, J = 4.8 Hz, 1H), 8.54 (d, J = 4.8 Hz, 1H)1H), 8.04-7.91 (m, 8H), 7.86-7.78 (m, 4H), 7.71-7.65 (m, 6H), 7.36 (d, J = 7.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  144.91, 141.59, 141.31, 141.26, 140.40, 140.35, 140.22, 139.33, 138.63, 136.89, 135.13, 134.98, 134.54, 133.51, 133.40, 133.06, 132.71, 132.46, 132.33, 131.30, 131.18, 130.66, 130.54, 130.27, 128.44, 128.34, 127.84, 127.79, 127.48, 127.36, 126.98, 126.94, 126.78, 125.51, 124.37, 123.79, 121.38, 120.86, 120.15, 115.92, 105.97; FD-MS m/z 718 (M<sup>+</sup>); MALDI-TOF-MS m/z 718 (M<sup>+</sup>); EI-HRMS calcd. for C<sub>48</sub>H<sub>28</sub>N<sub>4</sub>Ni (M<sup>+</sup>): 718.1667. Found: 718.1659. Characterization data for **5**: UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon \times 10^{-4}$ ) = 592 (0.49), 550 (0.77), 435 (12.07); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.78 (d, *J* = 4.8 Hz, 1H), 8.66–8.62 (m, 3H), 8.50 (d, *J* = 5.2 Hz, 1H), 8.48 (d, *J* = 4.8 Hz, 1H), 8.29 (d, *J* = 4.8 Hz, 1H), 8.05 (dd, *J* = 3.2, 2.4 Hz, 2H), 8.01–7.97 (m, 6H), 7.78–7.75 (m, 3H), 7.71–7.65 (m, 10H), 7.04 (t, *J* = 4.5 Hz, 1H); MALDI-TOF-MS *m*/*z* 754 (M<sup>+</sup>); EI-HRMS calcd. for C<sub>48</sub>H<sub>29</sub>ClN<sub>4</sub>Ni (M<sup>+</sup>): 754.1434. Found: 754.1470.

#### 4.7. PtCl<sub>2</sub> induced thermal cycloaromatization of nickel(II) 2,3bis(trimethylsilylethynyl)-5,10,15,20-tetraphenylporphyrin (**2a**)

A mixture of 2a (100 mg, 0.12 mmol) and PtCl<sub>2</sub> (31 mg, 0.12 mmol) in toluene (2.0 mL) was heated in pressure tube at 125 °C for 24 h. The dark green reaction mixture was cooled to 25 °C and diluted with 10 mL CH<sub>2</sub>Cl<sub>2</sub>. After evaporation of solvent under reduced pressure, the residue was loaded on Si-gel column and eluted with 25% CH<sub>2</sub>Cl<sub>2</sub> in hexane to produce phenanthroporphyrins 4b and 6 in 45% and 5% yields, respectively. Characterization data for 4b: same as given above. Characterization data for **6**: UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ ) = 611 (0.99), 561 (0.79), 445 (13.80); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.53 (d, J = 4.8 Hz, 1H), 9.09 (d, J = 7.2 Hz, 1H), 9.06 (s, 1H), 9.00 (d, J = 7.6 Hz, 1H), 8.89 (d, J = 4.8 Hz, 1H), 8.72 (d, J = 4.8 Hz, 1H), 8.69 (d, J = 5.2 Hz, 1H), 8.60 (d, J=4.8 Hz, 1H), 8.54 (d, J=4.8 Hz, 1H), 8.04–7.93 (m, 7H), 7.88-7.82 (m, 4H), 7.71-7.65 (m, 6H), 7.54 (s, 1H), 0.43 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si); MALDI-TOF-MS m/z 790 (M<sup>+</sup>); EI-HRMS calcd. for C<sub>51</sub>H<sub>37</sub>N<sub>4</sub>NiSi (MH<sup>+</sup>): 791.2140. Found: 791.2147.

#### 4.8. PtCl<sub>2</sub> induced thermal cycloaromatization of nickel(II) 2,3bis(phenylethynyl)-5,10,15,20-tetraphenylporphyrin (**2c**)

A mixture of 2c (50 mg, 0.06 mmol) and PtCl<sub>2</sub> (15 mg, 0.056 mmol) in toluene (1.0 mL) was heated in pressure tube at 115 °C for 40 h. After completion of the reaction, the mixture was cooled to 25 °C and diluted with 10 mL CH<sub>2</sub>Cl<sub>2</sub>. To this solution, neutral aluminum oxide was added and solvent was evaporated off under reduced pressure. The resulting powder was loaded on activated neutral aluminum oxide column and eluted by 50% CH<sub>2</sub>Cl<sub>2</sub> in hexane as solvent. The major green fraction was collected, which on evaporation affords a mixture of compounds. The mixture was further repurified on Si-gel preparative TLC by using CH<sub>2</sub>Cl<sub>2</sub>:hexane (30:70) as solvent. Only two major compounds 4c and 3c were obtained in 35% and 10% yields, respectively. The efforts to separate other minor products were unsuccessful due their close  $R_f$ . Characterization data for **4c**: UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  $(\epsilon \times 10^{-4}) = 611$  (1.0), 562 (0.82), 448 (14.15); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.53 (d, J = 4.8 Hz, 1H), 8.92 (d, J = 4.8 Hz, 1H), 8.78 (d, J = 7.2 Hz, 1H), 8.70 (d, J = 4.8 Hz, 1H), 8.62 (d, J = 4.8 Hz, 1H), 8.59 (d, *J* = 4.8 Hz, 1H), 8.55 (d, *J* = 5.2 Hz, 1H), 8.02 (br, 6H), 7.74–7.66 (m, 10H), 7.48-7.43 (m, 6H), 7.41 (s, 1H), 7.23-7.19 (m, 4H), 7.13-7.11 (m, 2H); MALDI-TOF-MS m/z 870 (M<sup>+</sup>); EI-HRMS calcd. for C<sub>60</sub>H<sub>36</sub>N<sub>4</sub>Ni (M<sup>+</sup>): 870.2293. Found: 870.2292. Characterization data for **3c**: UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ ) = 633 (2.59), 584 (0.62), 541 (0.50), 455 (15.96); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.70 (d, J = 5.2 Hz, 2H), 9.43 (d, J = 7.6 Hz, 2H), 8.94 (d, J = 4.8 Hz, 2H), 8.48 (s, 2H), 8.08-8.06 (m, 4H), 7.96-7.91 (m, 4H), 7.74-7.70 (m, 6H), 7.58-7.56 (m, 4H), 7.51–7.44 (m, 8H); EI-HRMS calcd. for C<sub>60</sub>H<sub>34</sub>N<sub>4</sub>Ni (M<sup>+</sup>): 868.2136. Found: 868.2124.

#### 4.9. PtCl<sub>2</sub> induced thermal cycloaromatization of nickel(II) 2,3bis(propylethynyl)-5,10,15,20-tetraphenylporphyrin (**2d**)

A mixture of **2d** (50 mg, 0.062 mmol) and  $PtCl_2$  (16 mg, 0.06 mmol) in toluene (1.0 mL) was heated in pressure tube at reflux temperature (115 °C) for 29 h. After completion of the

reaction, the mixture was cooled to 25 °C and diluted with 10 mL  $CH_2Cl_2$ . To this solution, neutral aluminum oxide was added and solvent was evaporated off under reduced pressure. The resulting powder was loaded on activated neutral aluminum oxide column and eluted by 50%  $CH_2Cl_2$  in hexane as solvent. The major green fraction was collected, which upon evaporation affords a mixture of compounds. Proton NMR of mixture showed the presence of corresponding phenanthroporphyrin **4d** and picenoporphyrin **3d** with other minor products. The efforts to separate these compounds in pure form were unsuccessful.

#### 4.10. PtCl<sub>2</sub> induced thermal cycloaromatization of nickel(II) 2,3bis(isopropylethynyl)-5,10,15,20-tetraphenylporphyrin (**2e**)

A mixture of **2e** (50 mg, 0.062 mmol) and PtCl<sub>2</sub> (16 mg, 0.06 mmol) in toluene (1.0 mL) was heated at 115 °C for 24 h. After completion of the reaction, the mixture was cooled to 25 °C and diluted with 10 mL CH<sub>2</sub>Cl<sub>2</sub>. To this solution, neutral aluminum oxide was added and solvent was evaporated to dryness. The resulting powder was loaded on activated neutral aluminum oxide column and eluted by 25-50% CH<sub>2</sub>Cl<sub>2</sub> in hexane as solvent. The reduced alkyne product 7 and benzoporphyrin 8 were obtained in 10% and 5% yields, respectively. Further, the column was eluted with CH<sub>2</sub>Cl<sub>2</sub>:hexane (1:1) and major green band was collected, which on evaporation produced an inseparable mixture of desired phenanthroporphyrin 4e and picenoporphyrin 3e along with other minor products on the basis of proton NMR. The purification of these compounds were unsuccessful due to their close R<sub>f</sub>. Characterization data for **7**: UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ ) = 574 (0.60), 539 (1.54), 424 (21.76); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.67 (s, 2H), 8.58 (d, J = 4.8 Hz, 2H), 8.53 (br s, 2H), 7.98–7.96 (m, 4H), 7.84 (br s, 4H), 7.69–7.64 (m, 6H), 7.58 (dd, J = 7.6, 7.2 Hz, 2H), 7.52–7.47 (m, 4H), 5.55 (d, *I* = 7.6 Hz, 2H, 2CH), 2.54–2.47 (m, 2H, 2CH), 1.00 (d, *I* = 6.0 Hz, 6H, 2CH<sub>3</sub>), 0.89 (d, *I* = 2.4 Hz, 6H, 2CH<sub>3</sub>); EI-HRMS calcd. for C<sub>54</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>4</sub>Ni (M<sup>+</sup>): 874.2140. Found: 874.2136. Characterization data for **8**: UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon \times 10^{-4}$ ) = 608 (0.57), 564 (0.73), 443 (9.30); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.47–8.42 (m, 4H), 8.32 (d, I = 4.8 Hz, 1H), 8.09 (d, I = 4.8 Hz, 1H), 8.00–7.90 (m, 4H), 7.84–7.79 (m, 4H), 7.67-7.58 (m, 12H), 7.52 (s, 1H), 3.47-3.42 (m, 1H, CH), 2.92–2.88 (m, 1H, CH), 1.30 (d, J=6.8 Hz, 12H, 4CH<sub>3</sub>); EI-HRMS calcd. for C<sub>54</sub>H<sub>41</sub>ClN<sub>4</sub>Ni (M<sup>+</sup>): 838.2373. Found: 838.2366.

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#### Appendix A. Supplementary material

CCDC 804628–804635 (for 9 compounds) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.cccdc.cam.ac.uk/data-request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.07.008.

#### References

- F. D'Souza, E. Maligaspe, A.S.D. Sandanayaka, N.K. Subbaiyan, P.A. Karr, T. Hasobe, O. Ito, J. Phys. Chem. A 114 (2010) 10951.
- [2] T. Hasobe, Phys. Chem. Chem. Phys. 12 (2010) 44.
- [3] E. Maligaspe, A.S.D. Sandanayaka, T. Hasobe, O. Ito, F. D'Souza, J. Am. Chem. Soc. 132 (2010) 8158.
- [4] P.K. Poddutoori, A.S.D. Sandanayaka, T. Hasobe, O. Ito, A.v.d. Est, J. Phys. Chem. B 114 (2010) 14348.
- [5] M. Vizuete, M.J. Gomez-Escalonilla, J.L.G. Fierro, A.S.D. Sandanayaka, T. Hasobe, M. Yudasaka, S. lijima, O. Ito, F. Langa, Chem.—Eur. J. 16 (2010) 10752.

- [6] A.N. Cammidge, P.J. Scaife, G. Berber, D.L. Hughes, Org. Lett. 7 (2005) 3413.
- [7] N.K.S. Davis, M. Pawlicki, H.L. Anderson, Org. Lett. 10 (2008) 3945.
- [8] T. Kopke, M. Pink, J.M. Zaleski, Synlett (2008) 1882.
- [9] A.K. Sahoo, S. Mori, H. Shinokubo, A. Osuka, Angew. Chem., Int. Ed. 45 (2006) 7972.
- [10] D.-M. Shen, C. Liu, Q.-Y. Chen, Chem. Commun. (2005) 4982.
- [11] S.S. Bhattacharyya, J.M. Zaleski, Prog. Inorg. Chem. 55 (2007) 355.
- [12] J. Akhigbe, M. Zeller, C. Bruckner, Org. Lett. 13 (2011) 1322.
- [13] N.K.S. Davis, A.L. Thompson, H.L. Anderson, J. Am. Chem. Soc. 133 (2011) 30.
- [14] H.-K. Chang, S. Datta, A. Das, A. Odedra, R.-S. Liu, Angew. Chem., Int. Ed. (2007) 4744.
- [15] C.-Y. Lo, M.P. Kumar, H.-K. Chang, S.-F. Lush, R.-S. Liu, J. Org. Chem. 70 (2005) 10482.
- [16] A.J. Jimenez, C. Jeandon, J.-P. Gisselbrecht, R. Ruppert, Eur. J. Org. Chem. (2009) 5725
- H. Aihara, L. Jaquinod, D.J. Nurco, K.M. Smith, Angew. Chem., Int. Ed. 40 (2001) [17] 3439.

- [18] S.G. DiMagno, V.S.Y. Lin, J.J. Therien, J. Org. Chem. 58 (1993) 5983.
- [19] J.K. Stille, Angew. Chem., Int. Ed. Engl. 25 (1986) 508.
- [20] L. Jaquinod, R.G. Khoury, K.M. Shea, K.M. Smith, Tetrahedron 55 (1999) 13151. [21] G. Menz, B. Wrackmeyer, Z. Naturforsch., B 32B (1977) 1400.
- [22] J.K. Stille, J.H. Simpson, J. Am. Chem. Soc. 109 (1987) 2138.
   [23] M. Nath, J.C. Huffman, J.M. Zaleski, Chem. Commun. (2003) 858.
- [24] M. Nath, M. Pink, J.M. Zaleski, J. Am. Chem. Soc. 127 (2005) 478.
- [25] M. Nath, J.C. Huffman, J.M. Zaleski, J. Am. Chem. Soc. 125 (2003) 11484.
- [26] C. Bruckner, J.R. McCarthy, H.W. Daniell, Z.D. Pendon, R.P. Ilagan, T.M. Francis,
- L. Ren, R.R. Birge, H.A. Frank, Chem. Phys. 294 (2003) 285.
- [27] M. Gouterman, J. Chem. Phys. 30 (1959) 1139.
  [28] M. Gouterman, J. Mol. Spectrosc. 6 (1961) 138.
- [29] M. Gouterman, G.H. Wagniere, L.C. Snyder, J. Mol. Spectrosc. 11 (1963) 108
- [30] E.J. Baerends, G. Ricciardi, A. Rosa, S.J.A.v. Gisbergen, Coord. Chem. Rev. 230 (2002) 5.