

Article

Palladium-Catalyzed Polyfluorophenylation of Porphyrins with Bis(polyfluorophenyl)zinc Reagents

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Abstract: A facile and efficient method for the synthesis of pentafluorophenyl- and related polyfluorophenyl-substituted porphyrins has been achieved via palladium-catalyzed cross-coupling reactions of brominated porphyrins with bis(polyfluorophenyl)zinc reagents. The reaction is applicable to a variety of free-base bromoporphyrins, their metal complexes, and a number of bis(polyfluorophenyl)zinc reagents.

Keywords: porphyrin; polyfluorophenylation; bis(polyfluorophenyl)zinc; palladium; cross-coupling

1. Introduction

The construction of porphyrins and related tetrapyrrolic macrocycles has attracted much interest [1–6] because they have a variety of important applications in many fields [7,8], including catalysis [9–14], medicine [15–18], and materials [19–27]. It is also well documented that the chemical, physical, and biological properties of porphyrin macrocycles can be systematically tuned by the electronic, steric and conformational environments of their peripheral substituents [7,8]. Penta-fluoro-phenyl and related polyfluorophenyl groups are one of the most important peripheral substituents in that their strong electron-withdrawing nature can greatly affect the electronic properties of a porphyrin core [25,27]. Conventional approaches to synthesizing pentafluorophenyl-substituted porphyrins involve multiple condensation reactions of pentafluorobenzaldehydes by using various monopyrroles or substituted dipyrromethanes under acidic conditions, followed by oxidation of the

resulting porphyrinogen intermediates [26–30]. However, these multiple-condensation methods have low yields, significant side products, and difficult purifications. Palladium and related transition metal-catalyzed cross-couplings of polyfluoroarenes with aryl halides [31–34] would facilitate alternative synthetic pathways to pentafluorophenyl-substituted porphyrins. However, to our knowledge, only one report to date, by Therien *et al.* [35], evaluates such palladium-catalyzed methods for preparing pentafluorophenyl-substituted porphyrins. They used Pd(dppf) as the catalyst and investigated couplings of C₆F₅ZnCl by using only two examples of zinc complexes of bromoporphyrins, [2-bromo-5,10,15,20-tetraphenylporphinato]zinc(II) and [5,15-dibromo-10,20-diphenylporphinato]zinc(II), as the substrates; however, no further reports have alluded to any extension of this methodology [35].

We wanted to investigate whether this protocol could be extended to other bromoporphyrins, particularly those of free bases. We report herein a general method for synthesizing polyfluorophenyl-substituted porphyrins from the corresponding bromoporphyrins utilizing bis(polyfluorophenyl)zinc reagents as the coupling partner and Pd(OAc)₂/*t*-Bu₃P as the catalyst system. The present catalytic protocol can be carried out in high yields under mild conditions and can easily be applied to a variety of bromoporphyrins, such as *meso*-mono-, *meso*-di-, and β-mono-bromoporphyrins, enabling the synthesis not only of *meso*- and β-mono-polyfluorophenylated porphyrins but also of *meso*-bis(poly-fluorophenyl)-substituted derivatives.

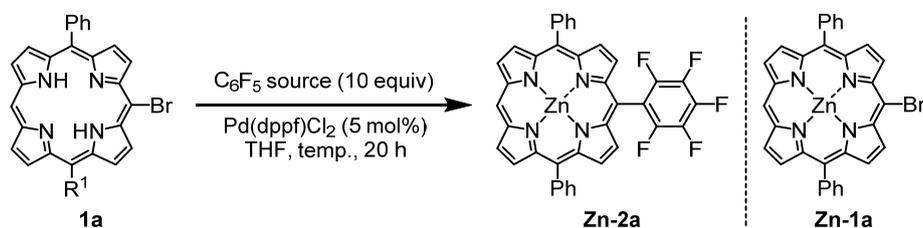
2. Results and Discussion

At the outset of our work, we examined the catalytic pentafluorophenylation of 5,15-diphenylporphyrin **1a** with C₆F₅ZnCl in accordance with the method developed by Therien *et al.* [35]. We thus achieved coupling of porphyrin **1a** with the organozinc reagent in the presence of Pd(dppf)Cl₂ (5 mol%) as a catalyst in THF at 25 °C and 60 °C (Table 1, entries 1 and 2). However, unfortunately, we did not obtain the desired fluorinated product **Zn-2a** after 20 h. Instead, the reactions produced zinc complexes of the starting bromoporphyrin **Zn-1a** as undesired byproducts in quantitative yields. Despite these disappointing results, we continued our investigation by changing the C₆F₅ source from C₆F₅ZnCl to commercially available (C₆F₅)₂Zn, and we were pleased to obtain the desired product **Zn-2a** in 12% yield (Table 1, entry 3).

Encouraged by this result, a series of palladium catalysts, ligands, and solvents were investigated to identify the variable(s) that affect the yield of the pentafluorophenylation product in the coupling reaction of the free-base *meso*-bromoporphyrin **1a** with the organozinc reagent (C₆F₅)₂Zn. As shown in Table 2, most of the palladium tertiary phosphine complexes we examined, either generated *in situ* or preformed, were ineffective for the coupling reaction, affording only low yields of the desired fluorinated product **Zn-2a** and the zinc complex of the starting bromoporphyrin **Zn-1a**. However, use of an electron-rich bulky monophosphine ligand, *t*-Bu₃P, can effectively catalyze the reaction in combination with both palladium complexes, Pd(dba)₂ and Pd(OAc)₂ (entries 9 and 14). We selected Pd(OAc)₂ as the palladium catalyst of choice for further investigation because of its high catalytic activity and low cost. A brief investigation of solvents found that ethereal solvents, such as THF and dioxane, were suitable reaction media (entries 14–17). Among which, THF was the solvent of choice in terms of yield of the desired fluorinated product **Zn-2a** (entry 14). Nonpolar solvent such as toluene did not promote the coupling reaction and gave no desired product (entry 17). Thus, with respect to optimized conditions the reaction of **1a** with 5 equiv of (C₆F₅)₂Zn in the presence of 5 mol%

$\text{Pd}(\text{OAc})_2$ and 10 mol% $t\text{-Bu}_3\text{P}\cdot\text{HBF}_4$ in THF at 60 °C afforded pentafluorophenyl-substituted product **Zn-2a** in 95% yield within 3 h (entry 14).

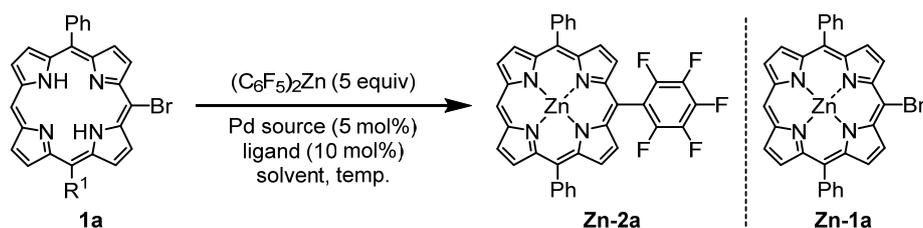
Table 1. Palladium-catalyzed coupling of free-base bromoporphyrin **1a** with pentafluorophenylzinc reagents, $\text{C}_6\text{F}_5\text{ZnCl}$ and $(\text{C}_6\text{F}_5)_2\text{Zn}$.



Entry	C_6F_5 source	Temp. (°C)	Yield ^a (%) of Zn-2a	Yield ^a (%) of Zn-1a
1	$\text{C}_6\text{F}_5\text{ZnCl}$	25	0	>99
2	$\text{C}_6\text{F}_5\text{ZnCl}$	60	trace	95
3	$(\text{C}_6\text{F}_5)_2\text{Zn}^b$	60	12	84

^a Isolated yield. ^b Using 5 equiv of $(\text{C}_6\text{F}_5)_2\text{Zn}$.

Table 2. Screening of palladium catalyst for coupling of *meso*-bromoporphyrin **1a** with bis(pentafluorophenyl)zinc.



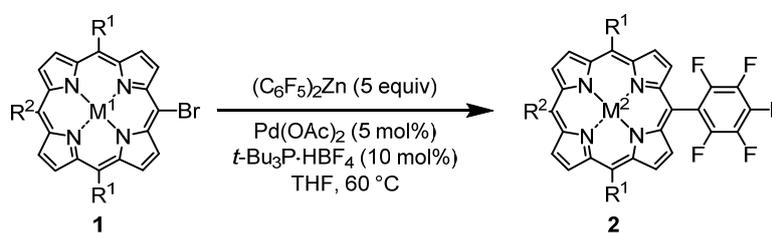
Entry	Pd source	Ligand	Solvent/temp	<i>t</i> (h)	Yield ^a (%) of Zn-2a	Yield ^a (%) of Zn-1a
1	$\text{Pd}(\text{dppf})\text{Cl}_2^b$	-	THF/60 °C	12	12	84
2	$\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$	-		20	0	>99
3	$\text{Pd}(\text{Ph}_3\text{P})_4$	-		12	23	69
4	$\text{Pd}(\text{dppe})_2^c$	-		20	0	>99
5	$\text{Pd}(\text{dba})_2$	dppf	THF/60 °C	12	14	82
6		Ph_3P		10	10	83
7		Cy_3P		10	23	74
8		SPhos ^d		20	trace	95
9		$t\text{-Bu}_3\text{P}\cdot\text{HBF}_4$		3	94	0
10	$\text{Pd}(\text{OAc})_2$	dppf	THF/60 °C	18	trace	97
11		Ph_3P		12	11	85
12		Cy_3P		12	18	77
13		SPhos		20	0	>99
14		$t\text{-Bu}_3\text{P}\cdot\text{HBF}_4$		3	95	0
15	$\text{Pd}(\text{OAc})_2$	$t\text{-Bu}_3\text{P}\cdot\text{HBF}_4$	dioxane/60 °C	3	89	0
16			dioxane/95 °C	2	92	0
17			toluene/110 °C	20	0	>99

^a Isolated yield.

Having identified optimized conditions for the pentafluorophenylation of porphyrins, we explored the substrate scope of this process by using $(\text{C}_6\text{F}_5)_2\text{Zn}$ (Table 3). These conditions were compatible with various phenyl substituents, including alkyl, alkoxy, alkenyl, and alkynyl groups on the

meso-brominated free-base diarylporphyrins, and we obtained the corresponding pentafluorophenyl-substituted zinc complexes in high yields (entries 1–6). Other free bases, including 10,20-dialkyl- and 10,15,20-trisubstituted bromoporphyrins, also participated in the catalytic pentafluorophenylation (entries 7 and 8). Central metal ions, such as Zn and Ni, could be incorporated into the products without greatly affecting the efficiency of the pentafluorophenylation (entries 9 and 10). Furthermore, we successfully employed β -bromoporphyrin **1i**, affording the desired β -pentafluorophenyl-substituted product **Zn-2i** in 92% yield (Scheme 1). The reaction also occurred with dibromoporphyrin **1j** to provide porphyrin **Zn-2j**, which contained two pentafluorophenyl substituents at the *meso* positions, in 86% yield (Scheme 2).

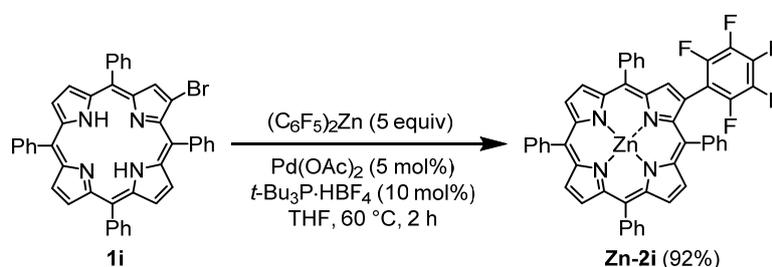
Table 3. Palladium-catalyzed coupling of bis(pentafluorophenyl)zinc with various bromoporphyrins.

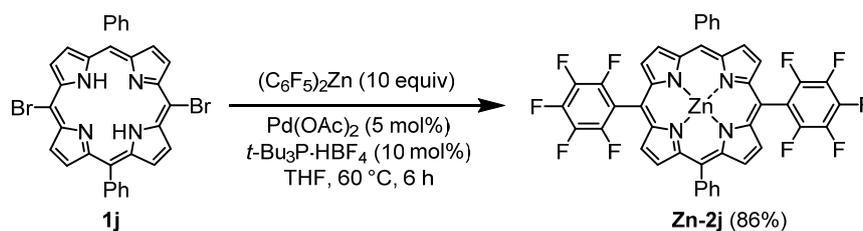


Entry	R ¹	R ²	M ¹	M ²	Substrate	Product	t (h)	Yield ^a (%)
1	Ph	H	2H	Zn	1a	Zn-2a	3	95
2	<i>p</i> -tolyl	H	2H	Zn	1b	Zn-2b	4	93
3	3-(CH ₂ =CH)C ₆ H ₄	H	2H	Zn	1c	Zn-2c	4	88
4	4-(<i>i</i> -Pr ₃ SiC≡C)C ₆ H ₄	H	2H	Zn	1d	Zn-2d	2	97
5	2,4,6-Me ₃ C ₆ H ₂	H	2H	Zn	1e	Zn-2e	4	90
6	3-(MeO)C ₆ H ₄	H	2H	Zn	1f	Zn-2f	4	89
7	<i>i</i> -Bu	H	2H	Zn	1g	Zn-2g	3	94
8	Ph	Ph	2H	Zn	1h	Zn-2h	3	96
9	Ph	H	Zn	Zn	Zn-1a	Zn-2a	1	99
10	Ph	H	Ni	Ni	Ni-1a	Ni-2a	1	97

^a Isolated yield.

Scheme 1. Preparation of β -pentafluorophenyl-substituted porphyrin **Zn-2i**.



Scheme 2. Preparation of bis(pentafluorophenyl)porphyrin **Zn-2j**.**Table 4.** Palladium-catalyzed coupling of **1a** with various bis(polyfluorophenyl)zinc reagents.

Entry	$(\text{F}_n\text{Ar})_2\text{Zn}$	Product	t (h)	Yield ^a (%)
1		Zn-2a	3	95
2		Zn-3	3	96
3		Zn-4	2	98
4		Zn-5	2	93
5		Zn-6	1	95
6		Zn-7	12	70

^a Isolated yield.

We next investigated the scope of bis(polyfluorophenyl)zinc reagents, which can readily be prepared *in situ* from the corresponding polyfluorophenyl Grignard reagents and $\text{Zn}(\text{OMe})_2$ in THF, by using *meso*-bromoporphyrin **1a**, as depicted in Table 4. In addition to standard pentafluorophenylation with $(\text{C}_6\text{F}_5)_2\text{Zn}$, related zinc reagents possessing 2,3,5,6-tetrafluoro-, 3,4,5-trifluoro-, and 3,6-difluorophenyl groups reacted to produce the corresponding polyfluorophenyl-substituted products in high yields (entries 1–4). An alkoxy-substituted zinc reagent also reacted to produce the desired product in 95% yield (entry 5). Furthermore, we effectively incorporated a highly electrophilic CF_3 -substituted tetrafluorophenyl group into the product, although a longer reaction time was required to complete the reaction and we obtained a slightly lower product yield (entry 6).

3. Experimental Section

^1H and ^{13}C NMR spectra were recorded at room temperature on 400 and 500 MHz spectrometers using perdeuterated solvents as internal standards. Chemical shifts of ^1H and ^{13}C spectra are given in ppm relative to residual protiated solvent and relative to the solvent respectively. ^{19}F NMR spectra were recorded at rt on a 500 MHz spectrometer using benzotrifluoride as an external standard. The chemical shift values are expressed as δ values (ppm) and the couple constants values (J) are in Hertz (Hz). The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. UV–visible spectra were recorded using a dual-beam grating spectrophotometer with a 1 cm quartz cell. The melting point data were not available for the porphyrin derivatives obtained because these compounds are infusible below 300 °C.

Reactions involving moisture sensitive reagents were carried out under an argon atmosphere using standard vacuum line techniques and glassware that was flame-dried and cooled under argon before use. Dry THF was purchased for the reactions and used without further desiccation. Bromoporphyrin derivatives, **1a–1c** [36], **1d** [6], **1e–1j** [36], **Zn-1a** [36], and **Ni-1a** [36] were prepared according to the method described in literature. Other chemicals were purchased from commercial sources and used as received unless stated otherwise.

Preparation of Bis(polyfluorophenyl)zinc Reagents: Bis(polyfluorophenyl)zinc reagents, bis(2,3,5,6-tetrafluorophenyl)zinc, bis(3,4,5-trifluorophenyl)zinc, bis(2,6-difluorophenyl)zinc, bis(2,6-difluoro-4-methoxyphenyl)zinc, and bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)zinc, were prepared according to the method described in literature [37] as follows. An oven-dried 20 mL two-necked flask equipped with magnetic stirring bar and rubber septum charged with $\text{Zn}(\text{OMe})_2$ (118 mg, 0.925 mmol) was added dry THF (4.0 mL) at rt. The heterogeneous solution was stirred for 5 min and cooled to 0 °C for another 10 min. A solution of polyfluorophenylmagnesium bromide (1.85 mL, 1.85 mmol, 1 M in THF) was added dropwise with vigorous stirring over 10 min at 0 °C, and the heterogeneous solution was allowed to stir at rt for 1 h. The mixture was then filtered and the Ar_2Zn solution (*ca.* 0.15 M) was used immediately.

A solution of bis(pentafluorophenyl)zinc in THF (*ca.* 0.15 M) was prepared as follows. An oven-dried 20 mL two-necked flask equipped with magnetic stirring bar and rubber septum charged with bis(pentafluorophenyl)zinc (370 mg, 0.925 mmol) was added dry THF (6.0 mL) at room temperature. The mixture was stirred for 10 min and used immediately.

General Procedure for the Palladium-Catalyzed Reaction of Bromoporphyrins with Bis(polyfluorophenyl)zinc Reagents: An oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar and rubber septum was charged with a free base bromoporphyrin **1** (0.185 mmol), $\text{Pd}(\text{OAc})_2$ (2.1 mg, 9.3 μmol , 5 mol%), and $t\text{-Bu}_3\text{P}\cdot\text{HBF}_4$ (5.4 mg, 18.5 μmol , 10 mol%). The reaction vessel was evacuated and flushed with argon (three times), and then dry THF (30 mL) was added. To the solution was slowly added *ca.* 0.15 M THF solution of a bis(polyfluorophenyl)zinc reagent (6.0 mL, *ca.* 0.9 mmol, 5 equiv.) at rt via a cannula. The mixture was stirred at 60 °C for several hours (1–12 h), having been monitored by TLC (1:1 hexane/toluene). Upon completion of the reaction, the mixture was allowed to reach rt. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with water and brine. The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (1:1 toluene/hexane). The first red purple band

eluted was collected, and taken to dryness. Recrystallization from hexane/CH₂Cl₂ gave the pure product.

[5,15-Diphenyl-10-pentafluorophenylporphyrinato]zinc(II) (**Zn-2a**). Prepared from bromoporphyrin **1a** (100.2 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 121.9 mg, 95% yield; $R_f = 0.60$ (1:1 hexane/toluene); ¹H NMR (THF-*d*₈, 400 MHz) δ 10.32 (1H, s), 9.42 (2H, d, $J = 4.4$ Hz), 9.06 (4H, d, $J = 4.4$ Hz), 9.01 (2H, d, $J = 4.4$ Hz), 8.35–8.23 (4H, m), 7.87–7.74 (6H, m); ¹³C NMR (THF-*d*₈, 100 MHz) δ 150.9, 150.3, 150.1, 149.3, 147.0 (2C, d, $J_{CF} = 246.6$ Hz), 143.3, 141.9 (1C, d, $J_{CF} = 248.3$ Hz), 137.8 (2C, d, $J_{CF} = 250.8$ Hz), 134.7, 132.8, 132.1, 131.9, 129.3, 127.4, 126.4, 120.8, 118.5, 107.2, 100.6; ¹⁹F NMR (THF-*d*₈, 466 MHz) δ -141.2 (2F, ddd, $J_{FF} = 24.6, 8.1, 5.9$ Hz), -158.9 (1F, tt, $J_{FF} = 20.9, 5.9$ Hz), -167.3 (2F, ddd, $J_{FF} = 24.6, 20.9, 8.0$ Hz); IR (KBr) 3055, 3028, 2970, 2924, 2866, 2804, 1493, 1065, 991, 860, 764, 702 cm⁻¹; UV/vis (CHCl₃) λ_{max} (log ϵ) 417.0 (5.7), 546.5 (4.3) nm; HRMS (EI) calcd. for C₃₈H₁₉F₅N₄Zn 690.0821, found 690.0822.

This compound was also synthesized from zinc complex of bromoporphyrin **Zn-1a** (111.9 mg, 0.185 mmol) and bis(pentafluorophenyl)zinc following the general procedure (see, Table 3, entry 9); 126.5 mg, 99% yield.

[5,15-Di(*p*-tolyl)-10-pentafluorophenylporphyrinato]zinc(II) (**Zn-2b**). Prepared from bromoporphyrin **1b** (105.4 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 124.1 mg, 93% yield; $R_f = 0.61$ (1:1 hexane/toluene); ¹H NMR (CDCl₃, 500 MHz) δ 9.76 (1H, s), 9.10 (2H, d, $J = 4.6$ Hz), 9.03 (2H, d, $J = 4.6$ Hz), 8.91 (4H, d, $J = 4.6$ Hz), 8.05 (4H, d, $J = 7.6$ Hz), 7.57 (4H, d, $J = 7.6$ Hz), 2.74 (6H, s); ¹³C NMR (CDCl₃, 125 MHz) δ 150.6, 150.3, 149.2, 148.9, 146.6 (2C, d, $J_{CF} = 245.2$ Hz), 141.7 (1C, d, $J_{CF} = 255.5$ Hz), 139.3, 137.4 (2C, d, $J_{CF} = 252.4$ Hz), 137.3, 134.5, 133.4, 132.5, 131.8, 129.5, 127.4, 121.2, 117.6, 106.9, 101.2, 21.5; ¹⁹F NMR (CDCl₃, 466 MHz) δ -138.7 (2F, ddd, $J_{FF} = 24.5, 8.5, 6.4$ Hz), -155.1 (1F, tt, $J_{FF} = 21.0, 6.4$ Hz), -164.2 (2F, ddd, $J_{FF} = 24.5, 21.0, 8.4$ Hz); IR (KBr) 3113, 3086, 3024, 2920, 2873, 2804, 1724, 1489, 1319, 1180, 1065, 995, 791 cm⁻¹; UV/vis (CHCl₃) λ_{max} (log ϵ) 418.0 (5.6), 547.0 (4.2) nm; HRMS (EI) calcd. for C₄₀H₂₃F₅N₄Zn 718.1134, found 718.1138.

[5,15-Bis(3-vinylphenyl)-10-pentafluorophenylporphyrinato]zinc(II) (**Zn-2c**). Prepared from bromoporphyrin **1c** (109.8 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 121.4 mg, 88% yield; $R_f = 0.57$ (1:1 hexane/toluene); ¹H NMR (CDCl₃, 500 MHz) δ 10.22 (1H, s), 9.34 (2H, d, $J = 4.6$ Hz), 9.06 (2H, d, $J = 4.6$ Hz), 9.05 (2H, d, $J = 4.6$ Hz), 8.86 (2H, d, $J = 4.6$ Hz), 8.29 (2H, s), 8.13 (2H, d, $J = 7.6$ Hz), 7.84 (2H, d, $J = 7.9$ Hz), 7.71 (2H, dd, $J = 7.9, 7.6$ Hz), 7.00 (2H, dd, $J = 17.7, 11.0$ Hz), 5.98 (2H, d, $J = 17.7$ Hz), 5.40 (2H, d, $J = 11.0$ Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 150.6, 150.0, 149.7, 149.0, 146.6 (2C, d, $J_{CF} = 246.2$ Hz), 143.1, 141.5 (1C, d, $J_{CF} = 254.5$ Hz), 137.3 (2C, d, $J_{CF} = 251.4$ Hz), 136.9, 135.7, 134.2, 133.1, 132.5, 132.4, 132.0, 129.4, 126.6, 125.2, 120.5, 118.0, 114.7, 107.2, 100.7; ¹⁹F NMR (CDCl₃, 466 MHz) δ -138.7 (2F, ddd, $J_{FF} = 23.8, 7.2, 5.3$ Hz), -154.9 (1F, tt, $J_{FF} = 21.0, 5.3$ Hz), -164.1 (2F, ddd, $J_{FF} = 23.8, 21.0, 8.5$ Hz); IR (KBr) 3089, 3020, 2981, 2924, 1489, 1319, 1173, 1065, 991, 910, 856, 791, 710 cm⁻¹; UV/vis (CHCl₃) λ_{max} (log ϵ) 418.0 (5.7), 546.5 (4.3) nm; HRMS (EI) calcd. for C₄₂H₂₃F₅N₄Zn 742.1134, found 742.1131.

[5,15-Bis[4-{2-(triisopropylsilyl)ethynyl}phenyl]-10-pentafluorophenylporphyrinato]zinc(II) (**Zn-2d**). Prepared from bromoporphyrin **1d** (166.9 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid (recrystallized from MeOH/CH₂Cl₂); 189.1 mg, 97%; *R_f* = 0.68 (1:1 hexane/toluene); ¹H NMR (CDCl₃, 400 MHz) δ 9.67 (1H, s), 9.08 (2H, d, *J* = 4.9 Hz), 8.97 (2H, d, *J* = 4.9 Hz), 8.94 (2H, d, *J* = 4.9 Hz), 8.83 (2H, d, *J* = 4.9 Hz), 8.09 (4H, d, *J* = 8.3 Hz), 7.92 (4H, d, *J* = 8.3 Hz), 1.50-1.12 (42H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 150.3, 150.0, 149.4, 149.2, 146.8 (2C, d, *J_{CF}* = 244.1 Hz), 142.4, 142.0 (1C, d, *J_{CF}* = 252.4 Hz), 137.6 (2C, d, *J_{CF}* = 254.9 Hz), 134.5, 133.3, 132.3, 132.1, 130.4, 129.9, 123.2, 120.4, 117.5, 107.3, 107.1, 101.9, 92.1, 18.9, 11.6; ¹⁹F NMR (CDCl₃, 466 MHz) δ -138.6 (2F, ddd, *J_{FF}* = 24.5, 7.6, 5.5 Hz), -154.7 (1F, tt, *J_{FF}* = 20.9, 5.5 Hz), -163.9 (2F, dd, *J_{FF}* = 24.5, 20.9, 8.0 Hz); IR (KBr) 3097, 3035, 2947, 2866, 1516, 1385, 1319, 1219, 1065, 995, 945, 818, 671 cm⁻¹; UV/vis (CHCl₃) λ_{max} (log ε) 419.5 (5.7), 549.0 (4.4) nm; HRMS-FAB⁺ ([M + H]⁺) calcd for C₆₀H₆₀F₅N₄Si₂Zn 1051.3568, found 1051.3578.

[5,15-Bis(2,4,6-trimethylphenyl)-10-pentafluorophenylporphyrinato]zinc(II) (**Zn-2e**). Prepared from bromoporphyrin **1e** (115.7 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 128.9 mg, 90% yield; *R_f* = 0.64 (1:1 hexane/toluene); ¹H NMR (CDCl₃, 500 MHz) δ 10.24 (1H, s), 9.36 (2H, d, *J* = 4.6 Hz), 8.92 (2H, d, *J* = 4.6 Hz), 8.91 (2H, d, *J* = 4.6 Hz), 8.83 (2H, d, *J* = 4.6 Hz), 7.31 (4H, s), 2.65 (6H, s), 1.82 (12H, s); ¹³C NMR (CDCl₃, 125 MHz) δ 150.6, 150.1, 149.7, 149.0, 146.6 (2C, d, *J_{CF}* = 246.2 Hz), 141.7 (1C, d, *J_{CF}* = 251.4 Hz), 139.3, 138.5, 137.7, 137.4 (2C, d, *J_{CF}* = 253.5 Hz), 132.7, 132.2, 131.5, 130.1, 127.8, 119.6, 117.4, 107.0, 100.7, 21.7, 21.5; ¹⁹F NMR (CDCl₃, 466 MHz) δ -138.7 (2F, ddd, *J_{FF}* = 24.3, 8.9, 6.7 Hz), -154.9 (1F, tt, *J_{FF}* = 21.0, 6.7 Hz), -164.1 (2F, ddd, *J_{FF}* = 24.3, 21.0, 8.5 Hz); IR (KBr) 3097, 2966, 2920, 2858, 1489, 1381, 1061, 995, 941, 852, 787 cm⁻¹; UV/vis (CHCl₃) λ_{max} (log ε) 417.5 (5.7), 545.5 (4.3) nm; HRMS (EI) calcd for C₄₄H₃₁F₅N₄Zn 774.1760, found 774.1755.

[5,15-Bis(3-methoxyphenyl)-10-pentafluorophenylporphyrinato]zinc(II) (**Zn-2f**). Prepared from bromoporphyrin **1f** (111.3 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 124.2 mg, 89% yield; *R_f* = 0.45 (1:1 hexane/toluene); ¹H NMR (THF-*d*₈, 400 MHz) δ 10.25 (1H, s), 9.37 (2H, d, *J* = 4.6 Hz), 9.11 (4H, d, *J* = 4.6 Hz), 8.88 (2H, d, *J* = 4.6 Hz), 7.81 (2H, d, *J* = 7.5 Hz), 7.75 (2H, s), 7.65 (2H, dd, *J* = 8.4, 7.5 Hz), 7.32 (2H, d, *J* = 8.4 Hz), 3.95 (6H, s); ¹³C NMR (THF-*d*₈, 100 MHz) δ 159.3, 151.6, 151.1, 151.0, 150.2, 147.8 (2C, d, *J_{CF}* = 243.3 Hz), 145.4, 142.8 (1C, d, *J_{CF}* = 254.9 Hz), 138.6 (2C, d, *J_{CF}* = 249.9 Hz), 133.7, 133.0, 132.7, 130.2, 128.5, 128.0, 121.8, 121.5, 119.3, 114.0, 108.0, 101.5, 55.7; ¹⁹F NMR (THF-*d*₈, 466 MHz) δ -138.5 (2F, ddd, *J_{FF}* = 24.5, 8.4, 6.3 Hz), -155.1 (1F, tt, *J_{FF}* = 21.0, 6.3 Hz), -164.3 (2F, ddd, *J_{FF}* = 24.5, 21.0, 8.5 Hz); IR (KBr) 3097, 2931, 2862, 2839, 1593, 1489, 1281, 1161, 1061, 991, 783 cm⁻¹; UV/vis (CHCl₃) λ_{max} (log ε) 417.5 (5.6), 546.0 (4.3) nm; HRMS (EI) calcd for C₄₀H₂₃F₅N₄O₂Zn 750.1033, found 750.1031.

[5,15-Di(*i*-butyl)-10-pentafluorophenylporphyrinato]zinc(II) (**Zn-2g**). Prepared from bromoporphyrin **1g** (92.8 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 113.6 mg, 94% yield; *R_f* = 0.59 (1:1 hexane/toluene); ¹H NMR (THF-*d*₈, 400 MHz) δ 10.01 (1H, s), 9.53 (2H, d, *J* = 4.6 Hz), 9.52 (2H, d, *J* = 4.6 Hz), 9.30 (2H, d, *J* = 4.6 Hz), 8.77 (2H, d, *J* = 4.6 Hz), 4.86 (4H, d, *J* = 7.3 Hz), 2.80-2.69 (2H, m), 1.14 (12H, d, *J* = 6.7 Hz); ¹³C NMR (THF-*d*₈, 100 MHz) δ 152.4, 151.8, 150.0, 149.3, 147.8 (2C, d, *J_{CF}* = 241.7 Hz), 142.6 (1C, d, *J_{CF}* = 251.6 Hz), 138.6 (2C, d,

$J_{CF} = 252.4$ Hz), 132.7, 131.2, 130.5, 130.1, 119.9, 119.8, 107.1, 100.1, 44.4, 38.1, 23.6; ^{19}F NMR (THF- d_8 , 466 MHz) δ -138.8 (2F, ddd, $J_{FF} = 24.7, 8.9, 6.8$ Hz), -156.0 (1F, tt, $J_{FF} = 20.6, 6.8$ Hz), -164.9 (2F, ddd, $J_{FF} = 24.7, 20.6, 8.8$ Hz); IR (KBr) 3113, 3028, 2958, 2870, 1493, 1381, 1315, 1165, 1076, 987, 949, 849, 775 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 417.0 (5.7), 549.0 (4.3) nm; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{27}\text{F}_5\text{N}_4\text{Zn}$ 650.1447, found 650.1451.

[5-Pentafluorophenyl-10,15,20-triphenylporphyrinato]zinc(II) (**Zn-2h**). Prepared from bromoporphyrin **1h** (114.2 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 136.1 mg, 96% yield; $R_f = 0.62$ (1:1 hexane/toluene); ^1H NMR (THF- d_8 , 400 MHz) δ 8.98 (2H, d, $J = 4.8$ Hz), 8.91 (2H, d, $J = 4.8$ Hz), 8.89 (2H, d, $J = 4.8$ Hz), 8.81 (2H, d, $J = 4.8$ Hz), 8.27-8.17 (6H, m), 7.82-7.70 (9H, m); ^{13}C NMR (THF- d_8 , 100 MHz) δ 151.7, 151.3, 151.1, 150.6, 147.9 (2C, d, $J_{CF} = 242.5$ Hz), 144.4, 144.3, 142.8 (1C, d, $J_{CF} = 252.4$ Hz), 138.7 (2C, d, $J_{CF} = 251.6$ Hz), 135.4 (6C), 133.8, 132.8, 132.5, 130.3, 128.3 (3C), 127.3, 127.2, 123.5, 122.3, 119.3, 101.3; ^{19}F NMR (THF- d_8 , 466 MHz) δ -139.1 (2F, ddd, $J_{FF} = 24.5, 8.4, 6.3$ Hz), -155.8 (1F, tt, $J_{FF} = 20.9, 6.3$ Hz), -164.8 (2F, ddd, $J_{FF} = 24.5, 20.9, 8.5$ Hz); IR (KBr) 3055, 3024, 2962, 2920, 2858, 1489, 1338, 1068, 995, 941, 868, 756, 702 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 422.5 (5.7), 552.0 (4.3) nm; HRMS (EI) calcd. for $\text{C}_{44}\text{H}_{23}\text{F}_5\text{N}_4\text{Zn}$ 766.1134, found 766.1133.

[2-Pentafluorophenyl-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**Zn-2i**). Prepared from bromoporphyrin **1i** (128.3 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 144.0 mg, 92% yield; $R_f = 0.63$ (1:1 hexane/toluene); ^1H NMR (THF- d_8 , 400 MHz) δ 8.94 (1H, s), 8.91 (2H, d, $J = 4.9$ Hz), 8.89 (2H, d, $J = 4.9$ Hz), 8.84 (1H, d, $J = 4.9$ Hz), 8.71 (1H, d, $J = 4.9$ Hz), 8.33-8.18 (6H, m), 8.13-8.04 (2H, m), 7.82-7.68 (9H, m), 7.57-7.42 (3H, m); ^{13}C NMR (THF- d_8 , 100 MHz) δ 151.85 (4C), 151.8, 151.0, 148.3, 146.5, 144.7 (2C, d, $J_{CF} = 243.3$ Hz), 144.4 (2C), 144.3, 143.1, 140.9 (1C, d, $J_{CF} = 249.1$ Hz), 138.3 (2C, d, $J_{CF} = 242.5$ Hz), 136.8, 135.5 (2C), 135.4 (4C), 135.0 (2C), 133.0, 132.8, 132.7 (2C), 132.6, 132.3, 128.6, 128.4, 128.3, 128.2 (2C), 127.3 (6C), 126.6 (2C), 122.1, 121.99, 121.96, 121.5, 116.7; ^{19}F NMR (THF- d_8 , 466 MHz) δ -140.0 (2F, ddd, $J_{FF} = 24.3, 7.6, 5.5$ Hz), -161.3 (1F, tt, $J_{FF} = 20.5, 5.5$ Hz), -167.8 (2F, ddd, $J_{FF} = 24.3, 20.5, 7.5$ Hz); IR (KBr) 3055, 3032, 2962, 2920, 2858, 2792, 2727, 1493, 1331, 1072, 995, 864, 795, 752 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 426.0 (5.7), 556.0 (4.3) 597.5 (3.8) nm; HRMS-FAB $^+$ (M^+) calcd for $\text{C}_{50}\text{H}_{27}\text{F}_5\text{N}_4\text{Zn}$ 842.1447, found 842.1445.

[5,15-Bis(pentafluorophenyl)-10,20-diphenylporphyrinato]zinc(II) (**Zn-2j**). The general procedure with dibromoporphyrin **1i** (114.8 mg) and 10 equiv, instead of 5 equiv, of bis(pentafluorophenyl)zinc (12 mL of its ca. 0.15 M solution in THF, ca. 1.8 mmol) gave the title compound as a red-purple solid (136.3 mg, 86% yield); $R_f = 0.71$ (1:1 hexane/toluene); $R_f = 0.71$ (1:1 hexane/toluene); ^1H NMR (THF- d_8 , 400 MHz) δ 8.99 (4H, d, $J = 4.9$ Hz), 8.98 (4H, d, $J = 4.9$ Hz), 8.30-8.22 (4H, m), 7.85-7.73 (6H, m); ^{13}C NMR (THF- d_8 , 100 MHz) δ 151.9, 150.5, 147.7 (4C, d, $J_{CF} = 241.7$ Hz), 143.9, 142.9 (2C, d, $J_{CF} = 253.2$ Hz), 138.7 (4C, d, $J_{CF} = 249.9$ Hz), 135.4, 133.9, 130.8, 128.5, 127.3, 122.8, 118.9, 103.1; ^{19}F NMR (THF- d_8 , 466 MHz) δ -138.7 (4F, ddd, $J_{FF} = 24.3, 8.0, 5.9$ Hz), -154.5 (2F, tt, $J_{FF} = 21.0, 5.9$ Hz), -163.9 (4F, ddd, $J_{FF} = 24.3, 21.0, 8.5$ Hz); IR (KBr) 3105, 3059, 3020, 2927, 2854, 1493, 1338, 1076, 991, 941, 768, 706 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 421.5 (5.8), 551.5 (4.3) nm; HRMS-FAB $^+$ (M^+) calcd for $\text{C}_{44}\text{H}_{18}\text{F}_{10}\text{N}_4\text{Zn}$ 856.0663, found 856.0662.

[5,15-Diphenyl-10-pentafluorophenylporphyrinato]nickel(II) (**Ni-2a**). Prepared from nickel complex of bromoporphyrin **Ni-1a** (110.7 mg) and bis(pentafluorophenyl)zinc following the general procedure; Red-purple solid; 126.8 mg, 97% yield; $R_f = 0.65$ (1:1 hexane/toluene); ^1H NMR (CDCl_3 , 400 MHz) δ 9.55 (1H, s), 8.89 (2H, d, $J = 4.9$ Hz), 8.84 (2H, d, $J = 4.9$ Hz), 8.77 (2H, d, $J = 4.9$ Hz), 8.68 (2H, d, $J = 4.9$ Hz), 8.02–7.95 (4H, m), 7.74–7.61 (6H, m); ^{13}C NMR (CDCl_3 , 100 MHz) δ 146.4 (2C, d, $J_{\text{CF}} = 247.5$ Hz), 143.4, 143.2, 142.8, 141.96, 141.94 (1C, d, $J_{\text{CF}} = 253.2$ Hz), 140.8, 137.6 (2C, d, $J_{\text{CF}} = 249.1$ Hz), 133.8, 133.5, 132.6, 132.5, 129.9, 127.9, 126.9, 119.3, 116.0, 105.9, 100.8; ^{19}F NMR (CDCl_3 , 466 MHz) δ -138.5 (2F, ddd, $J_{\text{FF}} = 24.1, 8.5, 6.4$ Hz), -154.5 (1F, tt, $J_{\text{FF}} = 21.0, 6.4$ Hz), -163.7 (2F, ddd, $J_{\text{FF}} = 24.1, 21.0, 8.0$ Hz); IR (KBr) 3059, 3032, 1493, 1385, 1335, 1161, 1072, 995, 941, 856, 764, 702 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 406.0 (5.4), 521.5 (4.2) 553.5 (3.9) nm; HRMS (EI) calcd for $\text{C}_{38}\text{H}_{19}\text{F}_5\text{N}_4\text{Ni}$ 684.0883, found 684.0880.

[5,15-Diphenyl-10-(2,3,5,6-tetrafluorophenyl)porphyrinato]zinc(II) (**Zn-3**). Prepared from bromoporphyrin **1a** (100.2 mg) and bis(2,3,5,6-tetrafluorophenyl)zinc following the general procedure; Red-purple solid; 119.4 mg, 96% yield; $R_f = 0.60$ (1:1 hexane/toluene); ^1H NMR (CDCl_3 , 400 MHz) δ 10.14 (1H, s), 9.26 (2H, d, $J = 4.8$ Hz), 8.97 (2H, d, $J = 4.8$ Hz), 8.96 (2H, d, $J = 4.8$ Hz), 8.82 (2H, d, $J = 4.8$ Hz), 8.21–8.15 (4H, m), 7.73–7.65 (6H, m), 7.51 (1H, tt, $J_{\text{HF}} = 10.0, 7.1$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 150.5, 150.0, 149.6, 148.8, 146.3 (2C, d, $J_{\text{CF}} = 245.8$ Hz), 145.6 (2C, d, $J_{\text{CF}} = 249.1$ Hz), 142.9, 134.5, 132.8, 132.2, 131.7, 129.3, 127.2, 126.3, 123.9, 120.6, 106.9, 106.1, 102.0; ^{19}F NMR (CDCl_3 , 466 MHz) δ -139.8 (2F, ddd, $J_{\text{FF}} = 22.5, 7.8$ Hz, $J_{\text{FH}} = 5.6$ Hz), -141.7 (2F, ddd, $J_{\text{FF}} = 22.5, 7.5$ Hz, $J_{\text{FH}} = 8.8$ Hz); IR (KBr) 3059, 2974, 2877, 2746, 1593, 1493, 1385, 1315, 1173, 1065, 999, 941, 852, 783, 710 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 417.0 (5.7), 546.0 (4.3) nm; HRMS-FAB $^+$ (M^+) calcd for $\text{C}_{38}\text{H}_{20}\text{F}_4\text{N}_4\text{Zn}$ 672.0916, found 672.0918.

[5,15-Diphenyl-10-(3,4,5-trifluorophenyl)porphyrinato]zinc(II) (**Zn-4**). Prepared from bromoporphyrin **1a** (100.2 mg) and bis(3,4,5-trifluorophenyl)zinc following the general procedure; Red-purple solid; 119.2 mg, 98% yield; $R_f = 0.58$ (1:1 hexane/toluene); ^1H NMR (CDCl_3 , 400 MHz) δ 10.17 (1H, s), 9.32 (2H, d, $J = 4.8$ Hz), 9.02 (2H, d, $J = 4.8$ Hz), 8.95 (2H, d, $J = 4.8$ Hz), 8.85 (2H, d, $J = 4.8$ Hz), 8.25–8.16 (4H, m), 7.83 (2H, dd, $J_{\text{HF}} = 8.3, 6.8$ Hz), 7.79–7.70 (6H, m); ^{13}C NMR (CDCl_3 , 100 MHz) δ 150.3, 150.0, 149.8, 149.2 (2C, d, $J_{\text{CF}} = 250.8$ Hz), 148.7, 143.0, 139.7 (1C, d, $J_{\text{CF}} = 252.4$ Hz), 139.6, 134.5, 132.2, 132.0, 131.6, 130.4, 127.2, 126.3, 120.4, 118.5, 116.5, 105.9; ^{19}F NMR (CDCl_3 , 466 MHz) δ -138.7 (2F, ddd, $J_{\text{FF}} = 20.5, 8.0$ Hz, $J_{\text{FH}} = 8.6$ Hz), -164.4 (1F, tt, $J_{\text{FF}} = 20.5$ Hz, $J_{\text{FH}} = 5.7$ Hz); IR (KBr) 3062, 2958, 2927, 2862, 2804, 1608, 1527, 1435, 1377, 1234, 1045, 999, 791, 725 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 417.5 (5.7), 546.0 (4.3) nm; HRMS (EI) calcd for $\text{C}_{38}\text{H}_{21}\text{F}_3\text{N}_4\text{Zn}$ 654.1010, found 654.1010.

[10-(2,6-Difluorophenyl)-5,15-diphenylporphyrinato]zinc(II) (**Zn-5**). Prepared from bromoporphyrin **1a** (100.2 mg) and bis(2,6-difluorophenyl)zinc following the general procedure; Red-purple solid; 109.5 mg, 93% yield; $R_f = 0.51$ (1:1 hexane/toluene); ^1H NMR (CDCl_3 , 400 MHz) δ 10.13 (1H, s), 9.27 (2H, d, $J = 4.4$ Hz), 8.98 (2H, d, $J = 4.4$ Hz), 8.93 (2H, d, $J = 4.4$ Hz), 8.85 (2H, d, $J = 4.4$ Hz), 8.24–8.15 (4H, m), 7.75–7.61 (7H, m), 7.28 (2H, dd, $J_{\text{HF}} = 8.3$ Hz, $J_{\text{HH}} = 6.8$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.6 (2C, dd, $J_{\text{CF}} = 247.0, 6.2$ Hz), 150.3, 150.0, 149.5, 149.4, 143.1, 134.5, 132.3, 132.0, 131.5, 130.1 (1C, t, $J_{\text{CF}} = 9.9$ Hz), 130.0, 127.1, 126.2, 120.5 (1C, t, $J_{\text{CF}} = 21.5$ Hz), 120.2, 110.8 (2C, dd, $J_{\text{CF}} = 19.0, 6.6$ Hz), 106.3, 105.0; ^{19}F NMR (CDCl_3 , 466 MHz) δ -110.5 (2F, ddd,

$J_{\text{FF}} = 7.8$ Hz, $J_{\text{FH}} = 8.5, 5.6$ Hz); IR (KBr) 3062, 3024, 2970, 2877, 2742, 1589, 1462, 1315, 1065, 995, 849, 787, 710 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 416.5 (5.6), 545.5 (4.2) nm; HRMS (EI) calcd. for $\text{C}_{38}\text{H}_{22}\text{F}_2\text{N}_4\text{Zn}$ 636.1104, found 636.1097.

[10-(2,6-Difluoro-4-methoxyphenyl)-5,15-diphenylporphyrinato]zinc(II) (**Zn-6**). Prepared from bromoporphyrin **1a** (100.2 mg) and bis(2,6-difluoro-4-methoxyphenyl)zinc following the general procedure; Red-purple solid; 117.6 mg, 95% yield; $R_f = 0.47$ (1:1 hexane/toluene); ^1H NMR (CDCl_3 , 400 MHz) δ 10.06 (1H, s), 9.23 (2H, d, $J = 4.4$ Hz), 8.95 (2H, d, $J = 4.4$ Hz), 8.89 (2H, d, $J = 4.4$ Hz), 8.86 (2H, d, $J = 4.4$ Hz), 8.21–8.12 (4H, m), 7.71 (2H, d, $J_{\text{HF}} = 8.3$ Hz), 7.70–7.62 (6H, m), 4.23 (3H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.6 (2C, dd, $J_{\text{CF}} = 249.1, 6.6$ Hz), 150.2, 150.0, 149.8, 149.0, 143.1, 138.5 (1C, t, $J_{\text{CF}} = 9.1$ Hz), 136.0 (1C, t, $J_{\text{CF}} = 14.1$ Hz), 134.5, 132.2, 131.8, 131.5, 130.7, 127.1, 126.2, 120.2, 118.5 (2C, dd, $J_{\text{CF}} = 16.1, 7.0$ Hz), 117.4, 105.7, 61.8; ^{19}F NMR (CDCl_3 , 466 MHz) δ -133.0 (2F, dd, $J_{\text{FF}} = 8.0$ Hz, $J_{\text{FH}} = 5.5$ Hz); IR (KBr) 3059, 3020, 2951, 2862, 1574, 1516, 1435, 1346, 1246, 999, 860, 791, 748, 702 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 417.5 (5.6), 547.0 (4.2) nm; HRMS (EI) calcd for $\text{C}_{39}\text{H}_{24}\text{F}_2\text{N}_4\text{OZn}$ 666.1210, found 666.1210.

[5,15-Diphenyl-10-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)porphyrinato]zinc(II) (**Zn-7**). Prepared from bromoporphyrin **1a** (100.2 mg) and bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)zinc following the general procedure; Red-purple solid; 96.5 mg, 70% yield; $R_f = 0.65$ (1:1 hexane/toluene); ^1H NMR (CDCl_3 , 400 MHz) δ 10.13 (1H, s), 9.24 (2H, d, $J = 4.6$ Hz), 8.95 (2H, d, $J = 4.6$ Hz), 8.95 (2H, d, $J = 4.6$ Hz), 8.77 (2H, d, $J = 4.6$ Hz), 8.20–8.10 (4H, m), 7.74–7.61 (6H, m); ^{13}C NMR (CDCl_3 , 100 MHz) δ 150.7, 150.0, 149.7, 148.1, 146.6 (2C, d, $J_{\text{CF}} = 248.3$ Hz), 143.8 (2C, d, $J_{\text{CF}} = 260.7$ Hz), 142.7, 134.6 (1C, q, $J_{\text{CF}} = 29.8$ Hz), 134.5, 133.1, 132.3, 131.8, 128.8, 127.3, 126.3, 121.2 (1C, q, $J_{\text{CF}} = 274.8$ Hz), 120.8, 109.8, 107.3, 99.9; ^{19}F NMR (CDCl_3 , 466 MHz) δ -57.6 (3F, t, $J_{\text{FF}} = 22.3$ Hz), -137.2 (2F, dd, $J_{\text{FF}} = 21.4, 7.6$ Hz), -143.4 (2F, qdd, $J_{\text{FF}} = 22.3, 21.4, 8.7$ Hz); IR (KBr) 3059, 1643, 1462, 1319, 1146, 991, 957, 748, 702 cm^{-1} ; UV/vis (CHCl_3) λ_{max} (log ϵ) 418.0 (5.7), 547.5 (4.3) nm; HRMS (EI) calcd for $\text{C}_{39}\text{H}_{19}\text{F}_7\text{N}_4\text{Zn}$ 740.0789, found 740.0794.

4. Conclusions

In summary, we have developed an efficient and facile palladium-catalyzed polyfluorophenylation of porphyrins. The success of this reaction relies on the use of readily accessible bis(polyfluorophenyl)zinc reagents as the polyfluorophenylation agent; furthermore, *t*- Bu_3P was the only effective ligand. The method is compatible with a wide array of free-base *meso*-mono-, *meso*-di-, and β -bromo-substituted porphyrins, their metal complexes, and a variety of bis(polyfluorophenyl)zinc reagents. The reaction generally achieves good to excellent yields. We anticipate that this method will find broad application among practitioners of porphyrin chemistry.

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Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

1. Shinokubo, H.; Osuka, A. Marriage of Porphyrin Chemistry with Metal-Catalysed Reactions. *Chem. Commun.* **2009**, 1011–1021.
2. Lindsey, J.S. Synthetic Routes to *meso*-Patterned Porphyrins. *Acc. Chem. Res.* **2010**, *43*, 300–311.
3. Senge, M.O. Stirring the Porphyrin Alphabet Soup—Functionalization Reactions for Porphyrins. *Chem. Commun.* **2011**, *47*, 1943–1960.
4. Yorimitsu, H.; Osuka, A. Organometallic Approaches for Direct Modification of Peripheral C–H Bonds in Porphyrin Cores. *Asian J. Org. Chem.* **2013**, *2*, 356–373.
5. Takanami, T. Functionalization of Porphyrins through C–C Bond Formation Reactions with Functional Group-Bearing Organometallic Reagents. *Heterocycles* **2013**, *87*, 1659–1689.
6. Sugita, N.; Hayashi, S.; Hino, F.; Takanami, T. Palladium-Catalyzed Kumada Coupling Reaction of Bromoporphyrins with Silylmethyl Grignard Reagents: Preparation of Silylmethyl-substituted Porphyrins as a Multipurpose Synthone for Fabrication of Porphyrin Systems. *J. Org. Chem.* **2012**, *77*, 10488–10497.
7. *The Porphyrin Handbook*; Kadish, K.M., Smith, K.M., Guillard, R., Eds.; Academic Press: San Diego, CA, USA, 1999–2003; Volume 1–20.
8. *Handbook of Porphyrin Science*; Kadish, K.M., Smith, K.M., Guillard, R., Eds.; World Scientific: Singapore, 2010; Volume 1–25.
9. Che, C.-M.; Lo, V.K.-Y.; Zhou, C.-Y.; Huang, J.-S. Selective Functionalisation of Saturated C–H Bonds with Metalloporphyrin Catalysts. *Chem. Soc. Rev.* **2011**, *40*, 1950–1975.
10. Lu, H.; Zhang, X.P. Catalytic C–H Functionalization by Metalloporphyrins: Recent Developments and Future Directions. *Chem. Soc. Rev.* **2011**, *40*, 1899–1909.
11. Takanami, T.; Suda, K. Metalloporphyrins and Phthalocyanines as Efficient Lewis Acid Catalysts with a Unique Reaction-Field. *J. Synth. Org. Chem. Jpn.* **2009**, *67*, 595–605.
12. Tachinami, T.; Nishimura, T.; Ushimaru, R.; Noyori, R.; Naka, H. Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 50–53.
13. Fujiwara, K.; Kurahashi, T.; Matsubara, S. Cationic Iron(III) Porphyrin-Catalyzed [4 + 2] Cycloaddition of Unactivated Aldehydes with Simple Dienes. *J. Am. Chem. Soc.* **2012**, *134*, 5512–5515.
14. Liu, W.; Huang, X.; Cheng, M.-J.; Nielsen, R.J.; Goddard III, W.A.; Groves, J.T. Oxidative Aliphatic C–H Fluorination with Fluoride Ion Catalyzed by a Manganese Porphyrin. *Science* **2012**, *337*, 1322–1325.

15. Therrien, B. Transporting and Shielding Photosensitisers by Using Water-Soluble Organometallic Cages: A New Strategy in Drug Delivery and Photodynamic Therapy. *Chem. Eur. J.* **2013**, *19*, 8378–8386.
16. Kamkaew, A.; Lim, S.H.; Lee, H.B.; Kiew, L.V.; Chung, L.Y.; Burgess, K. BODIPY Dyes in Photodynamic Therapy. *Chem. Soc. Rev.* **2013**, *42*, 77–88.
17. Ethirajan, M.; Chen, P.; Ohulchanskyy, T.Y.; Goswami, L.N.; Gupta, A.; Srivatsan, A.; Dobhal, M.P.; Missert, J.R.; Prasad, P.N.; Kadish, K.M.; *et al.* Regioselective Synthesis and Photophysical and Electrochemical Studies of 20-Substituted Cyanine Dye–Purpurinimide Conjugates: Incorporation of Ni^{II} into the Conjugate Enhances its Tumor-Uptake and Fluorescence-Imaging Ability. *Chem. Eur. J.* **2013**, *19*, 6670–6684.
18. Kumar, D.; Mishra, B.A.; Chandra Shekar, K.P.; Kumar, A.; Kusaka, E.; Ito, T. Remarkable Photocytotoxicity of a Novel Triazole-Linked Cationic Porphyrin- β -Carboline Conjugate. *Chem. Commun.* **2013**, *49*, 683–685.
19. Son, H.-J.; Jin, S.; Patwardhan, S.; Wezenberg, S.J.; Jeong, N.C.; So, M.; Wilmer, C.E.; Sarjeant, A.A.; Schatz, G.C.; Snurr, R.Q.; *et al.* Light-Harvesting and Ultrafast Energy Migration in Porphyrin-Based Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2013**, *135*, 862–869.
20. Bandi, V.; Ohkubo, K.; Fukuzumi, S.; D'Souza, F. A Broad-Band Capturing and Emitting Molecular Triad: Synthesis and Photochemistry. *Chem. Commun.* **2013**, *49*, 2867–2869.
21. Adams, H.; Chekmeneva, E.; Hunter, C.A.; Misuraca, M.C.; Navarro, C.; Turega, S.M. Quantification of the Effect of Conformational Restriction on Supramolecular Effective Molarities. *J. Am. Chem. Soc.* **2013**, *135*, 1853–1863.
22. Matsumura, M.; Tanatani, A.; Azumaya, I.; Masu, H.; Hashizume, D.; Kagechika, H.; Muranaka, A.; Uchiyama, M. Unusual Conformational Preference of an Aromatic Secondary Urea: Solvent-Dependent Open-Closed Conformational Switching of *N,N'*-Bis(porphyrinyl)urea. *Chem. Commun.* **2013**, *49*, 2290–2292.
23. Berova, N.; Pescitelli, G.; Petrovica, A.G.; Pronic, G. Probing Molecular Chirality by CD-Sensitive Dimeric Metalloporphyrin Hosts. *Chem. Commun.* **2009**, 5958–5980.
24. Hembury, G.A.; Borovkov, V.V.; Inoue, Y. Chirality-Sensing Supramolecular Systems. *Chem. Rev.* **2008**, *108*, 1–73.
25. Borhan *et al.* reported that incorporation of pentafluorophenyl groups onto the *meso* carbons of porphyrin zinc complexes can significantly lower the LUMO energy and thus increase the Lewis acidity compared to their non-fluorinated analogues, see: ref [27].
26. Rao, P.D.; Dhanalekshmi, S.; Littler, B.J.; Lindsey, J.S. Rational Syntheses of Porphyrins Bearing up to Four Different Meso Substituents. *J. Org. Chem.* **2000**, *65*, 7323–7344.
27. Li, X.; Tanasova, M.; Vasileiou, C.; Borhan, B. A Powerful Reporter of Absolute Configuration for *erythro* and *threo* Diols, Amino Alcohols, and Diamines. *J. Am. Chem. Soc.* **2008**, *130*, 1885–1893.
28. Fang, Z.; Breslow, R. Metal Coordination-Directed Hydroxylation of Steroids with a Novel Artificial P-450 Catalyst. *Org. Lett.* **2006**, *8*, 251–254.
29. Dogutan, D.K.; Bediako, D.K.; Teets, T.S.; Schwalbe, M.; Nocera, D.G. Efficient Synthesis of Hangman Porphyrins. *Org. Lett.* **2010**, *12*, 1036–1039.

30. Jurow, M.; Farley, C.; Pabon, C.; Hageman, B.; Dolor, A.; Drain, C.M. Facile Synthesis of a Flexible Tethered Porphyrin Dimer That Preferentially Complexes Fullerene C₇₀. *Chem. Commun.* **2012**, *48*, 4731–4733.
31. Ashburn, B.O.; Carter, R.G. Diels–Alder Approach to Polysubstituted Biaryls: Rapid Entry to Tri- and Tetra-ortho-substituted Phosphorus-Containing Biaryls. *Angew. Chem. Int. Ed.* **2006**, *45*, 6737–6741.
32. Korenaga, T.; Kosaki, T.; Fukumura, R.; Ema, T.; Sakai, T. Suzuki-Miyaura Coupling Reaction Using Pentafluorophenylboronic Acid. *Org. Lett.* **2005**, *7*, 4915–4917.
33. Molander, G.A.; Biolatto, B. Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions of Potassium Aryl- and Heteroaryltrifluoroborates. *J. Org. Chem.* **2003**, *68*, 4302–4314.
34. Frohn, H.-J.; Adonin, N.Y.; Bardimb, V.V.; Starichenko, V.F. Highly Efficient Cross-Coupling Reactions with the Perfluoroorganotrifluoroborate Salts K [R_FBF₃] (R_F = C₆F₅, CF₂=CF). *Tetrahedron Lett.* **2002**, *43*, 8111–8114.
35. DiMagno, S.G.; Lin, V.S.-Y.; Therien, M.J. Facile Elaboration of Porphyrins via Metal-Mediated Cross-Coupling. *J. Org. Chem.* **1993**, *58*, 5983–5993.
36. Takanami, T.; Yotsukura, M.; Inoue, W.; Inoue, N.; Hino, F.; Suda, K. A Facile and Efficient Synthesis of Mono- and Bis-Functionalized *meso*-Substituted Porphyrins via Palladium-Catalyzed Negishi Cross-Coupling. *Heterocycles* **2008**, *76*, 439–453.
37. Côté, A.; Charette, A.B. General Method for the Expedient Synthesis of Salt-Free Diorganozinc Reagents Using Zinc Methoxide. *J. Am. Chem. Soc.* **2008**, *130*, 2771–2773.

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