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Brief Communication

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Aluminum Chloride Mediated Alkynylation of Boron Subphthalocyanine Chloride Using Trimethylsilyl-Capped Acetylenes

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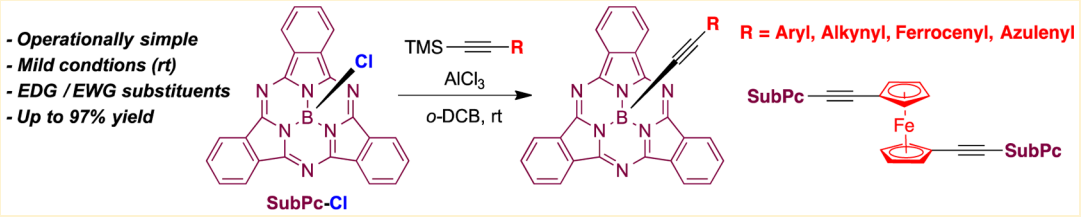
Supporting Information



ABSTRACT: A mild and versatile procedure is presented for functionalization of boron chloride subphthalocyanine at the axial boron position with trimethylsilyl-protected alkyne nucleophiles in the presence of aluminum chloride. The method allows a large variety of substituents on the alkyne units, including electron-donating/withdrawing aryl groups, silyl-protected alkynyl groups, as well as ferrocenyl and azulenyl groups. In addition, ferrocene itself reacts smoothly under these conditions allowing for directly anchoring it to the boron of the subphthalocyanine.

Subphthalocyanines (SubPc's) are redox-active chromophores, which are readily synthesized in a cyclotrimerization reaction of phthalonitrile in the presence of boron trichloride,[1] and they have for these reasons found significant interest as molecular entities for organic photovoltaics.[2−6] To advance their use, efficient functionalization methods are pursued,[3] for example, at the axial boron position. An important protocol has been developed for substitution of the chloride of the readily achievable boron chloride SubPc (**SubPc-Cl**)[1] via the triflate intermediate.[7] Direct attachment of an acetylide to the boron, forming a SubPc-C≡C-R compound, is possible via Grignard reactions, which preclude, however, the use of base-sensitive or electrophilic substrates.[6,8−10] The noninvertible nature of the boron center of SubPc is reminiscent of other systems such as adamantyl bromide[11] and perchloroazatriquinacene,[12] both of which have been shown to undergo $AlCl_3$-mediated substitution reactions. Indeed, Morse and Bender[13] have demonstrated the use of $AlCl_3$ in axial functionalization of **SubPc-Cl** with oxygen-, sulfur-, and nitrogen-based nucleophiles. Furthermore, Torres and co-workers[14] have recently shown that trimethylsilyl (TMS) capped nucleophiles can be added axially to **SubPc-Cl** with the expulsion of volatile trimethylsilyl chloride as the driving force. Rather harsh conditions were, however, necessary (reflux in toluene or nitrobenzene), and the conditions did not allow (trimethylsilyl)acetylenes as substrates. Inspired by the work of Bender and Torres, we sought to expand upon the axial reactivity of **SubPc-Cl** toward trimethylsilyl-protected terminal alkynes assisted by $AlCl_3$.

We treated **SubPc-Cl** with a large selection of TMS-protected alkynes (**1a−k**) in the presence of $AlCl_3$ in *o*-dichlorobenzene (*o*-DCB) at room temperature, which furnished the SubPc products **2a−k** (Scheme 1), in generally good to high yields as listed in Table 1 (only **2d** was isolated in rather low yield), but with various reaction times needed (until no further change was observed by TLC inspection, not always corresponding to complete reaction). Gratifyingly, both electron-poor and electron-rich TMS-protected arylacetylenes turned out to be reactive under these conditions (entries 1−5). In addition, the aryl triflate **1f** (prepared in two steps from 4-bromo-2,6-dimethylphenol, see the Experimental Section) was almost quantitatively converted to the product **2f** (entry 6). We do not attribute the modest yield of the dimethylaniline product **2d** (entry 4) to an inefficient reaction as spot-to-spot conversion was observed by TLC, but rather to stability issues of the product toward silica gel during chromatographic purification.

The procedure was also successful toward alkyne substrates **1g** and **1h**, furnishing the desired products **2g** and **2h** in yields of 65 and 97%, respectively (entries 7 and 8). These products are like the iodide **2b** and triflate **2f** potential building blocks for further acetylenic scaffolding. We have recently shown that a terminal alkyne at the axial position, separated by a CH_2CH_2O spacer to boron, is a convenient handle for a variety of metal-catalyzed cross-coupling reactions.[15]

Ferrocene is often used in conjunction with SubPc, targeting systems for which light-induced charge-separation can be achieved,[8,16−19] and therefore, we wanted to explore the procedure's susceptibility toward substrates incorporating ferrocene. Using an excess of the readily achievable mono-/

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Scheme 1. Axial Functionalization of Boron Subphthalocyanine (for Yields and Details, See Table 1)

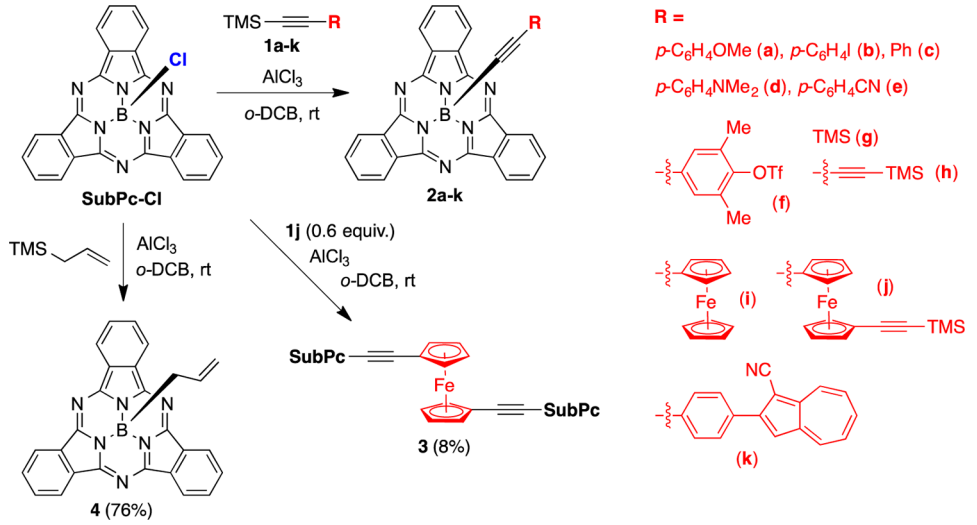

Table 1. Yields of Axially Functionalized Subphthalocyanines (See Scheme 1)

entry	alkyne substrate (equiv)	$AlCl_3$ (equiv)	reaction time (h)	product (yield, %)	recovered alkyne substrate (%)
1	**1a** (10)	5	15	**2a** (69)	
2	**1b** (6)	5	16	**2b** (89)	
3	**1c** (10)	5	17	**2c** (88)	
4	**1d** (10)	5	2	**2d** (28)	
5	**1e** (8)	12	3.5	**2e** (86)	
6	**1f** (10)	5	18	**2f** (93)	
7	**1g** (10)	6	40	**2g** (65)	
8	**1h** (9)	6	0.5	**2h** (97)	
9	**1i** (10)	6	2	**2i** (89)	78
10	**1j** (9)	6	2	**2j** (57)	51
11	**1j** (0.6)	3	4	**3** (8)	
12	**1k** (8)	12	5 days	**2k** (65)	82
13	allyltrimethylsilane (10)	5	17	**4** (76)	

diethynylferrocene substrates **1i** and **1j**,[20,21] **SubPc-Cl** was converted to the SubPc–Fc conjugates **2i** and **2j** (Fc = ferrocenyl) in yields of 78 and 57%, respectively (entries 9 and 10). In the latter case, 4% of the SubPc–Fc–SubPc triad **3** was isolated as well. Conjugate **2i** has previously been prepared in a yield of 26% by Nemykin and co-workers[8] via the Grignard reagent of ethynylferrocene and **SubPc-Cl**, and our procedure hence presents a significant improvement. In addition, by subjecting the substrate **1j** to an excess of **SubPc-Cl** (1.8 equiv), the procedure provided direct access to the triad **3**, albeit only in 8% yield (entry 11). The azulene moiety was readily incorporated via the substrate **1k** (for its preparation, see the Experimental Section), furnishing the conjugate **2k** in a yield of 65% (entry 12). Interestingly, with the cyano-containing substrates **1e** and **1k**, a larger excess of $AlCl_3$ was necessary to carry out the desired substitutions. A possible explanation could be that the $AlCl_3$-reserve is depleted by the CN groups of the TMS nucleophiles. Finally, **SubPc-Cl** was treated with allyltrimethylsilane and $AlCl_3$, which gave the product **4** in a yield of 76% (entry 13). Conveniently, when the TMS-protected alkyne is either expensive or difficult to obtain, the excess can to a large extent be reisolated (entries 9, 10, and 12). In most cases, 8–10 equiv of the alkyne was employed, but entry 2 shows an example with successful conversion using only 6 equiv. The structures of **2a**, **2j**, and **2k** were confirmed by X-ray crystallographic analysis (Figure 1) as was the structure of **2i** (see the Supporting Information; structure has been reported previously[8]). In regard to the optical properties, the variation in axial substitution had little influence on the characteristic longest wavelength SubPc absorption maximum (ca. 566–570 nm in $CHCl_3$; for absorption spectra, see the Supporting Information).

The reaction conditions were also found to facilitate a Friedel–Crafts like reaction between **SubPc-Cl** and parent ferrocene to furnish the SubPc–Fc conjugate **5** in a yield of

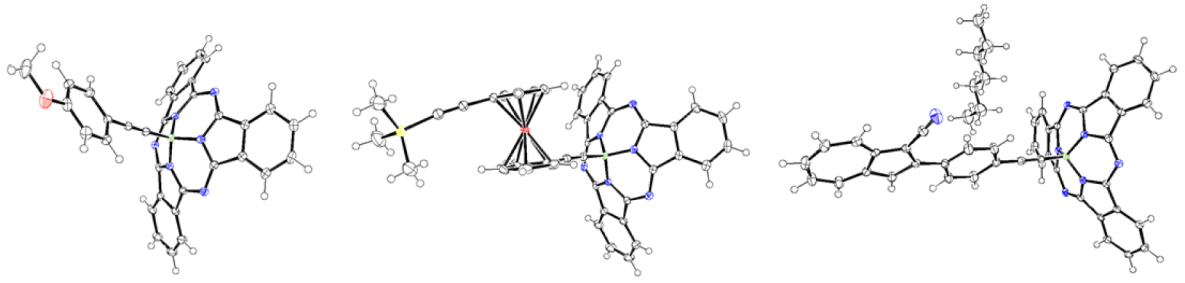

Figure 1. Molecular structures (with displacement ellipsoids at 50% probability for non-H atoms) of **2a** (left; crystals grown from $CHCl_3$/heptane; CCDC 1439146), **2j** (middle; crystals grown from EtOAc/heptane; CCDC 1439351), and **2k** with co-crystallized heptane molecule (right; crystals grown from benzene/heptane; CCDC 1439324).

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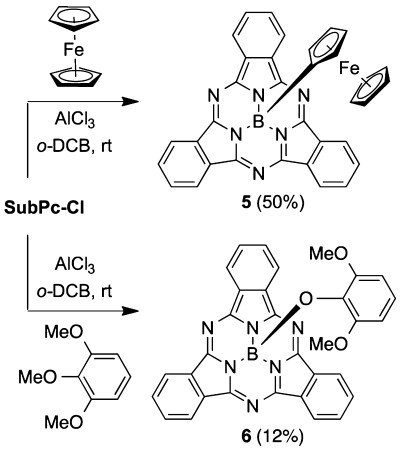
50% where ferrocene is directly anchored to boron (Scheme 2), confirmed by X-ray crystallography (see the Supporting Information). This compound was previously synthesized via the monolithioferrocene and **SubPc-Cl** in a yield of 21%;[8] again, the present procedure is a significant improvement. Finally, 1,2,3-trimethoxybenzene was subjected to the reaction conditions in the hope that this highly activated aromatic substrate would give access to another Friedel–Crafts like product. However, rather than reacting via the C-5 position, the central methoxy group had gone through a demethylation and reacted through the oxygen to form the *O*-substituted SubPc **6**, albeit in low yield.

Scheme 2. Reactions with Ferrocene and 1,2,3-Trimethoxybenzene Nucleophiles



In conclusion, a mild and versatile procedure for the axial functionalization of **SubPc-Cl** with electron-poor/rich TMS-protected alkynes has been developed, allowing for ready preparation of subphthalocyanine-ferrocene/azulene conjugates. The protocol is operationally very simple, not requiring inert conditions. Some of the products, in particular those containing a silylprotected alkyne unit, are potential building blocks for further acetylenic scaffolding.

EXPERIMENTAL SECTION

General Methods. All reagents and solvents were obtained from commercial suppliers and used as received unless otherwise stated. Boron subphthalocyanine chloride (**SubPc-Cl**) was prepared according to a literature procedure.[15] Dry THF was obtained by distillation from a Na/benzophenone couple. Dry pyridine was obtained from storage over KOH. Purification by column chromatography was carried out on silica gel (SiO_2, 60 Å, 40–63 μm). Thin-layer chromatography (TLC) was carried out using commercially available aluminum sheets precoated with silica gel with fluorescence indicator and visualized under UV light at 254 or 360 nm. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz instrument equipped with a noninverse cryoprobe. The ^{11}B NMR spectra were recorded on a 500 MHz instrument equipped with a broad-band probe. Chemical shift values are quoted in ppm and coupling constants (J) in Hz. ^{1}H and ^{13}C NMR spectra are referenced against the residual solvent peak ($CDCl_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm; C_6D_6 δ_H = 7.16 ppm, δ_C = 128.06 ppm). ^{11}B NMR spectra are referenced against an external standard of BF_3 diethyl etherate ($BF_3{\cdot}(OC_2H_5)_2$; δ_B = 0 ppm). HR-MS MALDI spectra were recorded on an ESP-MALDI-FT-ICR instrument equipped with a 7T magnet (prior to the experiments, the instrument was calibrated using NaTFA cluster ions). IR spectra were recorded on an FT-IR instrument using the attenuated total reflectance (ATR) sampling technique, and the measurements were carried out on a thin film of each sample obtained by evaporation from a solution of deuterated chloroform or benzene. UV–vis absorption measurements were performed in a 1 cm path-length cuvette, and the neat solvent was used as baseline; sh = shoulder. All melting points are uncorrected.

4-Bromo-2,6-dimethylphenyl Trifluoromethanesulfonate. To a stirring solution of 4-bromo-2,6-xylenol (1.98 g, 9.84 mmol) in dry pyridine (10 mL) cooled in an ice bath under an argon atmosphere was added dropwise triflic anhydride (2 mL, 11.9 mmol). The cooling bath was removed, and the contents of the vessel were allowed to stir at ambient temperature for 16 h. The contents of the vessel were diluted with Et_2O (50 mL) and washed with aqueous 1 M $CuSO_4$ (3 × 50 mL). The organic phase was dried over $MgSO_4$ and filtered, and the crude oil purified by flash column chromatography (10% CH_2Cl_2/petroleum spirit) afforded the title compound (2.23 g, 68%) as a colorless oil. R_f = 0.49 (10% CH_2Cl_2/petroleum spirit). IR: 2977, 2931, 1606, 1571 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (s, 2H), 2.36 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.9, 133.8, 132.7, 121.5, 118.7 (q, J = 320 Hz), 17.2 ppm. GCMS (EI) m/z: [M, $^{79/81}$Br]$^{\bullet+}$ calcd for $[C_9H_8BrF_3O_3S]^{\bullet+}$ 332 (100), 334 (97), found 332 (98), 334 (100). Anal. Calcd for $C_9H_8BrF_3O_3S$ (333.12): C, 32.45; H, 2.42. Found: C, 32.60; H, 2.27.

*2,6-Dimethyl-4-(trimethylsilyl)ethynyl)phenyl Trifluoromethanesulfonate (**1f**).* To a degassed solution of 4-bromo-2,6-dimethylphenyl trifluoromethanesulfonate (1.08 g, 3.24 mmol), (trimethylsilyl)-acetylene (0.7 mL, 4.9 mmol) in diisopropylamine (30 mL), and THF (50 mL) were added $Pd(PPh_3)_2Cl_2$ (124 mg, 0.177 mmol) and CuI (33 mg, 0.173 mmol), and the resulting mixture was heated to 70 °C for 1 h under inert atmosphere. The solvent was removed under reduced pressure, and the residue subjected to flash column chromatography (10% CH_2Cl_2/heptane) to give **1f** (649 mg, 57%) as a colorless oil. R_f = 0.45 (10% CH_2Cl_2/heptane). IR: 2963, 2901, 2161, 1592 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (s, 2H), 2.35 (s, 6H), 0.24 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.8, 133.4, 131.8, 123.3, 118.7 (q, J = 320 Hz), 103.4, 95.8, 17.1, 0.0 ppm. HRMS (MALDI + ve): m/z [M + Na]$^+$ calcd for $[C_{14}H_{17}F_3O_3SSiNa]^+$ 373.0512, found 373.0545. Anal. Calcd for $C_{14}H_{17}F_3O_3SSi$ (350.43): C, 47.99; H, 4.89. Found: C, 47.72; H, 4.77.

*2-(4-((Trimethylsilyl)ethynyl)phenyl)azulene-1-carbonitrile (**1k**).* To a degassed solution of 2-(4-iodophenyl)azulene-1-carbonitrile[22] (463 mg, 1.30 mmol), (trimethylsilyl)acetylene (1.0 mL, 7.0 mmol) in Et_3N (5 mL), and toluene (30 mL) were added $Pd(PPh_3)_2Cl_2$ (55 mg, 0.078 mmol) and CuI (19 mg, 0.10 mmol), and the resulting mixture was stirred overnight at ambient temperature under inert atmosphere. The solvent was removed under reduced pressure and the residue subjected to column chromatography (90% toluene/heptane) to give **1k** (418 mg, 99%) as a dark purple solid. R_f = 0.38 (90% toluene/heptane). Mp: 158–159.5 °C. IR: 2958, 2898, 2202, 2155, 1604, 1590sh, 1577, 1537 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.64 (dd, J = 9.8, 1.6 Hz, 1H), 8.40 (d, J = 9.8 Hz, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.79 (t, J = 9.8 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.56–7.52 (m, 2H), 7.49 (t, J = 9.8 Hz, 1H), 0.28 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.0, 145.9, 142.6, 139.3, 138.3, 136.1, 134.4, 132.8, 128.5, 128.3, 128.1, 124.3, 118.1, 116.6, 104.8, 96.7, 94.2, 0.1 ppm. HRMS (MALDI + ve): m/z [M]$^{\bullet+}$ calcd for $[C_{22}H_{19}NSi]^{\bullet+}$ 325.1281, found 325.1288. UV–vis ($CHCl_3$) λ_{max} (ε): 632sh, 578 (6.83 × 10^2 M^{-1} cm^{-1}), 549 (6.60 × 10^2 M^{-1} cm^{-1}), 406sh, 391 (1.57 × 10^4 M^{-1} cm^{-1}), 331 (5.69 × 10^4 M^{-1} cm^{-1}), 292sh nm. Anal. Calcd for $C_{22}H_{19}NSi$ (325.49): C, 81.18; H, 5.88; N, 4.30. Found: C, 80.98; H, 5.95; N, 4.30.

Alkynylation of SubPc-Cl. *Compound **2a**.* To a stirring suspension of **SubPc-Cl** (50 mg, 0.12 mmol) and (4-methoxyphenylethynyl)trimethylsilane (0.25 mL, 1.2 mmol) in *o*-dichlorobenzene (4 mL) was added $AlCl_3$ (76 mg, 0.58 mmol), and the resulting mixture was stirred for 15 h at rt. Pyridine (0.1 mL) was added, and the reaction mixture was filtered through a short plug of neutral Brockman I Al_2O_3 using gradient elution from toluene to 10% EtOAc/toluene. The filtrate was concentrated in vacuo, and subjected to flash column chromatography (30% EtOAc/heptane) to furnish **2a** (42 mg, 69%) as a golden brown crystalline solid. Crystals suitable for

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X-ray crystallography were grown from $CHCl_3$/heptane. R_f = 0.35 (5% EtOAc/toluene). Mp > 230 °C. IR: 3060, 3002, 2953, 2932, 2835, 2178, 1603, 1569, 1507 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.86 (dd, J = 5.9, 3.0 Hz, 6H), 7.89 (dd, J = 5.9, 3.0 Hz, 6H), 6.67 (d, J = 9.1 Hz, 2H), 6.46 (d, J = 9.1 Hz, 2H), 3.61 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3, 150.6, 133.0, 131.1, 129.7, 122.2, 114.7, 113.4, 94.2, 55.2 (1C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ −21.3 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{33}H_{20}BN_6O]^+$ 527.1786, found 527.1792. UV−vis ($CHCl_3$) λ_{max} (ε): 568 (8.44 × 10^4 M^{-1} cm^{-1}), 550sh, 520sh, 308 (5.15 × 10^4 M^{-1} cm^{-1}), 269 (4.95 × 10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{33}H_{19}BN_6O$ (526.17): C, 75.30; H, 3.64; N, 15.97; Found: C, 74.96; H, 3.52; N, 16.10.

Compounds **2b−k** and **3−6** were prepared analogously to the above procedure.

Compound ***2b*** *(known compound[9]).* Golden brown crystalline solid (68 mg, 89%). Reactants: **SubPc-Cl** (53 mg, 0.12 mmol), (4-iodophenylethynyl)trimethylsilane (230 mg, 0.77 mmol), and $AlCl_3$ (81 mg, 0.61 mmol). R_f = 0.34 (20% EtOAc/heptane). Mp > 230 °C. IR: 3059, 2922, 2850, 2182, 1613 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.86 (dd, J = 5.9, 3.0 Hz, 6H), 7.89 (dd, J = 5.9, 3.0 Hz, 6H), 7.27 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.4, 136.8, 132.9, 130.9, 129.7, 122.1, 121.9, 93.7 (2C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ −21.3 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{32}H_{17}BIN_6]^+$ 623.0647, found 623.0652. UV−vis ($CHCl_3$) λ_{max} (ε): 569 (8.31 × 10^4 M^{-1} cm^{-1}), 551sh, 521sh, 308 (5.23 × 10^4 M^{-1} cm^{-1}), 531 (5.29 × 10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{32}H_{16}BIN_6$ (622.06): C, 61.77; H, 2.59; N, 13.51; Found: C, 61.85; H, 2.52; N, 13.44.

Compound ***2c***. Golden brown crystalline solid (50 mg, 88%). Reactants: **SubPc-Cl** (50 mg, 0.12 mmol), trimethyl(phenylethynyl)-silane (0.23 mL, 1.2 mmol), and $AlCl_3$ (83 mg, 0.62 mmol). R_f = 0.27 (3% EtOAc/toluene). Mp > 230 °C. IR: 3060, 2924, 2852, 2180, 1739, 1712, 1613, 1596, 1570, 1565 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.86 (dd, J = 5.9, 3.0 Hz, 6H), 7.89 (dd, J = 5.9, 3.0 Hz, 6H), 7.04−6.96 (m, 1H), 6.95−6.90 (m, 2H), 6.75−6.71 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 131.5, 131.0, 129.8, 127.9, 127.8, 122.5, 122.2 (2C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ −21.2 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{32}H_{18}BN_6]^+$ 497.1681, found 497.1687. UV−vis ($CHCl_3$) λ_{max} (ε): 569 (9.61 × 10^4 M^{-1} cm^{-1}), 550sh, 525sh, 308 (5.90 × 10^4 M^{-1} cm^{-1}), 258 (5.08 × 10^4 M^{-1} cm^{-1}) nm.

Compound ***2d***. Brown crystalline solid (19 mg, 28%). Reactants: **SubPc-Cl** (54 mg, 0.12 mmol), *N*,*N*-dimethyl-4-((trimethylsilyl)-ethynyl)aniline (262 mg, 1.21 mmol), and $AlCl_3$ (88 mg, 0.66 mmol). R_f = 0.34 (30% EtOAc/heptane). Mp > 230 °C. IR: 3087, 3058, 2922, 2853, 2806, 2188, 2136sh, 1606, 1520 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.85 (dd, J = 5.9, 3.0 Hz, 6H), 7.88 (dd, J = 5.9, 3.0 Hz, 6H), 6.61 (d, J = 9.1 Hz, 2H), 6.24 (d, J = 9.1 Hz, 2H), 2.77 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 149.8, 132.6, 131.1, 129.6, 122.2, 111.4, 109.4, 40.2 (2C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ −21.2 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{34}H_{23}BN_7]^+$ 540.2103, found 540.2109. UV−vis ($CHCl_3$) λ_{max} (ε): 568 (9.22 × 10^4 M^{-1} cm^{-1}), 550sh, 525sh, 306 (8.21 × 10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{34}H_{22}BN_7$ (539.20): C, 75.71; H, 4.11; N, 18.18. Found: C, 75.90; H, 3.95; N, 17.97.

Compound ***2e***. Golden brown crystalline solid (65 mg, 86%). Reactants: **SubPc-Cl** (62 mg, 0.14 mmol), 4-((trimethylsilyl)ethynyl)-benzonitrile (230 mg, 1.15 mmol), and $AlCl_3$ (232 mg, 1.74 mmol). R_f = 0.32 (25% EtOAc/heptane). Mp > 230 °C. IR: 3087sh, 3060, 2227, 2185, 1613, 1602, 1567 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.86 (dd, J = 5.8, 3.0 Hz, 6H), 7.90 (dd, J = 5.8, 3.0 Hz, 6H), 7.23 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.4, 131.8, 131.4, 130.8, 129.8, 127.4, 122.1, 118.3, 111.0, 92.4 (1C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ −21.3 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{33}H_{17}BN_7]^+$ 522.1633, found 522.1641. UV−vis ($CHCl_3$) λ_{max} (ε): 570 (8.82 × 10^4 M^{-1} cm^{-1}), 552sh, 525sh, 308 (5.74 × 10^4 M^{-1} cm^{-1}), 526 (5.87 × 10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{33}H_{16}BN_7$ (521.16): C, 76.03; H, 3.09; N, 18.81. Found: C, 76.12; H, 3.03; N, 18.71.

Compound ***2f***. Golden brown crystalline solid (83 mg, 93%). Reactants: **SubPc-Cl** (57 mg, 0.13 mmol), **1f** (469 mg, 1.34 mmol), and $AlCl_3$ (88 mg, 0.66 mmol). R_f = 0.36 (25% EtOAc/heptane). Mp > 230 °C. IR: 3060, 2970, 2930, 2182, 1614, 1592 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.86 (dd, J = 5.9, 3.0 Hz, 6H), 7.89 (dd, J = 5.9, 3.0 Hz, 6H), 6.51 (s, 2H), 2.06 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.4, 146.1, 132.6, 131.1, 130.9, 129.7, 122.4, 122.2, 122.1, 119.7, 117.1, 114.6, 92.5, 16.6 (1C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ −21.3 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ Calcd for $[C_{35}H_{21}BF_3N_6O_3S]^+$ 673.1435, found 673.1441. UV−vis ($CHCl_3$) λ_{max} (ε): 569 (7.99 × 10^4 M^{-1} cm^{-1}), 553sh, 525sh, 308 (4.95 × 10^4 M^{-1} cm^{-1}), 261 (4.18 × 10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{35}H_{20}BF_3N_6O_3S$ (672.14): C, 62.52; H, 3.00; N, 12.50. Found: C, 62.60; H, 2.85; N, 12.53.

Compound ***2g***. Deep purple shiny crystalline solid (39.0 mg, 65%). Reactants: **SubPc-Cl** (53 mg, 0.12 mmol), (trimethylsilylethynyl)-trimethylsilane (214 mg, 1.26 mmol), and $AlCl_3$ (99 mg, 0.74 mmol). R_f = 0.34 (20% EtOAc/heptanes). Mp > 230 °C. IR: 2951, 2917, 2849, 2361, 2338 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.85 (dd, J = 5.9, 3.1 Hz, 6H), 7.88 (dd, J = 5.9, 3.1 Hz, 6H), −0.37 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 131.0, 129.7, 128.5, 122.2, 101.3, −0.3 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{29}H_{22}BN_6Si]^+$ 493.1763, found 493.1770. UV−vis ($CHCl_3$) λ_{max} (ε): 569 (8.91 × 10^4 M^{-1} cm^{-1}), 552sh, 527sh, 308 (5.49 × 10^4 M^{-1} cm^{-1}), 272sh nm. Anal. Calcd for $C_{29}H_{21}BN_6Si$ (492.41): C, 70.74; H, 4.30; N, 17.07. Found: C, 70.58; H, 4.39; N, 16.96.

Compound ***2h***. Bright pink solid (85 mg, 97%). Reactants: **SubPc-Cl** (73 mg, 0.170 mmol), 1,4-bis(trimethylsilyl)buta-1,3-diyne (303 mg, 1.56 mmol), and $AlCl_3$ (145 mg, 1.09 mmol). R_f = 0.35 (EtOAc/heptane 1:3). Mp > 230 °C. IR: 3062, 2959, 2079, 1614 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.84 (dd, J = 6.0, 3.0 Hz, 6H), 7.88 (dd, J = 6.0, 3.0 Hz, 6H), −0.08 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.4, 130.9, 129.9, 122.3, 87.5, 84.7, −0.6 (2C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = −21.8 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{31}H_{22}BN_6Si]^+$ 517.1763, found 517.1770. UV−vis ($CHCl_3$) λ_{max} (ε): 570 (8.53 × 10^4 M^{-1} cm^{-1}), 552sh, 526sh, 308 (5.27 × 10^4 M^{-1} cm^{-1}), 278sh nm. Anal. Calcd for $C_{31}H_{21}BN_6Si$ (516.45): C, 72.10; H, 4.10; N, 16.27. Found: C, 71.94; H, 4.02; N, 16.50.

Compound ***2i*** *(Known Compound[8]).* Bright purple solid (93 mg, 89%). In addition, recovered **1i** (378 mg, 78%) was isolated. Reactants: **SubPc-Cl** (74 mg, 0.172 mmol), **1i** (486 mg, 1.72 mmol), and $AlCl_3$ (142 mg, 1.06 mmol). R_f = 0.39 (25% EtOAc/heptane). Mp > 230 °C. IR: 3088, 3059, 2924, 2184, 2170sh, 1613 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.87 (dd, J = 5.9, 3.0 Hz, 6H), 7.89 (dd, J = 5.9, 3.0 Hz, 6H), 3.82 (t, J = 1.9 Hz, 2H), 3.78 (s, 5H), 3.76 (t, J = 1.9 Hz, 2H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = −21.4 ppm. HRMS (MALDI + ve): m/z $[M]^{\bullet+}$ calcd for $[C_{36}H_{21}BFeN_6]^{\bullet+}$ 604.1265, found 604.1272.

Compound ***2j***. Bright purple solid (72 mg, 57%). In addition, the triad **3** (8 mg, 4%) was isolated as a dark purple solid as well as recovered **1j** (327 mg, 51%). Reactants: **SubPc-Cl** (78 mg, 0.181 mmol), **1j** (644 mg, 1.70 mmol), and $AlCl_3$ (137 mg, 1.03 mmol). R_f = 0.31 (25% EtOAc/heptane). Mp > 230 °C. IR: 3086, 3058, 2957, 2895, 2184, 2164, 2149, 1614 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.86 (dd, J = 5.9, 3.1 Hz, 6H), 7.88 (dd, J = 5.9, 3.1 Hz, 6H), 4.06 (t, J = 1.9 Hz, 2H), 3.85 (t, J = 1.9 Hz, 2H), 3.77 (t, J = 1.9 Hz, 2H), 3.73 (t, J = 1.9 Hz, 2H), 0.11 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.5, 131.0, 129.7, 122.2, 103.5, 92.2 (br), 91.0, 73.1, 72.8, 71.7, 71.5, 65.5, 65.3, 0.3 (1C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = −21.3 ppm. HRMS (MALDI + ve): m/z $[M]^{\bullet+}$ Calcd for $[C_{41}H_{29}BFeN_6Si]^{\bullet+}$ 700.1660, found 700.1667. UV−vis ($CHCl_3$) λ_{max} (ε): 568 (8.34 × 10^4 M^{-1} cm^{-1}), 552sh, 525sh, 306 (5.35 × 10^4 M^{-1} cm^{-1}), 272sh nm.

Compound ***2k***. Deep purple solid (51 mg, 67%). In addition, recovered **1k** (248 mg, 82%) was isolated. Reactants: **SubPc-Cl** (50 mg, 0.12 mmol), **1k** (301 mg, 0.925 mmol), and $AlCl_3$ (186 mg, 1.39 mmol). R_f = 0.27 (5% EtOAc/toluene). Mp > 230 °C. IR: 2917, 2849, 2204, 2178, 1738, 1611, 1605, 1575 cm^{-1}. ^1H NMR (500 MHz, C_6D_6) δ 8.78 (dd, J = 5.9, 3.1 Hz, 6H), 8.23 (d, J = 9.8 Hz, 1H), 7.54 (d, J =

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9.8 Hz, 1H), 7.50 (d, J = 8.7 Hz, 2H), 7.40 (dd, J = 5.9, 3.1 Hz, 6H), 6.86 (t, J = 9.8 Hz, 1H), 6.75 (s, 1H), 6.72 (d, J = 8.7 Hz, 2H), 6.60 (t, J = 9.8 Hz, 1H), 6.58 (t, J = 9.8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, C_6D6) δ 151.0, 150.6, 145.37, 141.9, 138.0, 137.3, 135.6, 133.8, 132.4, 131.7, 129.5, 127.2, 127.0, 124.1, 122.1, 117.2, 116.6, 95.3, 94.6 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{43}H_{23}BN_7]^+$ 648.2103, found 648.2112. UV−vis ($CHCl_3$) λ_{max} (ε): 569 (8.25×10^4 M^{-1} cm^{-1}), 552sh, 526sh, 409sh, 393 (1.99×10^4 M^{-1} cm^{-1}), 331 (6.58×10^4 M^{-1} cm^{-1}), 311 (7.85×10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{43}H_{22}BN_7$ (647.51): C, 79.76; H, 3.42; N, 15.14; Found: C, 79.83; H, 3.39; N, 14.92.

Compound **3**. Dark purple solid (20 mg, 8%). Reactants: **SubPc-Cl** (100 mg, 0.232 mmol), **1j** (48 mg, 0.13 mmol), and $AlCl_3$ (88 mg, 0.66 mmol). R_f = 0.54 (5% EtOAc/CH_2Cl_2). Mp > 230 °C. IR: 3063, 2184, 1613 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.82 (dd, J = 5.9, 3.0 Hz, 12H), 7.87 (dd, J = 5.9, 3.0 Hz, 12H), 3.48 (d, J = 1.9 Hz, 4H), 3.31 (d, J = 1.9 Hz, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.5, 131.0, 129.7, 122.2, 77.7, 71.8, 71.7 (2C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = −21.5 ppm. HRMS (MALDI + ve): m/z $[M]^{\bullet+}$ calcd for $[C_{62}H_{32}B_2FeN_{12}]^{\bullet+}$ 1022.2403, found 1022.2412. UV−vis ($CHCl_3$) λ_{max} (ε): 567.5 (1.36×10^5 M^{-1} cm^{-1}), 550sh, 518sh, 307 (8.87×10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{62}H_{32}B_2FeN_{12}$ (1022.49): C, 72.83; H, 3.15; N, 16.44; Found: C, 72.79; H, 2.94; N, 16.28.

Compound **4**. Brown crystalline solid (42 mg, 76%). Reactants: **SubPc-Cl** (54 mg, 0.12 mmol), allyltrimethylsilane (0.20 mL, 1.2 mmol), and $AlCl_3$ (88 mg, 0.66 mmol). R_f = 0.31 (20% EtOAc/toluene). Mp > 230 °C. IR: 3061, 2966, 2913, 2869, 1726, 1628, 1612, 1584 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82 (dd, J = 5.9, 3.0 Hz, 6H), 7.86 (dd, J = 5.9, 3.0 Hz, 6H), 4.20−4.08 (m, 2H), 3.83−3.74 (m, 1H), −1.16 (d, J = 5.6 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 133.3, 130.9, 129.6, 122.1, 113.6, 25.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ −15.8 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{27}H_{18}BN_6]^+$ 437.1681, found 437.1687. UV−vis ($CHCl_3$) λ_{max} (ε): 566 (8.83×10^4 M^{-1} cm^{-1}), 549sh, 522sh, 311 (4.54×10^4 M^{-1} cm^{-1}) nm.

Compound **5** *(Known Compound*[8]*)*. Bright purple solid (50 mg, 50%). In addition, recovered ferrocene (230 mg, 75%) was isolated. Reactants: **SubPc-Cl** (74 mg, 0.172 mmol), ferrocene (305 mg, 1.64 mmol), and $AlCl_3$ (145 mg, 1.09 mmol). R_f = 0.39 (25% EtOAc/heptane). Mp > 230 °C. IR: 3087, 3059, 1613 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.86 (dd, J = 5.9, 3.1 Hz, 6H), 7.89 (dd, J = 5.9, 3.1 Hz, 6H), 3.56 (s, 5H), 3.50 (t, J = 1.8 Hz, 2H), 2.37 (t, J = 1.8 Hz, 2H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = −16.1 ppm. HRMS (MALDI + ve): m/z $[M]^{\bullet+}$ calcd for $[C_{34}H_{21}BFeN_6]^{\bullet+}$ 580.1265, found 580.1272.

Compound **6**. Bright pink solid (12 mg, 12%). Reactants: **SubPc-Cl** (78 mg, 0.181 mmol), 1,2,3-trimethoxybenzene (297 mg, 1.77 mmol), and $AlCl_3$ (142 mg, 1.06 mmol). R_f = 0.30 (33% EtOAc/heptane). Mp > 230 °C. IR: 3059, 2956, 2927, 2853, 2834, 1727, 1614, 1594 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.83 (dd, J = 5.9, 3.0 Hz, 6H), 7.87 (dd, J = 5.9, 3.0 Hz, 6H), 6.55 (t, J = 8.3 Hz, 1H), 6.03 (d, J = 8.3 Hz, 2H), 3.23 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.1, 150.8, 131.2, 129.6, 122.2, 122.0, 104.4, 55.5 (1C missing) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = −15.3 ppm. HRMS (MALDI + ve): m/z $[M + H]^+$ calcd for $[C_{32}H_{22}BN_6O_3]^+$ 549.1841, found 549.1849. UV−vis ($CHCl_3$) λ_{max} (ε): 564 (8.63×10^4 M^{-1} cm^{-1}), 546sh, 522sh, 304 (3.71×10^4 M^{-1} cm^{-1}), 269 (3.50×10^4 M^{-1} cm^{-1}) nm. Anal. Calcd for $C_{32}H_{21}BN_6O_3$ (548.37): C, 70.09; H, 3.86; N, 15.33. Found: C, 70.11; H, 3.93; N, 15.41.

■ ASSOCIATED CONTENT

Supporting Information

TThe Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02719.

NMR and UV−vis absorption spectra (PDF)
X-ray data for **2a** (CIF)
X-ray data for **2j** (CIF)
X-ray data for **2k** (CIF)
X-ray data for **2i** (CIF)
X-ray data for **5** (CIF)

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Notes

The authors declare no competing financial interest.

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