Synthesis of *meso*-Substituted Tetraarylalkynylporphyrins via Rhenium-Catalyzed Formation of Naphthalene Units

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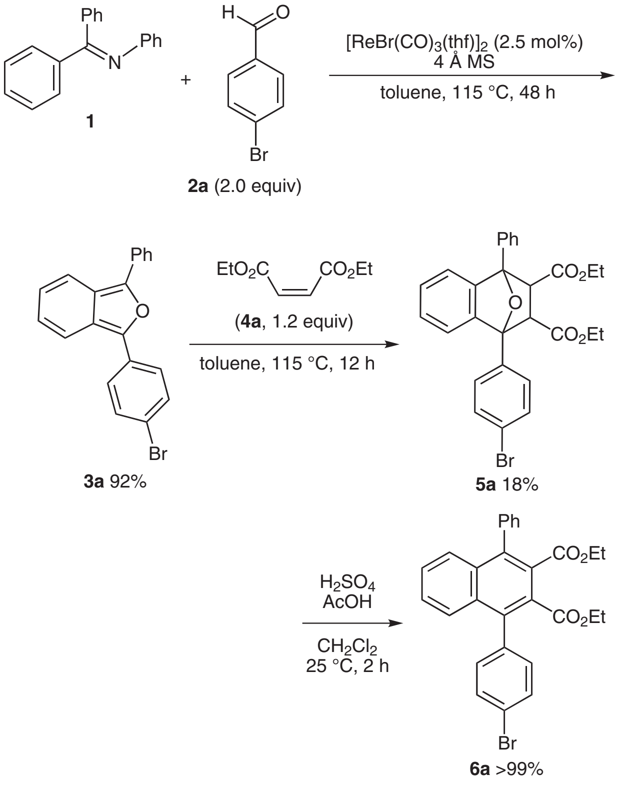
Abstract: Rhenium-catalyzed synthesis of naphthalene-substituted aryl bromides or iodides via C–H bond activation, and its use for palladium-catalyzed cross-coupling reactions with tetraethynylporphyrin are described. A series of novel *meso*-substituted tetraalkynylporphyrins with naphthalene moieties were obtained.

Key words: rhenium catalyst, C–H bond activation, naphthalene derivative, Sonogashira coupling, *meso*-substituted tetraalkynylporphyrin

The continuing interest in porphyrins can be explained by their peculiar optical and electronic properties that make them attractive targets as physiologically active compounds[1] and for a variety of applications.[2] Thus, porphyrin derivatives with conjugated connections at the *meso* positions have attracted much interest for their potential applications in electronic materials such as nonlinear optics[3,4] and light harvesting.[5] Electronic distributions in the porphyrin rings can be easily modified by changing the peripheral substituents, which influence the physicochemical and conformational properties of the porphyrin derivatives.[6] The synthesis of *meso*-tetraarylporphyrins has been intensively studied.[7] In contrast, extending the π-conjugate systems of porphyrin cores with aryl groups by linking them with acetylene bridges is one of the most efficient methods for extending the π-conjugate systems between aryl substituents and porphyrin macrocycles.[5,8] Since the acetylene cores are linear, the structures cannot be twisted to break the conjugation with the porphyrin skeletons. In this paper, we present our strategy for the synthesis of functionalized aryl halides that could be coupled with *meso*-tetraethynylporphyrin to afford a new family of *meso*-tetraarylalkynylporphyrins.

Recently, we reported a rhenium-catalyzed synthesis of naphthalene skeletons via C–H bond activation.[9] Due to our continuing interests in rhenium-catalyzed synthesis of multisubstituted aromatic compounds,[10] we decided to investigate the synthesis of our target molecules based on this C–H bond transformation. Treatment of aromatic ketimine **1**, 4-bromobenzaldehyde (**2a**), and molecular sieves with a catalytic amount of a rhenium complex, [ReBr(CO)$_3$(thf)]$_2$, in toluene at 115 °C gave isobenzofuran derivative **3a** in 92% yield (Scheme 1). The isobenzofuran **3a** was trapped with diethyl maleate (**4a**) by a Diels–Alder reaction to afford Diels–Alder adduct **5a** in only 18% yield due to its instability. In fact, **5a** was decomposed during the purification by column chromatography on silica gel. Therefore, the problem can be solved by one-pot operation as described in Table 1 (entry 1). The Diels–Alder adduct was exposed to acidic conditions causing dehydrative aromatization, and the functionalized naphthalene derivative with a bromine atom (**6a**) was obtained quantitatively. The bromine atom was retained in these reaction steps.



Scheme 1

By the reaction of aromatic ketimine **1**, 4-iodobenzaldehyde (**2b**), and *N*-methylmaleimide (**4b**) as a dienophile in the presence of catalytic amounts of the rhenium complex and molecular sieves, the Diels–Alder adduct **5b** was isolated in 91% yield. Diene formation was not affected by the presence of maleimide **4b**. The Diels–Alder adduct

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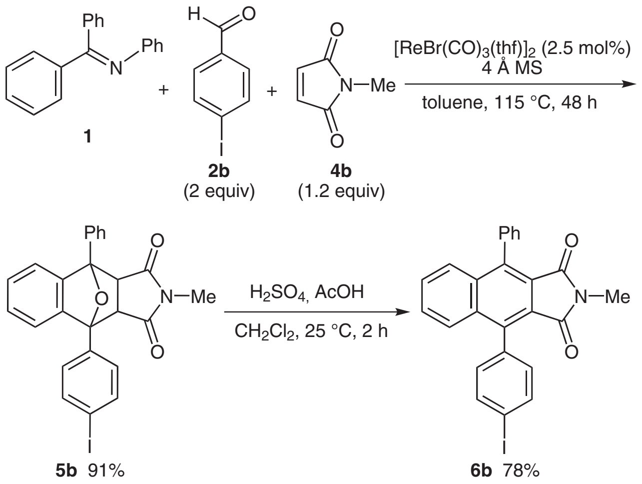
was treated with sulfuric acid and acetic acid in dichloromethane at room temperature for 2 hours. As a result, the desired naphthalene derivative bearing an iodine atom (**6b**) was afforded in 78% yield (Scheme 2). These reactions proceeded without loss of the iodine atom.

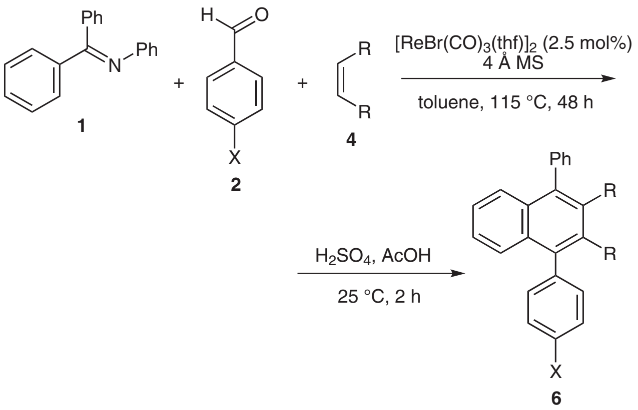


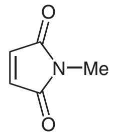
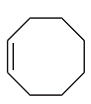
Scheme 2

The generality of this methodology was further extended to the one-pot synthesis of naphthalene derivatives with a halogen atom. Treatment of aromatic ketimine **1**, 4-bromobenzaldehyde (**2a**), olefin **4a**, and molecular sieves (4 Å) with a catalytic amount of [ReBr(CO)$_3$(thf)]$_2$ in toluene at 115 °C for 48 hours and successive dehydration under acidic conditions led to the corresponding naphthalene derivative **6a** in 78% yield without isolation of the formed Diels–Alder adduct **5a** (Table 1, entry 1). The one-pot synthesis of the naphthalene derivative bearing a halogen atom is advantageous compared with the stepwise method (Scheme 1) from the viewpoint of easy procedure and good total yield. By using this method, the corresponding naphthalene derivatives **6** with several types of substituents were obtained in good to excellent overall yields (Table 1, entries 2–8). Substituents such as esters and amides were tolerated under the reaction conditions and no significant electronic and/or steric effects were observed for the olefin substituents. In addition, it is noteworthy that aryl halides remain intact under the rhenium catalysis.

The preparation of 5,10,15,20-*meso*-tetraethynylporphyrin **8** by desilylation of porphyrin derivative **7**[11] using tetrabutylammonium fluoride is a key step for applying the Sonogashira cross-coupling towards the construction of the extended conjugated porphyrin derivatives.[12] When naphthalene derivatives with bromine atoms (**6a** and **6c**) were used to couple with 5,10,15,20-*meso*-tetraethynylporphyrin **8**, a complex mixture of porphyrins was obtained. In contrast, the desired porphyrin derivatives could be synthesized easily using the naphthalene-substituted aryl iodides as shown in Table 2. The coupling reaction of porphyrin **8** with aryl iodide **6d** was carried out in a mixture of triethylamine and THF using palladium complex Pd$_2$(dba)$_3$ and AsPh$_3$, resulting in efficient formation of the desired *meso*-substituted tetraarylalkynylporphyrin **9a** in 92% yield (Table 2, entry 1). UV-vis spectra of *meso*-tetraethynylporphyrin **8** and *meso*-tetraarylalkynylporphyrin **9a** were measured. As a result, the absorptions were observed at λ = 450 nm and 475 nm, respectively, and long-wavelength shift was caused by introducing the naphthalene moieties. These results indicate that the π-conjugate system is expanded by the connection between porphyrin and naphthalene skeletons using the alkyne moieties. In a similar manner, other *meso*-substituted tetraarylalkynylporphyrins **9b**–**f** could be synthesized in moderate to good yields (Table 2, entries 2–6).

Table 1 One-Pot Synthesis of Naphthalene Derivatives with a Halogen Atom[a]

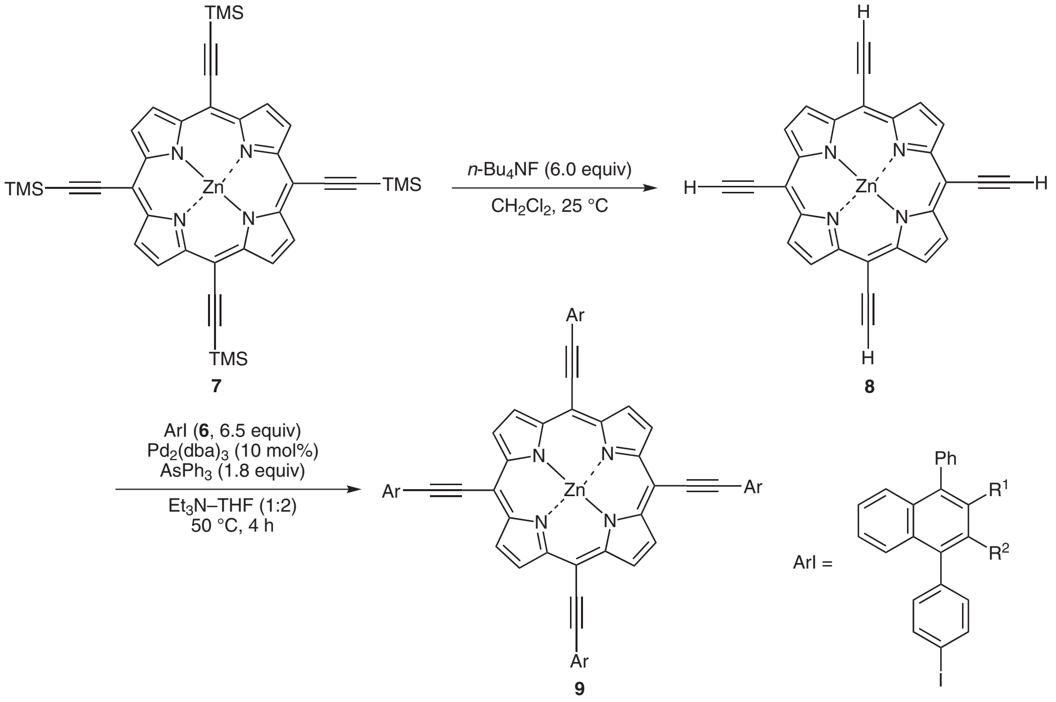


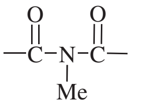
Entry	Aldehyde **2**	Olefin **4**	Product **6**	Yield (%)
1	**2a** X = Br	**4a** R = CO$_2$Et	**6a**	78
2	**2a**	**4c** R = CO$_2$Me	**6c**	64
3	**2b** X = I	**4a** R = CO$_2$Et	**6d**	66
4	**2b**	**4c** R = CO$_2$Me	**6e**	58
5	**2b**	**4d** R = CO$_2$*n*-Bu	**6f**	71
6	**2b**	**4e** R = *n*-Pr	**6g**	34
7	**2b**	 **4b**	**6b**	72
8	**2b**	 **4f**	**6h**	94

[a] Conditions: aldehyde **2** (2 equiv), olefin **4** (1.2 equiv).

In summary, we have succeeded in the one-pot synthesis of naphthalene derivatives with a bromine or iodine atom via C–H bond activation by the reaction of *N*-(diphenylmethylene)aniline and 4-halobenzaldehydes with dienophiles in the presence of the rhenium catalyst [ReBr(CO)$_3$(thf)]$_2$ and successive dehydration.[13] The coupling reaction of the naphthalene derivatives with *meso*-tetraethynylporphyrin provided a series of extended conjugated *meso*-tetraarylalkynylporphyrins.[14] These new compounds are expected to show high potential as new functional materials for optical memories and solar cell devices. Optical and electrochemical properties of synthesized *meso*-tetraarylalkynylporphyrins are under way.

Table 2 Coupling Reactions of *meso*-Tetraethynylporphyrin **8** with Aryl Iodides **6**



Entry	ArI	R^1	R^2	Yield (%)
1	**6d**	CO_2Et	CO_2Et	**9a** 92
2	**6e**	CO_2Me	CO_2Me	**9b** 93
3	**6f**	CO_2*n*-Bu	CO_2*n*-Bu	**9c** 86
4	**6g**	*n*-Pr	*n*-Pr	**9d** 51
5	**6b**	 $—\overset{O}{\overset{\Vert}{C}}—\underset{\underset{Me}{\vert}}{N}—\overset{O}{\overset{\Vert}{C}}—$		**9e** 56
6	**6h**	$–(CH_2)_6–$		**9f** 81

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(13) **General Procedure for the Synthesis of Naphthalene Derivatives 6 by One-Pot Reaction**
A mixture of *N*-(diphenylmethylene)aniline (**1**, 129 mg, 0.500 mmol), 4-bromobenzaldehyde (**2a**, 1.00 mmol) or 4-iodobenzaldehyde (**2b**, 1.00 mmol), olefin (**4**, 0.600 mmol), 4 Å MS (200 mg), $[\mathrm{ReBr(CO)_3(thf)}]_2$ (10.6 mg, 0.0125 mmol), and toluene (1.0 mL) was stirred at 115 °C for 48 h. Then, AcOH (3.0 mL) and H_2SO_4 (1.0 mL) were added, and the mixture was stirred at r.t. for 2 h. The crude product was extracted with hexane and purified by column chromatography on silica gel or recrystallized from EtOH to give naphthalene derivative **6**.

(14) **Typical Procedure for the Synthesis of *meso*-Substituted Tetraarylalkynylporphyrin 9a**
Porphyrins **7**[11] and **8**[12a] were prepared according to the reported methods. To a degassed solution of zinc(II) 5,10,15,20-tetraethynylporphyrin (**8**, 10 mg, 0.021 mmol), 1-(4-iodophenyl)-4-phenylnaphthalene-2,3-dicarboxylic acid diethyl ester (**6d**, 75.4 mg, 0.137 mmol), and $AsPh_3$ (12 mg, 0.038 mmol) in a mixture of anhyd THF (10 mL) and Et_3N (5.0 mL) was added $Pd_2(dba)_3$ (2.0 mg, 0.0020 mmol). The reaction mixture was stirred at 50 °C for 4 h under an argon atmosphere. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel using $CHCl_3$ as an eluent to give a dark green solid **9a** (41.7 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.2$ Hz, 12 H), 1.17 (t, $J = 7.2$ Hz, 12 H), 4.03 (q, $J = 7.2$ Hz, 8 H), 4.19 (q, $J = 7.2$ Hz, 8 H), 7.43–7.55 (m, 28 H), 7.68–7.71 (m, 12 H), 7.85 (d, $J = 8.4$ Hz, 4 H), 8.27 (d, $J = 8.0$ Hz, 8 H), 9.48 (s, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.6$, 13.9, 61.4, 61.6, 66.7, 92.8, 96.9, 102.7, 123.7, 127.1, 127.5, 127.8, 127.9, 128.1, 129.0, 129.2, 130.2, 130.7, 131.2, 131.5, 132.6, 132.8, 137.7, 138.3, 138.4, 139.3, 151.3, 168.3, 168.4. IR (Nujol): 480, 771, 941, 1132, 1166, 1222, 1300, 1676, 1685, 1716, 1734, 2213, 2924 cm^{-1}.