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Reductive 3-Silylation of Benzofuran Derivatives via Coupling Reaction with Chlorotrialkylsilane

Suhua Zheng, Tianyuan Zhang, and Hirofumi Maekawa*

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ABSTRACT: Reductive silylation of benzofurans with an electron-withdrawing group by a magnesium metal and the subsequent oxidative rearomatization by DDQ gave the selective formation of less reported 3-silylated benzofurans in moderate to good yields under mild reaction conditions with wide substituent scope. The silyl group introduced on the five-membered ring by the reductive coupling could survive with no elimination throughout the oxidation process. The silylated heteroaromatic skeleton is useful as an intermediate in organic synthesis, and its practical utility was also demonstrated by several transformation reactions.

INTRODUCTION

A benzofuran structure can be frequently seen in the skeleton of naturally occurring compounds and has been focused by medicinal chemists and pharmacologists due to its potent bioactivities.[1] Silylated compounds such as vinylsilanes, allylsilanes, and arylsilanes are of particular importance as useful intermediates in the field of organic syntheses,[2] materials science,[3] and medicinal chemistry[4] because they behave as superior nucleophiles. From these backgrounds, extensive attention has been paid to the introduction of silyl groups into heteroaromatics, especially benzofurans and indoles to construct novel bioactive groups of compounds.[5] Conventionally, 2-silylation of heteroaromatics can be easily achieved by a reaction with an organometallic reagent followed by the electrophilic attack of chlorotrialkylsilanes (Scheme 1A).[6] In comparison with traditional methods, many of the recent synthetic approaches to silylated benzofurans are investigated such as the catalytic direct silylation by C−H activation (Scheme 1B)[7] and the intramolecular cyclization of alkynylsilanes (Scheme 1C).[8] These processes are generally useful and reliable; however, the main products in almost all of the reactions are 2-silylated benzofuran derivatives except for some examples[7a,8d] and the reactions sometimes demand hazardous reactants or the troublesome preparation of starting materials. Therefore, the development of new strategies toward the silylation of heteroaromatics, especially the less reported 3-silylated benzofurans[7a,8d] or indoles[7b] from simple feedstocks under mild reaction conditions still remains an attractive and vital task.

We have previously developed a series of magnesium-promoted silylation of electron-deficient aromatic alkenes or alkynes under mild reaction conditions.[9] However, the reductive silylation of benzofuran or indole was not achieved due to their high stability and more negative reduction potentials.[10] In this study, 2-acetylbenzofuran was first selected as the benchmark substrate, and the reductive silylation to the

Scheme 1. (A−D) Scope of Silylation of Benzofuran and Analogues

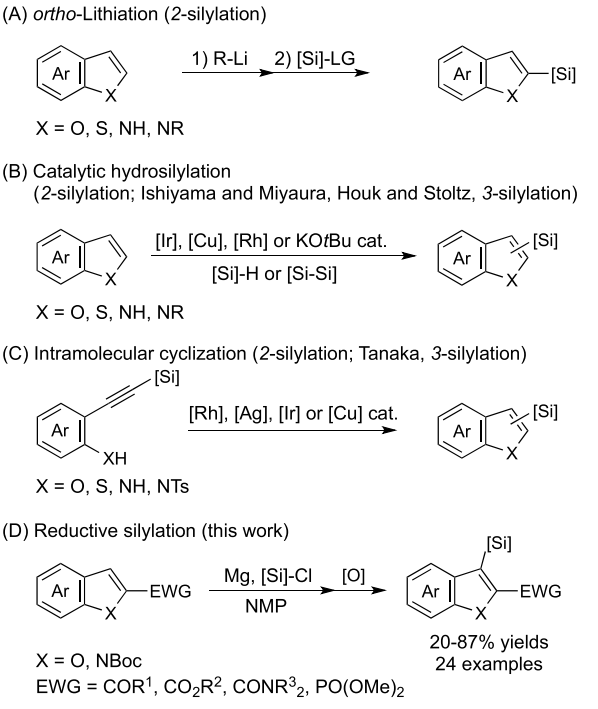

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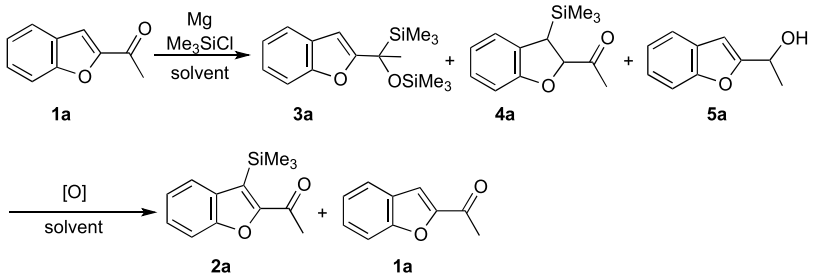
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	temp (°C)	[O] conditions	yield of **2a** (%)
1	NMP	25	air oxidation	(25)[b]
2	NMP	25	DDQ/CH_2Cl_2	48
3	NMP	−15	DDQ/CH_2Cl_2	31
4	NMP	0	DDQ/CH_2Cl_2	60 (52)[c]
5	DMI	25	DDQ/CH_2Cl_2	26
6	DMF	0	DDQ/CH_2Cl_2	20
7	DMA	0	DDQ/CH_2Cl_2	40
8	THF	0	DDQ/CH_2Cl_2	no reaction
9	NMP	0	DDQ/CH_2Cl_2	29[d]
10	NMP	0	DDQ/CH_2Cl_2	33[e]

[a]Reaction conditions: (1) **1a** (2 mmol), Mg (4 equiv), Me_3SiCl (6 equiv), solvent (15 mL, 0.13 M), N_2 atmosphere, and 3 h. (2) DDQ (1 equiv), CH_2Cl_2 (1 M, 2 mL), 25 °C, and 6 h. Yields were determined by gas chromatography using *n*-undecane as the internal standard. Isolated yields are shown in the parentheses. [b]Air oxidation for 24 h instead of DDQ oxidation afforded a mixture of **2a** (25%), **3a** (13%), **4a** (7%), **5a** (16%), and **1a** (10%). [c]Starting material **1a** was reproduced in 11% yield. [d]NMP (5 mL, 0.40 M) was used. [e]NMP (25 mL, 0.08 M) was used. See the Supporting Information for detailed optimization on equivalents of reagents.

five-membered ring was investigated. As a result, the reductive coupling of benzofuran derivatives with chlorotrimethylsilane followed by the subsequent oxidative aromatization allowed the efficient delivery of the corresponding benzofurans silylated at the 3-position as the main product (Scheme 1D).

RESULTS AND DISCUSSION

Our study was initiated by reduction of 2-acetylbenzofuran **1a** with magnesium turnings in the presence of chlorotrimethylsilane in *N*-methylpyrrolidone (NMP), and the desired product, 3-silylated benzofuran **2a**, was obtained in 25% yield after air oxidation, accompanying with the disilylated compound of the carbonyl group **3a** (13%), 3-silylated dihydrobenzofuran **4a** (7%), and simply reduced product of the carbonyl group **5a** (16%) as the side products (Table 1, entry 1). Oxidative aromatization facilitated by addition of DDQ (see the Supporting Information for detailed optimization) and investigation on the reaction temperature gave the desired product **2a** at 0 °C in 60% yield with only a small amount of the starting material (Table 1, entry 4), while reactions at −15 °C or room temperature gave slightly lower yields (Table 1, entries 2 and 3). Then, extensive screening of the solvent effect suggested the requirement of the aprotic polar solvent for the coupling, and NMP was found to be the best solvent (Table 1, entries 4−8). On the other hand, the investigation of the substrate concentration showed no improvement on yields (Table 1, entries 9 and 10).

Under the optimized reaction conditions, the substrate scope and generality of this reaction were carefully screened (Scheme 2). First, substitution by a methoxy group or a bromine atom at the 7-position of 2-acetylbenzofurans showed undesired reaction efficiency, and the target product **2b** or **2c** was obtained in only 25 and 20% yields, respectively, with a much amount of dimers and recovery of the starting material. Pleasingly, the replacement of the acetyl group to an ester group led to a dramatic decrease of side products and the yields of **2d** and **2e** were enhanced to 70 and 87%, respectively. A range of benzofurans, with a methyl group, a methoxy group, or a halogen atom, were well compatible with this reductive coupling under the optimal reaction conditions, which allowed the efficient transformation into 3-silylated benzofurans **2f** to **2o** in 38 to 84% yields. A naphthofuran ring was also tolerated under the standard conditions, albeit in diminished yields (**2p**). Furthermore, the scope of the electron-withdrawing group at the 2-position was extended to carboxamides, which allowed the facile synthesis of products **2q**−**2s** in moderate to good yields. In addition, this protocol can also be extended to other silylating agents, and silyl groups such as ethyldimethylsilyl, chloromethyldimethylsilyl, and triethylsilyl groups were selectively introduced to the 3-position of benzofurans in moderate yields (**2t**−**2v**, respectively).

To increase the utility of this reaction, we next switched our attention to the investigation of benzofurans with other types of electron-withdrawing groups and indole derivatives. As shown in Scheme 3, under the designated reaction conditions, silylation of dimethyl phosphonate **6** gave the 3-silylated product **7** in 35% yield, while 2-cyanobenzofuran **8** was transformed into an unpredicted tris-silylated product **9** in 30% yield. Furthermore, the reaction of Boc-protected indole **10b** also gave a positive result, while the reaction of *N*-methylindole **10a** gave aroylsilane **11** in 46% yield.[11] The contrast results of indoles may be explained by the difference of electron density of the five-membered ring,[12] which will be referred to the reaction mechanism.

The synthetic usability of the products **2q** and **2r** was demonstrated in Scheme 4.[2b] First, the substrate **2q** was converted into an *ipso*-substitution product, 2-acetyl-3-iodobenzofuran **13**, by addition of 4 equiv of ICl at ambient temperature, and the substrate **2r** was also transformed into

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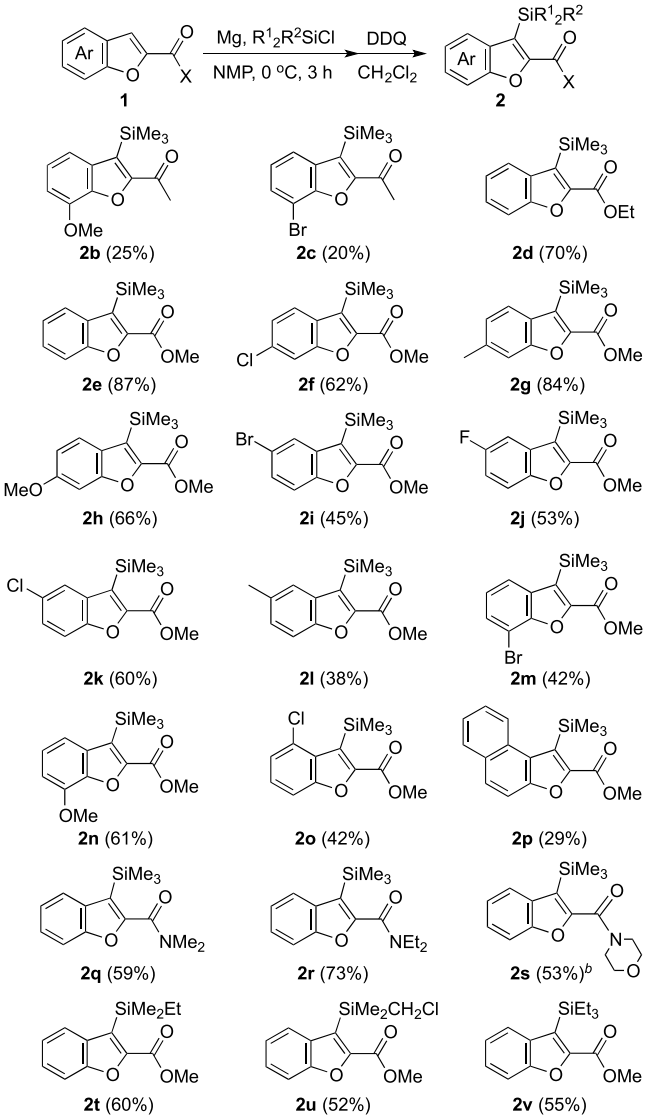
Scheme 2. Scope of the Reductive Silylation of Benzofuran Derivatives[a]

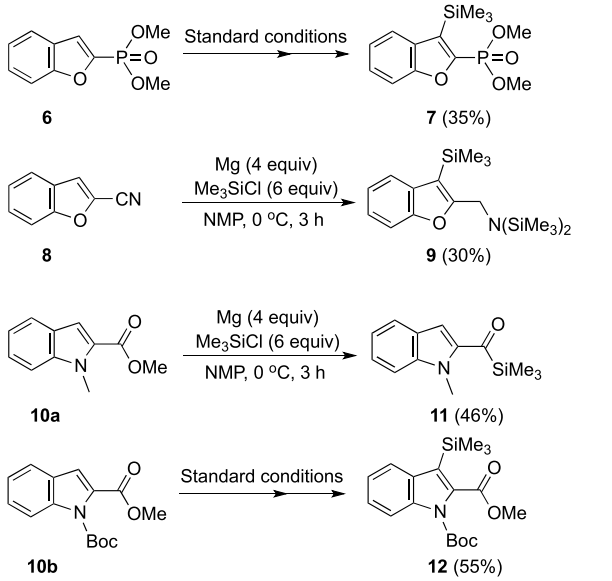


[a]Reaction conditions: substrate **1** (2 mmol), Mg (4 equiv), silylating agent (6 equiv), NMP (15 mL, 0.13 M), N_2 atmosphere, and 3 h; DDQ (1 equiv), CH_2Cl_2 (2 mL, 1 M), 25 °C, and 6 h. Yields are shown in the parentheses. [b]At the first step, the reaction mixture was stirred for 20 h.

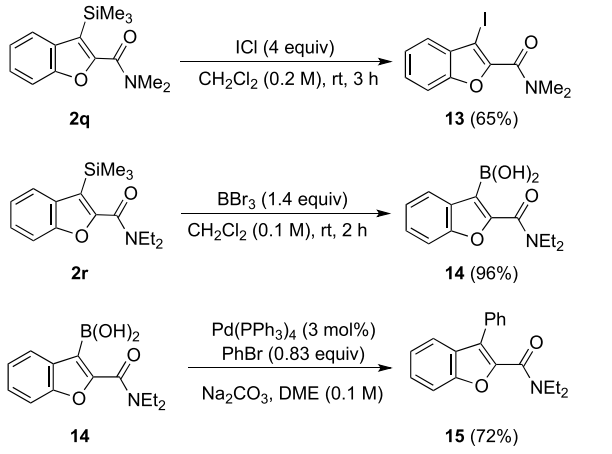
boronic acid **14**, quantitatively. Boronic acid **14** is regarded as a good reagent for Suzuki−Miyaura coupling reactions, and in fact, the palladium-catalyzed coupling of **14** with bromobenzene afforded a biaryl compound **15** in 72% yield. Benzofuran-2-carboxamides including biaryl compounds like **15** were reported to have the bioactive potential on anti-inflammatory, analgesic, and antipyretic activities,[13] and these two-step reactions from arylsilane **2** to biaryl compounds may be dedicated to the synthesis of a series of potential drug candidates.

Finally, to gain insight into the reaction mechanism, several control experiments were executed (Scheme 5). No reaction was observed without magnesium in the presence of chlorotrimethylsilane; then, zinc turnings, which had the lower reducibility than magnesium, were applied to this coupling instead of magnesium, and a mixture of pinacol

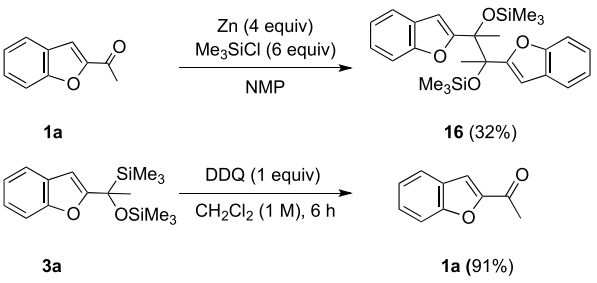
Scheme 3. Reactions of Benzofurans with Other Electron-Withdrawing Groups and Indole Derivatives



Scheme 4. Synthetic Applications of 3-Silylated Benzofurans



Scheme 5. Mechanistic Studies



isomer **16** was obtained in 32% yield with no detection of the C-silylated product. On the basis of this result, it was rationalized that the conjugation system including the carbonyl group could be easily reduced by the single electron transfer from the metal. Furthermore, DDQ oxidation of the isolated disilylated compound **3a** under the same reaction conditions afforded the starting material **1a** and this result suggested that the crude reaction mixture composed of **3a**, **4a**, and **5a** would be convergent to a mixture of **2a** and the starting material **1a** by DDQ oxidation (see Table 1). In addition, it is remarkable

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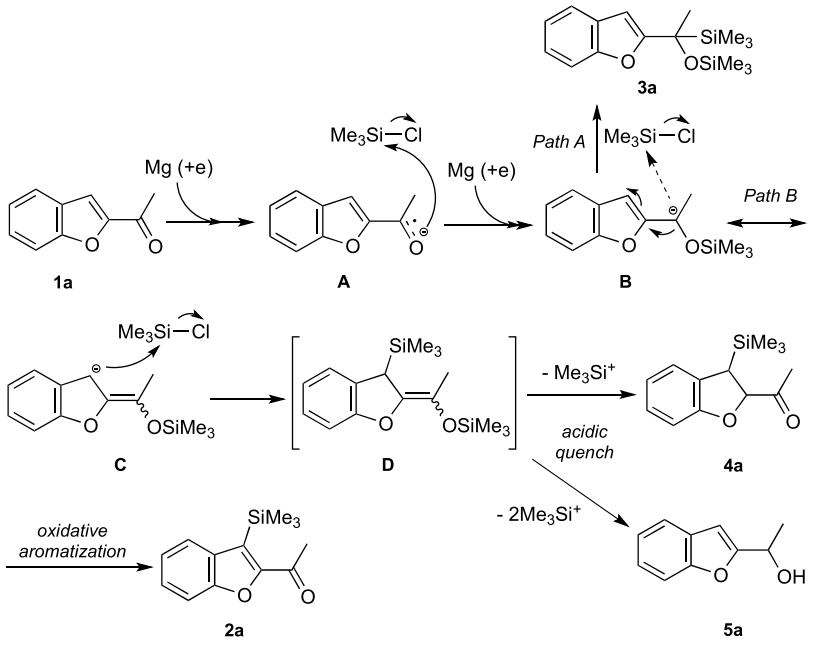
Scheme 6. Proposed Reaction Mechanism



that the silyl group on the five-membered ring of **4a** survived during DDQ oxidation, while the silyl group of **3a** on a carbon atom of the side chain had been completely removed.

Based on the above observations and previous research,[14] a plausible reaction mechanism on the formation of **2a** is descripted in Scheme 6. Initially, a single electron transfer from the magnesium metal to 2-acetylbenzofuran **1a** affords an anion radical species **A**, which will attack chlorotrimethylsilane to give **B** after the second electron transfer from magnesium. Then, a direct attack of the anionic intermediate **B** to chlorotrimethylsilane will furnish a side product **3a** disilylated at the carbonyl group through pathway A. The compound **3a** and simply reduced product **5a** will be transformed into the starting material **1a** after DDQ oxidation. Meanwhile, in pathway B, the attack of **C** through the resonance with the furan ring to chlorotrimethylsilane occurs on the 3-position of the benzofuran ring to yield intermediate **D**. The compounds **4a** and **5a** may be formed through the hydrolysis of **D**, and the oxidative aromatization of **4a** will give the product **2a** with no elimination of the silyl group from the 3-position.

CONCLUSIONS

In conclusion, magnesium-promoted reductive silylation of benzofurans and Boc-protected indoles with an electron-withdrawing group at the 2-position and the subsequent oxidative aromatization led to the selective formation of the corresponding 3-silylated products. It is noteworthy that the oxidative aromatization proceeded without elimination of the introduced silyl group and this two-step silylation has a broad functional group tolerance. The reaction is characterized by a simple process, mild reaction conditions, easily available silylating agent, and use of an Earth-abundant metal. Selectively prepared silylated heteroaromatics were also proved to be promising intermediates for the synthesis of natural products and pharmaceutical drugs by some transformation reactions.

EXPERIMENTAL SECTION

General Information. All commercially available chemicals were used without further purification, unless otherwise noted. All solvents were distilled by standard techniques prior to use. Chlorotrialkylsilanes were simply distilled before use. All starting materials except **1o**[15] are known compounds, and they were synthesized according to the procedures from the literature studies, **1a−1c**,[16] **1d−1n**,[17] **1p**,[17] **1q−1s**,[18] **6**,[19] **8**,[20] **10a**,[21] and **10b**.[22] ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{19}F NMR, and ^{31}P{^{1}H} NMR spectra were measured on a JEOL JNM AL-400 (400 MHz) spectrometer at 20 °C. Proton chemical shifts were expressed in parts per million (ppm) downfield from the residual signal of chloroform (7.26 ppm). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm ($CDCl_3$). Fluorine chemical shifts were referenced to the external fluorine signal of trifluoroacetic acid at −76.50 ppm. A phosphorus chemical shift was referenced to the external phosphorus signal of triphenylphosphine at −5.65 ppm. Infrared (IR) spectra were recorded on a JASCO 470Plus FTIR spectrometer. A low mass spectrum was recorded on a Shimadzu GCMS-QP2010 spectrometer (quadrupole, EI). High-resolution mass spectra were recorded on a JEOL JMS-600H spectrometer (double-focusing, EI), and spectra of **2a**, **2n**, and **11** were recorded on a JEOL JMS-T200GC spectrometer (TOF, EI). Melting point determinations were performed using a Yanaco MP-J3 instrument and are uncorrected. Cyclic voltammograms were measured with an ALS model 600.

General Procedure for 3-Silylation of Benzofurans and Indoles. In a round-bottom flask, a mixture of magnesium (194 mg, 8 mmol, 4 equiv), chlorotrimethylsilane (1.52 mL, 12 mmol, 6 equiv), and NMP (5 mL) was stirred for 30 min at room temperature under a nitrogen atmosphere. Then, to the mixture was added a solution of benzofuran or indole (2 mmol) in NMP (10 mL). After stirring for 3 h at room temperature, the reaction mixture was poured into 50 mL of 1 M sulfuric acid and products were extracted with diethyl ether (30 mL × 3). The combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and then concentrated *in vacuo*. The crude products were transferred into another round-bottom flask, and a dichloromethane (2 mL) solution of DDQ (454 mg, 2 mmol, 1 equiv) was added. The mixture was stirred for 6 h at room temperature. The reaction mixture was quenched by 50 mL of 1 M sodium hydroxide solution, and the product was extracted with diethyl ether (30 mL × 3). The combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After

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concentration *in vacuo*, the final product was purified by flash column chromatography.

*1-[3-(Trimethylsilyl)benzofuran-2-yl]ethanone (**2a**).* 52% yield (242 mg); hexane/ethyl acetate = 5:1; R_f = 0.7; white solid; mp 98.7−101.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (1H, d, J = 8.3 Hz), 7.57 (1H, d, J = 8.3 Hz), 7.45 (1H, t, J = 8.3 Hz), 7.28 (1H, t, J = 8.3 Hz), 2.66 (3H, s), 0.45 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 190.9, 156.9, 155.1, 132.3, 127.3, 124.7, 123.3, 122.2, 112.0, 27.5, −0.2. IR (KBr): 3098, 2957, 2902, 1681, 1521 (cm^{-1}). HRMS (EI-TOF) m/z: [M]$^+$ calcd for $C_{13}H_{16}O_2Si$, 232.0914; found, 232.0935.

*[1-(Benzofuran-2-yl)-1-(trimethylsilyloxy)ethyl]trimethylsilane (**3a**).* 13% yield (77 mg); hexane/ethyl acetate = 5:1; R_f = 0.8; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (1H, d, J = 8.0 Hz), 7.42 (1H, d, J = 8.0 Hz), 7.21−7.18 (2H, m), 6.40 (1H, s), 1.68 (3H, s), 0.05 (9H, s), 0.03 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 164.1, 154.6, 129.0, 122.9, 122.4, 120.2, 110.8, 100.6, 69.1, 22.6, 2.2, −4.1. IR (neat): 3066, 2958, 2900, 2869, 1577, 1569, 1455, 1250 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{16}H_{26}O_2Si_2$, 306.1471; found, 306.1495.

*1-[3-(Trimethylsilyl)-2,3-dihydrobenzofuran-2-yl]ethanone (**4a**).* 7% yield (34 mg); hexane/ethyl acetate = 5:1; R_f = 0.75; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.13−7.08 (2H, m), 6.88−6.86 (2H, m), 5.17 (1H, d, J = 9.9 Hz), 3.06 (1H, d, J = 9.9 Hz), 2.23 (3H, s), 0.11 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 209.0, 158.8, 129.5, 127.3, 124.0, 121.1, 109.5, 89.8, 35.7, 28.1, −1.3. IR (neat): 3070, 2956, 2926, 2903, 2856, 1715, 1522 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{18}O_2Si$, 234.1076; found, 234.1063.

*1-(Benzofuran-2-yl)ethanol (**5a**).* 16% yield (53 mg); known compounds;[23] hexane/ethyl acetate = 5:1; R_f = 0.2; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (1H, d, J = 8.0 Hz), 7.50 (1H, d, J = 8.0 Hz), 7.31 (1H, t, J = 8.0 Hz), 7.26 (1H, t, J = 8.0 Hz), 6.61 (1H, s), 5.02 (1H, q, J = 6.8 Hz), 3.09 (1H, broad, s), 1.65 (3H, d, J = 6.8 Hz). MS (EI) m/z: [M]$^+$ 162.

*1-[7-Methoxy-3-(trimethylsilyl)benzofuran-2-yl]ethanone (**2b**).* 25% yield (133 mg); hexane/ethyl acetate = 5:1; R_f = 0.3; pale yellow solid; mp 117.1−118.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (1H, d, J = 8.0 Hz), 7.19 (1H, t, J = 8.0 Hz), 6.93 (1H, d, J = 8.0 Hz), 4.03 (3H, s), 2.69 (3H, s), 0.44 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 190.8, 157.0, 145.9, 144.8, 134.0, 123.8, 122.5, 116.6, 108.6, 56.1, 27.5, −0.2. IR (KBr): 3080, 3046, 3002, 2958, 2898, 1683, 1580 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{14}H_{18}O_3Si$, 262.1025; found, 262.1015.

*1-[7-Bromo-3-(trimethylsilyl)benzofuran-2-yl]ethanone (**2c**).* 20% yield (124 mg); hexane/ethyl acetate = 5:1; R_f = 0.6; pale yellow solid; mp 85.0−86.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (1H, d, J = 7.8 Hz), 7.61 (1H, d, J = 7.8 Hz), 7.16 (1H, t, J = 7.8 Hz), 2.70 (3H, s), 0.44 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 190.8, 157.0, 152.3, 133.5, 130.1, 124.5, 123.8, 123.1, 104.7, 27.5, −0.3. IR (KBr): 3075, 3041, 2999, 2956, 2899, 1685, 1521 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{15}O_2SiBr$, 310.0025; found, 310.0003.

*Ethyl 3-(Trimethylsilyl)benzofuran-2-carboxylate (**2d**).* 70% yield (368 mg); hexane/ethyl acetate = 5:1; R_f = 0.6; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (1H, d, J = 8.0 Hz), 7.60 (1H, d, J = 8.0 Hz), 7.41 (1H, t, J = 8.0 Hz), 7.26 (1H, t, J = 8.0 Hz), 4.47 (2H, q, J = 7.2 Hz), 1.45 (3H, t, J = 7.2 Hz), 0.48 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.3, 155.2, 149.7, 132.0, 127.0, 124.2, 123.8, 123.1, 112.1, 61.5, 14.3, 0.3. IR (neat): 3051, 2984, 2954, 2901, 1717, 1538 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{14}H_{18}O_3Si$, 262.1025; found, 262.1010.

*Methyl 3-(Trimethylsilyl)benzofuran-2-carboxylate (**2e**).* 87% yield (431 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (1H, d, J = 8.0 Hz), 7.59 (1H, d, J = 8.0 Hz), 7.41 (1H, t, J = 8.0 Hz), 7.26 (1H, t, J = 8.0 Hz), 3.99 (3H, s), 0.49 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.4, 155.1, 149.2, 131.8, 127.0, 124.2, 124.1, 123.1, 112.0, 52.0, 0.1. IR (neat): 3033, 2952, 2900, 2844, 1724, 1538 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{16}O_3Si$, 248.0869; found, 248.0868.

*Methyl 6-Chloro-3-(trimethylsilyl)benzofuran-2-carboxylate (**2f**).* 62% yield (350 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (1H, d, J = 8.5 Hz), 7.56 (1H, s), 7.23 (1H, d, J = 8.5 Hz), 3.98 (3H, s), 0.46 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.2, 155.3, 149.8, 133.0, 130.5, 124.7, 124.13, 124.08, 112.4, 52.2, 0.0. IR (neat): 3085, 2953, 2926, 2902, 2855, 1725, 1538 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{15}O_3SiCl$, 282.0479; found, 282.0458.

*Methyl 6-Methyl-3-(trimethylsilyl)benzofuran-2-carboxylate (**2g**).* 84% yield (442 mg); hexane/ethyl acetate = 5:1; R_f = 0.6; yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (1H, d, J = 7.6 Hz), 7.38 (1H, s), 7.09 (1H, d, J = 7.6 Hz), 3.98 (3H, s), 2.48 (3H, s), 0.47 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.6, 155.7, 148.7, 137.8, 129.5, 124.9, 124.4, 123.6, 112.0, 52.1, 21.8, 0.1. IR (neat): 3088, 3024, 2952, 2900, 2854, 1716, 1538 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{14}H_{18}O_3Si$, 262.1025; found, 262.1049.

*Methyl 6-Methoxy-3-(trimethylsilyl)benzofuran-2-carboxylate (**2h**).* 66% yield (365 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; pale yellow solid; mp 72.2−74.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (1H, d, J = 7.7 Hz), 7.07 (1H, s), 6.90 (1H, d, J = 7.7 Hz), 3.97 (3H, s), 3.86 (3H, s), 0.45 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.5, 160.1, 156.6, 148.5, 125.3, 124.8, 124.5, 113.2, 95.4, 55.6, 52.0, 0.1. IR (KBr): 3087, 3018, 2995, 2953, 2899, 2837, 1713, 1616 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{14}H_{18}O_4Si$, 278.0974; found, 278.0981.

*Methyl 5-Bromo-3-(trimethylsilyl)benzofuran-2-carboxylate (**2i**).* 45% yield (291 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; white solid; mp 42.0−44.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96 (1H, s), 7.50 (1H, d, J = 9.0 Hz), 7.44 (1H, d, J = 9.0 Hz), 3.98 (3H, s), 0.46 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.2, 153.9, 150.2, 133.8, 130.1, 126.7, 123.6, 116.4, 113.5, 52.3, 0.1. IR (KBr): 3097, 3076, 3029, 2951, 2907, 2841, 1721, 1538 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{15}O_3SiBr$, 325.9974; found, 325.9978.

*Methyl 5-Fluoro-3-(trimethylsilyl)benzofuran-2-carboxylate (**2j**).* 53% yield (282 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; yellow solid; mp 43.1−44.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54−7.49 (2H, m), 7.18−7.13 (1H, m), 3.99 (3H, s), 0.46 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.3, 159.2 (d, $^1J_{CF}$ = 237.7 Hz), 151.5, 150.8, 132.6 (d, $^3J_{CF}$ = 11.0 Hz), 124.2, 115.3 (d, $^2J_{CF}$ = 26.1 Hz), 112.7 (d, $^3J_{CF}$ = 10.0 Hz), 109.4 (d, $^2J_{CF}$ = 30.1 Hz), 52.3, 0.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −119.54 (m). IR (KBr): 3107, 3049, 3014, 2963, 2908, 2849, 1716, 1584 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{15}O_3FSi$, 266.0775; found, 266.0770.

*Methyl 5-Chloro-3-(trimethylsilyl)benzofuran-2-carboxylate (**2k**).* 60% yield (338 mg); hexane/ethyl acetate = 5:1; R_f = 0.6; pale yellow solid; mp 103.8−104.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (1H, s), 7.51 (1H, d, J = 8.8 Hz), 7.39 (1H, d, J = 8.8 Hz), 3.99 (3H, s), 0.47 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.3, 153.6, 150.4, 133.2, 128.9, 127.5, 123.7, 113.5, 113.1, 52.3, 0.1. IR (KBr): 3098, 3075, 3004, 2955, 2909, 2848, 1721, 1537 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{15}O_3SiCl$, 282.0479; found, 282.0480.

*Methyl 5-Methyl-3-(trimethylsilyl)benzofuran-2-carboxylate (**2l**).* 38% yield (198 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; pale yellow solid; mp 87.0−88.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63 (1H, s), 7.47 (1H, d, J = 8.5 Hz), 7.24 (1H, d, J = 8.5 Hz), 3.98 (3H, s), 2.45 (3H, s), 0.47 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.6, 153.7, 149.3, 132.7, 132.0, 128.6, 124.0, 123.8, 111.6, 52.1, 21.5, 0.2. IR (KBr): 3070, 3034, 2954, 2919, 2861, 1718, 1533 (cm^{-1}). HRMS (EI) m/z: [M]$^+$ calcd for $C_{14}H_{18}O_3Si$, 262.1025; found, 262.1049.

*Methyl 7-Bromo-3-(trimethylsilyl)benzofuran-2-carboxylate (**2m**).* 42% yield (274 mg); hexane/ethyl acetate = 5:1; R_f = 0.6; white solid; mp 91.2−93.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.80 (1H, d, J = 7.9 Hz), 7.59 (1H, d, J = 7.9 Hz), 7.15 (1H, t, J = 7.9 Hz), 3.99 (3H, s), 0.47 (9H, s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 160.3, 152.5, 149.8, 133.0, 129.9, 125.1, 124.4, 123.3, 104.6, 52.3, 0.1. IR (KBr): 3068, 2997, 2951, 2907, 2842, 1720,

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1538 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{13}H_{15}O_3SiBr$, 325.9974; found, 325.9985.

Methyl 7-Methoxy-3-(trimethylsilyl)benzofuran-2-carboxylate (**2n**). 61% yield (341 mg); hexane/ethyl acetate = 5:1; R_f = 0.4; yellow solid; mp 74.0−75.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (1H, d, J = 8.1 Hz), 7.19 (1H, t, J = 8.1 Hz), 6.91 (1H, d, J = 8.1 Hz), 4.01 (3H, s), 3.97 (3H, s), 0.47 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.5, 149.4, 145.9, 144.9, 133.5, 124.5, 123.7, 116.0, 108.2, 55.9, 52.1, 0.1. IR (KBr): 3104, 3027, 3006, 2981, 2947, 2898, 2837, 1721, 1542 (cm^{-1}). HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{14}H_{18}O_4Si$, 278.0969; found, 278.0994.

Methyl 4-Chloro-3-(trimethylsilyl)benzofuran-2-carboxylate (**2o**). 42% yield (236 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48 (1H, d, J = 7.2 Hz), 7.34−7.29 (2H, m), 3.96 (3H, s), 0.47 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.3, 155.6, 150.7, 130.6, 128.3, 127.1, 124.8, 120.2, 110.5, 52.7, 1.7. IR (neat): 3024, 2952, 2928, 2901, 2855, 1736, 1530 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{13}H_{15}O_3SiCl$, 282.0479; found, 282.0458.

Methyl 3-(Trimethylsilyl)naphtho[2,1-b]furan-2-carboxylate (**2p**). 29% yield (174 mg); hexane/ethyl acetate = 5:1; R_f = 0.8; white solid; mp 80.2−82.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.37 (1H, d, J = 7.8 Hz), 7.96 (1H, d, J = 7.8 Hz), 7.86 (1H, d, J = 7.8 Hz), 7.71 (1H, d, J = 7.8 Hz), 7.62 (1H, t, J = 7.8 Hz), 7.52 (1H, t, J = 7.8 Hz), 4.01 (3H, s), 0.57 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.1, 153.4, 149.3, 131.2, 129.3, 129.10, 129.05, 127.0, 126.1, 125.9, 124.7, 123.1, 112.5, 52.4, 1.4. IR (KBr): 3055, 2988, 2951, 2926, 2854, 1732, 1531 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{17}H_{18}O_3Si$, 298.1025; found, 298.1030.

N,N-Dimethyl-3-(trimethylsilyl)benzofuran-2-carboxamide (**2q**). 59% yield (307 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (1H, d, J = 7.9 Hz), 7.51 (1H, d, J = 7.9 Hz), 7.34 (1H, t, J = 7.9 Hz), 7.26 (1H, t, J = 7.9 Hz), 3.08 (6H, broad, s), 0.39 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 163.3, 154.4, 153.5, 131.7, 125.1, 123.0, 122.8, 115.2, 111.4, 38.3, 35.2, −0.4. IR (neat): 3066, 2953, 2928, 2900, 2856, 1652, 1583, 1444 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{14}H_{19}NO_2Si$, 261.1185; found, 261.1178.

N,N-Diethyl-3-(trimethylsilyl)benzofuran-2-carboxamide (**2r**). 73% yield (422 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (1H, d, J = 7.8 Hz), 7.50 (1H, d, J = 7.8 Hz), 7.33 (1H, t, J = 7.8 Hz), 7.26 (1H, t, J = 7.8 Hz), 3.56 (2H, q, J = 7.1 Hz), 3.31 (2H, q, J = 7.1 Hz), 1.29−1.21 (6H, m), 0.41 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 162.7, 154.3, 154.2, 131.8, 124.9, 122.9, 122.8, 114.8, 111.4, 43.0, 39.8, 14.3, 12.5, −0.4. IR (KBr): 3068, 2963, 2899, 1645, 1428 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{16}H_{23}NO_2Si$, 289.1498; found, 289.1526.

Morpholino-4-yl-[3-(trimethylsilyl)benzofuran-2-yl]methanone (**2s**). 53% yield (322 mg); hexane/ethyl acetate = 3:2; R_f = 0.6; pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (1H, d, J = 7.6 Hz), 7.48 (1H, d, J = 7.6 Hz), 7.32 (1H, t, J = 7.6 Hz), 7.24 (1H, t, J = 7.6 Hz), 3.78−3.75 (4H, m), 3.65−3.63 (2H, m), 3.47−3.45 (2H, m), 0.40 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.8, 154.2, 152.8, 131.5, 125.3, 123.1, 122.9, 116.6, 111.4, 66.9, 66.6, 47.3, 42.6, −0.3. IR (neat): 3067, 2961, 2899, 2855, 1647, 1430 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{16}H_{21}NO_3Si$, 303.1291; found, 303.1277.

Methyl 3-(Ethyldimethylsilyl)benzofuran-2-carboxylate (**2t**). 60% yield (313 mg); hexane/ethyl acetate = 5:1; R_f = 0.3; colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (1H, d, J = 7.6 Hz), 7.60 (1H, d, J = 7.6 Hz), 7.43 (1H, t, J = 7.6 Hz), 7.28 (1H, t, J = 7.6 Hz), 3.99 (3H, s), 1.01−0.96 (5H, m), 0.47 (6H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.6, 155.2, 149.3, 132.2, 127.1, 124.3, 123.5, 123.2, 112.1, 52.2, 7.49, 7.47, −2.1. IR (neat): 3088, 3051, 3030, 2953, 2910, 2874, 2844, 1724, 1535 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{14}H_{18}O_3Si$, 262.1025; found, 262.1052.

Methyl 3-[(Chloromethyl)dimethylsilyl]benzofuran-2-carboxylate (**2u**). 52% yield (292 mg); hexane/ethyl acetate = 5:1; R_f = 0.3; yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (1H, d, J = 7.9 Hz), 7.61 (1H, d, J = 7.9 Hz), 7.46 (1H, t, J = 7.9 Hz), 7.31 (1H, t, J = 7.9 Hz), 4.01 (3H, s), 3.25 (2H, s), 0.62 (6H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.5, 155.3, 149.8, 131.6, 127.5, 124.0, 123.6, 121.1, 112.2, 52.5, 30.2, −2.9. IR (neat): 3049, 3031, 2955, 2926, 2849, 1719, 1540 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{13}H_{15}O_3SiCl$, 282.0479; found, 282.0505.

Methyl 3-(Triethylsilyl)benzofuran-2-carboxylate (**2v**). 55% yield (317 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (1H, d, J = 7.8 Hz), 7.49 (1H, d, J = 7.8 Hz), 7.31 (1H, t, J = 7.8 Hz), 7.16 (1H, t, J = 7.8 Hz), 3.87 (3H, s), 0.95−0.85 (15H, m). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.7, 155.2, 149.5, 132.6, 127.1, 124.4, 123.2, 121.7, 112.0, 52.2, 7.6, 3.8. IR (neat): 3051, 3031, 2954, 2910, 2875, 2733, 1724, 1533 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{16}H_{22}O_3Si$, 290.1338; found, 290.1327.

Dimethyl 3-(Trimethylsilyl)benzofuran-2-yl Phosphonate (**7**). 35% yield (210 mg); hexane/ethyl acetate = 3:2; R_f = 0.3; colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (1H, d, J = 7.7 Hz), 7.57 (1H, d, J = 7.7 Hz), 7.38 (1H, t, J = 7.7 Hz), 7.26 (1H, t, J = 7.7 Hz), 3.83 (6H, d, $^3J_{HP}$ = 11.5 Hz), 0.52 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 156.4 (d, $^3J_{CP}$ = 11.6 Hz), 148.8 (d, $^1J_{CP}$ = 238.3 Hz), 131.3 (d, $^3J_{CP}$ = 14.9 Hz), 128.0 (d, $^2J_{CP}$ = 31.4 Hz), 126.4, 123.7, 123.0, 111.7, 53.0 (d, $^2J_{CP}$ = 6.0 Hz), 0.6. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm): 8.37. IR (neat): 3066, 2954, 2926, 2853, 1249, 1033 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{13}H_{19}O_4SiP$, 298.0790; found, 298.0788.

N,N,3-Tris(trimethylsilyl)-2-benzofuranmethanamine (**9**). 30% yield (216 mg); hexane/ethyl acetate = 5:1; R_f = 0.6; yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24 (1H, d, J = 8.0 Hz), 7.19 (1H, t, J = 8.0 Hz), 6.94 (1H, t, J = 8.0 Hz), 6.90 (1H, d, J = 8.0 Hz), 3.92 (2H, s), 0.24 (9H, s), 0.19 (18H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 164.7, 158.7, 128.0, 125.4, 124.7, 122.3, 121.3, 109.3, 33.3, 3.1, −0.7. IR (neat): 3078, 3037, 2954, 2900, 1644, 1606, 1479, 1463 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{18}H_{33}NOSi_3$, 363.1870; found, 363.1857.

1-Methyl-2-(trimethylsilyl)carbonyl 1H-Indole (**11**). 46% yield (213 mg); hexane/ethyl acetate = 5:1; R_f = 0.5; yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (1H, d, J = 7.3 Hz), 7.43−7.36 (3H, m), 7.18 (1H, t, J = 7.3 Hz), 4.07 (3H, s), 0.46 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 226.8, 139.3, 139.2, 126.2, 126.1, 123.0, 120.5, 114.4, 110.3, 32.0, −1.3. IR (neat): 3126, 3059, 2956, 2900, 1613, 1580 (cm^{-1}). HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{13}H_{17}NOSi$, 231.1074; found, 231.1091.

1-(1,1-Dimethylethyl) 2-Methyl 3-(Trimethylsilyl)-1H-indole-1,2-dicarboxylate (**12**). 55% yield (379 mg); hexane/ethyl acetate = 5:1; R_f = 0.7; white solid; mp 62.6−64.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.16 (1H, d, J = 7.9 Hz), 7.73 (1H, d, J = 7.9 Hz), 7.37 (1H, t, J = 7.9 Hz), 7.26 (1H, t, J = 7.9 Hz), 3.93 (3H, s), 1.64 (9H, s), 0.40 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 164.8, 148.9, 136.2, 135.5, 132.8, 125.2, 122.9, 122.6, 117.6, 115.2, 84.7, 52.2, 27.8, −0.2. IR (KBr): 3096, 3074, 3050, 3006, 2981, 2959, 2903, 1743, 1732, 1524 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{18}H_{25}NO_4Si$, 347.1553; found, 347.1580.

3-Iodo-N,N-dimethylbenzofuran-2-carboxamide (**13**). 65% yield (205 mg); hexane/ethyl acetate = 5:1; R_f = 0.3; yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41−7.32 (3H, m), 7.26 (1H, t, J = 7.2 Hz), 3.08 (3H, s), 3.07 (3H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 160.7, 153.5, 147.9, 130.2, 127.0, 123.9, 122.3, 111.6, 68.0, 38.3, 35.4. IR (neat): 3061, 3016, 2929, 2865, 1652, 1444 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{11}H_{10}NO_2I$, 314.9757; found, 314.9751.

2-(Diethylaminocarbonyl)-3-benzofuranboronic Acid (**14**). 96% yield (250 mg); hexane/ethyl acetate = 5:1; R_f = 0.2; white solid; mp 123.7−124.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (2H, s), 8.27 (1H, d, J = 7.2 Hz), 7.49 (1H, d, J = 7.2 Hz), 7.41 (1H, t, J = 7.2 Hz), 7.33 (1H, t, J = 7.2 Hz), 3.77−3.48 (4H, m), 1.51−1.10 (6H, m). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 162.8, 153.9, 153.7, 130.9, 126.6, 125.2, 123.8, 110.9, 44.1, 42.5, 14.6, 12.5. IR (neat): 3303, 2984, 2943, 2909, 2880, 2830, 2764, 1593, 1560, 1479, 1452,

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1313, 1303 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{13}H_{16}BNO_4$, 261.1172; found, 261.1155.

*N,N-Diethyl-3-phenylbenzofuran-2-carboxamide (**15**).* 72% yield (88 mg); hexane/ethyl acetate = 5:1; R_f = 0.3; yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (1H, d, *J* = 7.4 Hz), 7.62 (2H, d, *J* = 7.4 Hz), 7.56 (1H, d, *J* = 7.4 Hz), 7.47 (2H, t, *J* = 7.4 Hz), 7.41 (1H, t, *J* = 7.4 Hz), 7.39 (1H, t, *J* = 7.4 Hz), 7.32 (1H, t, *J* = 7.4 Hz), 3.53 (2H, q, *J* = 7.1 Hz), 3.17 (2H, q, *J* = 7.1 Hz), 1.20 (3H, t, *J* = 7.1 Hz), 0.92 (3H, t, *J* = 7.1 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.9, 154.2, 144.7, 131.0, 128.81, 128.77, 128.0, 127.0, 125.7, 123.4, 120.9, 120.5, 111.9, 43.0, 39.5, 14.0, 12.4. IR (neat): 3060, 2976, 2935, 2874, 1639, 1446 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{19}H_{19}NO_2$, 293.1416; found, 293.1438.

*4,5-Di(benzofuran-2-yl)-2,2,4,5,7,7-hexamethyl-3,6-dioxa-2,7-disilaoctane (**16**).* 32% yield (151 mg); meso/dl = 1:1; hexane/ethyl acetate = 5:1; R_f = 0.6; colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 (1H, d, *J* = 7.6 Hz), 7.58−7.54 (2H, m), 7.37−7.30 (2H, m), 7.26−7.25 (3H, m), 6.73 (1H, s), 6.53 (1H, s), 1.89 (3H, s), 1.77 (3H, s), 0.21 (9H, s), 0.08 (9H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 161.6, 160.9, 154.6, 154.3, 128.5, 128.4, 123.4, 123.3, 122.4, 122.2, 120.7, 120.6, 111.0, 110.9, 104.3, 104.2, 79.9, 79.6, 22.8, 22.3, 2.0, 1.8. IR (neat): 3116, 3085, 3066, 3035, 2993, 2956, 2899, 2862, 1580, 1455 (cm^{-1}). HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{26}H_{34}O_4Si_2$, 466.1996; found, 466.1948.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01995.

Copies of ^1H NMR spectrum for **5a**; ^1H NMR spectra and $^{13}C\{^1H\}$ NMR spectra for **1o**, **2a**−**2v**, **3a**, **4a**, **7**, **9**, and **11**−**16**; ^{19}F NMR spectrum for **2j**; $^{31}P\{^1H\}$ NMR spectrum for **7**; and DEPT-135 spectrum for **9** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Hirofumi Maekawa − *Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan;* orcid.org/0000-0002-8192-8518; Email: maekawa@vos.nagaokaut.ac.jp

Authors

Suhua Zheng − *Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan*

Tianyuan Zhang − *Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c01995

Notes

The authors declare no competing financial interest.

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