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Cs_2CO_3-PROMOTED VINYLATION OF PHENOLS WITH TRICHLOROETHYLENE: FACILE SYNTHESIS OF (*E*)-1,2-DICHLORO-1-PHENOXYETHENES

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Abstract – An efficient method for the synthesis of (*E*)-1,2-dichloro-1-phenoxyethenes **2** has been developed. The reaction of phenol derivatives **1** with trichloroethylene at ambient temperature by means of Cs_2CO_3-DMSO system furnished the corresponding aryl vinyl ethers **2** in excellent yields. On the other hand, the same reaction of phenol derivatives **1i**, **1k** and **1p** possessing an electron-withdrawing group at the *o*- or *p*-position of the hydroxy group required a harsh reaction conditions to heat at 70 °C for the synthesis of the desired products **2i**, **2k** and **2p**.

Aryl vinyl ethers are recognized to serve as valuable building blocks in the fields of organic synthesis. Among them, (*E*)-1,2-dichloro-1-phenoxyethene derivatives were employed in the construction of different types of functional groups and carbon skeletons (Figure 1). For example, (1) synthesis of tetra-substituted alkenes[1] or (2) ynol ethers[2] using *n*-BuLi, (3) construction of tri-substituted alkenes utilizing Pd catalyzed-coupling reaction,[3] (4) synthesis of benzofuran derivatives *via* sequential Suzuki-Miyaura coupling and cyclization by means of C-H activation,[4] have been reported to date. Moreover, usefulness of ynol ethers and ynolates,[5] readily available from the corresponding vinyl ethers, in organic synthesis and also in functional group transformations had been demonstrated by many research groups. Therefore, it is important to establish an efficient method for the facile construction of (*E*)-1,2-dichloro-1-phenoxyethene derivatives under mild reaction conditions.

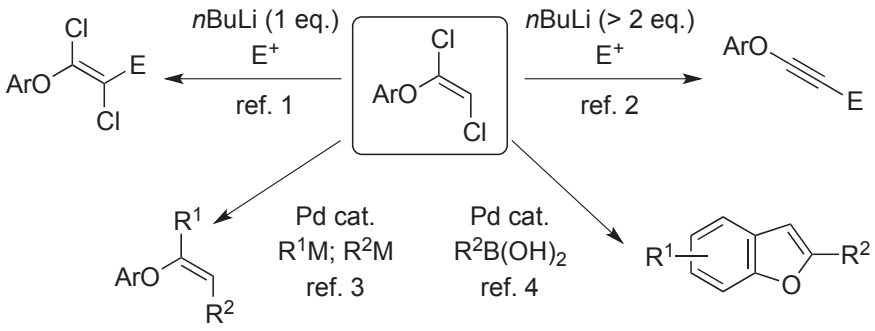


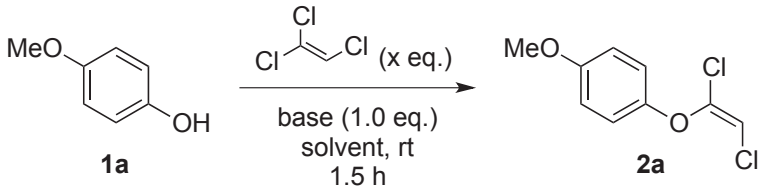
Figure 1. Synthesis of various types of compounds *via* aryl vinyl ether

Generally, the preparation of aryl vinyl ethers has been achieved by treatment of phenol derivatives with a base, such as KH,[3] NaOH[6] and K_2CO_3,[7] and subsequent addition of trichloroethylene. However, KH is documented as a pyrophoric reagent, and highly required to avoid its use in this reaction. On the other hand, when NaOH was employed as a base, a prolonged reaction time was needed, since the poor solubility of NaOH in organic solvent. Furthermore, when the reaction did not proceed immediately, the product yields were generally decreased, probably due to occurrence of decomposition of 1,2-dichloroacetylene, generated in the reaction of trichloroethylene with a base, prior to the reaction with phenol derivatives.[8] As alternative new methods developed recently for the preparation of aryl vinyl ethers, Blouin reported the copper(II)-promoted vinylation of phenols with tetravinyltin under an oxygen atmosphere.[9] However, at least 1 equivalent of tetravinyltin was required to achieve a >90% conversion, though tetravinyltin would be able to deliver more than one vinyl unit per mole, theoretically. In 2008, O'Shea published the availability of 2,4,6-trivinylcyclotriboroxane-pyridine complex, a synthetic equivalent of unstable vinylboronic acid, in the preparation of aryl vinyl ethers.[10] The new methods developed so far, however, have encountered some disadvantages, e.g. requirement of expensive and/or toxic reagents, a prolong reaction time and so on. Thus, we are interested in developing a facile synthetic procedure for aryl vinyl ethers, and describe here a general, easy handling, highly efficient method for the preparation of the target compounds. The present protocol seems to have a general applicability to phenolic compounds bearing a variety of functional groups.

First, the optimal reaction conditions for the preparation of aryl vinyl ether **2a**, were investigated as shown in Table 1. To establish a mild reaction conditions, the reaction temperature was fixed at room temperature. The reaction of **1a** with trichloroethylene in DMSO in the presence of NaOH afforded the corresponding product **2a** in 72% yields (entry 1). With the use of K_2CO_3 as the base, **2a** was obtained only in 5% yield (entry 2), though Sales reported that the same reaction at 70 °C gave **2a** in excellent yields.[7] On the other hand, the similar reaction of phenol **1a** with trichloroethylene (1.3 equiv) in DMSO in the presence of Cs_2CO_3 gave **2a** in excellent yields (entry 3).[11] Moreover, lowering the amount of

trichloroethylene to 1 equivalent reduced the yield to 87% (entry 4), while using 1.5 equivalents of trichloroethylene provided the desired product in the same yield as in the case of entry 3 (entry 5). Although the solvent effects were also investigated by using polar solvents, such as DMF and MeCN, in this reaction, the yields of the desired product **2a** were dramatically decreased (entries 6 and 7).

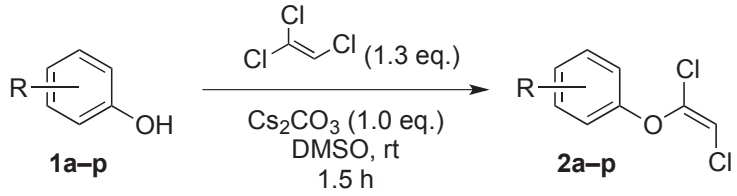
Table 1. Attempted optimization of reaction conditions for the synthesis of aryl vinyl ether **2a**

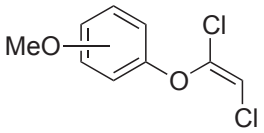


entry	x eq.	base	solvent	yield (%)
1	1.3	NaOH	DMSO	72
2	1.3	K_2CO_3	DMSO	5
3	1.3	Cs_2CO_3	DMSO	92
4	1.0	Cs_2CO_3	DMSO	87
5	1.5	Cs_2CO_3	DMSO	92
6	1.3	Cs_2CO_3	DMF	61
7	1.3	Cs_2CO_3	MeCN	0

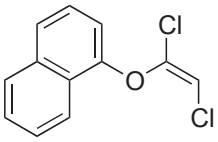
Establishing the optimal reaction conditions as above (Table 1, entry 3), the similar reaction of regioisomeric phenol derivatives **1b** and **1c** was carried out to afford the desired products **2b** and **2c** in 93% and 99% yields, respectively (Table 2). The reaction of cresols **1d–f** under the same reaction conditions gave vinyl ethers **2d–f** in 82-91% yields. Again, in the reaction of naphthols **1g** and **1h**, the naphthyl ethers **2g** and **2h** were produced in 70 and 77% yields, respectively. The reaction of *m*-cyanophenol (**1j**) possessing the electron-withdrawing substituent gave the corresponding aryl ether **2j** in 89% yield. Unfortunately *p*- and *o*-cyanophenols (**1j**) and (**1k**) did not afford the desired product at ambient temperature, probably due to the weak reactivity of phenoxide.[4] However, the reaction of *p*- and *o*-cyanophenols proceeded successfully to furnish **2j** and **2k** in 99% and 95% yields, respectively, when the reaction was carried out at 70 °C. Even the reaction of *o*-iodophenol **1l** or sterically bulky *o*-*tert*-butylphenol **1m** could provide **2l** and **2m** in high yields. Phenol derivatives **1n** and **1o** having halogen group at the *p*-position of the hydroxy group also gave **2n** and **2o** in high yields. As the same as the case of **1i** and **1k**, the reaction of *p*-nitrophenol (**1p**) proceeded at 70 °C to afford **2p** in 99% yield.

Table 2. Synthesis of aryl vinyl ethers **2**

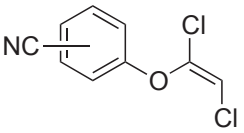




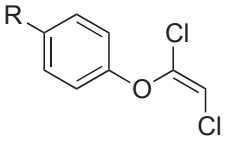
2a: *p*-MeO (92%)
2b: *m*-MeO (93%)
2c: *o*-MeO (99%)



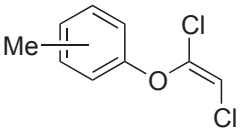
2g (70%)



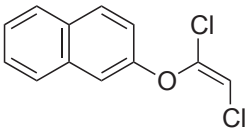
2i: *p*-CN (99%)[a]
2j: *m*-CN (89%)
2k: *o*-CN (95%)[a]



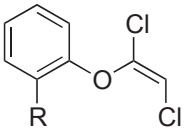
2n: R = F (88%)
2o: R = Br (91%)
2p: R = NO_2 (99%)[a]



2d: *p*-Me (82%)
2e: *m*-Me (91%)
2f: *o*-Me (88%)



2h (77%)

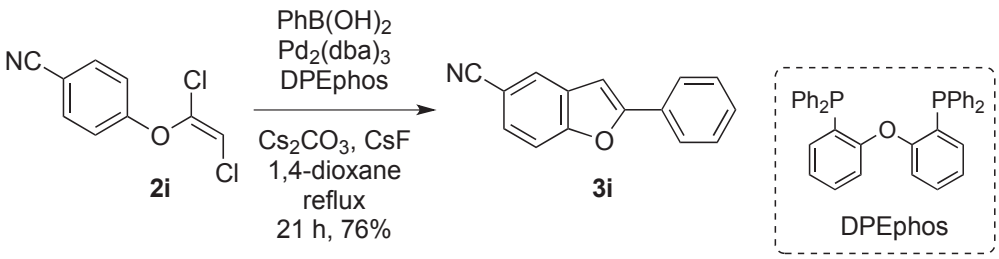


2l: R = I (90%)
2m: R = *t*Bu (89%)

[a] The reaction was carried out Cs_2CO_3 (1.3 eq.) at 70 °C.

The stereochemistry of the products could not be determined on the basis of NMR analysis, unfortunately. Thus, the authentic samples with known stereochemistries were prepared by following the literature known methods. All the stereochemistries of the synthesized compounds were determined by direct comparison with already-identified specimen.

Finally, Pd-catalyzed coupling reaction of aryl vinyl ether **2i** with phenylboronic acid, followed by cyclization reaction *via* C-H activation afforded 2-phenylbenzofuran **3i** in 76% yield under Hultins' conditions (Scheme 1).[4]



Scheme 1. Synthesis of 2-phenylbenzofuran

In conclusion, we have developed an efficient and convenient synthetic method for the preparation of aryl vinyl ether **2** by using Cs_2CO_3 as the base at ambient temperature. It is noteworthy that the phenol derivatives **1i**, **1k** and **1p** having the electron-withdrawing groups at the *o*- or *p*-position of the hydroxy group furnished **2i**, **2k** and **2p** in excellent yields by heating at 70 °C. The methodology developed here has improved generality and provides efficient construction of a variety of the aryl vinyl ethers **2**.

EXPERIMENTAL

IR spectra were obtained using a IRPrestige-21 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AV III 400 (^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz) instrument for solutions in $CDCl_3$, and chemical shifts are reported on the δ scale using TMS as an internal standard of 0.00 for ^{1}H-NMR spectra and $CDCl_3$ as an internal standard of δ 77.00 for ^{13}C-NMR spectra, respectively. Mass spectra of all aryl vinyl ethers did not indicate their molecular ion peak (M^+) or the corresponding fragment ion peaks by EI, CI, ESI^+ and ESI^- - MS, unfortunately, because the corresponding ethers **2** were unstable under attempted measurement conditions.

(*E*)-1-(1,2-Dichlorovinyloxy)-4-methoxybenzene[12,13] **(2a).** To a flask were added 4-methoxyphenol (**1a**) (1.01 g, 8.06 mmol) and trichloroethylene (1.38 g, 10.5 mmol). After the flask was flushed with Ar, DMSO (6 mL) and Cs_2CO_3 (2.63 g, 8.07 mmol) were added to the reaction mixture at ambient temperature. After stirring for 1.5 h at the same temperature, the reaction was quenched with H_2O. The reaction mixture was extracted with $CHCl_3$. The extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo to leave a residue, which was purified by column chromatography on silica gel using hexane-AcOEt (19:1, v/v) as a eluent to give vinyl ether **2a** (1.63 g, 92%) as a colorless oil; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.01 (2H, d, J = 9.2 Hz), 6.88 (2H, d, J = 9.2 Hz), 5.88 (1H, s), 3.80 (3H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 156.5, 147.5, 140.6, 118.4, 114.6, 102.5, 55.5.

(*E*)-1-(1,2-Dichlorovinyloxy)-3-methoxybenzene[13] **(2b).** Etherification of 3-methoxyphenol (**1b**) (10.0 g, 80.6 mmol) was carried out according to the same procedure as described for **2a** to give **2b** (13.7 g, 93%) as a colorless oil [eluent: hexane]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.26 (1H, d, J = 8.2 Hz), 6.71 (1H, ddd, J = 8.2, 2.4, 0.8 Hz), 6.66 (1H, ddd, J = 8.2, 2.4, 0.8 Hz), 6.63 (1H, t, J = 2.4 Hz), 5.96 (1H, s), 3.81 (3H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 160.8, 154.8, 139.8, 130.1, 110.0, 108.9, 104.0, 103.2, 55.4.

(*E*)-1-(1,2-Dichlorovinyloxy)-2-methoxybenzene[12] **(2c).** Etherification of 2-methoxyphenol (**1c**) (7.01 g, 56.5 mmol) was carried out according to the same procedure as described for **2a** to give **2c** (12.3 g, 99%) as a colorless oil [eluent: hexane-AcOEt (39:1, v/v)]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.15 (1H, ddd, J = 8.1, 7.5, 1.6 Hz), 7.03 (1H, dd, J = 8.0, 1.6 Hz), 6.98 (1H, dd, J = 8.1, 1.4 Hz), 6.94 (1H, ddd, J = 8.0, 7.5, 1.4 Hz), 5.85 (1H, s), 3.90 (3H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 150.2, 142.4, 140.4, 125.4, 120.6,

118.1, 112.7, 101.4, 56.0.

(*E*)-1-(1,2-Dichlorovinyloxy)-4-methylbenzene[4] **(2d).** Etherification of *p*-cresol (**1d**) (0.99 g, 9.23 mmol) was carried out according to the same procedure as described for **2a** to give **2d** (1.54 g, 82%) as a colorless oil [eluent: hexane]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.16 (2H, d, *J* = 8.1 Hz), 6.96 (2H, d, *J* = 8.1 Hz), 5.92 (1H, s), 2.34 (3H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 151.6, 140.2, 134.1, 130.2, 117.0, 103.2, 20.7.

(*E*)-1-(1,2-Dichlorovinyloxy)-3-methylbenzene[4] **(2e).** Etherification of *m*-cresol (**1e**) (1.01 g, 9.34 mmol) was carried out according to the same procedure as described for **2a** to give **2e** (1.73 g, 91%) as a colorless oil [eluent: hexane]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.26-7.22 (1H, m), 6.98 (1H, d, *J* = 7.3 Hz), 6.88 (1H, s), 6.87 (1H, d, *J* = 7.0 Hz), 5.95 (1H, s), 2.37 (3H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 153.7, 140.1, 140.0, 129.4, 125.3, 117.6, 113.9, 103.6, 21.4.

(*E*)-1-(1,2-Dichlorovinyloxy)-2-methylbenzene[14] **(2f).** Etherification of *o*-cresol (**1f**) (1.01 g, 9.34 mmol) was carried out according to the same procedure as described for **2a** to give **2f** (1.66 g, 87%) as a colorless oil [eluent: hexane]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.23-7.17 (2H, m), 7.08 (1H, dt, *J* = 7.4, 1.1 Hz), 6.93 (1H, dd, *J* = 8.1, 1.1 Hz), 5.91 (1H, s), 2.32 (3H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) 152.3, 140.5, 131.6, 128.6, 127.1, 124.7, 116.2, 102.6, 16.0.

(*E*)-1-(1,2-Dichlorovinyloxy)naphthalene[14,15] **(2g).** Etherification of 1-naphthol (**1g**) (5.03 g, 34.9 mmol) was carried out according to the same procedure as described for **2a** to give **2g** (5.84 g, 70%) as pale yellow oil [eluent: hexane-AcOEt (39:1, v/v)]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 8.24-8.22 (1H, m), 7.88-7.87 (1H, m), 7.67 (1H, d, *J* = 8.3 Hz), 7.57-7.54 (1H, m), 7.43 (1H, t, *J* = 8.0 Hz), 7.08 (1H, dd, *J* = 7.6, 0.8 Hz), 6.06 (1H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 149.5, 140.2, 134.7, 127.6, 126.3, 126.8, 125.4, 125.2, 124.3, 121.4, 110.4, 103.9.

(*E*)-2-(1,2-Dichlorovinyloxy)naphthalene[14] **(2h).** Etherification of 2-naphthol (**1h**) (1.00 g, 6.94 mmol) was carried out according to the same procedure as described for **2a** to give **2h** (1.28 g, 77%) as a colorless oil [eluent: hexane-AcOEt (39:1, v/v)]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.84 (2H, t, *J* = 8.3 Hz), 7.80 (1H, d, *J* = 8.1 Hz), 7.50 (1H, t, *J* = 7.5 Hz), 7.45 (1H, d, *J* = 7.1 Hz), 7.42-7.41 (1H, br m), 7.27 (1H, dd, *J* = 8.9, 1.9 Hz), 6.03 (1H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 151.5, 140.0, 133.8, 130.7, 130.1, 127.8, 127.3, 126.9, 125.3, 117.8, 112.5, 104.1.

(*E*)-4-(1,2-Dichlorovinyloxy)benzonitrile[4] **(2i).** To a flask were added 4-cyanophenol (**1i**) (0.29 g, 2.51 mmol) and trichloroethylene (0.43 g, 3.23 mmol). After the flask was flushed with Ar, DMSO (1.9 mL) and Cs_2CO_3 (1.07 g, 3.28 mmol) were added to the reaction mixture at ambient temperature. After stirring for 1.5 h at 70 °C, the reaction was quenched with H_2O. The reaction mixture was extracted with $CHCl_3$. The extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo to leave a residue, which was purified by column chromatography on silica gel using hexane-AcOEt (19:1, v/v) as a eluent

to give vinyl ether **2i** (0.55 g, 99%) as a white solid; Mp 69–70 °C; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.70 (1H, d, *J* = 9.0 Hz, 1H), 7.16 (1H, d, *J* = 9.0 Hz, 1H), 6.10 (s, 1H); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 156.8, 138.5, 134.2, 118.2, 117.3, 108.1, 106.1.

(*E*)-3-(1,2-Dichlorovinyloxy)benzonitrile[4] **(2j).** Etherification of 3-cyanophenol (**1j**) (1.01 g, 8.48 mmol) was carried out according to the same procedure as described for **2a** to give **2j** (1.60 g, 88%) as a colorless oil [eluent: hexane-AcOEt (39:1, v/v)]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.56-7.46 (2H, m), 7.35-7.30 (2H, m), 6.07 (1H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 153.6, 138.6, 130.7, 127.9, 121.4, 119.9, 117.6, 113.6, 105.5, 130.7.

(*E*)-2-(1,2-Dichlorovinyloxy)benzonitrile[4] **(2k).** Etherification of 2-cyanophenol (**1k**) (0.30 g, 2.53 mmol) was carried out according to the same procedure as described for **2h** to give **2k** (0.51 g, 95%) as a white solid [eluent: hexane-AcOEt (19:1, v/v)]; Mp 72–74 °C; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.69 (1H, dd, *J* = 7.7, 1.7 Hz), 7.62 (1H, ddd, *J* = 8.5, 7.7, 1.7 Hz), 7.27 (1H, dt, *J* = 7.7, 1.0 Hz), 7.13 (1H, dd, *J* = 8.5, 1.0 Hz), 6.11 (1H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 155.1, 138.5, 134.3, 134.1, 124.6, 115.9, 114.9, 106.2, 103.7.

(*E*)-1-(1,2-Dichlorovinyloxy)-2-iodobenzene[14,16] **(2l).** Etherification of 2-iodophenol (**1l**) (1.01 g, 4.59 mmol) was carried out according to the same procedure as described for **2a** to give **2l** (1.29 g, 89%) as a colorless oil [eluent: hexane]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.84 (1H, dd, *J* = 7.9, 1.6 Hz), 7.35 (1H, ddd, *J* = 8.2, 7.4, 1.6 Hz), 7.00 (1H, dd, *J* = 8.2, 1.4 Hz), 6.92 (1H, ddd, *J* = 7.9, 7.4, 1.4 Hz), 6.00 (s, 1H); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 153.1, 140.0, 139.8, 129.6, 126.2, 116.4, 104.2, 86.5.

(*E*)-1-*tert*-Butyl-2-(1,2-dichlorovinyloxy)benzene[14] **(2m).** Etherification of 2-*tert*-butylphenol (**1i**) (1.01 g, 8.48 mmol) was carried out according to the same procedure as described for **2a** to give **2m** (1.45 g, 88%) as a pale yellow oil [eluent: hexane]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.38 (1H, dd, *J* = 7.8, 1.7 Hz, 1H), 7.21 (1H, ddd, *J* = 8.1, 7.5, 1.7 Hz), 7.10 (1H, ddd, *J* = 7.8, 7.5, 1.3 Hz), 6.93 (1H, dd, *J* = 8.1, 1.3 Hz), 5.99 (1H, s); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 152.2, 139.3, 139.2, 127.4, 127.0, 124.1, 116.0, 103.7, 34.7, 30.0.

(*E*)-1-(1,2-Dichlorovinyloxy)-4-fluorobenzene[17] **(2n).** Etherification of 4-fluorophenol (**1n**) (1.01 g, 9.01 mmol) was carried out according to the same procedure as described for **2a** to give **2n** (1.63 g, 87%) as a colorless oil [eluent: hexane]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.05 (5H, m), 5.94 (s, 1H); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 160.7, 158.2, 149.7, 149.7, 140.2, 118.6, 118.5, 116.4, 116.2, 103.6.

(*E*)-1-Bromo-4-(1,2-dichlorovinyloxy)benzene[18] **(2o).** Etherification of 4-bromophenol (**1o**) (1.01 g, 5.48 mmol) was carried out according to the same procedure as described for **2a** to give **2o** (1.41 g, 90%) as a colorless oil [eluent: hexane]; IR ν max 3100, 1632, 1590, 1482, 1203, 1065 cm^{-1}; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.48 (1H, d, *J* = 9.0 Hz), 6.96 (1H, d, *J* = 9.0 Hz), 5.98 (s, 1H); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 152.8, 139.6, 132.7, 118.7, 117.2, 104.4.

(*E*)-1-(1,2-Dichlorovinyloxy)-4-nitrobenzene[4,13] **(2p).** Etherification of 4-nitrophenol (**1p**) (0.30 g, 2.17 mmol) was carried out according to the same procedure as described for **2h** to give **2p** (0.50 g, 99%) as a yellow oil [eluent: hexane-AcOEt (19:1, v/v)]; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 8.29 (1H, d, *J* = 9.3 Hz), 7.19 (1H, d, *J* = 9.3 Hz), 6.13 (s, 1H); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 158.2, 144.1, 138.4, 125.8, 116.7, 106.3.

2-Phenylbenzofuran-5-carbonitrile[19] **(3i).** To a flask were added phenylboronic acid (60.0 mg, 0.49 mmol), $Pd_2(dba)_3$ (12.0 mg, 13.1 μmol), bis[2-diphenylphosphino]phenyl]ether (DPEphos: 13.0 mg, 24.1 μmol), Cs_2CO_3 (0.46 g, 1.41 mmol) and CsF (227.0 mg, 1.49 mmol). After the flask was flushed with Ar, a solution of vinyl ether **2i** (0.10 g, 0.47 mmol) in 1,4-dioxane (1.2 mL) was added to the reaction mixture at ambient temperature. After stirring for 21 h at reflux, the reaction was quenched with H_2O. The reaction mixture was extracted with $CHCl_3$. The extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo to leave a residue, which was purified by column chromatography on silica gel using hexane-AcOEt (37:3, v/v) as a eluent to give benzofuran **3i** (79.0 mg, 76%) as a white solid; Mp 146–148 °C; ^{1}H-NMR ($CDCl_3$; 400 MHz) δ 7.93 (1H, dd, *J* = 1.6, 0.7 Hz), 7.91-7.84 (1H, m), 7.61 (1H, d, *J* = 8.5 Hz), 7.56 (1H, dd, *J* = 8.5, 1.6 Hz), 7.52-7.45 (1H, m), 7.46-7.38 (1H, m), 7.07 (1H, d, *J* = 0.7 Hz); ^{13}C-NMR ($CDCl_3$; 100 MHz) δ 158.3, 156.4, 129.9, 129.5, 129.3, 129.0, 127.9, 125.7, 125.2, 119.5, 112.3, 106.8, 100.7.

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