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DIRECT ARYLATION OF BENZOTHIOPHENE AND BENZOFURAN CATALYZED BY A DINUCLEAR PALLADIUM COMPLEX

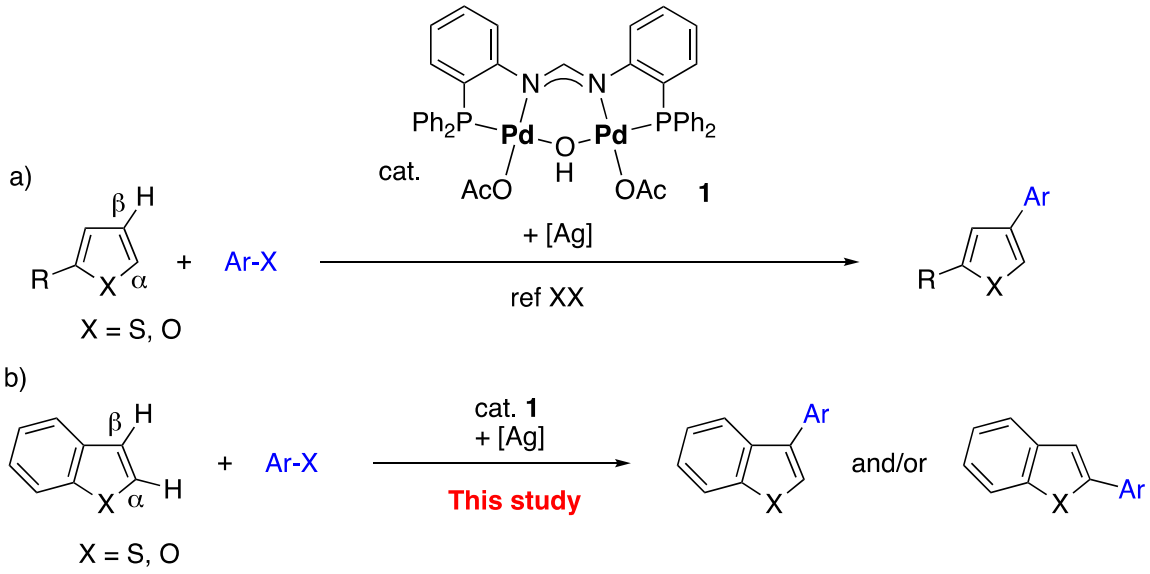
Takuma Mochizuki, Keiryu Seto, Yuma Sugiyama, and Naofumi Tsukada*

Department of Chemistry, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan. e-mail:tsukada.naofumi@shizuoka.ac.jp

Abstract – Direct arylation of benzothiophene and benzofuran with iodoarenes proceeded in the presence of a dinuclear palladium complex formed by a chelate-bridging ligand. In the reaction of benzothiophene, *β*-arylbenzothiophenes were selectively obtained by using silver acetate as an additive. In the reaction of benzofuran, *α*-arylbenzofurans were selectively obtained by using silver sulfonate as an additive.

Direct arylation of aryl C-H bonds catalyzed by transition metal complexes has emerged as an alternative to the conventional palladium-catalyzed cross-coupling reactions.[1] The direct arylation of 5-membered heteroarenes such as furan, thiophene and their derivatives is a valuable and important method for the construction of arylated heteroarenes, which are prevalent in natural products,[2] pharmaceuticals,[3] and organic materials.[4] However, difficulty in controlling of site-selectivity is a significant problem for the direct arylation because several aryl C-H bonds exist in starting materials in most cases.

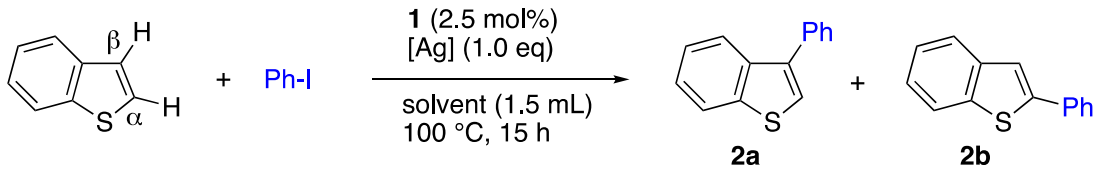
In the course of our studies on dinuclear complexes,[5] we found that dinuclear complex **1** worked as an effective catalyst for the arylation of thiophenes and furans (Scheme 1a).[6] Furthermore, catalyst **1** showed unusual site-selectivity. In the presence of **1**, β-arylated products are selectively obtained, while there are a lot of reports for α-arylation reactions.[7] Herein, we report the site-selectivity of **1** for the direct arylation of benzothiophene and benzofuran, which have different reactivity from thiophene and furan due to fusion with a benzene ring (Scheme 1b).



Scheme 1. Direct arylation of thiophenes and furans with haloarenes catalyzed by dinuclear complex **1**

In the case of the direct arylation of thiophene with haloarenes, β-selective reaction has been less known than α-selective reaction.[6b,7,8] Similarly, β-selective reaction is rather limited for the direct arylation of benzothiophene with haloarenes.[8d,9,10] Initially, the site-selectivity of **1** in the arylation of benzothiophene with iodobenzene was investigated (Table 1). Addition of silver carbonate, which is effective for the arylation of ethylthiophene,[6b] did not gave satisfactory results (entry 1). Both of the yield and the β-selectivity for 3-phenylbenzothiophene **2a** are low. The β-selectivity was significantly improved by using silver salts of carboxylic acids (entries 2 and 3). Unexpectedly, the site-selectivity was inverted by using silver oxides. In the arylation with AgO or Ag_2O, 2-phenylbenzothiophene **2b** was obtained as a sole product (entries 5 and 6). The yield of **2a** was also improved by using 2-propanol as a solvent (entries 7-11). Finally, **2a** was obtained in 97% yield with high site-selectivity after optimization of several reaction conditions (entry 12). The use of 2-propanol was also effective for improvement of the yield in the arylation with silver oxide. However, the high α-selectivity for **2b** was not observed (entries 13 and 14).

Table 1. Direct arylation of benzothiophene catalyzed by dinuclear palladium complex **1**[a]



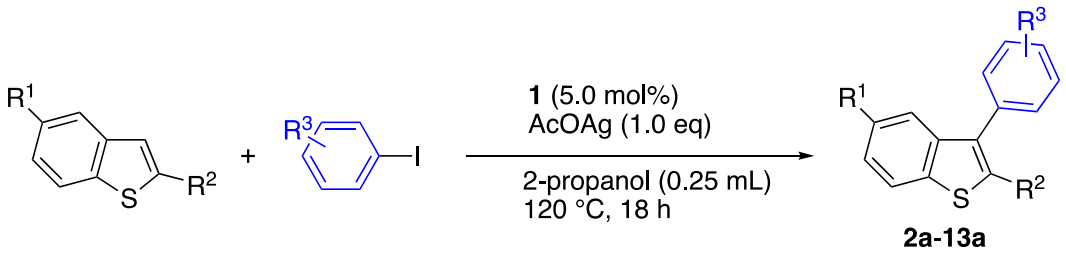
Entry	[Ag]	Solvent	Yield[b] (%)	**2a**:**2b**[b]
1	Ag_2CO_3	CPME	25	60:40
2	AcOAg	CPME	47	>95:<5
3	$C_6H_5CO_2Ag$	CPME	12	>95:<5

4	*tert*-$C_4H_9CO_2Ag$	CPME	11	64:36
5	AgO	CPME	14	<5:>95
6	Ag_2O	CPME	18	<5:>95
7	AcOAg	1,4-dioxane	31	90:10
8	AcOAg	toluene	35	>95:<5
9	AcOAg	DMF	22	82:18
10	AcOAg	HFIP	20	>95:<5
11	AcOAg	2-propanol	64	95:5
12[c]	AcOAg	2-propanol	97	>95:<5
13[c]	AgO	2-propanol	60	70:30
14[c]	Ag_2O	2-propanol	47	23:77

[a] A mixture of benzothiophene (0.45 mmol), iodobenzene (0.30 mmol), and a silver salt (0.30 mmol) in a solvent (1.5 mL) was stirred at 100 °C for 15 h in the presence of **1** (7.5 μmol). CPME: cyclopentyl methyl ether. HFIP: hexafluoroisopropyl alcohol. [b] Determined by GC using dodecane as an internal standard. [c] 0.25 mL of 2-propanol, 120 °C.

Table 2 summarizes the results of the reaction of several benzothiophenes and various iodoarenes in the presence of **1**. 3-Phenylbenzothiophene **2a** was isolated in 81% yield from the reaction carried out under the above reaction conditions (Table 1, entry 12). Electron-donating substituents on haloarenes did not affect the yield and the selectivity of products. Tolylbenzothiophene **3a** and anisylbenzothiophene **4a** were obtained in high yields and with high β-selectivity (Table 2, entries 2 and 3). Electron-withdrawing substituents decreased the β-selectivity. While acetyl and methoxycarbonyl groups slightly decreased the selectivity (entries 4 and 5), strong electron-withdrawing substituents such as cyano and nitro decreased the selectivity to 76% (entries 6 and 7). *Ortho* and *meta* substituents affect only the reactivity of iodoarenes. The reaction of *o*-iodotoluene and *m*-iodotoluene afforded 3-arylbenzothiophene **10a** or **11a** with high site-selectivity although the yields were lower (entries 9 and 10). The reaction of substituted benzothiophenes was also investigated. A methyl group at C5 position did not affect the high β-selectivity (entry 11). A methyl group at C2 position restricted the arylation reaction (entry 12).

Table 2. Direct arylation of several benzothiophenes with various iodoarenes[a]



2a-13a

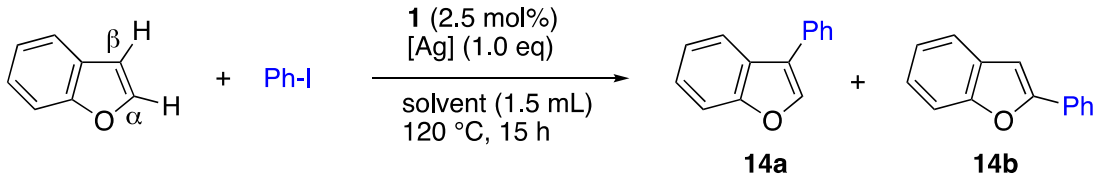
Entry	R^1	R^2	R^3	Product	Yield[b] (%)	β Selectivity[c]
1	H	H	H	**2a**	81	>95
2	H	H	*p*-Me	**3a**	84	>95
3	H	H	*p*-OMe	**4a**	100	>95
4	H	H	*p*-COMe	**5a**	79	93
5	H	H	*p*-CO_2Me	**6a**	88	94
6	H	H	*p*-CF_3	**7a**	100	87
7	H	H	*p*-CN	**8a**	46	76
8	H	H	*p*-NO_2	**9a**	78	76
9[d]	H	H	*m*-Me	**10a**	62	>95
10[d]	H	H	*o*-Me	**11a**	64	>95
11	Me	H	H	**12a**	21	>95
12	H	Me	H	**13a**	0	-

[a] A mixture of a benzothiophene (0.45 mmol), a iodoarene (0.30 mmol), AcOAg (0.30 mmol) in 2-propanol (0.25 mL) was stirred at 120 °C for 18 h in the presence of **1** (15 mmol). [b] Isolated yields. [c] Determined by ^{1}H NMR spectrum. [d] Reaction time: 42 h.

Most of the direct arylation of benzofuran with haloarenes proceeds with high α-selectivity, giving 2-arylbenzofuran.[10b,11] For β-selective arylation, there are no reports for the reaction with haloarenes, and only a few reports for the reaction with azoarenes or the oxidative reaction with arenes.[12] Therefore, the site-selectivity of dinuclear palladium complex **1** in the arylation of benzofuran with iodobenzene was investigated (Table 3). The reaction in the presence of **1** gave 3-phenylbenzofuran **14a** as a major product under reaction conditions similar to the reaction of benzothiophene (entry 1). However, both of the yield and the β-selectivity was low. Changing 2-propanol to other solvents did not improve the yield and the β-selectivity (entries 2-5). The reaction in acetic acid afforded 2-phenylbenzofuran **14b** as a major product (entry 3). Changing AcOAg to other silver salts improved the yield. When silver tosylate and silver 10-camphorsulfonate were used as as additive, the reaction proceeded with high α-selectivity, giving phenylbenzofuran **14** in 43% and 56% yields, respectively. After optimization of reaction conditions, 2-phenylbenzofuran **14b** was obtained in 84% yield with high site-selectivity.

These silver sulfonates were also effective for conventional catalytic systems for α-selective direct arylation of benzofuran. For example, the reaction catalyzed by Pd(OCO-*t*-Bu)$_2$/dppb instead of **1** afforded only α-phenylbenzofuran **14b** in high yield. The use of silver sulfonates did not affect the site-selectivity in the reaction of benzothiophene. The reaction of benzothiophene in the presence of TsOAg gave only β-phenylthiophene **2a** with high site-selectivity.

Table 3. Direct arylation of furan catalyzed by dinuclear palladium complex **1**[a]



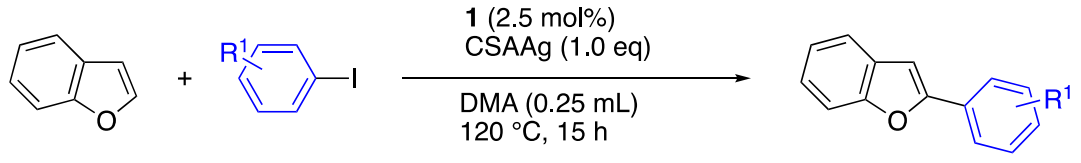
14a **14b**

Entry	[Ag]	Solvent	Yield[b] (%)	**14a**:**14b**[b]
1	AcOAg	2-propanol	19	67:33
2	AcOAg	HFIP	30	22:78
3	AcOAg	acetic acid	39	10/90
4	AcOAg	CPME	19	69:31
5	AcOAg	NMP	15	77:23
6	AgO	NMP	8	41:59
7	Ag_2O	NMP	8	27:73
8	TsOAg	NMP	43	5:95
9	CSAAg	NMP	56	6:94
10	TsONa	NMP	2	61:39
11	$(TsO)_2Cu$	NMP	22	30:70
12[x]	TsOAg	DMA	67	<5:>95
13[x]	CSAAg	DMA	84	<5:>95

[a] A mixture of benzofuran (0.30 mmol), iodobenzene (0.30 mmol), and a silver salt (0.30 mmol) in a solvent (0.25 mL) was stirred at 120 °C for 15 h in the presence of **1** (7.5 μmol). TsOAg: silver *p*-toluenesulfonate. CSAAg: silver 10-camphorsulfonate. [b] Determined by GC using dodecane as an internal standard. [c] 0.60 mmol of iodobenzene was used.

Table 4 summarizes the results of the α-arylation of benzofuran and several iodoarenes in the presence of **1**. Both of electron-donating and electron-withdrawing groups on iodoarenes did not affect the site-selectivity. In all cases, 2-arylbenzofurans were obtained with high α-selectivity.

Table 4. Direct arylation of benzofuran with several iodoarenes[a]



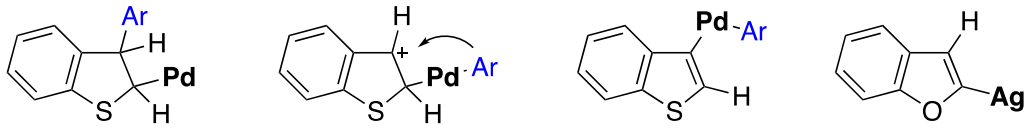
15b-18b

Entry	R^1	Product	Yield[b] (%)	α Selectivity[c]
1	*p*-Me	**15b**	85	>95
2	*p*-OMe	**16b**	45	>95
3	*p*-CO_2Me	**17b**	84	>95

4	*p*-Cl	**18b**	72	>95

[a] A mixture of benzofuran (0.30 mmol), a iodoarene (0.60 mmol), and CSAAg (0.30 mmol) in DMA (0.25 mL) was stirred at 120 °C for 15 h in the presence of **1** (7.5 μmol). [b] Isolated yields. [c] Determined by ^{1}H NMR spectrum.

Reaction mechanism for the above direct arylation has not been clear. For the mechanism of β-selective arylation of benzothiophene with haloarenes, Larrosa proposed a Heck-type pathway through intermediate **19**,[9b] and Itami proposed a electrophilic attack of cationic palladium, generating intermediate **20**, and followed by aryl ligand migration.[9c] These mechanism may be plausible for the reaction catalyzed by **1**. However, a CMD pathway[13] through intermediate **21** should be considered because the addition of acetate anion improved the yield and site-selectivity (Table 1). While the CMD pathway has been proposed for α-arylation of benzothiophene,[10a,10b,13] the reaction catalyzed by **1** proceed with high β-selectivity. The difference of site-selectivity could be caused by the dinuclear structure of **1** although a precise mechanism cannot be discussed. The above arylation of benzofuran proceeded with high α-selectivity by addition of silver sulfonates (Table 3). The reaction may proceed through a C-H activation with silver ion through intermediate **22**.[10h] Silver ion is more easily dissociated from sulfonates than from carboxylates.



19 **20** **21** **22**

In summary, we found that the dinuclear palladium complex **1** was effective for the β-selective arylation of benzothiophene with iodoarenes. The addition of silver acetate was necessary for the high yield and selectivity. Although the β-selective arylation of benzofuran was not achieved, the addition of silver sulfonated such as TsOAg and CSAAg was found to be effective for the α-selective arylation of benzofuran with iodoarenes.

EXPERIMENTAL

All reactions were carried out under nitrogen atmosphere. Dry solvents were purchased and used directly as received. Benzothiophene, benzofuran and iodoarenes were purchased and used without further purification. Complex **1** were prepared according to the literature procedure.[6b] ^{1}H NMR spectra were measured at 25 °C on a 600 MHz spectrometer. Chemical shifts are reported in the scale relative to tetramethylsilane (0 ppm). ^{13}C{1H} NMR spectra were measured at 25 °C on a 151 MHz spectrometer.

Chemical shifts are reported in the scale relative to $CDCl_3$ (77.0 ppm). The structures of the products **2-18** were determined by comparing their ^1H NMR spectra with those in the literature.[9b,11a,13,15]

General procedure for arylation of benzothiophene with iodoarenes (Table 2).

To a mixture of **1** (13.6 mg, 5.0 mol%, 15 mmol), AgOAc (50 mg, 0.30 mmol) and a thiophene (0.45 mmol) were added 2-propanol (0.25 mL) and then a iodoarene (0.30 mmol) in a pressure vial. After stirring at 120 °C for 18 h, the mixture was cooled and then filtered through a short plug of silica gel using EtOAc as an eluent. After evaporation of volatiles in the filtrate, the products were separated from the residue by silica gel column chromatography.

3-Phenylbenzo[*b*]thiophene (2a):[9b] ^1H NMR ($CDCl_3$): δ 7.92 (m, 2H), 7.59 (d, *J* = 6.9 H, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43-7.36 (m, 4H).

3-(*p*-Tolyl)benzo[*b*]thiophene (3a):[9b] ^1H NMR ($CDCl_3$): δ 7.91 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.38 (m, 2H), 7.37 (s, 1H), 7.30 (d, *J* = 8.3 Hz), 2.43 (s, 3H).

3-(4-Methoxyphenyl)benzo[*b*]thiophene (4a):[9b] ^1H NMR ($CDCl_3$): δ 7.89 (m, 2H), 7.50 (m, 2H), 7.37 (m, 2H), 7.31 (s, 1H), 7.01 (m, 2H), 3.86 (s, 3H).

3-(4-Acetylphenyl)benzo[*b*]thiophene (5a):[9b] ^1H NMR ($CDCl_3$): δ 8.09 (m, 2H), 7.94 (m, 1H), 7.92 (m, 1H), 7.70 (m, 2H), 7.50 (s, 1H), 7.45-7.39 (m, 2H), 2.67 (s, 3H).

Methyl 4-(benzo[*b*]thiophen-3-yl)benzoate (6a):[9b] ^1H NMR ($CDCl_3$): δ 8.16 (d, *J* = 8.3 Hz, 2H), 7.94 (m, 1H), 7.91 (m, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.49 (s, 1H), 7.45-7.38 (m, 2H), 3.96 (s, 3H).

3-(4-(Trifluoromethyl)phenyl)benzo[*b*]thiophene (7a):[9b] ^1H NMR ($CDCl_3$): δ 7.93 (m, 1H), 7.87 (m, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.45 (s, 1H), 7.44-7.38 (m, 2H).

4-(Benzo[*b*]thiophen-3-yl)benzonitrile (8a):[13] ^1H NMR ($CDCl_3$): δ 7.95 (m, 1H), 7.87 (m, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.51 (s, 1H), 7.45-7.41 (m, 2H).

3-(4-Nitrophenyl)benzo[*b*]thiophene (9a):[9b] ^1H NMR ($CDCl_3$): δ 8.30 (d, *J* = 8.3 Hz, 2H), 7.90-7.82 (m, 4H), 7.73 (s, 1H), 7.44-7.36 (m, 2H).

3-(*m*-Tolyl)benzo[*b*]thiophene (10a):[9b] ^1H NMR ($CDCl_3$): δ 7.93-7.89 (m, 2H), 7.41-7.35 (m, 6H), 7.22 (m , 1H), 2.43 (s, 3H).

3-(*o*-Tolyl)benzo[*b*]thiophene (11a): ^1H NMR ($CDCl_3$):[9b] δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37-7.25 (m, 7H), 2.17 (s, 3H).

5-Methyl-3-phenylbenzo[*b*]thiophene (12a):[15] ^1H NMR ($CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.70 (s, 1H), 7.58 (m, 2H), 7.49 (m, 2H), 7.40 (m, 1H), 7.36 (s, 1H), 7.22 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.46 (s, 3H).

General procedure for arylation of benzofuran with iodoarenes (Table 4).

To a mixture of **1** (6.9 mg, 2.5 mol%, 7.5 μmol), silver 10-camphorsulfonate (102 mg, 0.30 mmol) and a furan (0.30 mmol) were added DMA (0.25 mL) and then a iodoarene (0.60 mmol) in a pressure vial. After stirring at 120 °C for 15 h, the mixture was cooled and then filtered through a short plug of silica

gel using EtOAc as an eluent. After evaporation of volatiles in the filtrate, the products were separated from the residue by silica gel column chromatography.

2-Phenylbenzo[*b*]furan (14b):[11a] ^{1}H NMR ($CDCl_3$): δ 7.86 (m, 2H), 7.58 (d, *J* = 6.9 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 (m, 2H), 7.35 (m, 1H), 7.28 (m, 1H), 7.23 (m, 1H), 7.02 (s, 1H).

2-(*p*-Tolyl)benzo[*b*]furan (15b):[11a] ^{1}H NMR ($CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.23 (m, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.21 (m, 1H), 6.95 (s, 1H), 2.39 (s, 3H).

2-(4-Methoxyphenyl)benzo[*b*]furan (16b):[11a] ^{1}H NMR ($CDCl_3$): δ 7.80 (m, 2H), 7.55 (dd, *J* = 1.4, 6.9 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.27-7.19 (m, 2H), 6.98 (m, 2H), 6.89 (s, 1H), 3.87 (s, 3H).

Methyl 4-(benzo[*b*]furan-2-yl)benzoate (17b):[11a] ^{1}H NMR ($CDCl_3$): δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 8.3 Hz, 1H), 7.25 (t, *J* = 6.9 Hz, 1H), 7.14 (s, 1H), 3.94 (s, 3H).

2-(4-Chlorophenyl)benzo[*b*]furan (18b):[11a] ^{1}H NMR ($CDCl_3$): δ 7.78 (m, 2H), 7.58 (d, 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.41 (m, 2H), 7.29 (m, 1H), 7.23 (m, 1H), 7.00 (s, 1H).

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