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SYNTHESIS OF BENZO[*b*]NAPHTHO[2,3-*d*]THIOPHENE-6,11-DIONES *VIA* PALLADIUM(II) ACETATE-MEDIATED CYCLIZATION OF 3-ARYLTHIO-1,4-NAPHTHOQUINONE

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Abstract – Palladium(II)-mediated oxidative cyclization of 3-arylthio-1,4-naphthoquinone (**4**) giving biologically important benzo[*b*]naphtho-[2,3-*d*]thiophene-6,11-diones (**2**) has been performed with a stoichiometric amount of palladium(II) acetate in distillated acetic acid.

INTRODUCTION

Palladium-mediated annulation methodology has been effectively employed for the preparation of new heterocyclic systems.[1] Compounds containing the quinone group represent an important class of biologically active molecules that are widespread in nature.[2-3] The heterocyclic benzo[*b*]naphtho[2,3-*d*]furan-6,11-dione derivatives (**1**) have received attention due to their potential biological activities (Figure 1).[4]

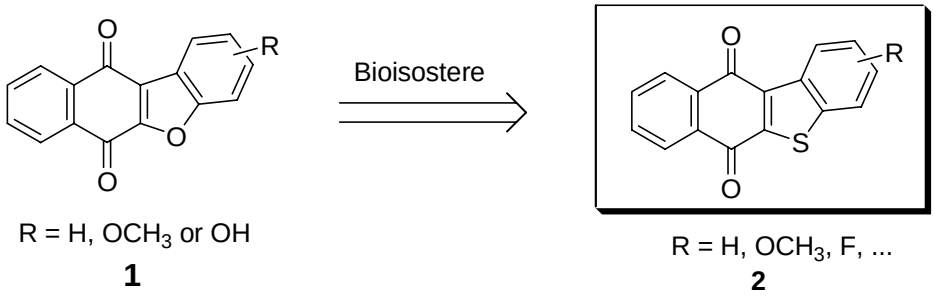
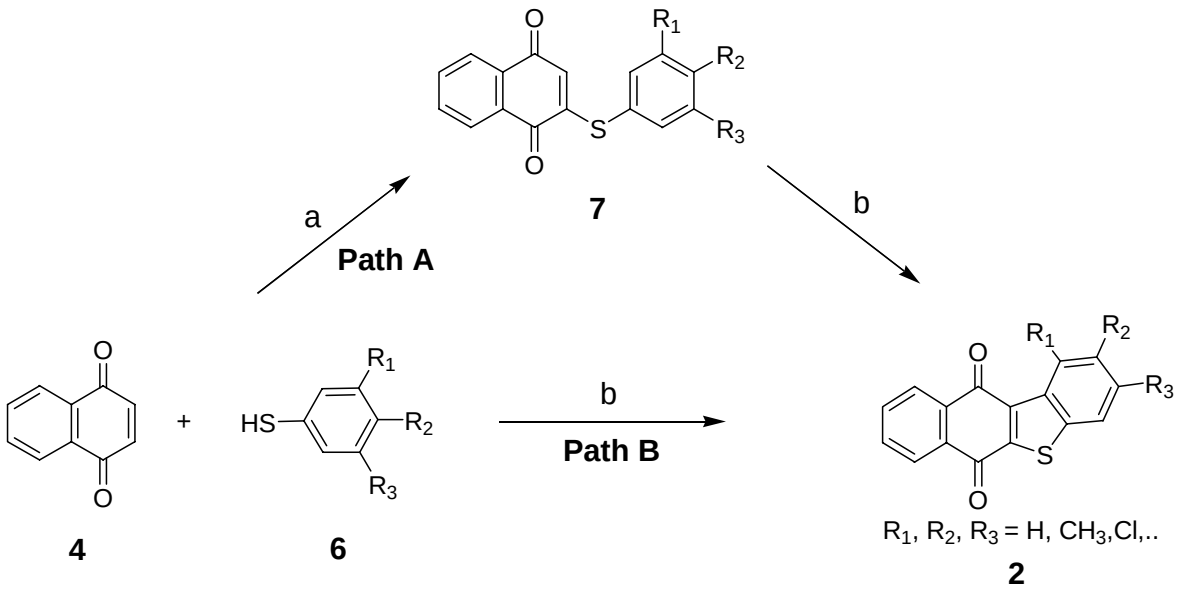


Figure 1

This fact prompted us to consider an bioisosteric substitution of the 5'-oxygen (O) by sulfur (S). The quinone analogues containing a sulfur such as benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-diones (**2**) could have similar activity as compounds (**1**) because sulfur is isoelectronic with oxygen. Therefore, we

synthesized benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-diones (**2**) as a bioisostere of the compounds (**1**) (Figure 1).

As shown in Scheme 1, compounds (**2**) could be synthesized by either one-pot (Path B) or two step synthesis (Path A) from 1,4-naphthoquinone (**4**) and appropriate arylthiols (**6**). Although one-pot synthesis of compounds (**2**) seem to be much more attractive, the two step synthesis is much easier than one-pot synthesis as a result of the difficulty in both the substitution reaction and the C-C coupling. Herein, we report efficient two-step synthesis of compounds (**2**) *via* quantitative palladium(II) acetate-mediated cyclization of 3-arylthio-1,4-naphthoquinones (**7**).

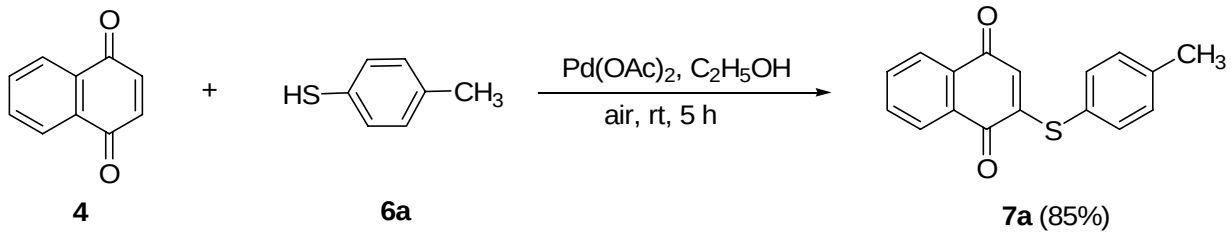


Reagents and conditions
a) 0.05 equiv. $Pd(OAc)_2$, C_2H_5OH, rt, 4~6 h
b) 1 equiv. $Pd(OAc)_2$, HOAc, reflux, argon, 2~40 h

Scheme 1

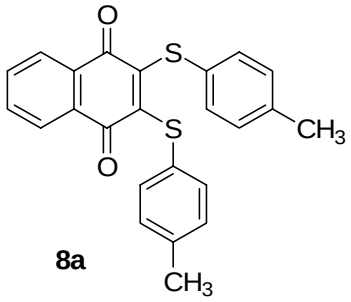
RESULTS AND DISCUSSION

The first step in Path A synthesis was preparation of 3-arylthio-1,4-naphthoquinones (**7**) according to known process[5] with modification (Scheme 1). For example, the substitution of 4-methylbenzenethiol (**6a**) to the quinone (**4**) in the presence of 0.05 equivalent palladium(II) acetate as a catalyst in air at room temperature for 5 h afforded 3-(4-methylphenylthio)-1,4-naphthoquinone (**7a**) in moderate yield (Scheme 2).



Scheme 2 Substitution of 4-methylbenzenethiol (**6a**) to 1,4-naphthoquinone (**4**)

Otherwise, reactions in absence of the palladium(II) acetate provided the compound (**7a**) with poor yields (15%) along with 2,3-bis(4-methylphenylthio)-1,4-naphthoquinone (**8a**) as a by-product (67%). The desired product (**7a**) and the by-product (**8a**) were separated by column chromatography on silica gel using $CHCl_3$ as eluent.



Ethanol for the reaction seems to be the best solvent. Acetic acid and THF were also tried, and in the solvents the product (**7a**) were observed with lower yield than in ethanol (Table 1).

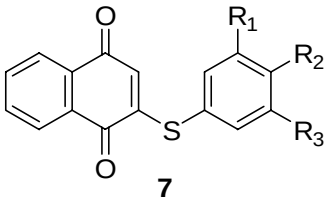
Table 1 Substitution of 4-methylbenzenethiol (**6a**) to 1,4-naphthoquinone (**4**)

entry	reaction condition	**7** (%)[a)]	**8** (%)	**7/8** ratio
1	C_2H_5OH/ air/ reflux/ 5 h	52	34	6 : 4
2	HOAc/ air/ reflux/ 5 h	41	23	2 : 1
3	0.05 equiv. $Pd(OAc)_2$/ C_2H_5OH/ air/ reflux/ 5 h	85	0	-
4	0.05 equiv. $Pd(OAc)_2$/ HOAc/ air/ reflux/ 5 h	6	0	-
3	0.05 equiv. $Pd(OAc)_2$/ THF/ air/ reflux/ 5 h	70	0	-

a) isolated yield

A number of 3-arylthio-1,4-naphthoquinones (**7**) synthesized by employing the optimized reaction condition (Scheme 1 and Table 1). The various 3-arylthio-1,4-naphthoquinones (**7**) were prepared by the substitution of appropriate arylthiols (**6**) to the quinone (**4**) in the presence of 0.05 equivalent palladium(II) acetate as a catalyst in air at room temperature for 5 h in moderate yield, respectively (Table 2).

Table 2 Structure of afforded 3-arylthio-1,4-naphthoquinones (**7**)

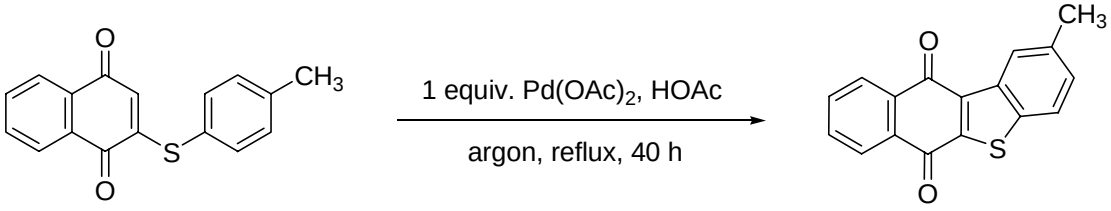


7

compounds	R_1	R_2	R_3	yield (%)
7a	H	CH_3	H	85
7b	Cl	H	H	55
7c	H	H	H	62
7d	H	Cl	H	65
7e	CH_3	H	CH_3	74
7f	H	F	H	65
7g	F	H	H	56

Reaction condition: 1.0 mmol quinone (**4**)/ 0.05 mmol $Pd(OAc)_2$/ C_2H_5OH/ air/ rt/ 6 h

The second step in Path A synthesis was palladium(II)-mediated oxidative cyclization of compounds (**7**) in acetic acid provided the desired products (**2**) (Scheme 1). For example, we refluxed the 3-(4-methylphenylthio)-1,4-naphthoquinone (**7a**) with stoichiometric amounts of palladium(II) acetate in the distilled acetic acid under an argon atmosphere for about 40 h to afford 2-methyl-benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2a**) (Scheme 3). The acetic acid seems to be the best solvent for the oxidative cyclization. The purity of acetic acid is of primary importance for the cyclization,[5] but the reason for this is not known. Ethanol and THF were also tried, but in these solvents no cyclization was observed (Table 3).



7a **2a** (55%)

Scheme 3 Oxidative cyclization of 3-(4-methylphenylthio)-1,4-naphthoquinone (**7a**)

Furukawa described the first palladium(II)-mediated oxidative cyclization of 3-phenylamino-1,4-benzoquinones to carbazole-1,4-quinones.[6] In the synthesis of benzo[*b*]carbarzole-6,11-diones, Knölker demonstrated that this reaction becomes catalytic in palladium by reoxidation of Pd(0) to Pd(II) with Cu(II).[7-8] We also tried, but the catalytic condition by reoxidation with cupper(II) acetate was not useful for getting the cyclized product (**2a**) (Table 3).

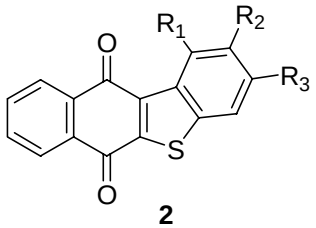
Table 3 Oxidative cyclization of the quinone (**7a**) for getting the cyclized product (**2a**)

entry	solvent	$Cu(OAc)_2$	time	atmosphere	yield (%)
1	HOAc	-	24 h	argon	30%
2	HOAc	-	40 h	argon	55%
3	HOAc	-	40 h	air	0
4	HOAc	2.5 equiv.	40 h	argon	trace
5	C_2H_5OH	2.5 equiv.	40 h	argon	0
6	C_2H_5OH	-	40 h	argon	0
7	THF	-	40 h	argon	trace

We refluxed the 0.2 mmol quinone (**7a**) with 0.2 mmol of $Pd(OAc)_2$ in various conditions

In order to determine the versatility of this intramolecular C-C coupling process on a quinone system, a number of benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-diones (**2**) were synthesized by employing the optimized reaction condition (Scheme 1 and Table 3). The various benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-diones (**2**) was obtained by clyclization of 3-arylthio-1,4-naphthoquinones (**7**) with stoichiometric amounts of palladium(II) acetate in refluxed acetic acid under an argon atmosphere for about 40 h (Table 4).

Table 4 Structure of benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-diones (**2**)

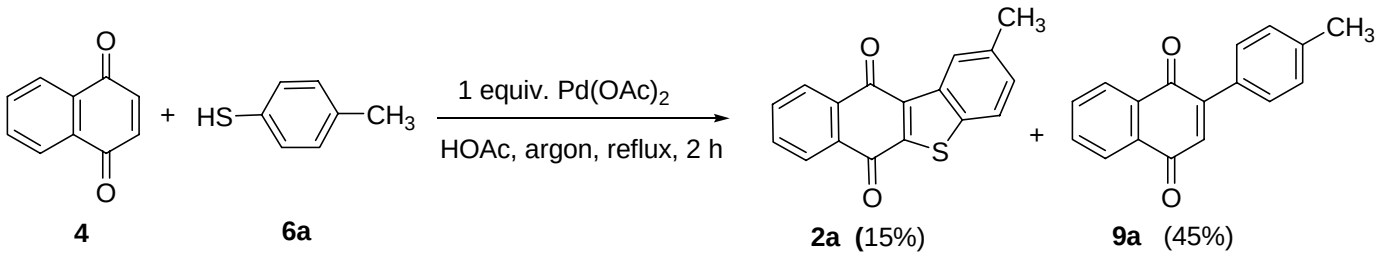


2

compounds	R_1	R_2	R_3	yield (%)
2a	H	CH_3	H	47
2b	Cl	H	H	25
2c	H	H	H	30
2d	H	Cl	H	41
2e	CH_3	H	CH_3	55
2f	H	F	H	26
2g	F	H	H	38

Reaction condition: 1 equiv. $Pd(OAc)_2$/ HOAc/ argon/ reflux/ 40 h.

As shown in Scheme 1, compounds (**2**) could be also synthesized by one pot synthesis of 1,4-naphthoquinone (**4**) with arylthiols (**6**) in both substitution reaction and the C-C coupling (Path B). For example of one pot synthesis, the quinone (**4**) was reacted with 4-methylthiophenol (**6a**) and stoichiometric amounts of palladium(II) acetate in refluxed acetic acid under an argon atmosphere for about 2 h. As a result of unexpected discovery, the one-pot synthesis provided 2-(4-methylphenyl)-1,4-naphthoquinone (**9a**) in major along with the desired product (**2a**) in low yields (Scheme 4**)**. Although the one-pot synthesis seems to be much more attractive than the two step route synthesis, the latter is more favorable for getting the cyclized product (**2a**) than one-pot synthesis occurring both intra- and intermolecular coupling all at once (Schemes 4 and 5).



Scheme 4 One-pot synthesis

In conclusion, we achieved an efficient palladium mediated synthesis of benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-diones (**2**). And we suggest that the palladium-mediated coupling has potential for even wider application to the quinone series or sulfur chemistry especially as shown in our study than described in the present work.

EXPERIMENTAL

All melting points were measured in open capillary tubes with a Büchi melting point B-545 and were uncorrected. The TLC was performed on precoated silica gel (60G 254, Merck) using chloroform as a solvent. The compounds were detected under UV light (254 nm) or by heating to 110 ^{o}C after spraying with a 30% H_2SO_4-vanillin solution. Column chromatography was performed on silica gel G60 (70-230 mesh, ASTM, Merck). ^{1}H-NMR spectra were recorded on Unity Varian INOVA 400 MHz FT-NMR spectrometer using $CDCl_3$ as a solvent, and chemical shifts were given in ppm with TMS as a standard. High-resolution mass (HRMS EI) spectra were taken from Jeol JMS AX505 WA. 1,4-Naphthoquinone, arylthiols, palladium(II) acetate, $CDCl_3$ and other reagents were purchased from Aldrich Chemical Co. Acetic acid was used after purification by the distillation.

General procedure for synthesis of 3-arylthio-1,4-naphthoquinones (7a-g)

A solution of 1,4-naphthoquinone (**4**) (158 mg, 1.0 mmol) and palladium(II) acetate (112 mg, 0.05 mmol) in 20 mL of 95% ethanol was added to a solution of arylthiols (**6**) (1.1 mmol) in 10 mL of 95% ethanol and then the mixture was stirred at rt for 4~6 h. After the reaction, the precipitate was collected by the filtration. The crude product was purified by silica gel column chromatography with EtOAc/n-hexane (1:2) or crystallized from 95% ethanol (Table 2).

2-(4-Methylphenylthio)-1,4-naphthoquinone (7a): Yellow powder (85%). mp 118℃ (lit.,[5] mp 118-120℃). ^{1}H-NMR ($CDCl_3$) δ 8.12 (d, J=7.5 Hz, 1H, benzene), 7.99 (d, J=7.5 Hz, 1H, Ph-H), 7.70 (m, 1H, Ph-H), 7.38 (m, 2H, Ph-H), 7.26 (m, 2H, Ph-H), 6.09 (s, 1H, quinone), 2.48 (s, 3H, CH_3). MS (m/z) 280 (M^+). HRMS Calcd for $C_{17}H_{12}O_2S$, 280.0558, Found: 280.0559.

2-(3-Chlorophenylthio)-1,4-naphthoquinone (**7b**): Yellow powder (55%). mp 155℃. ^{1}H-NMR ($CDCl_3$) δ 8.11 (d, J= 7.7 Hz, 1H, benzene), 8.00 (d, J=7.7 Hz, 1H, benzene), 7.70 (m, 1H, Ph-H), 7.60 (m, 2H, Ph-H), 7.57 (m, 1H, Ph-H), 7.45 (t, J=7.7 Hz, 1H, benzene), 7.36 (m, 1H, Ph-H)), 6.22 (s, 1H, quinone). MS (m/z) 300 (M^+). HRMS Calcd for $C_{16}H_9O_2ClS$, 300.0012, Found: 300.0012.

2-Phenylthio-1,4-naphthoquinone (7c): Yellow powder (62%). mp 159℃ (lit.,[5] mp 159℃). ^{1}H-NMR ($CDCl_3$) δ 8.15 (m, 1H, Ph-H), 8.03 (m, 1H, Ph-H), 7.73 (m, 1H, Ph-H), 7.54 (m, 5H, Ph-H), 6.12 (s, 1H, quinone). MS (m/z) 266 (M^+). HRMS Calcd for $C_{16}H_{10}O_2S$, 266.0401, Found: 266.0403.

2-(4-Chlorophenylthio)-1,4-naphthoquinone (7d): Yellow powder (65%). mp 149℃ (lit.,[5] mp 149-50℃). ^{1}H-NMR ($CDCl_3$) δ 8.15 (d, J=7.3 Hz, 1H, Ph-H), 8.03 (d, J=7.3 Hz, 1H, Ph-H), 7.74 (m, 2H, Ph-H), 7.46 (m, 4H, benzene), 6.08 (s, 1H, quinone). MS (m/z) 300 (M^+). HRMS Calcd for $C_{16}H_9O_2ClS$, 300.0012, Found: 300.0013.

2-(3,5-Dimethylphenylthio)-1,4-naphthoquinone (**7e**): Yellow powder (74%). mp 115℃. ^{1}H-NMR ($CDCl_3$) δ 8.11 (m, 1H, Ph-H), 8.00 (m, 1H, Ph-H), 7.70 (m, 1H, Ph-H), 7.12 (s, 1H, benzene), 7.10 (s, 2H, benzene), 6.13 (s, 1H, quinone), 2.78 (s, 6H, CH_3). MS (m/z) 294 (M^+). HRMS Calcd for $C_{18}H_{14}O_2S$, 294.0715, Found: 294.0714.

2-(4-Fluorophenylthio)-1,4-naphthoquinone (7f): Yellow powder (65%). mp 121℃. ^{1}H-NMR ($CDCl_3$) δ 8.11 (m, 1H, Ph-H), 8.02 (m, 1H, Ph-H), 7.71 (m, 1H, Ph-H), 7.51 (d, J=7.2Hz, 2H, Ph-H), 7.18 (d, J=7.2Hz, 2H, Ph-H), 6.06 (s, 1H, quinone). MS (m/z) 284 (M^+). HRMS Calcd for $C_{16}H_9O_2FS$, 284.0307, Found: 284.0308.

2-(3-Fluorophenylthio)-1,4-naphthoquinone (7g): Yellow powder (56%). mp 125℃. ^{1}H-NMR ($CDCl_3$) δ 8.15 (m, 1H, Ph-H), 8.05 (m, 1H, Ph-H), 7.73 (m, 2H, Ph-H), 7.50 (m, 1H, Ph-H), 7.36 (m, 1H, Ph-H), 7.30 (m, 1H, Ph-H), 7.23 (m, 1H, benzene), 6.14 (s, 1H, quinone). MS (m/z) 284 (M^+). HRMS Calcd for $C_{16}H_9O_2FS$, 284.0307, Found: 284.0306.

Synthesis of 2,3-bis(4-methylphenylthio)-1,4-naphthoquinone (8a)

A solution of 1,4-naphthoquinone (**4**) (158 mg, 1.0 mmol) in 20 mL of 95% ethanol was added to a solution of arylthiols (**6a**) (2.1 mmol) in 10 mL of 95% ethanol and then the mixture was stirred at rt for 4~6 h. After the reaction, the precipitate was collected by the filtration. The filtrated crude product was purified by silica gel column chromatography with $CHCl_3$. The compound (**7a**) was obtained with poor yields (15%) along with 2,3-bis(4-methylphenylthio)-1,4-naphthoquinone (**8a**) as a by-product (67%).

2,3-Bis(4-mehylphenylthio)-1,4-naphthoquinone (8a): Deep red plate (67%). mp 173-175℃ (lit.,[5] mp 173-174℃). ^{1}H-NMR ($CDCl_3$) δ 8.04 (s, 2H, Ph-H), 7.72 (d, J=7.1 Hz, 2H, benzene), 7.07 (d, J=7.1 Hz, 2H, benzene), 6.92 (m, 2H, Ph-H), 2.36 (s, 6H, CH_3). MS (m/z) 402 (M^+). HRMS Calcd for $C_{24}H_{18}O_2S_2$, 402.0748, Found: 402.0749.

General procedure for synthesis of benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-diones (2a-g)

A mixture of compounds (**7**) (2.0 mmol) and $Pd(OAc)_2$ (448 mg, 2.0 mmol) in 10 mL of acetic acid was refluxed und an argon atmosphere for about 40 h. The insoluble matter was filtered off and washed with acetic acid. The filtrate was evaporated in vacuum. The residue was purified by silica gel column chromatography with CH_3Cl/n-hexane or crystallized from 95% ethanol to give the compounds (**2a-g)** (Table 4).

2-Methylbenzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2a**): Yellow powder (35%). mp 201-203℃. ^{1}H-NMR ($CDCl_3$) δ 8.74 (s, 1H, Ph-H), 8.27 (m, 1H, Ph-H), 8.23 (m, 1H, Ph-H), 7.83 (m, 1H, Ph-H), 7.78 (m, 2H, Ph-H), 2.56 (s, 3H, CH_3). MS (m/z) 278 (M^+). HRMS Calcd for $C_{17}H_{10}O_2S$, 278.0402, Found: 278.0401. *Anal.* Calcd for $C_{17}H_{10}O_2S$: C, 73.36; H, 3.62, Found: C, 73.31; H, 3.64.

3-Chlorobenzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2b**): Yellow powder (25%). mp 249-251℃. ^{1}H-NMR ($CDCl_3$) δ 8.84 (m, 1H, Ph-H), 8.26 (m, 1H, Ph-H), 8.23 (m, 1H, Ph-H), 7.95 (m, 1H, Ph-H), 7.79 (m, 2H, Ph-H), 7.56 (m, 1H, Ph-H). MS (m/z) 298 (M^+). HRMS Calcd for $C_{16}H_7O_2ClS$, 297.9855, Found: 297.9856. *Anal.* Calcd for $C_{16}H_7O_2ClS$: C, 64.33; H, 2.36, Found: C, 64.29; H, 2.35.

Benzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2c**): Pale brown powder (30%). mp 199-201℃. ^{1}H-NMR ($CDCl_3$) δ 8.94 (m, 1H, Ph-H), 8.28 (m, 1H, Ph-H), 8.23 (m, 1H, Ph-H), 7.96 (m, 1H, Ph-H), 7.78 (m, 2H, Ph-H), 7.59 (m, 1H, Ph-H). MS (m/z) 264 (M^+). HRMS Calcd for $C_{16}H_8O_2S$, 264.0245, Found: 264.0244. *Anal.* Calcd for $C_{16}H_8O_2S$: C, 72.71; H, 3.05, Found: C, 72.73; H, 3.08.

2-Chlorobenzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2d**): Yellow powder (26%). mp 210-212℃. ^{1}H-NMR ($CDCl_3$) δ 8.86 (m, 1H, Ph-H), 8.20 (m, 1H, Ph-H), 8.17 (m, 2H, Ph-H), 7.80 (s, 1H, Ph-H), 7.72 (d, J=7.1 Hz, 1H, Ph-H), 7.45 (d, J=7.1 Hz, 1H, Ph-H). MS (m/z) 298 (M^+). HRMS Calcd for

$C_{16}H_7O_2ClS$, 297.9855, Found: 297.9857. *Anal.* Calcd for $C_{16}H_7O_2ClS$: C, 64.33; H, 2.36, Found: C, 64.35; H, 2.39

1,3-Dimethylbenzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2e**): Yellow powder (55%). mp 252-254℃. ^{1}H-NMR ($CDCl_3$) δ 8.21 (m, 1H, Ph-H), 8.18 (m, 1H, Ph-H), 7.78 (m, 2H, Ph-H), 7.73 (s, 1H, Ph-H), 7.58 (s, 1H, Ph-H), 7.19 (s, 1H, Ph-H), 2.90 (s, 3H, CH_3), 2.40 (s, 3H, CH_3). MS (m/z) 292 (M^+). HRMS Calcd for $C_{18}H_{12}O_2S$, 292.0558, Found: 292.0557. *Anal.* Calcd for $C_{18}H_{12}O_2S$: C, 73.95; H, 4.14, Found: C, 73.94; H, 4.17.

2-Fluorobenzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2f**): Yellow powder (26%). mp 194-196℃. ^{1}H-NMR ($CDCl_3$) δ 8.58 (m, 1H, Ph-H), 8.27 (m, 1H, Ph-H), 8.21 (m, 1H, Ph-H), 7.88 (s, 1H benzothiophene), 7.77 (d, J=7.3 Hz, 1H, Ph-H), 7.32 (d, J=7.3 Hz, 1H, Ph-H). MS (m/z) 282 (M^+). HRMS Calcd for $C_{16}H_7O_2FS$, 282.0151, Found: 282.0150. *Anal.* Calcd for $C_{16}H_7O_2FS$: C, 68.08; H, 2.50, Found: C, 68.07; H, 2.51

3-Fluorobenzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (**2g**): Yellow powder (38%). mp 227-229℃. ^{1}H-NMR ($CDCl_3$) δ 8.91 (m, 1H, Ph-H), 8.26 (m, 1H, Ph-H), 8.24 (m, 1H, Ph-H), 7.79 (m, 2H, Ph-H), 7.64 (m, 1H, Ph-H), 7.35 (d, 1H, Ph-H). MS (m/z) 282 (M^+). HRMS Calcd for $C_{16}H_7O_2FS$, 282.0151, Found: 282.0151, *Anal.* Calcd for $C_{16}H_7O_2FS$: C, 68.08; H, 2.51, Found: C, 68.09; H, 2.50

General procedure for one pot synthesis of 2-methylbenzo[*b*]naphtho[2,3-*d*]thiophene-6,11-dione (2a)

A mixture of compound (**4**) (316 mg, 2.0 mmol) and $Pd(OAc)_2$ (448 mg, 2.0 mmol) in 10 mL of acetic acid was added to a solution of the arylthiol (**6a**) (261 mg, 2.1 mmol) in 10 mL of acetic acid, and the mixture was refluxed for about 2 h under an argon atmosphere. The filtrate was evaporated in vacuum. After evaporation, compounds (**2a**) (15%) and (**9a**) (45%) were separated by silica gel column chromatography with CH_3Cl/n-hexane, and crystallized from 95% ethanol.

2-(4-Methylphenyl)-1,4-naphthoquinone (9a): Yellow powder (45%). mp 111-112℃ (lit.,[9] mp 111-112℃). ^{1}H-NMR ($CDCl_3$) δ 8.25 (s, 1H, Ph-H), 8.07 (d, J=7.7 Hz, 2H, benzene), 7.70 (d, J=7.7 Hz, 2H, benzene), 7.32 (m, 1H, Ph-H), 7.05 (m, 2H, Ph-H), 2.21 (s, 3H, CH_3). MS (m/z) 248 (M^+). HRMS Calcd for $C_{17}H_{12}O_2$, 248.0837, Found: 248.0838.

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