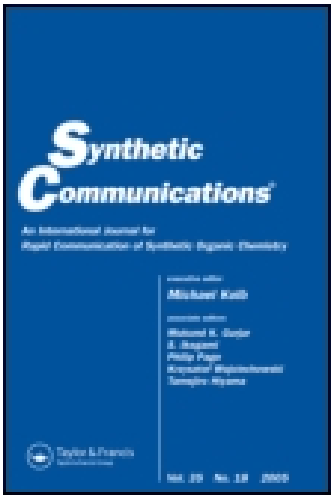

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 23 Nov 2006.

To cite this article: Chung-Kyu Ryu, Ik Hwa Choi, & Rae Eun Park (2006) Synthesis of Benzo[b]benzo[2,3-d]thiophen-6,9-diones via Palladium(II) Acetate-Mediated Cyclization of 5-Arylthiocyclohexa-2,5-diene-1,4-diones, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 36:22, 3319-3328, DOI: 10.1080/00397910600941208

To link to this article: http://dx.doi.org/10.1080/00397910600941208

Synthetic Communications®, 36: 3319–3328, 2006

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910600941208

Synthesis of Benzo[b]benzo[2,3-d]thiophen-6,9-diones via Palladium(II) Acetate–Mediated Cyclization of 5-Arylthiocyclohexa-2,5-diene-1,4-diones

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Abstract: Palladium(II)-mediated oxidative cyclization of 5-arylthiocyclohexa-2,5-diene-1,4-diones **4** giving biologically important benzo[b]benzo[2,3-d]thiophene-6,9-diones **2** has been performed with a stoichiometric amount of palladium(II) acetate in distillated acetic acid.

Keywords: 5-Arylthiocyclohexa-2,5-diene-1,4-dione, arylthiol, benzo[b]benzo[2,3-d]thiophene-6,9-dione, palladium acetate

Quinonoid compounds represent an important class of biologically active molecules that are widespread in nature.[1,2] The heterocyclic 9*H*-carbazole-1,4-dione derivatives **1** have received attention because of their potential biological activities[3–5] (Fig. 1). This fact prompted us to consider a bioisosteric substitution of the 5′-nitrogen (NH) by sulfur (S). The quinone analogues containing a sulfur such as benzo[b]benzo[2,3-d]thiophene-6,9-diones **2** could have similar activity as compounds **1** because sulfur is isoelectronic with nitrogen. There have not been any reports on benzo[b]benzo[2,3-d]thiophene-6,9-dione derivatives to the best of our knowledge. Therefore, we synthesized the compounds **2** as a bioisostere of the compounds **1**.

Received in Japan October 11, 2005
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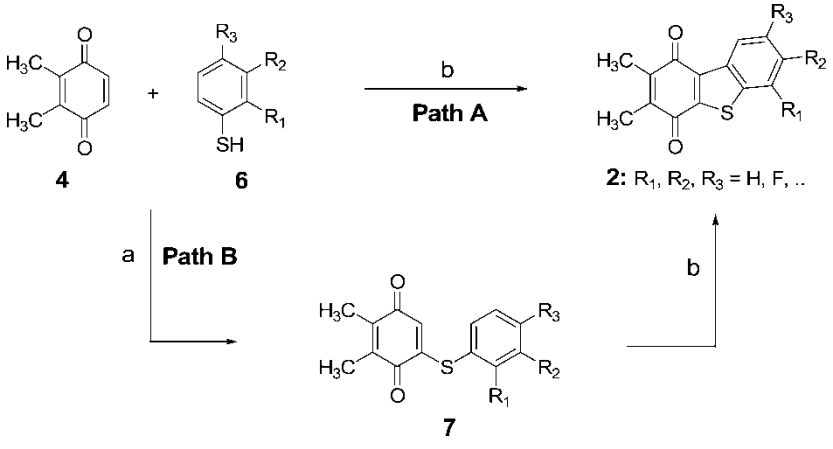
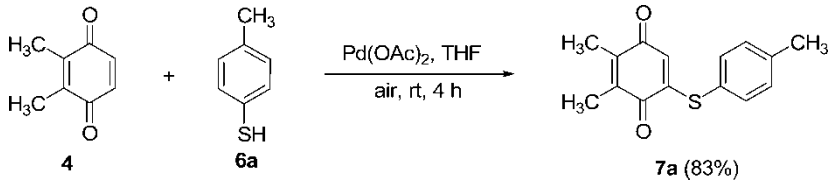
Figure 1. 9*H*-Carbazole-1,4-diones and benzo[b]benzo[2,3-d]thiophene-6,9-diones.

Palladium-mediated annulation methodology has been effectively employed for the preparation of new heterocyclic systems.[6] As shown in Scheme 1, compounds **2** should be synthesized by either one-pot (Path A) or two-step synthesis (Path B) from 2,3-dimethylcyclohexa-2,5-diene-1,4-dione (**4**) and appropriate arylthiols **6** with palladium(II) acetate. Although the one-pot synthesis of compounds **2** seem to be much more attractive, the two-step synthesis is much easier than the 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 palladium(II) acetate–mediated cyclization of 5-arylthio-2,3-dimethyl-cyclohexa-2,5-diene-1,4-diones **7**.

The first step in Path B synthesis was preparation of 5-arylthio-2,3-dimethyl-cyclohexa-2,5-diene-1,4-diones **7** (Scheme 1). For example, the substitution of 4-methylbenzenethiol (**6a**) to the quinone **4** in the presence of 0.05 equivalent of palladium(II) acetate as a catalyst in air at room temperature for 4 h afforded 2,3-dimethyl-5-(4-methylphenylthio)cyclohexa-2,5-diene-1,4-dione (**7a**) in good yield (Scheme 2). Otherwise, reactions



Scheme 1. Reagents and conditions: a) EtOH, 0.05M $Pd(OAc)_2$, rt, 4 h; b) CH_3COOH, 1M $Pd(OAc)_2$, reflux, Ar, 24 h.



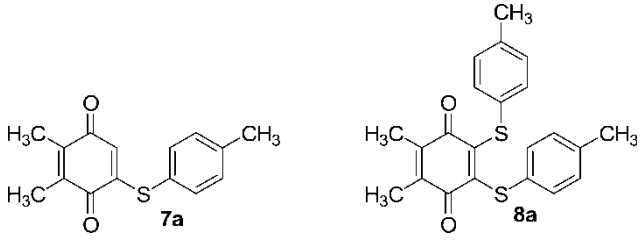
Scheme 2. Substitution of 4-methylbenzenethiol (**6a**) to the quinone **4**.

in absence of the palladium(II) acetate provided the compound **7a** with poor yields along with 5,6-bis(4-methylphenylthio)-2,3-dimethylcyclohexa-2,5-diene-1,4-dione (**8a**) as a by-product (Table 1). THF for the reaction seems to be the best solvent. Acetic acid and ethanol were also tried, and in those solvents the product **7a** was observed with lower yield than in THF.

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

The second step in Path A synthesis was palladium(II)-mediated oxidative cyclization of compounds **7** in acetic acid, which provided the desired products **2** (Scheme 1). For example, we refluxed the compound **7a** with stoichiometric amounts of palladium(II) acetate in the distilled acetic acid under an argon atmosphere for about 24 h to afford 2,7,8-trimethylbenzo[b]benzo[2,3-

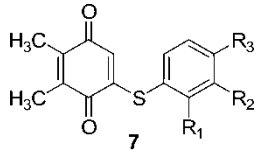
Table 1. Substitution of 4-methylbenzenethiol (**6a**) to the quinone **4**



Entry	Reaction condition	**7a** (%)[a]	**8a** (%)
1	C_2H_5OH, air, reflux, 10 h	55	24
2	HOAc, air, reflux, 4 h	53	21
3	THF, air, reflux, 4 h	39	42
3	0.05 equiv. $Pd(OAc)_2$, C_2H_5OH, air, reflux, 4 h	72	0
4	0.05 equiv. $Pd(OAc)_2$, HOAc, air, reflux, 4 h	59	0
5	0.05 equiv. $Pd(OAc)_2$, THF, air, reflux, 4 h	83	0

[a]Isolated yield.

Table 2. Structure of afforded 5-arylthio-2,3-dimethylcyclohexa-2,5-diene-1,4-diones **7**



7

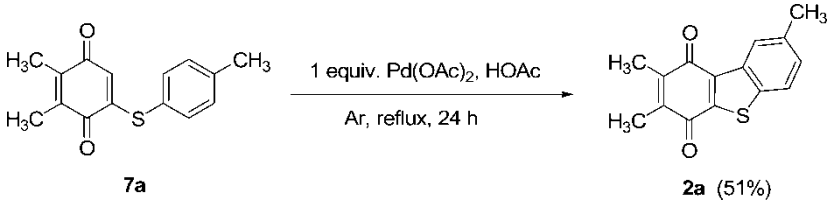
Compounds	R_1	R_2	R_3	Yield (%)
7a	H	H	CH_3	83
7b	H	H	F	45
7c	H	H	Cl	52
7d	H	H	H	55
7e	F	H	F	64
7f	H	H	CH_3O	55
7g	H	Cl	H	59

Notes: Reaction condition: 1.0 mmol quinone **4**, 1.1 mmol arylthiol **6**, 0.05 mmol $Pd(OAc)_2$, THF, air, rt, reflux, 4 h.

d]thiophene-6,9-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 cyclization,[7,8] but the reason for this is not known. Ethanol and THF were also tried, but in those solvents no cyclization was observed (Table 3).

Furukawa described the first palladium(II)-mediated oxidative cyclization of 3-phenylamino-1,4-benzoquinones to carbazole-1,4-quinones.[9] In the synthesis of benzo[b]carbarzole-6,9-diones, Knölker demonstrated that this reaction becomes catalytic in palladium by reoxidation of Pd(0) to Pd(II) with Cu(II).[10] We also tried, but the catalytic condition by reoxidation with copper(II) acetate was not useful for getting the cyclized product **2a** (Table 3).

To determine the versatility of this intramolecular C-C coupling process on a quinone system, a number of benzo[b]benzo[2,3-d]thiophene-6,9-diones **2** were synthesized by employing the optimized reaction condition (Scheme 3



7a **2a** (51%)

Scheme 3. Cyclization of 2,3-dimethyl-5-(4-methylphenylthio)cyclohexa-2,5-diene-1,4-dione (**7a**).

Table 3. Oxidative cyclization of the quinone **7a** to get the cyclized product **2a**

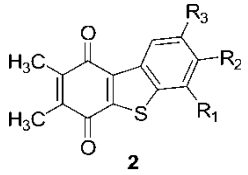
Entry	Solvent	$Cu(OAc)_2$	Time	Atmosphere	Yield (%)
1	HOAc	—	10 h	Argon	30
2	HOAc	—	24 h	Argon	51
3	HOAc	—	40 h	Air	35
4	HOAc	2.5 equiv.	24 h	Argon	Trace
5	C_2H_5OH	2.5 equiv.	24 h	Argon	0
6	C_2H_5OH	—	24 h	Argon	0
7	THF	—	24 h	Argon	Trace

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

and Table 3). The various compounds **2** was obtained by cyclization of 5-arylthio-2,3-dimethylcyclohexa-2,5-diene-1,4-diones **7** with stoichiometric amounts of palladium(II) acetate in refluxed acetic acid under an argon atmosphere for about 24 h (Table 4).

As shown in Scheme 1, compounds **2** could be also synthesized by one-pot synthesis of the quinone **4** with arylthiols **6** in both substitution reaction and the C-C coupling (Path A). For an example of the one-pot synthesis, the quinone **4** was reacted with 4-fluorothiophenol (**6b**) 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 2,3-dimethyl-5-(4-fluorophenyl)cyclohexa-2,5-

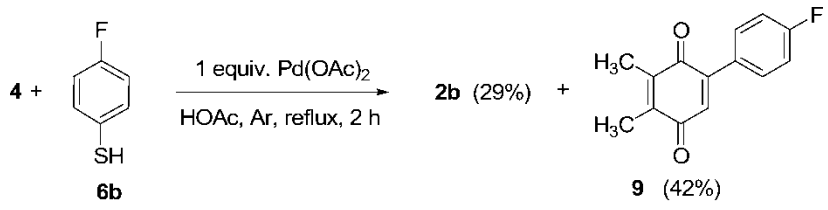
Table 4. Structure of benzo[b]benzo[2,3-d]thiophene-6,9-diones **2**



2

Compounds	R_1	R_2	R_3	Yield (%)
2a	H	H	CH_3	51
2b	H	H	F	23
2c	H	H	Cl	47
2d	H	H	H	37
2e	F	H	F	43
2f	H	H	CH_3O	39
2g	H	Cl	H	40

Note: Reaction condition: quinone **7**, $Pd(OAc)_2$, HOAc, Ar, reflux, 24 h.



Scheme 4. One-pot synthesis.

diene-1,4-dione (**9**) along with the desired product **2b** 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 **2b** than the one-pot synthesis, because both intra- and intermolecular coupling occur all at once (Schemes 3 and 4).

In conclusion, we achieved an efficient palladium-mediated synthesis of benzo[b]benzo[2,3-d]thiophene-6,9-diones **2**, and we suggest that the palladium-mediated coupling has potential for even wider application to the quinone series or sulfur chemistry than described in the present work.

EXPERIMENTAL

All melting points were measured in open capillary tubes with a Büchi melting-point B-545 apparatus and are uncorrected. The thin-layer chromatography (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°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 with a Jeol JMS AX505 WA. Arylthiols, palladium(II) acetate, $CDCl_3$, and other reagents were purchased from Aldrich Chemical Co. Acetic acid was used after purification by the distillation. 2,3-Dimethylcyclohexa-2,5-diene-1,4-dione (**4**) was prepared by the oxidation from 2,3-dimethylhydroquinone with ammonium cerium(IV) nitrate.

General Procedure for Synthesis of 5-Arylthio-2,3-dimethylcyclohexa-2,5-diene-1,4-diones 7a–g

A solution of 2,3-dimethyl-cyclohexa-2,5-diene-1,4-dione (**4**) (136 mg, 1.0 mmol) and palladium(II) acetate (112 mg, 0.05 mmol) in 20 mL of THF was added to a solution of arylthiols **6** (1.1 mmol) in 10 mL of THF, and

then the mixture was stirred at room temperature for 4 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.

2,3-Dimethyl-5-(4-methylphenylthio)cyclohexa-2,5-diene-1,4-dione (7a): yield: 83%. Mp: 68–70°C. ^{1}H NMR ($CDCl_3$): δ 7.35 (d, 2H, $J = 7.2$, benzene), 7.26 (d, 2H, $J = 7.2$, 2H, benzene), 5.83 (s, 1H, benzene), 2.41 (s, 3H, benzene), 2.06 (s, 3H, methyl), 2.00 (s, 3H, methyl). MS (m/z): 258 (M^+).

2,3-Dimethyl-5-(4-fluorophenylthio)cyclohexa-2,5-diene-1,4-dione (7b): yield: 45%. Mp: 82–84°C. ^{1}H NMR ($CDCl_3$): δ 7.47 (d, 2H, $J = 7.4$, benzene), 7.17 (d, 2H, $J = 7.4$, benzene), 5.79 (s, 1H, benzene), 2.06 (s, 3H, methyl), 2.00 (s, 3H, methyl). MS (m/z): 262 (M^+).

5-(4-Chlorophenylthio)-2,3-dimethylcyclohexa-2,5-diene-1,4-dione (7c): yield: 52%. Mp: 70–71°C. ^{1}H NMR ($CDCl_3$): δ 7.45 (d, 2H, $J = 7.2$, benzene), 7.43 (d, 2H, $J = 7.2$, benzene), 5.82 (s, 1H, benzene), 2.06 (s, 3H, methyl), 2.00 (s, 3H, methyl). MS (m/z): 278 (M^+).

5-Phenylthio-2,3-dimethylcyclohexa-2,5-diene-1,4-dione (7d): yield: 55%. Mp: 90–91°C. ^{1}H NMR ($CDCl_3$): δ 7.45 (m, 5H, benzene), 5.84 (s, 1H, benzene), 2.05 (s, 3H, methyl), 1.99 (s, 3H, methyl). MS (m/z): 244 (M^+).

5-(2,4-Difluorophenylthio)-2,3-dimethylcyclohexa-2,5-diene-1,4-dione (7e): yield: 64%. Mp: 76–78°C. ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 1H, benzene), 7.00 (m, 2H, benzene), 2.06 (s, 3H, methyl), 2.01 (s, 3H, methyl). MS (m/z): 280 (M^+).

2,3-Dimethyl-5-(4-methoxyphenylthio)cyclohexa-2,5-diene-1,4-dione (7f): yield: 59%. Mp: 109–110°C. ^{1}H NMR ($CDCl_3$): δ 7.38 (d, 2H, $J = 7.1$, benzene), 6.97 (d, 2H, $J = 7.1$, benzene), 5.81 (s, 1H, benzene), 3.85 (s, 3H, benzene), 2.05 (s, 3H, methyl), 2.00 (s, 3H, methyl). MS (m/z): 274 (M^+).

5-(3-Chlorophenylthio)-2,3-dimethylcyclohexa-2,5-diene-1,4-dione (7g): yield: 56%. Mp: 82–83°C. ^{1}H NMR ($CDCl_3$): δ 7.3–7.0 (m, 4H, benzene), 6.82 (s, 1H, benzoquinone), 1.97 (s, 3H, methyl), 1.91 (s, 3H, methyl), MS (m/z): 278 (M^+).

Synthesis of 5,6-bis(4-Methylphenylthio)-2,3-dimethylcyclohexa-2,5-diene-1,4-dione (8a)

A solution of the quinone **4** (136 mg, 1.0 mmol) in 20 mL of THF was added to a solution of 4-methylbenzenethiol **6a** (2.1 mmol) in 10 mL of THF, and then the mixture was stirred at room temperature for 4 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 moderate yields (39%) along with the compound **8a** as a by-product (42%).

5,6-bis(4-Methylphenylthio)-2,3-dimethylcyclohexa-2,5-diene-1,4-dione (8a): yield: 42%. Mp: 155–156°C. ^{1}H NMR ($CDCl_3$): δ 7.12 (m, 4H, benzene), 6,91 (m, 4H, benzene), 2.30 (s, 6H, methyl), 1.94 (s, 6H, methyl), MS (m/z): 380 (M^+).

General Procedure for Synthesis of Benzo[b]benzo[2,3-d]thiophene-6,9-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 under an argon atmosphere for about 24 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**.**

2,7,8-Trimethylbenzo[b]benzo[2,3-d]thiophen-6,9-dione (2a): orange powder (51%). Mp: 190–192°C. ^{1}H NMR ($CDCl_3$): δ 8.53 (s, 1H, benzothiophene), 7.78 (d, 1H, $J = 7.1$, benzothiophene), 7.33 (d, 1H, $J = 7.1$, benzothiophene), 2.52 (s, 3H, methyl), 2.15 (s, 6H, methyl), MS (m/z): 256 (M^+). HRMS calcd. for $C_{15}H_{12}O_2S$: 256.05581; found: 256.0559.

7,8-Dimethyl-2-fluorobenzo[b]benzo[2,3-d]thiophen-6,9-dione (2b): yellow powder (23%). Mp: 140–142°C. ^{1}H NMR ($CDCl_3$): δ 8.41 (d, 1H, $J = 7.6$, benzothiophene), 7.85 (d, 1H, $J = 7.6$, benzothiophene), 7.00 (m, 1H, benzothiophene), 2.52 (s, 6H, methyl), MS (m/z): 260 (M^+). HRMS calcd. for $C_{14}H_9FO_2S$: 260.0307; found: 260.0308.

2-Chloro-7,8-dimethylbenzo[b]benzo[2,3-d]thiophen-6,9-dione (2c): orange powder (47%). Mp: 189–190°C. ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 1H, benzothiophene), 7.83 (d, 1H, $J = 7.6$, benzothiophene), 7.45 (d, 1H, $J = 7.6$, benzothiophene), 2.19 (s, 6H, methyl), MS (m/z): 276 (M^+). HRMS calcd. for $C_{14}H_9ClO_2S$: 276.0012; found: 276.0012.

7,8-Dimethylbenzo[b]benzo[2,3-d]thiophen-6,9-dione (2d): bright brown powder (37%). Mp: 140–142°C. ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 1H, benzothiophene), 7.92 (d, 1H, benzothiophene), 7.53 (m, 2H, benzothiophene), 2.16 (s, 6H, methyl), MS (m/z): 242 (M^+). HRMS calcd. for $C_{14}H_{10}O_2S$: 242.0402; found: 242.0401.

2,4-Difluoro-7,8-dimethylbenzo[b]benzo[2,3-d]thiophen-6,9-dione (2e): yellow powder (43%). Mp: 142–144°C. ^{1}H NMR ($CDCl_3$): δ 8.25 (m, 1H,

benzothiophene), 7.04 (m, 1H, benzothiophene), 2.17 (s, 6H, methyl), MS (m/z): 278 (M^+). HRMS calcd. for $C_{14}H_8F_2O_2S$: 278.0213; found: 278.0212.

7,8-Dimethyl-2-methoxybenzo[b]benzo[2,3-d]thiophen-6,9-dione (2f): yellow powder (39%). Mp: 192–194°C. ^{1}H NMR ($CDCl_3$): δ 8.18 (s, 1H, $J = 7.1$, benzothiophene), 7.74 (d, 1H, $J = 7.12$, benzothiophene), 7.14 (d, 1H, $J = 7.1$, benzothiophene), 3.93 (s, 3H, methyl), 2.13 (s, 6H, methyl), MS (m/z): 272 (M^+). HRMS calcd. for $C_{15}H_{12}O_3S$: 272.0507; found: 272.0508.

3-Chloro-7,8-dimethylbenzo[b]benzo[2,3-d]thiophen-6,9-dione (2g): orange powder (40%). Mp: 228–229°C. ^{1}H NMR ($CDCl_3$): δ 8.66 (m, 1H, benzothiophene), 7.90 (s, 1H, benzothiophene), 7.50 (m, 1H, benzothiophene), 2.17 (s, 6H, methyl), MS (m/z): 276 (M^+). HRMS calcd. for $C_{14}H_9ClO_2S$: 276.0012; found: 276.0013.

Procedure for One-Pot Synthesis of the 7,8-Dimethyl-2-fluorobenzo[b]benzo[2,3-d]thiophen-6,9-dione (2b)

A mixture of compound **4** (272 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 4-fluorothiophenol (**6b**) (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 a vacuum. After evaporation, the compound **2b** (29%) and compound **9** were separated by silica-gel column chromatography with CH_3Cl/n-hexane and crystallized from 95% ethanol.

2,3-Dimethyl-5-(4-fluorophenyl)cyclohexa-2,5-diene-1,4-dione (9): Yellow powder (45%). Mp: 104–106°C. ^{1}H NMR ($CDCl_3$): δ 7.08 (m, 2H, benzene), 6.93 (m, 2H, benzene), 6.24 (S, 1H, p-benzoquinone), 2.23 (s, 3H methyl), 2.20 (s, 3H, methyl). MS (m/z): 230 (M^+).

ACKNOWLEDGMENTS

This study was supported by a grant of the Research Institute of Pharmaceutical Science, Ewha Womans University (2005).

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