

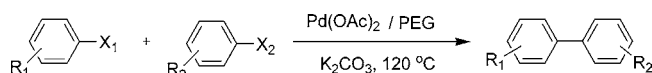
Palladium-Catalyzed Homocoupling and Cross-Coupling Reactions of Aryl Halides in Poly(ethylene glycol)

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The direct coupling of aryl halides to prepare symmetrical and unsymmetrical biaryls were performed successfully in poly(ethylene glycol) (PEG) using Pd(OAc)₂ as the catalyst in the absence of other additives or reductants. The selectivity toward biaryl depended on the amount of PEG used. Excessive PEGs induce the increase of hydrodehalogenation product, and the best selectivity to biaryl is obtained when the concentration of the hydroxyl group in PEG achieves 100 mol % relative to aryl halides. The catalyst system could be recycled and reused up to five times with no loss of catalytic activity.

Biaryls are important building blocks of numerous agrochemicals, pharmaceuticals, natural products, conducting materials, and asymmetric catalysts.¹ Due to their widespread applications, the development of straightforward and environmentally-friendly methods for the preparation of biaryls has aroused many attentions.² The cross coupling of aryl halides with arylmetals mediated by palladium is one of the effective methodologies for the synthesis of biaryls. Many different arylmetals, including arylboronic acids,³ arylstannanes,⁴ arylzinc,⁵ aryl Grignard reagents,⁶ and so on,⁷ have been thoroughly investigated. However, these methods require more than one equimolar amount of arylmetal reagents. The direct dimerization of aryl halides without the preparation step of arylmetal is considered to be a more convenient and straightforward method for the synthesis of biaryls. For example, the Ullmann reaction has long been employed to generate the C–C bond from aryl halides directly.⁸ Unfortunately, the relatively harsh conditions required

in the Ullmann reaction prevented the applications in the synthesis of functionalized biaryls.

Recently, the selective palladium-catalyzed coupling of aryl halides under mild conditions has been developed.⁹ The reaction is usually conducted in the presence of the reducing agents, such as formate salt,^{9b,c} hydrogen gas,^{9d} amines,^{9e} alcohols,^{9f,g} and zinc.^{9h–k} These reducing agents, however, diminish the selectivity in some cases due to the competitive chemisorption and hydride forming ability, which lead to the parallel reduction reaction. For example, undesired reductions of carbonyl and nitro group as well as the hydrodehalogenation are often observed when metal was employed as the reductants. Although organic reductants show some advantages over inorganic reductants in solubility and selectivity, the hydrodehalogenation of aryl halides is still problematic in many cases. On the other hand, the synthesis of unsymmetrical biaryls via palladium-catalyzed cross-coupling reaction of aryl halides is a relatively unexplored area.¹⁰

The preliminary studies of others and our group have revealed that PEG can be used as a reaction medium for selective reactions with easy recyclability of solvent and catalysts.¹¹ Unlike several of the “neoteric solvents” such as ionic liquids (ILs) where toxicity and environmental burden data are for the

(3) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Xiao, J.-C.; Shreeve, J. M. *J. Org. Chem.* **2005**, *70*, 3072. (c) Mathews, C. J.; Smith, P. J.; Welton, T. *Chem. Commun.* **2000**, 1249. (d) Miao, W.; Chan, T. H.; *Org. Lett.* **2003**, *5*, 5003. (e) Revell, J. D.; Ganesan, A. *Org. Lett.* **2002**, *4*, 3071.

(4) (a) Hudkins, R. L.; Diebold, J. L.; Marsh, F. D. *J. Org. Chem.* **1995**, *60*, 6218. (b) Barchin, B. M.; Valenciano, J.; Cuadro, A. M.; Builla-Alvarez, J.; Vaquero, J. J. *Org. Lett.* **1999**, *1*, 545. (c) Schubert, U. S.; Eschbaumer, C. *Org. Lett.* **1999**, *1*, 1027. (d) Baxter, P. N. W. *J. Org. Chem.* **2000**, *65*, 1257. (e) Handy, S. T.; Zhang, X. *Org. Lett.* **2001**, *3*, 233.

(5) (a) Jutand, A.; Mosleh, A. *Synlett.* **1993**, 568. (b) Jutand, A.; Mosleh, A. *J. Org. Chem.* **1997**, *62*, 261. (c) Hossain, K. M.; Shibata, T.; Takagi, K. *Synlett* **2000**, 1137.

(6) (a) Widdowson, D. A.; Zhang, Y.-Z. *Tetrahedron* **1986**, *42*, 2111. (b) Fechtenkoetter, A.; Saalwaechter, K.; Harbison, M. A.; Muellen, K.; Spiess, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3039. (c) Bumagin, N. A.; Luzikova, E. V. *J. Organomet. Chem.* **1997**, *532*, 271. (d) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889. (e) Spivey, A. C.; Fekner, T.; Spey, S. E. *J. Org. Chem.* **2000**, *65*, 3154.

(7) (a) Yamaguchi, S.; Ohno, S.; Tamao, K. *Synlett* **1997**, 1199. (b) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471. (c) Gouda, K.-I.; Hagiwara, E.; Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1996**, *61*, 7232. (d) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053. (e) Frid, M.; Pérez, D.; Peat, A. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9469.

(8) (a) Ullman, F. *Chem. Ber.* **1903**, *36*, 2389. (b) Fanta, P. E. *Chem. Rev.* **1945**, *36*, 139. (c) Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613.

(9) (a) Hennings, D. D.; Iwama, T.; Rawel, V. H. *Org. Lett.* **1999**, *1*, 1205. (b) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Wiener, H.; Sasson, Y. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2481. (c) Mukhopadhyay, S.; Rothenberg, G.; Qafisheh, N.; Sasson, Y. *Tetrahedron Lett.* **2001**, *42*, 6117. (d) Mukhopadhyay, S.; Rothenberg, G.; Wiener, H.; Sasson, Y. *Tetrahedron* **1999**, *55*, 14763. (e) Kuroboshi, M.; Waki, Y.; Tanaka, H. *J. Org. Chem.* **2003**, *68*, 3938. (f) Hassan, J.; Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron* **1998**, *54*, 13793. (g) Penalva, V.; Hassan, J.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron Lett.* **1998**, *39*, 2559. (h) Venkatraman, S.; Li, C.-J. *Org. Lett.* **1999**, *1*, 1133. (i) Shezad, N.; Clifford, A. A.; Rayner, C. M. *Green Chem.* **2002**, *4*, 64. (j) Li, J.-H.; Xie, Y. -X.; Yin, D. -L. *J. Org. Chem.* **2003**, *68*, 9867. (k) Venkatraman, S.; Li, C.-J. *Tetrahedron Lett.* **2000**, *41*, 4831. (l) Soon, B. P.; Howard, A. *Tetrahedron Lett.* **2004**, *45*, 5515. (m) Huo, S. *Org. Lett.* **2003**, *5*, 423.

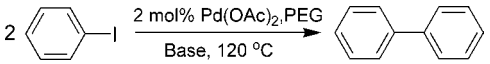
(10) Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. *Tetrahedron* **2001**, *57*, 7845.

(11) (a) Liu, L.; Zhang, Y.; Wang, Y. *J. Org. Chem.* **2005**, *70*, 6122. (b) Chandrasekhar, S.; Narsihmulu, Ch.; Sultana, S. S.; Reddy, N. R. *Org. Lett.* **2002**, *4*, 4399. (c) Luo, C.; Zhang, Y.; Wang, Y. *J. Mol. Catal. A: Chem.* **2005**, *229*, 7.

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(1) (a) Nicolaou, K. C.; Boddy, C. N. C.; Brase, S.; Winssinger, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2096. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405. (c) Tsuji, J. In *Palladium Reagents and Catalysts*; John Wiley and Sons: New York, 1995.

(2) (a) Wallow, T. I.; Norak, B. M. *J. Org. Chem.* **1994**, *59*, 5034. (b) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153. (c) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359.

TABLE 1. Homocoupling Reaction of Iodobenzene^a


entry	PEG	<i>m</i> _{PEG} (g)	base	conv (%)	yield Ph-H ^b (%)	yield Ph-Ph ^b (%)
1	PEG ₆₀₀	7.2	K ₂ CO ₃	>99	88	12
2	PEG ₆₀₀	4	K ₂ CO ₃	>99	58	42
3	PEG ₆₀₀	1.8	K ₂ CO ₃	>99	32	68
4	PEG ₆₀₀	0.6	K ₂ CO ₃	>99	9	91
5	PEG ₆₀₀	0.3	K ₂ CO ₃	90	8	82
6	PEG ₁₀₀₀	4	K ₂ CO ₃	>99	27	73
7	PEG ₁₀₀₀	1	K ₂ CO ₃	>99	7	93
8	PEG ₂₀₀₀	4	K ₂ CO ₃	>99	15	85
9	PEG ₂₀₀₀	2	K ₂ CO ₃	>99	7	93
10	PEG ₄₀₀₀	2	K ₂ CO ₃	92	14	86
11	PEG ₄₀₀₀	4	K ₂ CO ₃	>99	4	96
12	PEG ₄₀₀₀	6	K ₂ CO ₃	>99	8	92
13	PEG ₄₀₀₀	8	K ₂ CO ₃	>99	10	90
14	PEG ₄₀₀₀	4	Et ₃ N	90	8	82
15	PEG ₄₀₀₀	4	K ₃ PO ₄	59	7	52
16	PEG ₄₀₀₀	4	Na ₂ CO ₃	4	3	trace
17	PEG ₄₀₀₀	4	NaOAc	3	3	trace
18	PEG ₄₀₀₀	4	KOH	61	16	45
19	PEG ₄₀₀₀	4	KOC ₄ H ₉	>99	28	72
20	PEG ₄₀₀₀	4	Cs ₂ CO ₃	29	2	27
21	PEG ₄₀₀₀	4	K ₂ CO ₃	86	14	72 ^c
22	PEG ₄₀₀₀	4	K ₂ CO ₃	>99	4	96 ^d

^a Reaction conditions: iodobenzene (4 mmol), base (4 mmol), 2 mol % of Pd(OAc)₂ (0.04 mmol) relative to iodobenzene, 120 °C, 4 h. ^b GC yield. ^c 2 mL water was added. ^d The PEG 4000 was heated at 120 °C for 4 h in vacuo before the reaction, and the reaction was performed under the N₂ atmosphere.

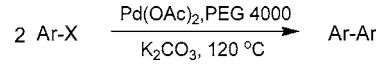
most part unknown, complete toxicity profiles are available for a range of poly(ethylene) glycol molecular weights, and a number of reviews have also covered PEG chemistry and its application in biotechnology and medicine.¹² PEGs have been applied as phase-transfer catalysts for palladium-catalyzed reactions,¹³ including the palladium-catalyzed reduction coupling.¹⁴ In this paper, we report a new palladium catalytic system made from PEG 4000 and Pd(OAc)₂ for the coupling of aryl halides to directly give the symmetrical and unsymmetrical biaryl products in high yields without the use of reductant and other organic solvents. The selectivity can be tailored by controlling the amount of PEG.

In the initial studies, iodobenzene was treated with 2 mol % of Pd(OAc)₂ and 2 equiv of K₂CO₃ in PEG 600 at 120 °C for 4 h in air. It was found that the selectivity of the homocoupling reaction strongly depended on the amount of PEG 600 used. When 7.2 g of PEG 600 was used as the reaction medium, the reaction afforded a small amount of the coupling product but delivered a large amount of hydrodehalogenation product of benzene (Table 1, entry 1). Decreasing the amount of PEG 600 resulted in a clear enhancement of the selectivity toward biphenyl, and the formation of hydrodehalogenation product was inhibited significantly (Table 1, entries 2 and 3). When the amount PEG 600 achieved 0.6 g (1 mmol), 91% selectivity toward biphenyl was observed (Table 1, entry 4), which is much

(12) (a) Ji, C.; Scott, K. S.; Jonathan, G. H.; Robin, D. R. *Green Chem.* **2005**, *7*, 64. (b) Akiya, N.; Savage, P. E. *Chem. Rev.* **2002**, *102*, 2725. (c) Lindstrom, U. M. *Chem. Rev.* **2002**, *102*, 2751.

(13) Li, J.-H.; Liu, W. -J.; Xie, Y. -X. *J. Org. Chem.* **2005**, *70*, 5409.

(14) (a) Mukhopadhyay, S.; Joshi, A. V.; Peleg, L.; Sasson, Y. *Org. Process Res. Dev.* **2003**, *7*, 44. (b) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Sasson, Y. *Org. Lett.* **2000**, *2*, 211.

TABLE 2. Homocoupling of Aryl Halides^a


entry	substrate	time (h)	product	yield ^b (%)
1	4-O ₂ N-Ph-I	4	(4-O ₂ N-Ph) ₂	97
2	4-EtO ₂ C-Ph-I	4	(4-EtO ₂ C-Ph) ₂	95
3	3-MeO ₂ C-Ph-I	4	(3-MeO ₂ C-Ph) ₂	92
4	2-MeO ₂ C-Ph-I	6	(2-MeO ₂ C-Ph) ₂	89
5	4-Cl-Ph-I	4	(4-Cl-Ph) ₂	97
6	Ph-I	4	Ph-Ph	95
7	4-Me-Ph-I	5	(4-Me-Ph) ₂	94
8	4-MeO-Ph-I	5	(4-MeO-Ph) ₂	96
9	4-O ₂ N-Ph-Br	8	(4-O ₂ N-Ph) ₂	94
10	3-O ₂ N-Ph-Br	10	(3-O ₂ N-Ph) ₂	82
11	4-NC-Ph-Br	6	(4-NC-Ph) ₂	96
12	3-NC-Ph-Br	10	(3-NC-Ph) ₂	94
13	4-MeOC-Ph-Br	8	(4-MeOC-Ph) ₂	82
14	4-Cl-Ph-Br	8	(4-Cl-Ph) ₂	95
15	Ph-Br	24	Ph-Ph	87 ^c
16	4-Me-Ph-Br	24	(4-Me-Ph) ₂	86 ^c
17	4-MeO-Ph-Br	28	(4-MeO-Ph) ₂	85 ^c
18	2-Br-Py	8	(2-Py) ₂	91
19	3-Br-Py	6	(3-Py) ₂	93
20	2-Br-C ₄ H ₃ S	10	(2-C ₄ H ₃ S) ₂	87
21	3-Br-C ₄ H ₃ S	7	(3-C ₄ H ₃ S) ₂	95

^a Reaction conditions: aryl halide (4 mmol), K₂CO₃ (4 mmol), PEG 4000 (4 g), 2 mol % of Pd(OAc)₂. ^b Isolated yield. ^c Temperature is 130 °C and Pd(OAc)₂ is 5 mol %.

better than using organic alcohols as the reductants, including those in which PEGs were used as phase-transfer catalyst.^{14a} Further reduction of the amount of PEG 600 has been proven to be negative to the selectivity and the reactivity (Table 1, entry 5). Although the larger chain length PEGs, such as PEG 1000, PEG 2000, and PEG 4000, proceeded in a similar manner to give the desired biphenyl and benzene (Table 1, entries 6–13), the selectivity toward biphenyl in larger chain length PEGs seems to be better than that in shorter chain length PEGs. The best selectivity of biphenyl was obtained using 4 g (1 mmol) of PEG 4000 (Table 1, entry 11), wherein only 4% hydrodehalogenation product was generated. The use of stronger base such as *t*-BuOK and KOH led to low yields for the coupling reaction (Table 1, entries 18 and 19). Et₃N and K₂CO₃ afforded good to excellent yields (Table 1, entries 11 and 13), while NaOAc, Na₂CO₃, and K₃PO₄ delivered very little coupling product (Table 1, entries 15–17).

Further investigations of the efficiency and scope of the method were performed, and the results are summarized in Table 2. The Pd(OAc)₂/PEG was proven to be a very active catalyst for the homocoupling of a broad spectrum of aryl iodides and bromides. As illustrated in Table 2, both electron-withdrawing (Table 2, entries 1–5) and electron-donating (Table 2, entries 6–8) aryl iodides were coupled cleanly to provide the corresponding biaryls in good to excellent yields. Aryl iodide with meta- and ortho-substituent delivered the corresponding biaryl in good yields (Table 2, entries 3–4), showing that the steric hindrance played little effect to the formation of intermediate arylpalladium complexes. In the case of aryl bromides, good to excellent biaryl yields were obtained after the prolongation of reaction times and the increasing of the amount of palladium acetate to 5 mol % (Table 2, entries 9–17). It should be noted that the desired biaryls were delivered in good yields in the PEG/Pd(OAc)₂ catalytic system without the reduction of nitro or carbonyl groups (Table 2, entries 1, 9, 10, and 13). However,

TABLE 3. Cross-Coupling of Aryl Halides^a

entry	Ar ₁ -I	Ar ₂ -Br	time (h)	yield	
				A ^b (%)	B ^c (%)
1	Ph-I	4-NC-Ph-Br	12	4	94
2	Ph-I	4-O ₂ N-Ph-Br	12	3	92
3	4-MeO-Ph-I	4-O ₂ N-Ph-Br	12	2	95
4	Ph-I	3-O ₂ N-Ph-Br	12	3	94
5	4-Me-Ph-I	3-O ₂ N-Ph-Br	12	2	95
6	Ph-I	3-NC-Ph-Br	12	5	91
7	4-MeO-Ph-I	3-NC-Ph-Br	12	4	93
8	Ph-I	2-O ₂ N-Ph-Br	20	11	85 ^d
9	4-Me-Ph-I	2-O ₂ N-Ph-Br	20	8	90 ^d
10	4-MeO-Ph-I	2-O ₂ N-Ph-Br	20	7	89 ^d
11	Ph-I	2-Br-Py	15	12	85
12	4-Me-Ph-I	2-Br-Py	15	7	91
13	Ph-I	3-Br-Py	12	11	85
14	4-Me-Ph-I	3-Br-Py	12	9	89
15	4-MeO-Ph-I	2-Br-C ₄ H ₃ S	10	7	90
16	4-MeO-Ph-I	3-Br-C ₄ H ₃ S	10	5	92

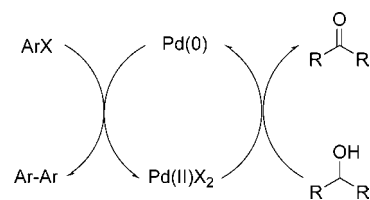
^a Reaction conditions: PEG 4000 (4 g), Ar₁-I (1 mmol), Ar₂-Br (2 mmol), K₂CO₃ (2 mmol), 5 mol % of Pd(OAc)₂. ^b GC yield. ^c Isolated yields. ^d 2-Nitrobromobenzene was 4 mmol.

the aryl halides bearing hydroxyl and amino substituents did not give the corresponding coupling products, possibly due to the interaction between palladium and these substituents, which may disturb the oxidative addition of the aryl halides.^{9e,10}

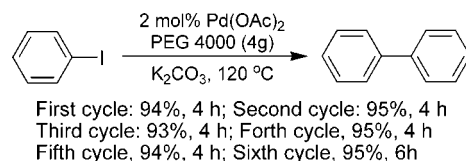
To obtain more insight to the Pd(OAc)₂/PEG system, the cross-coupling reaction of various aryl halides was investigated. Hassan et al. reported the synthesis of unsymmetrical biaryls via palladium-catalyzed coupling reaction of aryl halides in xylene, but the isolated yield was very low.¹⁰ In our experiment, the unsymmetrical biaryls were generated in high isolated yields through the cross-coupling of unactivated aryl iodides and activated aryl bromides (Table 3). Various aryl iodides coupled with *p*- and *m*-aryl bromides and produced the unsymmetrical biaryls in good selectivity (Table 3, entries 1–7). The cross-coupling reaction of *ortho*-substituted aryl bromides with aryl iodides led to the unsymmetrical biaryls with good selectivity, but longer reaction time and 4 equiv of 2-bromonitrobenzene were required (Table 3, entries 8–10). The cross-coupling of aryl iodides with bromopyridine was tested in the Pd(OAc)₂/PEG system, and good selectivity was also obtained (Table 3, entries 11–14). Encouraged by these results, we studied the cross-coupling of aryl iodides and bromothiophene. Unfortunately, the cross-coupling products of the iodobenzene and 4-methyliodobenzene were very difficult to be isolated with bromothiophene due to the very similar *R_f* value. 4-Methoxyiodobenzene delivered good selectivity and good yields of 2-(4-methoxyphenyl)thiophene and 3-(4-methoxyphenyl)thiophene (Table 3, entries 15 and 16). The small amount of homocoupling products of aryl iodides was always observed.

The exact mechanism of the direct coupling reaction of aryl halides in PEG is not clear at the moment. It has been reported that the reductants plays the key role in the palladium-catalyzed coupling reaction of aryl halides.⁹ In the coupling of using alcohols as reducing agents, the alcohol generally considered to be oxidized to the corresponding aldehyde/ketone by palladium(II) and completed the catalytic cycle (Scheme 1). Sasson and co-workers studied the palladium-catalyzed homocoupling of halides in the presence of PEG as phase transfer catalyst in

SCHEME 1



SCHEME 2



water and toluene.¹⁴ They reported the possibility of the terminal hydroxyl group in PEG acting as the reductant. In our cases, the addition of water in PEG was deleterious to the coupling reaction (Table 1, entry 21), but virtually identical results were obtained under the nitrogen and air (Table 1, entries 11 and 22).

The recycle experiments were carried out on iodobenzene with K₂CO₃ as the base in the Pd(OAc)₂/PEG 4000 system. A constant rate of conversion was obtained under the typical conditions without the addition Pd(OAc)₂ and PEG 4000 in the first five cycles (Scheme 2). This pronounced efficiency in the recycle, however, might imply that the PEG did not consume as reductant in the coupling reaction (1 mmol PEG 4000 = 4 g). Further investigations are needed to fully understand the mechanism.

In summary, the coupling reaction catalyzed by palladium acetate in PEGs provides a convenient and recyclable reaction system for the direct coupling involving organic halides in good selectivity and yield. The amount of PEG was important to determine the coupling efficiency and selectivity. The product is readily separated from the extraction with diethyl ether, and the catalyst-containing PEG phase can be reused for the coupling without the addition of catalyst or PEG.

Experimental Section

Representative Procedure for the Coupling Reaction. A mixture of aryl iodides (4 mmol), Pd(OAc)₂ (9 mg, 0.04 mmol, 2 mol %), K₂CO₃ (0.55 g, 4 mmol), and PEG 4000 (4 g) was stirred at 120 °C for the desired time until complete consumption of the starting material. For aryl bromides, the catalyst of Pd(OAc)₂ was increased to 5 mol % (22 mg, 0.1 mmol). After the reaction, the solution was cooled to room temperature and the resulting solid was extracted with anhydrous diethyl ether (4 × 15 mL). The residue was subjected to a second run with the same substrates without further addition of Pd(OAc)₂ and PEG. The combined diethyl ether phase was analyzed by GC/MS and then concentrated. Further purification of the product was achieved by flash chromatography on a silica gel column.

Biphenyl-4-carbonitrile: ¹H NMR (500 MHz, CDCl₃, TMS) δ 7.73 (d, 2 H, *J* = 8.5 Hz), 7.68 (d, 2 H, *J* = 8.5 Hz), 7.59 (t, 2 H, *J* = 4.5 Hz), 7.48 (t, 2 H, *J* = 7.5 Hz), 7.42 (m, 1 H) ppm; MS (EI) *m/z* 179 (100) [M⁺], 151 (16), 89 (10), 76 (14).

2-Phenylpyridine: ¹H NMR (500 MHz, CDCl₃, TMS) δ 8.70 (d, 1H, *J* = 4.5 Hz), 7.98 (d, 2 H, *J* = 7.5 Hz), 7.75 (m, 2 H), 7.48 (t, 2 H, *J* = 5.0 Hz), 7.42 (d, 1 H, *J* = 7.5 Hz), 7.24 (d, 1 H, *J* = 5.5 Hz) ppm; MS (EI) *m/z* 155 (100) [M⁺], 154 (21), 153 (7), 115 (7), 76 (9).

2-(4-Methoxyphenyl)thiophene: ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.53 (q, 2 H, $J = 3.0$ Hz), 7.20 (m, 2 H), 7.04 (m, 1 H), 6.91 (q, 2 H, $J = 3.0$ Hz), 3.83 (s, 3 H) ppm; MS (EI) m/z 190 (100) [M^+], 175 (16), 159 (12), 76 (5).

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Supporting Information Available: The experimental procedure and spectroscopic data (^1H NMR and MS) for the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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