

Palladium-Catalyzed Carbonylation and Coupling Reactions of Aryl Chlorides and Amines

Robert J. Perry* and B. David Wilson

Imaging Research and Advanced Development, Eastman Kodak Company,
Rochester, New York 14650-1705

Received May 10, 1996⁶

The palladium-catalyzed amidation of electron-deficient aryl chlorides proceeds readily in the presence of low CO pressures and a slight excess of an iodide salt. The rates of amidation are accelerated over those without added salt, and iodide is preferred over bromide or chloride. More electron-rich aryl chlorides were not effectively amidated, either with or without added iodide. We postulate that an intermediate anionic palladium(0) iodide complex is responsible for the enhanced reactivity.

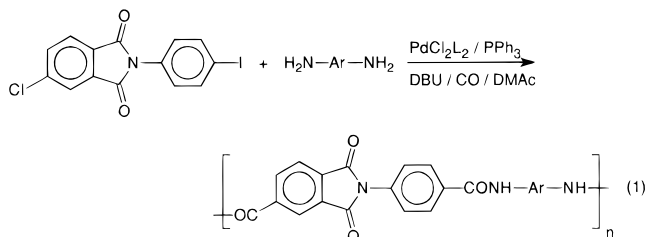
Introduction

We recently found that high molecular weight aramids,¹ polyimides,² poly(amide-ols),³ and poly(imide-amides)⁴ could be readily formed by the palladium-catalyzed carbonylation and condensation of diamines and aromatic diiodides. These polymerization reactions were efficient, but a concern over the expense of preparing the aromatic diiodides prompted an examination of alternate monomers for these types of polymer syntheses.

Chloro-substituted monomers were of interest because of their low cost, ease of preparation, and stability. While palladium-mediated carbonylations proceed readily with bromo- and iodoaromatic compounds, aromatic chlorides are generally less reactive. The use of high temperatures to induce oxidative addition has led to catalyst decomposition,⁵ although a temperature-resistant supported Pd(0) catalyst in the form of 5% Pd/C with K₂Cr₂O₇ was found to be effective in carbonylation reactions of chlorobenzenes.⁶ More commonly, aromatic chlorides have been activated through the introduction of Cr(CO)₃ moieties⁷ or other electron-withdrawing substituents,⁵ or inductive effects.⁸ An alternate method of carbonylating aryl chlorides has been to use strongly basic and sterically demanding ligands on palladium, such as triisopropylphosphine, tricyclohexylphosphine,⁹ or bis(diisopropylphosphino)propane.¹⁰ Carbonylation of aromatic chlorides has also been achieved with nickel catalysts¹¹ and with cobalt complexes.¹² Another means of activating aromatic chlorides utilized a Ni/Pd system containing

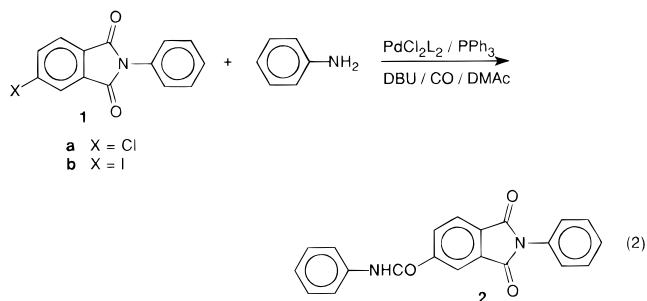
NaI.¹³ In that work, nickel catalyzed the conversion of a small amount of aryl chloride to aryl iodide, which subsequently reacted with palladium.

We recently found that a chloriodophthalimide monomer was sufficiently reactive in the presence of a palladium catalyst to undergo carbonylation and coupling reactions with diamines to give high molecular weight poly(imide-amides) (eq 1).¹⁴ The presence of iodide ion enhanced the polymerization rate and suggested that other aryl chlorides could be activated by iodide, thus providing a general route for the amidation of aromatic chlorides. Reported herein are the results of our study.



Results and Discussion

We initially investigated the carbonylation reaction of 4-chloro-*N*-phenylphthalimide, **1a**, with aniline (eq 2).



At 120 °C and elevated CO pressures (95 psig), conditions under which the iodo analogue, **1b**, rapidly reacted,

(10) (a) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1816. (b) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989**, *111*, 8742.

(11) Cassar, L.; Foa, M. *J. Organomet. Chem.* **1973**, *51*, 381.

(12) (a) Brunet, J.-J.; Sidot, C.; Caubere, P. *J. Org. Chem.* **1983**, *48*, 1166. (b) Foa, M.; Francalanci, F.; Bencini, E.; Gardano, A. *J. Organomet. Chem.* **1985**, *285*, 293. (c) Foa, M.; Francalanci, F. *J. Mol. Catal.* **1987**, *41*, 89. (d) Kudo, K.; Shibata, T.; Kashimura, T.; Mori, S.; Sugita, N. *Chem. Lett.* **1987**, 577.

(13) Bozell, J. J.; Vogt, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 2655.

* Current Address: GE Silicones, General Electric Company, 260 Hudson River Road, Waterford, NY 12188.

⁶ Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) (a) Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules* **1993**, *26*, 1509. (b) Turner, S. R.; Perry, R. J.; Blevins, R. W. *Macromolecules* **1992**, *25*, 4819.

(2) Perry, R. J.; Turner, S. R. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 159.

(3) Perry, R. J.; Wilson, B. D. *Macromolecules* **1994**, *27*, 40.

(4) Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules* **1994**, *27*, 4058.

(5) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

(6) Dufaud, V.; Thivolle-Cazat, J.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1990**, 426.

(7) (a) Mutin, R.; Lucas, C.; Thivolle-Cazat, J.; Dufaud, V.; Dany, F.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 896. (b) Dany, F.; Mutin, R.; Lucas, C.; Dufaud, V.; Thivolle-Cazat, J.; Basset, J. M. *J. Mol. Catal.* **1989**, *51*, L15. (c) Dufaud, V.; Thivolle-Cazat, J.; Basset, J. M.; Mathieu, R.; Jaud, J.; Waissermann, J. *Organometallics* **1991**, *10*, 4005. (d) Scott, W. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1755.

(8) Takeuchi, R.; Suzuki, K.; Sato, N. *J. Mol. Catal.* **1991**, *66*, 277.

(9) (a) Huser, M.; Youinou, M.-T.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1386. (b) Grushin, V. V.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1992**, 611.

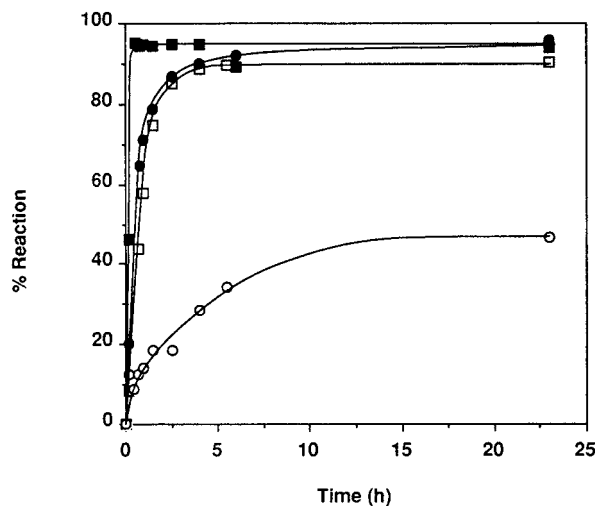


Figure 1. Effect of CO pressure and iodide on amidation of **1a** with aniline. Reaction in DMAc (0.22 M) at 120 °C, 1.2 equiv of DBU, 3% PdCl₂L₂, 6% L (L = PPh₃). Key: ■, 5 psig of CO, 1.2 equiv of NaI; □, 5 psig of CO, no NaI; ●, 95 psig of CO, 1.2 equiv of NaI; ○, 95 psig of CO, no NaI.

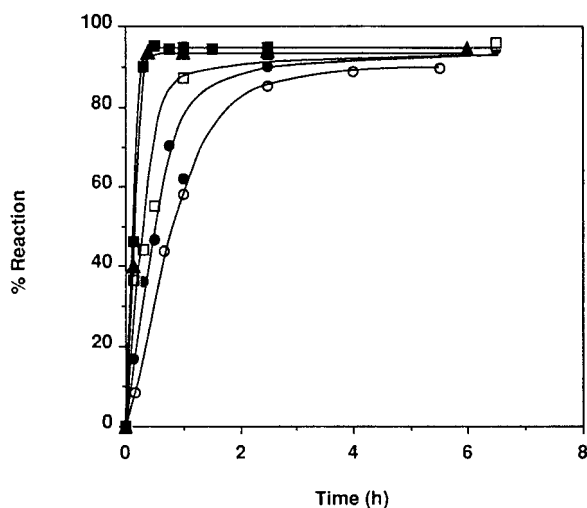


Figure 2. Effect of iodide concentration on amidation of **1a** with aniline. Reaction in DMAc (0.22 M) at 120 °C, 1.2 equiv of DBU, 5 psig of CO, 3% PdCl₂L₂, 6% L (L = PPh₃). Key: ○, no NaI; ●, 0.1 equiv of NaI; □, 0.5 equiv of NaI; ■, 1.2 equiv of NaI; ▲, 5.0 equiv of NaI.

some amidation of **1a** to **2** occurred, but the reaction was slow and tapered off after 6 h (Figure 1). Under the same conditions, but with 1.2 equiv of NaI present (based on **1a**), amidation occurred more quickly with 90% conversion in *ca.* 3 h. When the CO pressure was decreased to 5 psig and NaI omitted from the reaction, the amidation reaction had nearly the same rate as that seen for the high CO pressure with NaI. The fastest reaction was observed at 5 psig CO and in the presence of a slight excess of NaI in which 95% conversion had been achieved within 0.5 h.

To determine the optimum loading of NaI, a series of reactions were run with varying iodide concentrations. The fastest reactions were seen when at least a stoichiometric amount of iodide was present. Greater than 90% reaction was achieved in 0.5 h or less with 1.2–5 equiv of NaI (Figure 2). With 0.5 equiv of iodide in the reaction, the time for 90% completion of the reaction increased to 1.5 h. At lower levels (0.1 equiv), 2.5 h was needed for

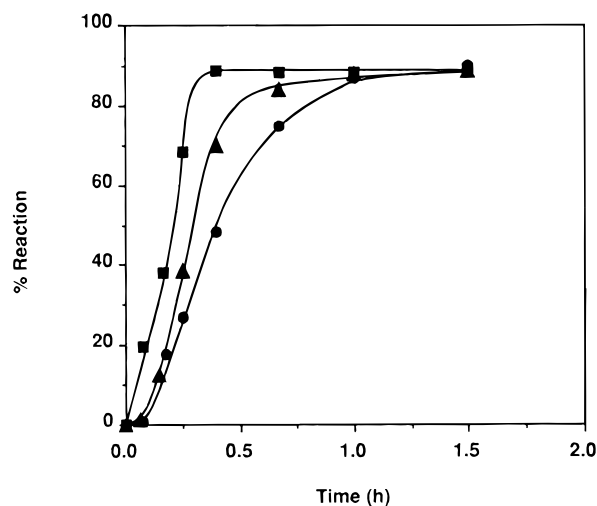


Figure 3. Effect of halide on amidation of **1a** with aniline. Reaction in DMAc (0.22 M) at 120 °C, 1.2 equiv of DBU, 3% PdCl₂L₂, 6% L (L = PPh₃), 1.2 equiv of LiX, 5 psig of CO. Key: ●, LiCl; ▲, LiBr; ■, LiI.

90% reaction. While the reactions were slower, they were still accelerated over the reaction without any added iodide.

A comparison of the different halides showed that iodide was the best in terms of rate enhancement. When LiCl, LiBr, and LiI were added to the reaction of **1a** and aniline, the iodide reaction was complete within 0.4 h (Figure 3). The bromide-containing reaction required 0.8 h and the chloride, 1.0 h, to reach the same level. The lithium salts were examined because of the greater solubility of LiCl in the reaction medium than that of NaCl.

Armatore¹⁵ and Negishi¹⁶ have described the formation of low coordinative zero-valent palladium complexes stabilized by halide anions. We suggest that similar palladium(0) ate complexes of the form [L_nPd(0)I]⁻Na⁺ are being formed in our system and that these reactive species are enhancing the oxidative addition reaction to the aryl chloride.

Similar [L_nPd(0)Cl]⁻Li⁺ complexes have been proposed to be the effective agents in cross-coupling reactions of aryl triflates and organostannanes.¹⁷ The formation of these anionic Pd(0) complexes and their reported enhanced reactivity in oxidative addition reactions provides an explanation for the overall rate increase seen in the amidation reactions. Oxidative addition reactions have been shown to be the slow step in the carbomethoxylation of aromatic bromides.¹⁸ Since the amidation reaction is an analogous carbonylation reaction and given that oxidative addition is slower to aryl chlorides than to bromides, an increase in the rate of this initial step results in an increase in the overall rate. The proposed reaction scheme is outlined in Scheme 1.

(14) Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules* **1995**, *28*, 2607.

(15) (a) Amatore, C.; Azzabi, M.; Jutand, A. *J. Organomet. Chem.* **1989**, *363*, C41. (b) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375. (c) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531.

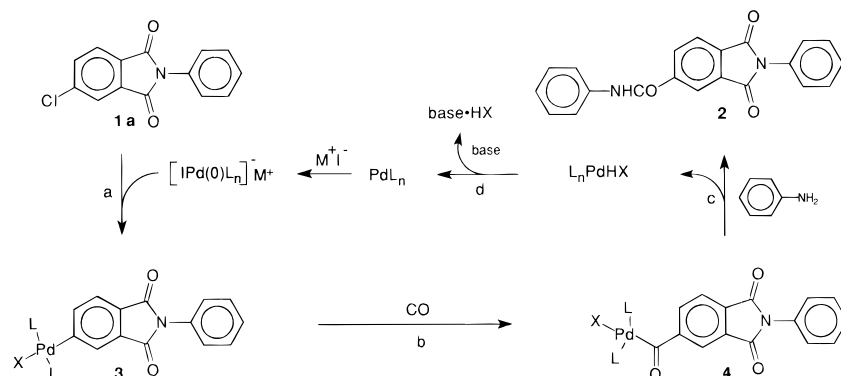
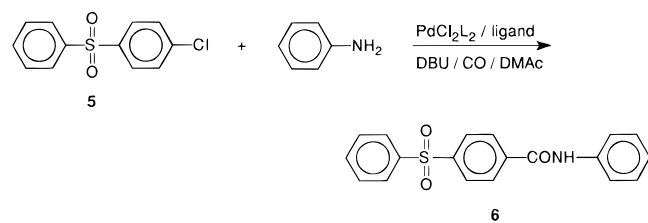
(16) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1338.

(17) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.

(18) Moser, W. R.; Wang, A. W.; Kildahl, N. K. *J. Am. Chem. Soc.* **1988**, *110*, 2816.

(19) (a) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979. (b) *Lange's Handbook of Chemistry*, 14th ed.; Dean, J. A., Ed.; McGraw Hill Book Co.: New York, 1992; pp 9.2–9.7.

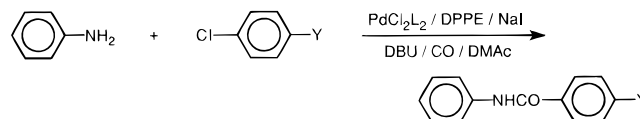
Scheme 1

Table 1. Optimization of Reaction of 5 with Aniline^a

entry	% catalyst ^b	% ligand ^c	salt (equiv)	CO pressure (psig)	time (h)	% product ^d
1	3	6		95	7	8
2	3	6		5	7	29
3	3	6	0.10 NaI	95	4	6
4	3	6	0.10 NaI	5	32	50
5	3	6	1.00 NaI	95	23	57
6	3	6	1.00 NaI	5	23	82
7	3	6	1.00 Bu ₄ N ⁺ I ⁻	5	23	36
8	3	6	1.00 KI	5	23	75
9	3	12	1.00 NaI	5	19	88
10	3		1.00 NaI	5	24	44
11	3 ^h		1.00 NaI	5	24	76
12	3	6 ^e	1.00 NaI	5	23	15
13	3	6 ^f	1.00 NaI	5	24	66
14	3	6 ^g	1.00 NaI	5	24	98

^a Reaction in DMAc at 115 °C with 1.2 equiv of DBU. ^b PdCl₂L₂ (L = PPh₃). ^c PPh₃. ^d Yield of **6** as determined by GC. ^e Tri-*o*-tolylphosphine as ligand. ^f Tri-*p*-tolylphosphine as ligand. ^g 1,2-Bis(diphenylphosphino)ethane as ligand. ^h PdL₄.

From the above experiments, it was clear that the phthalimide group was sufficient to activate the aryl chloride bond for oxidative addition reactions and that iodide had an accelerating effect on the overall amidation rate. Another such activating group is the sulfone moiety. A series of reactions for the amidation of 4-chlorophenyl phenyl sulfone were also performed to compare with the phthalimide. Table 1 shows that similar trends were found. Lower CO pressures gave higher yields of product (entries 1–6), and higher NaI concentrations gave greater yields (entries 2, 4, and 6). The addition of extra phosphine ligands provided a higher yield of amide (entry 9), while the removal of these ligands resulted in a drop in product formation (entry 10). The use of PdL₄ gave results similar to PdCl₂L₂ with 2 PPh₃ added (entry 11). These last results suggested, at least in the case of the 4-chlorophenyl phenyl sulfone, that the ligands were more important than in the phthalimide case where no difference in rate or yield was seen with variation in PPh₃ concentration. Tri-*o*- and tri-*p*-tolylphosphine were added as ligands with no advantageous effects (entry 12–13). However, the chelating phosphine, 1,2-bis(diphenylphosphino)ethane (DPPE),

Table 2. Effect of Substituent on Amidation Reaction^a

entry	Y	σ _p ^b	yield ^c (%)
1	SO ₂ Ph	0.67 ^d	91
2	CN	0.66	62
3	CF ₃	0.54	78
4	COMe	0.50	71
5	COPh	0.46	82
6	COOMe	0.39	59
7	F	0.06	<15% conversion
8	H	0.00	<3% conversion
9	Ph	-0.01	<12% conversion
10	Me	-0.17	<1% conversion
11	OMe	-0.27	0

^a Reactions run for 24 h at 115 °C using 3% PdCl₂L₂ and 6% DPPE at 5 psig of CO. ^b Hammett *para* substituent constants. ^c Isolated, purified yields; percent conversion was determined by GC and products were not isolated. ^d Estimated from Hammett *meta* constant.

showed essentially quantitative formation of the desired amide sulfone **6**, after 24 h (entry 14).

To determine the scope and limitation of this reaction, the optimum conditions for chlorophenyl phenyl sulfone amidation were applied to other substrates as shown in Table 2. Only those chlorides activated by strong electron withdrawing groups (entries 1–6) underwent successful amidation. GC analysis indicated complete reaction, and the isolated, purified yields of substituted benzamides ranged between 60 and 90%. Weakly withdrawing moieties and donating substituents reacted sluggishly or not at all.

Conclusion

We have shown that the palladium-catalyzed amidation of electron, deficient aryl chlorides proceeds readily in the presence of low CO pressures and a slight excess of an iodide salt. The rates of amidation are accelerated over those without added salt, and iodide is preferred over bromide or chloride. More electron-rich aryl chlorides were not effectively amidated, either with or without added iodide. We postulate that an intermediate anionic palladium(0) iodide complex is responsible for the enhanced reactivity.

Experimental Section

General Procedures. Reactions were performed in a 120 mL pressure reaction vessel (containing a Teflon-coated stir-bar), fitted with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample

withdrawal, in a well-ventilated hood and behind safety shields. Reactions were monitored on an HP 5890 gas chromatograph using a 15 m, 0.25 μ M DB-5 column (0.32 mm i.d.) and a flame ionization detector. Helium flow rate through the column was 4.0 mL/min. The GC parameters employed for analysis were as follows: injection port, 300 °C; detector, 350 °C; temperature ramp from 50 °C (hold 1 min) to 300 °C (hold 10 min) at 20 °C/min. Biphenyl was used as an internal standard to determine GC yields. ¹H NMR and ¹³C NMR spectra were acquired on a 300 MHz spectrometer using CDCl₃ or DMSO-*d*₆ as both solvent and reference. ³¹P NMR spectra were acquired on a 120 MHz spectrometer using DMF-*d*₇ as solvent and H₃PO₄ as an external reference. Fourier transform infrared spectra were recorded as KBr pellets. Elemental analyses were performed by the Analytical Technology Division of Eastman Kodak Company.

Chemicals. Aniline (dried over CaH₂) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were fractionally distilled under reduced pressure. Triphenylphosphine (PPh₃) was recrystallized from hexanes. NaI, KI, and NaBr were dried at 120 °C *in vacuo*. CO (Air Products, UPC grade), bis(triphenylphosphine)palladium(II) chloride (PdCl₂L₂), tetrakis(triphenylphosphine)palladium (PdL₄), tri(*o*-tolyl)phosphine, tri(*p*-tolyl)phosphine, 1,2-bis(diphenylphosphino)ethane (DPPE), *N,N*-dimethylacetamide (DMAc, anhydrous), tetra-*n*-butylammonium iodide, 4-chlorophenyl phenyl sulfone, 4-chlorobenzotri-fluoride, methyl 4-chlorobenzoate, 1-chloro-4-fluorobenzene, 4-chlorotoluene, 4-chloroanisole (all Aldrich), *p*-chlorobenzonitrile, 4'-chloroacetophenone, chlorobenzene (all Eastman Kodak), 4-chlorophthalic anhydride (Oxy Chem), and 4-chlorobiphenyl (Alfa) were used as received. 4-Iodophthalic anhydride was prepared as described previously.¹³

Preparation of Starting Materials. 4-Chloro-*N*-phenylphthalimide, 1a. A solution of 4-chlorophthalic anhydride (9.12 g, 50 mmol), aniline (4.65 g, 50 mmol), pyridine (12.01 g, 152 mmol), and DMAc (40 mL) was heated at 70 °C for 1 h under argon. Acetic anhydride (20.0 g, 196 mmol) was added, and the solution was allowed to stir at 80 °C for a total of 4 h. The reaction mixture was cooled to *ca.* 5 °C and the crystalline solid removed by filtration, washed with acetone and methanol, and dried *in vacuo* to give 9.0 g (70%) product that was recrystallized from acetic anhydride: mp 187–189 °C (lit. mp 189.5–191 °C);²⁰ ¹H NMR (CDCl₃) δ 7.90 (d, *J* = 1.6 Hz, 1), 7.88 (d, *J* = 8.0 Hz, 1), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1), 7.50 (m, 2), 7.41 (m, 3); ¹³C NMR (CDCl₃) {¹H} δ 166.2, 165.9, 141.1, 134.4, 133.5, 131.5, 129.9, 129.1, 128.2, 126.4, 124.9, 124.1.

4-Iodo-*N*-phenylphthalimide, 1b. As described above, 4-iodophthalic anhydride (2.0 g, 7.3 mmol), aniline (665 μ L, 7.3 mmol), pyridine (2.1 mL, 25.5 mmol), and DMAc (10 mL) were heated at 80 °C for 2 h, followed by continued heating in the presence of acetic anhydride (2.75 mL, 29.2 mmol) for 16 h. MeOH (5 mL) was added to the warm solution, which was then cooled to room temperature. The crystalline solid was removed by filtration, washed with MeOH, and dried *in vacuo* to give 1.96 g (77%) of product. The filtrate was concentrated and cooled to 0 °C to afford another 300 mg (11%) of product: total yield 88%; mp 178–179 °C; ¹H NMR (CDCl₃) δ 8.27 (d, *J* = 1.0 Hz, 1), 8.13 (dd, *J* = 7.5, 1.0 Hz, 1), 7.65 (d, *J* = 7.9 Hz, 1), 7.49 (m, 2), 7.40 (m, 3); ¹³C NMR (CDCl₃) {¹H} δ 166.6, 165.7, 143.3, 133.1, 132.8, 131.5, 131.0, 129.1, 128.2, 126.4, 124.9, 101.1. Anal. Calcd for C₁₄H₈INO₂: C, 48.16; H, 2.31; N, 4.01. Found: C, 47.81; H, 2.39; N, 3.95.

Representative Amidation Reactions. *N*-Phenyl-4-(carboxyanilino)phthalimide (2). A pressure bottle was charged with 4-chloro-*N*-phenylphthalimide, **1** (566 mg, 2.19 mmol), aniline (200 μ L, 2.19 mmol), PdCl₂L₂ (46 mg, 0.066 mmol), PPh₃ (35 mg, 0.132 mmol), NaI (395 mg, 2.63 mmol), DBU (395 μ L, 6.6 mmol), and DMAc (15 mL). The mixture was degassed and charged with 5 psig of CO and then heated to 115 °C for 16 h. The solution was filtered through Celite, concentrated *in vacuo*, and then slurried with MeOH to give an off-white solid. The solid was washed extensively with MeOH and dried to give 615 mg of product (82%): mp 266.5–268 °C; ¹H NMR (DMSO-*d*₆) δ 10.60 (s, 1), 8.50 (s, 1), 8.41 (dd, *J* = 7.5, 1.0 Hz, 1), 8.08 (d, *J* = 7.7 Hz, 1), 7.78 (d, *J* = 7.8

Hz, 2), 7.46 (m, 5), 7.35 (t, *J* = 7.8 Hz, 2), 7.11 (t, *J* = 7.3 Hz, 1); ¹³C NMR (DMSO-*d*₆) {¹H} δ 166.3, 166.2, 163.4, 140.2, 138.5, 134.1, 133.6, 131.7, 131.6, 128.7, 128.4, 127.9, 127.1, 124.0, 123.4, 122.0, 120.5. Anal. Calcd for C₂₁H₁₄N₂O₃: C, 73.68; H, 4.12; N, 8.18. Found: C, 73.71; H, 4.10; N, 7.94.

(4-Carboxyanilino)phenyl Phenylsulfone. A pressure bottle was charged with 4-chlorophenyl phenyl sulfone (1.387 g, 5.5 mmol), aniline (500 μ L, 5.5 mmol), PdCl₂L₂ (116 mg, 0.16 mmol), DPPE (131 mg, 0.3 mmol), NaI (823 mg, 6.6 mmol), DBU (985 μ L, 6.6 mmol) and DMAc (17 mL). The mixture was degassed and charged with 5 psig of CO and then heated to 115 °C for 6 h. GC analysis of the reaction indicated all the starting material had been consumed. The solution was filtered through Celite, concentrated *in vacuo*, and then slurried with MeOH to give an off-white solid. The solid was washed extensively with MeOH and dried to give 1.54 g of product (83%). The filtrate was concentrated and subjected to chromatography on silica gel, eluting with 1:1 hexanes: EtOAc, to give an additional 147 mg (8%) product: total yield 91%; mp 206–207.5 °C; ¹H NMR (CDCl₃) δ 10.43 (s, 1), 8.09 (s, 4), 7.98 (d, *J* = 8.0 Hz, 2), 7.65 (m, 5), 7.33 (t, *J* = 7.5 Hz, 2), 7.08 (t, *J* = 7.0 Hz, 1); ¹³C NMR (CDCl₃) {¹H} δ 164.2, 143.3, 140.6, 139.6, 138.7, 133.9, 129.8, 128.9, 128.6, 127.4, 124.0, 120.3. Anal. Calcd for C₁₉H₁₅NO₃S: C, 67.64; H, 4.48; N, 4.15. Found: C, 67.28; H, 4.60; N, 4.15.

The rest of the amidation reactions were performed on the same scale and in a similar manner, except as noted below.

4-Cyanobenzanilide. After 17 h reaction time, the reaction mixture was filtered, concentrated, dissolved in hot toluene, and chromatographed on silica gel eluting with toluene. The product obtained was recrystallized from toluene to give 761 mg of product (62%): mp 179.5–180 °C (lit.²¹ mp 175–176 °C); ¹H NMR (CDCl₃) δ 10.45 (s, 1), 8.08 (d, *J* = 8.3 Hz, 2), 8.03 (d, *J* = 8.3 Hz, 2), 7.75 (d, *J* = 8.0 Hz, 2), 7.34 (t, *J* = 7.8 Hz, 2), 7.10 (t, *J* = 7.3 Hz, 1); ¹³C NMR (CDCl₃) {¹H} δ 164.1, 138.9, 138.7, 132.4, 128.6, 128.4, 124.0, 120.4, 118.4, 113.8.

4-(Trifluoromethyl)benzanilide. After recrystallization from toluene, as above, 1.136 g (78%) of product was obtained: mp 202–203 °C (lit.²² mp 198 °C); ¹H NMR (CDCl₃) δ 10.44 (s, 1), 8.12 (d, *J* = 8.2 Hz, 2), 7.88 (d, *J* = 8.2 Hz, 2), 7.75 (d, *J* = 7.9 Hz, 2), 7.34 (t, *J* = 7.8 Hz, 2), 7.10 (t, *J* = 7.4 Hz, 1).

4-Acetylbenzanilide. After recrystallization from toluene, as above, 933 mg (71%) of product was obtained: mp 197–198 °C (lit.²³ mp 188–189 °C); ¹H NMR (CDCl₃) δ 10.40 (s, 1), 8.05 (s, 4), 7.77 (d, *J* = 8.1 Hz, 2), 7.34 (t, *J* = 7.8 Hz, 2), 7.09 (t, *J* = 7.3 Hz, 1), 2.61 (s, 3); ¹³C NMR (CDCl₃) {¹H} δ 197.6, 164.7, 138.9, 138.8, 138.7, 128.6, 128.1, 127.9, 123.9, 120.4, 26.9.

4-Benzoylbenzanilide. After recrystallization from toluene, as above, 1.351 g (82%) of product was obtained: mp 161–161.5 °C; ¹H NMR (CDCl₃) δ 10.44 (s, 1), 8.08 (d, *J* = 8.2 Hz, 2), 7.83 (d, *J* = 8.2 Hz, 2), 7.77 (m, 4), 7.69 (t, *J* = 7.5 Hz, 1), 7.56 (t, *J* = 7.5 Hz, 2), 7.34 (t, *J* = 7.8 Hz, 2), 7.10 (t, *J* = 7.3 Hz, 1); ¹³C NMR (CDCl₃) {¹H} δ 195.3, 164.7, 139.4, 138.9, 138.2, 136.6, 133.0, 129.6, 129.4, 128.6, 127.8, 123.5, 120.4. Anal. Calcd for C₂₀H₁₅NO₂: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.53; H, 5.15; N, 4.65.

4-Carbomethoxybenzanilide. After recrystallization from toluene, as above, 821 mg (59%) product was obtained: mp 191.5–192 °C (lit.²⁴ mp 192–193 °C); ¹H NMR (CDCl₃) δ 10.41 (s, 1), 8.05 (s, 4), 7.77 (d, *J* = 8.0 Hz, 2), 7.38 (t, *J* = 7.8 Hz, 2), 7.09 (t, *J* = 7.3 Hz, 1), 3.86 (s, 3); ¹³C NMR (CDCl₃) {¹H} δ 165.6, 164.6, 139.0, 138.8, 132.0, 129.1, 128.6, 128.0, 123.9, 120.4, 52.3.

JO960861J

(21) Bharucha, K. R.; Shah, R. C. *J. Univ. Bombay* **1949**, *17A*, 76.

(22) Yagupol'skii, L. M.; Gruz, B. E. *Ukr. Khim. Zh.* **1957**, *23*, 634. CA52:9980a.

(23) Suzuki, H.; Tsuji, J.; Hiroi, Y.; Sato, N.; Osuka, A. *Chem. Lett.* **1983**, 449.

(24) Schoenberg, A.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3327.