Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201400929

Arylthiolation of Arylamine Derivatives with (Arylthio)-pyrrolidine-2,5-diones

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Received: September 22, 2014; Revised: November 4, 2014; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400929.

Abstract: A simple and efficient method for arylthiolation of arylamines has been developed. The protocol uses (arylthio)pyrrolidine-2,5-diones as the arylthiolating reagents, acetonitrile as the solvent, and no catalyst and additive are required, which avoids contamination from the transition metal catalysts in the target products. Therefore, the present method should provide a convenient, efficient and practical strategy for the synthesis of other aryl sulfides.

Keywords: arylamine derivatives; aryl sulfides; arylthiolation; Friedel–Crafts reaction; synthetic methods

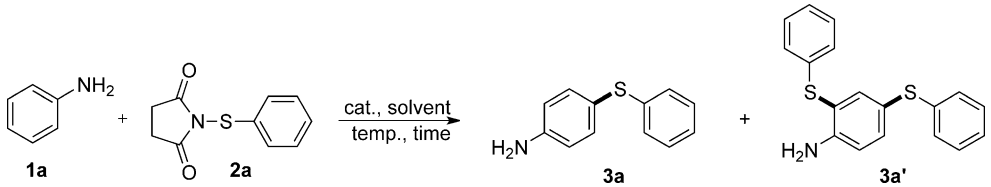
Introduction

Aryl sulfides widely occur in various fields,[1] and they are often found in biologically and pharmaceutically active molecules.[2] The traditional methods for the synthesis of aryl sulfides are through the coupling of thiols or disulfides with aryl halides or pseudohalides catalyzed by transition metals[3] such as palladium,[4] copper,[5] iron,[6] gold,[7] rhodium,[8] cobalt,[9] indium,[10] and nickel.[11] Other alternative methods include the transition metal-catalyzed reactions of arylmagnesium halides[12] or arylboronic acid derivatives[13] with suitable electrophilic arylsulfur reagents. Obviously, direct arylthiolation of the aryl C–H bond is attractive. However, the examples using this strategy are scarce. In 2006, Tudge and co-workers reported the halide-catalyzed sulfenylation of indoles.[14a] Recently, a $CeCl_3$-catalyzed sulfenylation of indoles with *N*-(arylthio)phthalimides has been developed.[14b] Yu's group developed a copper-catalyzed aerobic oxidative thiolation of 2-phenylpyridine with PhSH and MeSSMe.[15] Later, Doi and Batey reported an intramolecular C–S bond formation of 2-substituted benzothiazoles *via* C–H functionalization, respectively.[16] Fukuzawa and co-workers investigated the copper-catalyzed direct thiolation of benzoxazole with diaryl disulfides and aryl thiols using the CuI/2,2′-bipyridine complex as catalyst.[17] In 2010, Qing's research group demonstrated the direct use of DMSO as the reagent for Cu(II)-mediated C–H bond methylthiolation.[18] Cheng and co-workers reported a copper-catalyzed aerobic oxidative C–H bond thiolation of the di- or trimethoxybenzene species with disulfides.[19] In 2011, Beller's research group developed the palladium-catalyzed direct arylthiolation of electron-rich arenes with arylsulfonyl cyanides.[20] Liu and co-workers reported the copper-mediated aerobic synthesis of aryl- or alkyl-substituted 2-mercaptobenzothiazoles by the direct thiolation of benzothiazoles with aryl or alkyl thiols in the presence of stoichiometric CuI, 2,2′-bipyridine and Na_2CO_3.[21a] Li's group described $FeCl_3$/I_2-catalyzed synthesis of 4-chalcogen-substituted arylamines with disulfides.[21b] In 2012, Bolm reported a transition metal-free direct thiolation of 1,3,4-oxadiazoles and related heteroarenes in the presence of Cs_2CO_3.[22] The $AlCl_3$-mediated[23a] or palladium-catalyzed[23b] aryl(alkyl)thiolation of arenes was also described. Very recently, we have developed the iron- or boron-catalyzed C–H arylthiolation of substituted phenols at room temperature.[24] Herein, we report a simply and efficient arylthiolation of arylamines without addition of any catalyst and additive.

Results and Discussion

As shown in Table 1, the reaction of aniline (**1a**) with 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) leading to 4-(phenylthio)benzenamine (**3a**) was applied as the model to optimize the reaction conditions including

Table 1. Optimization of the conditions for the reaction of aniline (**1a**) with 1-(phenylthio)pyrrolidine-2,5-dione (**2a**).[a]



Entry	Catalyst	Solvent	Temperature [°C]	Time [h]	Yield of **3a** [%][b]	Yield of **3a′** [%][b]
1		DCE	100	24	72	4
2		DMF	100	24	8	0
3		DMSO	100	24	21	0
4		dioxane	100	24	0	0
5		THF	100	24	0	0
6		$CHCl_3$	100	24	70	4
7		MeCN	100	24	83	6
8		MeCN	100	12	49	Trace
9		MeCN	100	18	67	3
10		MeCN	80	24	58	trace
11		MeCN	60	24	22	0
12	$FeCl_3$	MeCN	100	24	53	trace
13	$BF_3{\cdot}OEt_2$	MeCN	100	24	67	3
14	$CuCl_2$	MeCN	100	24	64	3
15	$Pd(OAc)_2$	MeCN	100	24	0	0
16	$ZnCl_2$	MeCN	100	24	12	0
17	$AlCl_3$	MeCN	100	24	70	4
18	TFA	MeCN	100	24	77	4
19	H_2SO_4	MeCN	100	24	29	0

[a] *Reaction conditions:* without exclusion of air, aniline (**1a**) (0.3 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (**2a**) (0.33 mmol), catalyst (0.03 mmol), anhydrous solvent (2 mL), temperature (60–100 °C), reaction time (12–24 h).
[b] Isolated yield.

the catalysts, solvents and temperature. Seven solvents were screened (entries 1–7) in the absence of catalyst at 100 °C for 24 h, and MeCN gave the highest yield of **3a** while a small amount of the diarylthiolated product (**3a′**) was observed (entry 7). Yields decreased when reaction temperature or time was reduced (compare entries 7–11). We tested various Lewis acids (entries 12–19), and the results showed that their addition did not promote reactivity. As shown in Figure 1, the addition of transition metal salt could lead to the formation of complex **Ia** (entries 12–17), and reaction of an inorganic acid with aniline provided the corresponding ammonium species (**I′a**) (entries 18 and 19). The electron density of the phenyl ring in **Ia** and **I′a** is decreased in comparison with that of **1a**, which is not favorable for the electrophilic substitution.

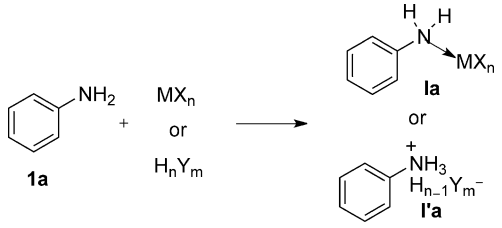
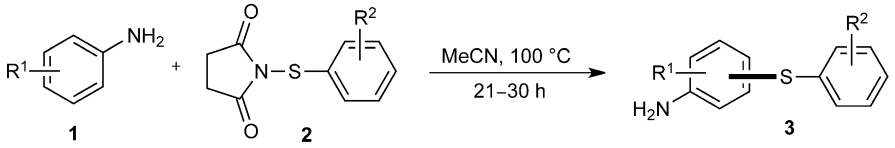


Figure 1. Treatment of aniline with Lewis acids.

After obtaining the optimized conditions, we investigated the scope of the arylthiolation of arylamine derivatives with (arylthio)pyrrolidine-2,5-diones. As shown in Table 2, all the tested substrates provided good to excellent yields, and the reaction efficiency was related to electronic and steric effects. For substituted arylamines, the substrates with electron-donating groups provided higher reactivity than those with electron-withdrawing groups. The site of arylthiolation depended on the electron density of the carbon on the phenyl ring and steric hindrance. For example, arylthiolation of aniline (**1a**) mainly occurred at the *para*-site to the amino function because of the low steric hindrance of the *para*-site, and *ortho*-substituted products were obtained when the *para*-site of the amino function was occupied by a substituent (entries 2, 5–7). For β-aminonaphthalene (**1s**), the arylthiolation occurred at the α-site because of the higher electron density of the α-carbon (entry 21). The site of arylthiolation of 3-methylaniline (**1w**) was dependent on both electronic and steric effects (entry 22). *N*-Substitued arylamines also were good substrates (entries 13, 22 and 28). For (arylthio)pyrrolidine-2,5-

Table 2. Arylthiolation of arylamine derivatives (**1**) with (arylthio)pyrrolidine-2,5-diones (**2**) leading to **3**.[a]



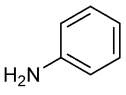
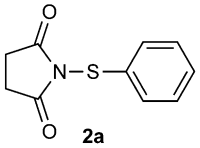
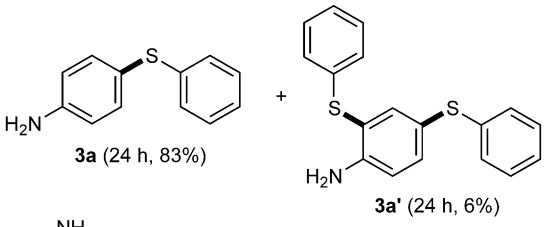
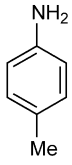
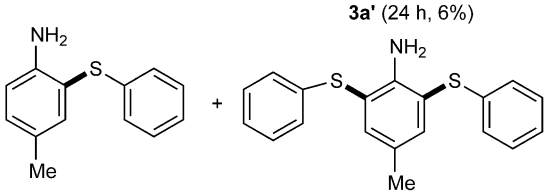
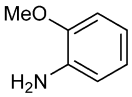
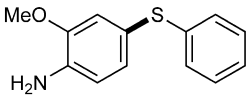
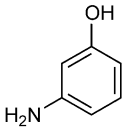
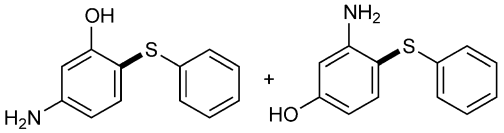
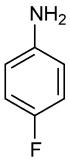
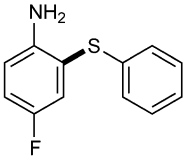
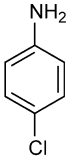
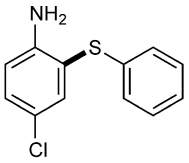
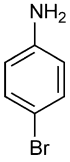
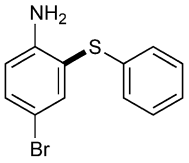
Entry	1	2	3 (Time, Yield[b])
1	 **1a**	 **2a**	 **3a** (24 h, 83%) + **3a'** (24 h, 6%)
2	 **1b**	**2a**	 **3b** (24 h, 76%) + **3b'** (24 h, 9%)
3	 **1c**	**2a**	 **3c** (21 h, 97%)
4	 **1d**	**2a**	 **3d** (24 h, 49%) + **3d''** (24 h, 25%)
5	 **1e**	**2a**	 **3e** (26 h, 52%)
6	 **1f**	**2a**	 **3f** (26 h, 61%)
7	 **1g**	**2a**	 **3g** (26 h, 66%)

Table 2. (Continued)

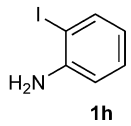
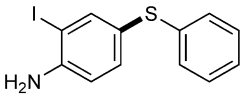
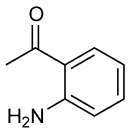
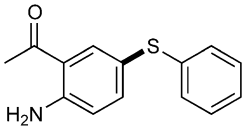
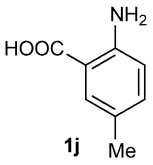
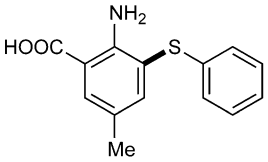
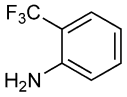
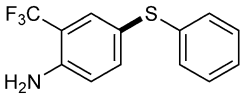
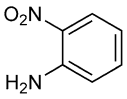
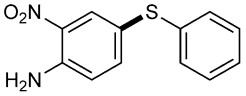
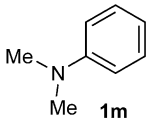
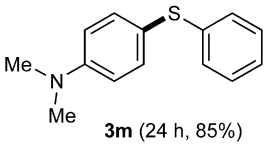
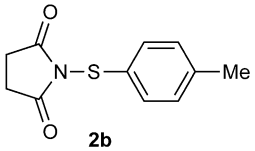
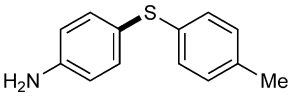
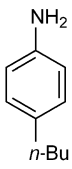
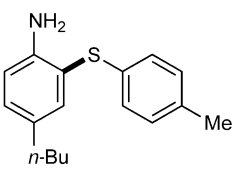
Entry	1	2	3 (Time, Yield[b])
8	 **1h**	**2a**	 **3h** (21 h, 69%)
9	 **1i**	**2a**	 **3i** (24 h, 73%)
10	 **1j**	**2a**	 **3j** (30 h, 67%)
11	 **1k**	**2a**	 **3k** (24 h, 67%)
12	 **1l**	**2a**	 **3l** (30 h, 62%)
13	 **1m**	**2a**	 **3m** (24 h, 85%)
14	**1a**	 **2b**	 **3n** (24 h, 75%)
15	 **1n**	**2b**	 **3o** (24 h, 86%)

Table 2. (Continued)

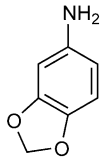
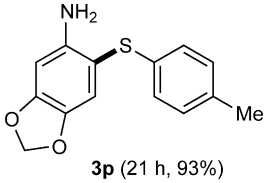
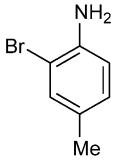
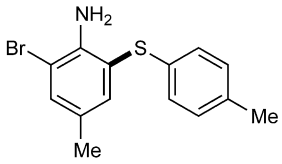
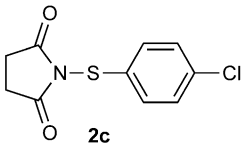
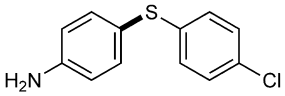
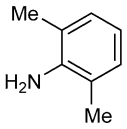
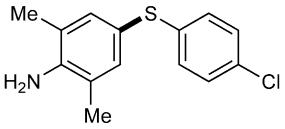
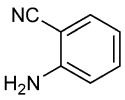
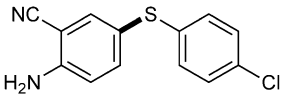
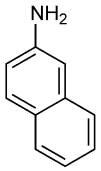
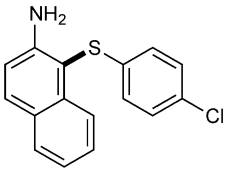
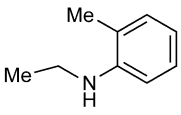
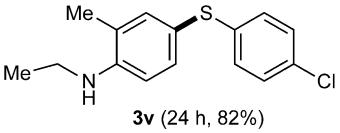
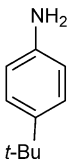
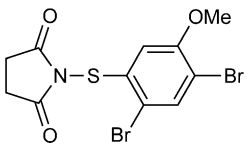
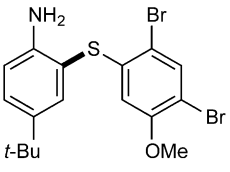
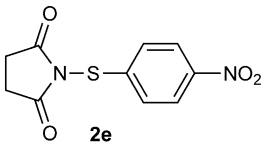
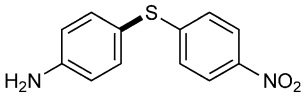
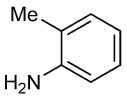
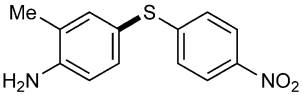
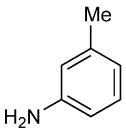
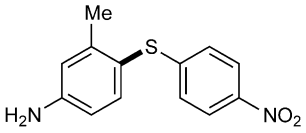
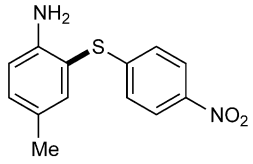
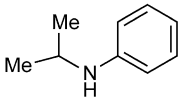
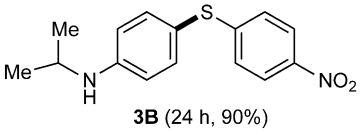
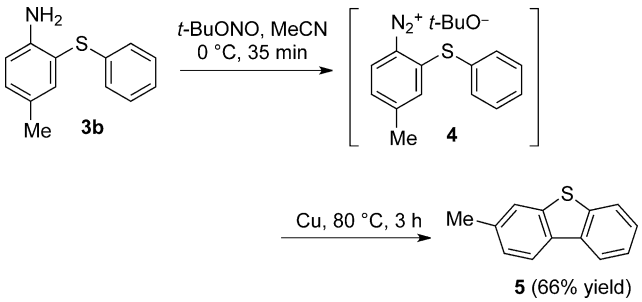
Entry	1	2	3 (Time, Yield[b])
16	 **1o**	**2b**	 **3p** (21 h, 93%)
17	 **1p**	**2b**	 **3q** (24 h, 76%)
18	**1a**	 **2c**	 **3r** (24 h, 77%)
19	 **1q**	**2c**	 **3s** (26 h, 75%)
20	 **1r**	**2c**	 **3t** (30 h, 58%)
21	 **1s**	**2c**	 **3u** (21 h, 87%)
22	 **1t**	**2c**	 **3v** (24 h, 82%)
23	 **1u**	 **2d**	 **3w** (21 h, 90%)

Table 2. (Continued)

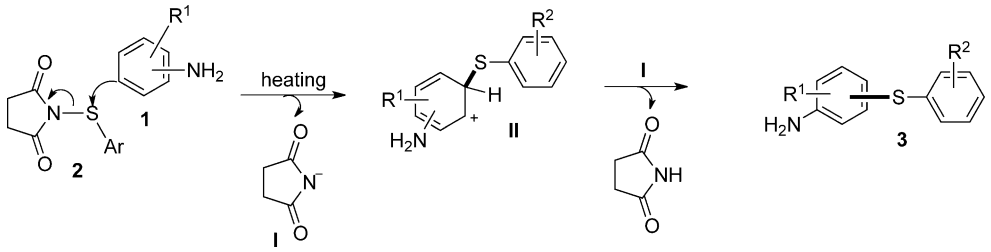
Entry	1	2	3 (Time, Yield[b])
24	**1a**	 **2e**	 **3x** (24 h, 88%)
25	 **1v**	**2e**	 **3y** (24 h, 92%)
26	 **1w**	**2e**	 **3z** (24 h, 89%)
27	**1b**	**2e**	 **3A** (24 h, 91%)
28	 **1x**	**2e**	 **3B** (24 h, 90%)

[a] *Reaction conditions:* substituted arylamine (**1**) (0.3 mmol), 1-(arylthio)pyrrolidine-2,5-dione (**2**) (0.33 mmol), dry CH_3CN (2 mL), temperature (100 °C), reaction time (21–30 h).
[b] Isolated yield.

diones, the substrates with electron-withdrawing groups on the aromatic rings gave higher yields than those with electron-donating groups. Arylthiolation of 3-aminophenol (**1d**) afforded two products **3d** and **3d″** because of the higher electronic density of the phenyl ring (entry 4). In addition, diarylthiolation of substrates **1a** and **1b** was found to occur (entries 1 and 2). For substrates containing halo and electron-withdrawing groups, some unknown by-products were observed by thin layer chromatography. The arylthiolation of arylamine derivatives could tolerate various functional groups including ethers (entries 3, 16 and 23), hydroxy (entry 4), C–F bond (entry 5), C–Cl bond (entries 6, 18–22), C–Br bond (entries 7, 17 and 23), C–I



Scheme 1. Application of synthesized **3b** in the synthesis of a sulfur heterocycle.



Scheme 2. Possible mechanism for the arylthiolation of arylamines with (arylthio)pyrrolidine-2,5-diones.

bond (entry 8), acetyl (entry 9), carboxyl (entry 10), trifluoromethyl (entry 11), nitro (entries 12, 24-28), and cyano (entry 20) groups.

Furthermore, we examined applications of the synthesized products. First, the reaction of 4-methyl-2-(phenylthio)benzenamine (**3b**) with 2 equiv. of *tert*-butyl nitrite at 0 °C provided the corresponding aryldiazonium salt (**4**), and then treatment of **4** in the presence of 2 equiv. of copper powder gave the corresponding S-heterocyle (3-methyldibenzo[*b*,*d*]thiophene) in 66% yield (Scheme 1).

A possible mechanism for the arylthiolation of substituted arylamines with (arylthio)pyrrolidine-2,5-diones is proposed in Scheme 2. Reaction of (arylthio)pyrrolidine-2,5-dione (**2**) with arylamine (**1**) gives **II**, freeing **I**, and treatment of **II** with **I** affords the target product (**3**) leaving succinimide.

Conclusions

We have developed a simple, efficient and practical method for the arylthiolation of arylamines. The protocol uses (arylthio)pyrrolidine-2,5-diones as the arylthiolation reagents for arylamine derivatives, acetonitrile as the solvent, and catalyst, additive and exclusion of air were not required, which avoided contamination by transition metal catalysts of the target products. Furthermore, applications of the synthesized arylthiolation products emphasise the great value of the present method. We believe that this environmentally friendly method will find wide applications.

Experimental Section

General Procedure for Synthesis of Compounds 3a-B

To a 25-mL Schlenk tube was charged with a magnetic stirrer, substituted arylamine (**1**) (0.3 mmol) and 1-(arylthio)-pyrrolidine-2,5-dione (**2**) (0.33 mmol), dry MeCN (2.0 mL) was added, the tube was sealed and the mixture was stirred at 100 °C until the reaction was completed (TLC determination). The resulting solution was concentrated on a rotary evaporator, and the residue was isolated by column chromatography on silica gel using petroleum ether/ethyl acetate, dichloromethane/hexane or dichloromethane/MeOH/AcOH as the eluent to give the desired target product (**3**).

Three representative examples are given below.

4-Bromo-2-(phenylthio)aniline (3g): Eluent: dichloromethane/hexane (1:5); yield: 55 mg (66%); brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.56$ (d, $J = 2.3$ Hz, 1H), 7.30 (dd, $J = 8.7$ Hz, 2.3 Hz, 1H), 7.24 (t, $J = 7.8$ Hz, 2H), 7.10–7.16 (m, 3H), 6.68 (d, $J = 8.7$ Hz, 1H), 3.87 (br.s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 147.5$, 139.0, 135.8, 133.8, 129.3, 127.2, 126.1, 117.1, 117.0, 109.7; EI-MS: $m/z = 279.3$, 281.3 (M^+).

1-(2-Amino-5-(phenylthio)phenyl)ethanone (3i): Eluent: dichloromethane/hexane (1:8); yield: 53 mg (73%); yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.92$ (d, $J = 1.4$ Hz, 1H), 7.37 (dd, $J = 8.7$ Hz, 1.4 Hz, 1H), 7.22 (t, $J = 7.3$ Hz, 2H), 7.09–7.13 (m, 3H), 6.65 (d, $J = 8.7$ Hz, 1H), 6.48 (br. s, 2H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 200.3$, 150.7, 140.9, 139.3, 139.2, 129.1, 127.2, 125.6, 118.9, 118.7, 117.5, 27.9; EI-MS: $m/z = 243.3$ (M^+).

4-(Phenylthio)-2-(trifluoromethyl)aniline (3k): Eluent: dichloromethane/hexane (1:3); yield: 54 mg (67%); yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.60$ (d, $J = 1.8$ Hz, 1H), 7.39 (dd, $J = 8.7$ Hz, 1.8 Hz, 1H), 7.21–7.25 (m, 2H), 7.12–7.16 (m, 3H), 6.70 (d, $J = 8.7$ Hz, 1H), 4.29 (br.s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 144.9$, 139.0, 138.4, 132.8 (q, $J = 4.8$ Hz), 129.1, 128.2, 126.1, 124.6 (q, $J = 273.2$ Hz), 120.9, 118.3, 114.5 (q, $J = 29.7$ Hz); EI-MS: $m/z = 269.1$ (M^+).

Acknowledgements

The authors wish to thank the National Natural Science Foundation of China (Grant Nos. 21172128, 21372139 and 21221062), and the Ministry of Science and Technology of China (Grant No. 2012CB722605) for financial support.

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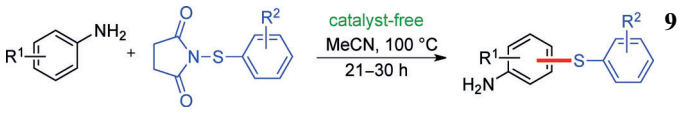
Arylthiolation of Arylamine Derivatives with (Arylthio)-pyrrolidine-2,5-diones



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