Preparation of Diarylamines and Arylhydrazines Using Palladium Catalysts

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Abstract: Aryl halides and aryl triflates (triflate = trifluoromethanesulfonyl) are coupled with *N*-compounds to give the corresponding arylamines or arylhydrazines in the presence of a palladium catalyst, a suitable ligand, and a base. Catalyst systems consisting of palladium (II) and BINAP or triphenylphosphine are generally effective for the amination of a wide range of aryl halides and aryl triflates with anilines and hydrazines.

Keywords: Aryl amination, Palladium catalyst, Solvent free conditions.

INTRODUCTION

N-Arylamines [1] and arylhydrazines [2] are interesting intermediates in drug discovery and synthesis, being particularly important in researching drugs for the pharmaceutical industry. Diarylamines have considerable potential in organic chemistry [3], act as precursors of a wide variety of compounds with pharmacological activity [4] and are useful synthetic intermediates for the preparation of substituted naphthylamines with antiangiogenesis activity [5] or other applications [6]. The preparation of functionalized diarylamines by classical methods was occasionally difficult and has renewed efforts in the search of versatile methodology. The classic Ullmann synthesis [7] has been complemented by new strategies including, cross coupling reaction catalyzed by Cu [8] or Ni [9], reaction using thallium [10], method of potassium fluoride alumina [11] and addition of arylmagnesiums to nitroarenes [12].

The catalytic amination of aryl halides reported by Buchwald [13-16] and Hartwig [17-20] represents an alternative to above cited methods of formation of these potentially useful compounds, and allowed the preparation of compounds which are inaccessible by other known synthetic routes. Buchwald *et al*., also described the synthesis of *N*-arylamines from triflates [21-22]. Both researcher groups have been motivated to seek out better reaction conditions for aryl amination and both have succeeded with apparent simple methods. The interesting work realized by Buchwald and Hartwig in the field of aromatic C-N bond formation has spurred others researchers to take part in this research line. For our part, we sought a simple methodology to form diarylamines and hydrazines as precursors of potential pharmaceutical agents from aryl halides and triflates and these results are reported.

RESULTS AND DISCUSSION

This work intends to develop general reaction conditions for the palladium-catalyzed diarylamines and arylhydrazines formation. Herein we describe our results (Tables **1-2**).

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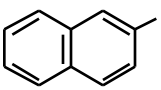
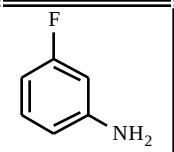
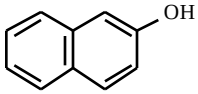
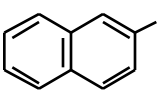
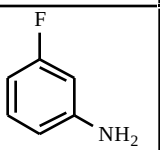
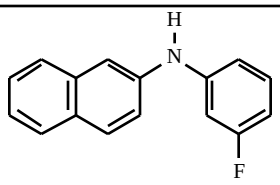
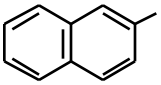
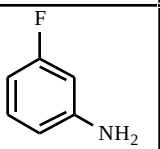
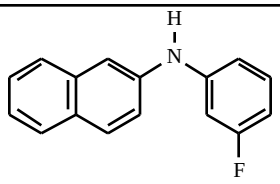
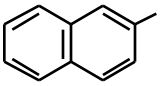
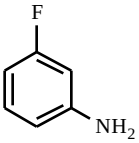
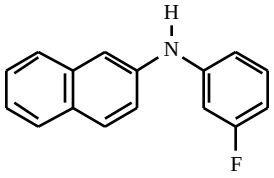
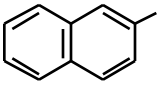
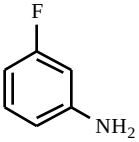
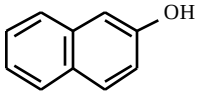
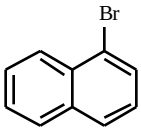
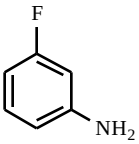
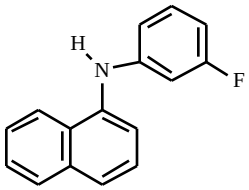
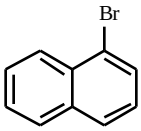
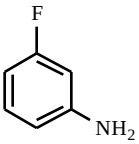
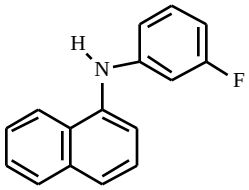
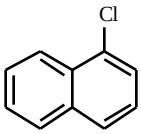
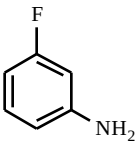
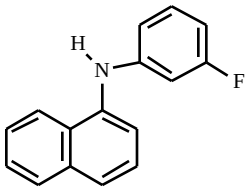
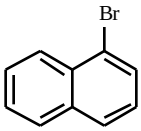
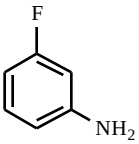
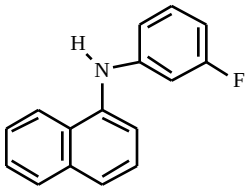
The conditions used for the *N*-arylation of several substrates were $Pd[P(o\text{-tolyl})_3]_2Cl_2$ as palladium precursor in a low concentration, chelating ligand 2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl (BINAP) or triphenylphosphine and cesium carbonate as a weak base without solvent. The reagents can be weighed in contact with air.

The conversion of triflates to aryl amines was also studied. Triflates are widely available from phenolic intermediates, and phenol derivatives, and are currently used in organic synthesis and in the synthesis of several therapeutic compounds. Thus, these compounds can be prepared from the hydroxyderivatives under classical conditions [23]. Triflates have been shown to be excellent substrates for metal-catalyzed amination with alkylamines and anilines [21-22]. These intermediate compounds were stable under the described reaction conditions, and no competing cleavage to phenol was observed, but the same reaction conducted without BINAP led to the recovery of the corresponding phenol (Table **1**, entry 5). The base used was also highly significant, a strong base such as NaO-*t*-Bu lad to the cleavage of the triflate and the recovery of the corresponding phenol (Table **1**, entry 1), when a weaker base, such as K_2CO_3, generated no cross coupled product. Nevertheless, Cs_2CO_3 provided aryl amines in acceptable chemical yields (Table **1**, entries 3 and 4).

Changing the ligand from BINAP to triphenylphosphine, which is less expensive, resulted in no significant modification of yields. Both ligands favored the coupling of aryl halides/aryl triflates and *N*-derivatives compounds (Table **1**, entry 9 versus entry 7; 15 versus 14, and 19 versus 18). In the same way, both racemic and non-racemic BINAP ((*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) gave similar results in all the tested transformations (Table **1**, entries 3 and 4, 6 and 7, 13 and 14). Moreover, addition of an excess of BINAP did not modify the yields under our experimental conditions. Earlier attempts in our laboratory to use $Pd(OAc)_2$ as catalyst, chelating bisphosphines such as BINAP, and NaO-*t*-Bu as a base, were unsuccessful, or gave the expected diarylamines in low yields when cesium carbonate was used (Table **1**, entries 1 and 2). No reaction occurred without addition of ligand BINAP or triphenylphosphine to $Pd[P(o\text{-tolyl})_3]_2Cl_2$, substrate, and

1570-1786/06 $50.00+.00

Table 1. Palladium-Catalyzed Amination of Aryl Halides and Triflates

Entry	Ar-X	R^1R^2NH	Catalyst (base)	Ligand	Time (h)	Product	Yield (%)*
1			$Pd(OAc)_2$ (*t*-BuONa)	BINAP	2		95
2			$Pd(OAc)_2$ (Cs_2CO_3)	BINAP	2		15
3			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	2		93
4			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	(±) BINAP	2		85
5			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	--	2		95
6			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	2		91
7			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	(±) BINAP	2		90
8			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	(±) BINAP	24		82
9			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	PPh_3	2		89

(Table 1). contd.....

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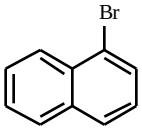
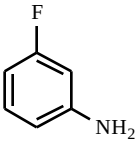
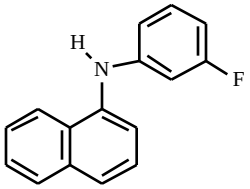
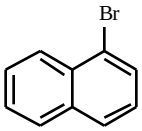
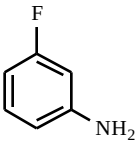
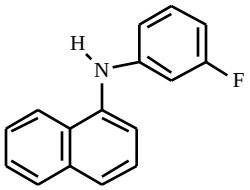
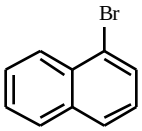
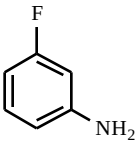
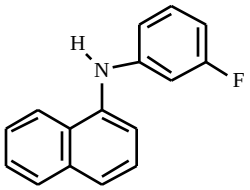
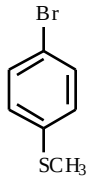
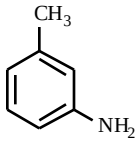
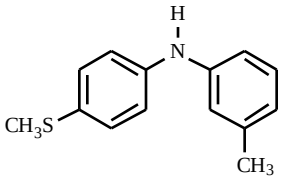
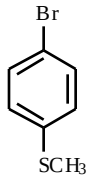
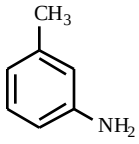
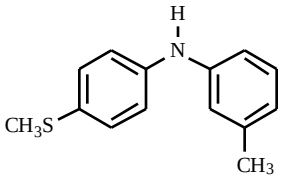
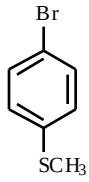
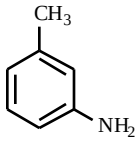
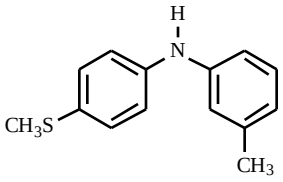
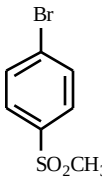
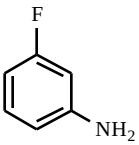
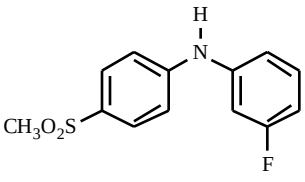
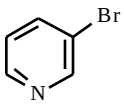
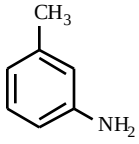
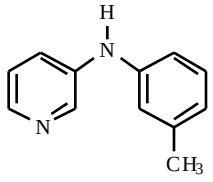
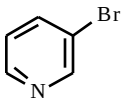
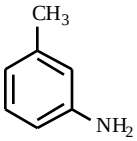
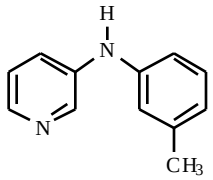
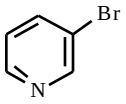
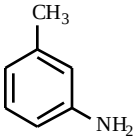
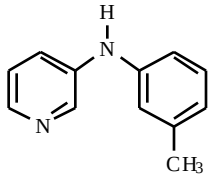
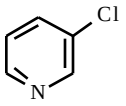
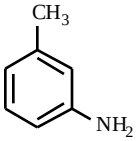
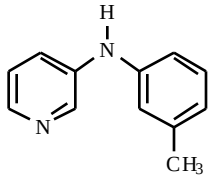
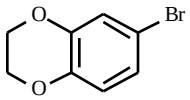
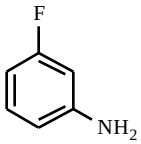
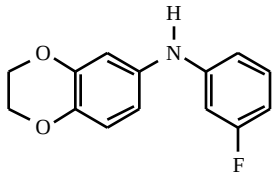
10			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	--	2		traces
11			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ ($BaCO_3$)	(±) BINAP	2		63
12			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (*t*-BuONa)	(±) BINAP	2		56
13			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	2		82
14			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	(±) BINAP	2		80
15			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	PPh_3	2		76
16			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	1		96
17			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	2		79

(Table 1). contd.....

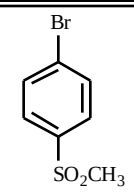
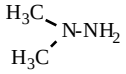
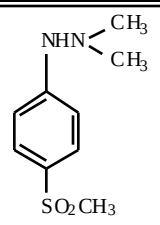
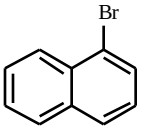
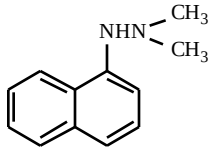
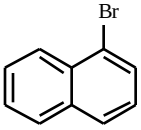
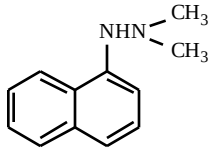
Entry	Ar-X	R^1R^2NH	Catalyst (base)	Ligand	Time (h)	Product	Yield (%)*
18			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	(±) BINAP	2		78
19			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	PPh_3	2		73
20			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	12		75
21			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	2		45

* Yields reported correspond to analytically pure isolated compounds (average of two or three runs). (±) BINAP racemic. BINAP ((*R*)-(+)-2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl). The reactions were conducted at 150ºC.

cesium carbonate (Table **1**, entries 5 and 10). Increasing the amount of catalyst did not improve the yield.

The reaction using aryl chlorides was slower than aryl bromides, but was successful in that the expected products were obtained in good yields (Table **1**, entries 8 and 20). Optimum results were obtained using $Pd[P(o\text{-tolyl})_3]_2Cl_2$, BINAP, aryl bromides, and cesium carbonate (Cs_2CO_3). The results showed that the $P(o\text{-tolyl})_3$ present in the catalyst

Table 2. Palladium-Catalyzed *N*-Arylation of Hydrazines

Entry	Ar-X	R^1R^2NH	Catalyst (base)	Ligand	Time (h)	Product	Yield (%)*
1			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	BINAP	1		76
2			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	(±) BINAP	2		83
3			$Pd[P(o\text{-tolyl})_3]_2Cl_2$ (Cs_2CO_3)	PPh_3	2		78

* Yields reported correspond to analytically pure isolated compounds (average of two or three runs). (±) BINAP racemic. BINAP ((*R*)-(+)-2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl). The reactions were conducted at 150ºC.

system was ineffective, even for the *N*-arylation of the activated substrates.

The reactions were successful using aryl chlorides and triflates, although the best results were obtained using aryl bromides. Moreover, this work confirms that electron-withdrawing (Table **1**, entry 16) as well as electron-donating substituents (Table **1**, entries 13, 14, 15, and 21) are tolerated under these conditions, although the withdrawing substituents favored the coupling reaction. Moreover, substrates containing other functional groups such as ether function or fluoro substituent were coupled giving the corresponding amines (Table **1**, entries 16 and 21).

Moreover, for an increase in substrate scope we also studied the arylation of substituted hydrazines. There are relatively few examples of catalytic amination reactions using protected hydrazines [24-29] and up to now, there are no report on the arylation of dialkyl hydrazines under palladium catalysis. Due to the importance of aryl hydrazines in the pharmaceutical industry, the same methodology was extended to the selective *N*-arylation of 1,1-dialkylhydrazines (Table **2**, entries 1-3).

In general, at 100 ºC in most cases, the reaction proceeded quickly (2h) and in acceptable yield, whereas at 150 ºC the yield was increased. The aromatic amination reaction is sensitive to the nature of the base, thus cesium carbonate was found to be the best for these transformations, whereas barium carbonate, potassium *tert*-butoxide, and sodium *tert*-butoxide gave the same coupled products but with yields significantly lower (Table **1**, entries 11 and 12).

In general, this coupling reaction was found to be temperature dependent, higher reaction temperature increasing the yield (100 to 150ºC); however raising the temperature to 200 ºC increased the amount of side products.

CONCLUSION

In conclusion, we report new conditions for the palladium-catalyzed amination of aryl halides and triflates which do not require the use of solvent or only drops of toluene (exceptional cases), and need low catalyst amounts, conditions that make the process more environment friendly. The fluorodiarylamines and the alkylarylhydrazines can be considered as intermediates for the preparation of interesting compounds with potential biological activity.

EXPERIMENTAL

Amination of Aryl Halides or Triflates (Tables 1-2). General Procedure

A flask was charged with aryl halide or triflate (1.0 mmol), amine (2 mmol), cesium carbonate (1 mmol), $Pd[P(o\text{-tolyl})_3]_2Cl_2$ (0.12 mol % Pd), and BINAP (0.0075 mmol) under argon without addition of solvent (just a drop of toluene was added only in exceptional cases). The flask was hermetically closed, and the mixture was heated at 100-150ºC (after the substrate and all reagents have been added without any period of incubation) with stirring until the starting material had been completely consumed as analyzed by TLC. The mixture was then allowed to cool to room temperature, and the crude product was then directly purified further by flash chromatography on silica gel, eluting with mixtures of hexane/ethyl acetate. All the commercially available reagents used were purchased from *Aldrich Chemical Co*. and were used without previous purification. The catalyst was acquired from *Strem* (Chemicals for Research). Yields reported correspond to analytically pure isolated compounds.

ACKNOWLEDGEMENTS

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[30] All compounds were characterized by NMR (^{1}H, ^{13}C). The spectroscopic data of the known compounds is in full agreement with that obtained from an authentic sample purchased from Aldrich. Combustion analyses were obtained for all new compounds, and for compounds which had been previously reported with limited analysis.
Analytical data of the synthesized compounds:
***N*-(3-Methylphenyl)-*N*-(4-methylthiophenyl)amine** *(Table 1, entries 13-15)*: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm), 2.29 (s, 3H, CH_3); 2.45 (s, 3H, CH_3); 5.60 (bs, 1H, NH); 6.78-6.82 (m, 1H, Ar); 6.89-6.91 (m, 2H, H-2'); 6.98 (d, *J* = 8.8 Hz, 2H, H-2, H-6); 7.16 (m, 1H, Ar); 7.25 (d, *J* = 8.8 Hz, 2H, H-3, H-5). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ (ppm), 17.9 (CH_3); 21.6 (CH_3); 114.8 (CH, Ar); 118.4 (CH, Ar); 118.5 (CH, C-2, C-6); 121.9 (CH, Ar); 128.8 (C, C-4); 129.2 (CH, Ar); 129.8 (CH, C-3, C-5); 139.2 (C, C-3'); 142.0 (C, C-1'); 142.8 (C, C-1). Anal. Calcd for $C_{14}H_{15}NS$: C, 73.32%; H, 6.59%; N, 6.11%. Found: C, 73.76%; H, 6.99%; N, 5.89%.
***N*-(3-Fluorophenyl)-*N*-(4-methylsulfonylphenyl)amine** *(Table 1, entry 16)*: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm), 3.04 (s, 3H, CH_3); 6.25 (bs, 1H, NH); 6.78-6.82 (m, 1H, Ar); 6.89-6.92 (m, 2H, Ar); 7.02 (d, *J* = 8.8 Hz, 2H, H-2, H-6); 7.24-7.27 (m, 1H, Ar); 7.81 (d, *J* = 8.8 Hz, 2H, H-3, H-5). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ (ppm), 44.9 (CH_3); 106.9 (CH, *J* = 24.2 Hz, C-2'); 109.7 (CH, *J* = 21 Hz, C-4'); 115.4 (CH, C-2, C-6); 115.7 (CH, *J* = 2.7 Hz, C-6'); 129.2 (CH,C-3, C-5); 130.5 (C, C-4); 130.7 (CH, *J* = 9.6 Hz, C-5'); 142.0 (C, *J* = Hz, C-1'); 148.1 (C, C-1); 163.4 (C, *J* = 245 Hz, C-3'). Anal. Calcd for $C_{13}H_{12}NO_2S$: C, 58.85%; H, 4.56%; N, 5.28%. Found: C, 59.12%; H, 4.32%; N, 5.18%.
***N*-(3-Methylphenyl)-*N*-(3-pyridinyl)amine** *(Table 1, entries 17-20)*: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm), 2.31 (s, 3H, CH_3); 5.93 (bs, 1H, NH); 6.87-6.91 (m, 2H, Ar); 6.91 (s, 1H, H-2'); 7.11-7.16 (m, 2H, Ar); 7.36-7.43 (m, 1H, H-4); 8.15 (dd, *J* = 4.4 Hz, *J* = 1 Hz, 1H, H-6); 8.38 (d, *J* = 2.8 Hz, 1H, H-2). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ (ppm), 21.5 (CH_3); 115.3 (CH, C-6'); 118.9 (CH, C-2'); 122.8 (CH, C-4'); 123.5 (C, C-5); 123.6 (CH, C-4); 129.3 (CH, C-5'); 139.4 (C, C-3'); 139.9 (CH, C-6); 141.5 (CH, C-2); 141.8 (C, C-1'). Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23%; H, 6.57%; N, 15.21%. Found: C, 77.92%; H, 6.87%; N, 14.89%.
***N*-(3-Fluorophenyl)-*N*-(2,3-dihydro-1,4-benzodioxin-6-yl)amine** *(Table 1, entry 21)*: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm), 4.25 (m, 4H, CH_2O-); 5.89 (bs, 1H, NH); 6.40-6.42 (m, 1H, Ar); 6.43 (m, 4H, Ar); 6.78-6.82 (m, 1H, Ar); 7.08-7.11 (m, 1H, Ar). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ (ppm), 64.3, and 64.5 (CH_2O); 101.9 (CH, *J* = 25 Hz, C-2'); 105.8 (CH, *J* = 21.5 Hz, C-4'); 110.2 (CH, C-5); 111.2 (CH, *J* = 3 Hz, C-6'); 114.6 (CH, C-8); 117.7 (CH, C-7); 103.2 (CH, *J* = 10 Hz, C-5'); 135.4 (C, C-6); 139.5 (C, C-8a); 143.4 (C, C-4a); 146.5 (C, *J* = 11 Hz, C-1'); 163.6 (C, *J* = 243 Hz, C-3'). Anal. Calcd for $C_{14}H_{12}FN_2O$: C, 68.56%; H, 4.93%; N, 5.71%. Found: C, 68.88%; H, 5.23%; N, 5.98%.
***N',N'*-(Dimethyl)-*N*-(4-methylsulfonylphenyl)hydrazine** *(Table 2, entry 1)*: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm), 2.55 (s, 6H, CH_3); 3.01 (s, 3H, CH_3); 4.84 (bs, 1H, NH); 6.90 (d, *J* = 7 Hz, 2H, H-2, H-6); 7.73 (d, *J* = 7 Hz, 2H, H-3, H-5). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ (ppm), 45.0 (CH_3); 47.6 (CH_3); 111.9 (CH, C-2, C-6); 128.9 (C, C-4); 129.2 (CH, C-3, C-5); 151.9 (C, C-1). Anal. Calcd for $C_9H_{14}N_2O_2S$: C, 50.44%; H, 6.59%; N, 13.07%. Found: C, 50.87%; H, 6.34%; N, 13.45%.
***N',N'*-(Dimethyl)-*N*-(1-naphthyl)hydrazine** *(Table 2, entries 2-3)*: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm), 2.64 (s, 6H, CH_3); 4.92 (bs, 1H, NH); 7.21-7.26 (m, 1H, Ar); 7.30-7.42 (m, 2H, Ar); 7.38-7.43 (m, 2H, Ar); 7.71-7.77 (m, 2H, Ar). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ (ppm), 47.8 (CH_3); 107.9 (CH, C-2); 119.2 (CH, C-4); 120.0 (CH, C-8); 122.9 (C, C-8a); 124.7 (CH,C-7); 125.5 (CH, C-6); 126.6 (CH, C-5); 128.5 (CH, C-3); 134.2 (C, C-4a); 142.1 (C, C-1). Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38%; H, 7.58%; N, 15.04%. Found: C, 76.98%; H, 7.87%; N, 15.02%.