Ruthenium(II)–Porphyrin Catalyzed Selective N-Imidation of Aromatic Nitrogen Heterocycles

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Received 19 January 2007; revised 1 March 2007

Abstract: Ruthenium(II)-porphyrin (0.5 mol%) catalyzed N-imidations of aromatic nitrogen heterocycles with phenyl(tosylimino)iodinane under mild conditions were achieved in good yields (<94%). The effects of substituent, catalyst, temperature, and solvent on the reaction have been investigated. It was found that the catalyst significantly affected the yield and selectivity of imidation reaction for aromatic nitrogen heterocycles at 30 °C.

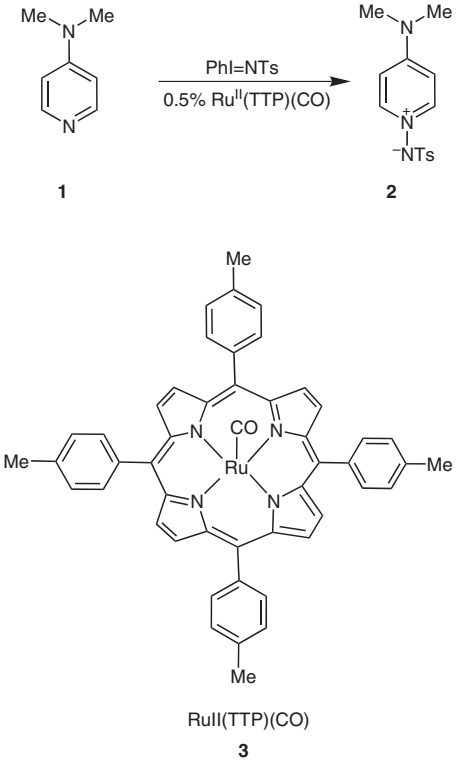
Key words: ruthenium porphyrin, N-imidation, aromatic nitrogen heterocycle, catalysis

Nitrene insertion catalyzed by transition metal complexes is an attractive reaction for the synthesis of amines and amine derivatives, and the structural modification of prodrugs.[1–14] It is also well known that amino-functionalized heterocycles are prevalent in many natural and therapeutic products of biological significance.[15–21]

The catalyzed N-imidation reaction of aromatic nitrogen heterocycles has been little explored. Reports exist of N–N bond formation either by acylation of 1-aminopyridinium salts followed by deprotonation[22] or by thermal decomposition of azides in the presence of pyridines.[23,24] However, challenges remain: (1) low yields in the imidation of aromatic nitrogen heterocycles resulting in N–N bond formation;[25–28] (2) formation of byproducts due to competing hydrogen abstraction and insertion reactions; and (3) the use of azides, which are extremely hazardous. Moreover, some imidation products are intermediates for the synthesis of bioactivity compounds. For example, *N*-imino aromatic nitrogen heterocycle ylides can be used for the synthesis of indolizine derivatives, which are the precursor of alkaloids[29] and 1*H*-1,2-diazepine derivatives,[30] important intermediates in the preparation of many natural products and pharmacologically active compounds. Therefore, it is significant to develop an efficient methodology for the preparation of *N*-imino aromatic nitrogen heterocycle ylides.

We were inspired by the work on carbonyl[*meso*-tetrakis(*p*-tolyl)porphyrinato]ruthenium(II) [Ru(II)(TTP)(CO)] (**3**) catalyzed imidation of *N*-phenylimidazole.[2] In the meanwhile, Jain and co-workers reported that copper-based catalysts[31] such as copper(II) triflate can catalyze the intermolecular imidation of pyridine, although the reactivity and selectivity are not ideal. In this direction, we wonder if ruthenium(II)–porphyrin can be used for N–N bond formation. Herein, we report an excellent method for intermolecular N-imidation using phenyl(tosylimino)iodinane (PhI=NTs, [(tosylimino)iodo]benzene) as the nitrogen source in the presence of a ruthenium(II)–porphyrin **3** (0.5 mol%) for the selective preparation of *N*-tosylimino-substituted aromatic nitrogen heterocycle ylides (Scheme 1).

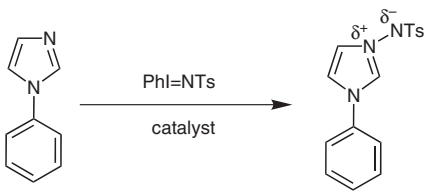
To evaluate the catalytic efficiency of various catalysts, the reaction of an aromatic nitrogen heterocycle **4** with phenyl(tosylimino)iodinane was studied using different catalysts with dichloromethane as the solvent (molar ratio substrate/PhI=NTs, 1:1.5) in the presence of 4 Å molecular sieves to give the nitrogen ylide **5** (Table 1). It is notable that although numerous catalysts were employed, only [Ru(II)(TTP)(CO)] was found to be effective for the inter-



Scheme 1

SYNTHESIS 2007, No. 10, pp 1459–1464
Advanced online publication: 02.05.2007
DOI: 10.1055/s-2007-966048; Art ID: F01507SS

Table 1 Optimization of Catalysts



4 5

Entry	Catalyst	Yield[a] (%)
1	10% [Co(TTP)(CO)]	trace
2	10% [Cu(TTP)(CO)]	trace
3	5% [Mn(TTP)(CO)]	trace
4	20% $Cu(OAc)_2$	trace
5	20% $[Cu(MeCN)_4]ClO_4$	trace
6	5% $Cu(hfacac)_2$	trace
7	20% CuI	trace
8	20% $Cu(OTf)_2$	trace
9	20% $Cu(OTf)_2$	trace[b]
10	20% $Cu(acac)_2$	trace
11	1% $Rh_2(OAc)_4$	trace
12	10% [Ru(TTP)(CO)]	91
13	–	0

[a] Reactions were performed in CH_2Cl_2 at 30 °C for 4 h with a catalyst.
[b] Reaction was performed in MeCN at 30 °C for 4 h.

molecular N-imidation of aromatic nitrogen heterocycles. Rhodium(II) acetate dimer, [Mn(TTP)(CO)], [Co(TTP)(CO)] and copper(II) acetate, copper(II) triflate, and copper(II) acetylacetonate were found to be poor catalysts for this intermolecular imidation reaction, and only a trace of **5** was found under similar conditions.

To examine the versatility of [Ru(II)(TTP)(CO)] as a catalyst, a variety of aromatic nitrogen heterocycle derivatives were reacted with the nitrene generated from phenyl(tosylimino)iodinane. Table 2 clearly shows that aromatic nitrogen heterocycles containing electron-donating groups (Table 2, entries 3, 5, 6) are more reactive and give better yields (88%, 86%, and 94%, respectively) of products. Similarly *ortho*-substituted aromatic nitrogen heterocycle derivatives (Table 2, entries 2, 4, 7, 11) were found to be less reactive compared to the corresponding substrates without an *ortho* substituent (Table 2, entry 1). However, aromatic nitrogen heterocycles substituted with electron-withdrawing groups (Table 2, entries 13–15) give the corresponding products in trace yields. In a similar manner, the reactivity of substrates with steric hindrance was low and only starting materials were recovered under strictly identical conditions (Table 2, entries 16–18).

On the other hand, metal–imido complexes **16**[1] (Figure 1) have tunable steric hindrance, causing sp^2-hybridized nitrogen imidation by metal–imido complexes to encounter larger steric hindrance than sp^2-hybridized nitrogen imidation by copper catalysts. Consequently, by replacing the catalyst with a metal–porphyrin, it is possible to control imidation selectively without the need to alter the steric hindrance of auxiliary ligand. This is a unique approach to adjust the relative reactivity of different nitrogen groups. The solvent effect on the N-imidation was also studied (Table 3). Various solvents were surveyed to ascertain the effect of the reaction medium on yield. Among these solvents studied, dichloromethane was found to be more effective for this reaction under similar reaction conditions than acetonitrile and toluene.

Table 2 Intermolecular N-Imidation of Aromatic Nitrogen Heterocycles

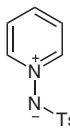
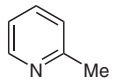
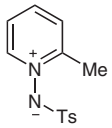
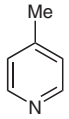
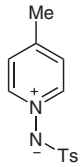
Entry	Substrate	Product		Yield[a,b] (%)
1			**6**	82
2			**7**	73
3			**8**	88

Table 2 Intermolecular N-Imidation of Aromatic Nitrogen Heterocycles (continued)

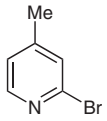
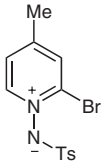
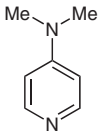
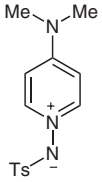
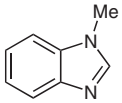
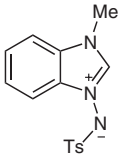
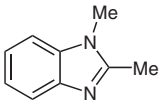
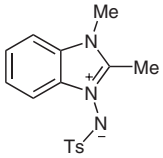
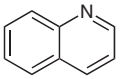
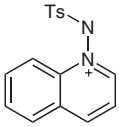
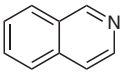
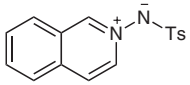
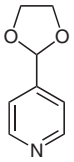
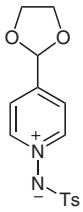
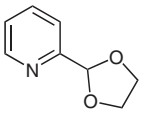
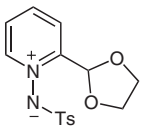
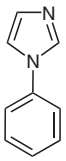
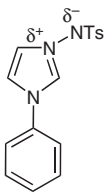
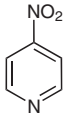
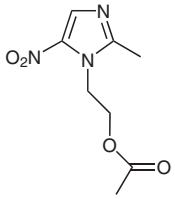
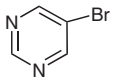
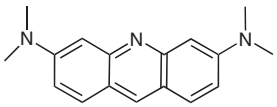
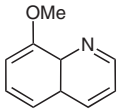
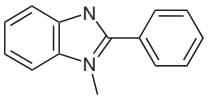
Entry	Substrate	Product		Yield[a,b] (%)
4			**9**	65
5			**2**	86
6			**10**	94
7			**11**	79
8			**12**	60
9			**13**	75
10			**14**	70
11			**15**	61
12			**5**	91[c]
13		–		trace

Table 2 Intermolecular N-Imidation of Aromatic Nitrogen Heterocycles (continued)

Entry	Substrate	Product	Yield[a,b] (%)
14		–	trace
15		–	trace
16		–	0
17		–	0
18		–	0

[a] Ratio [Ru(TTP)(CO)]/substrate/TsN=IPh, 0.005:1:1.5, 30 °C,2–6 h.
[b] Isolated yield.
[c] Ratio [Ru(TTP)(CO)]/substrate/TsN=IPh, 1:10:15, 40 °C, 2 h.

By using compound **1** as the substrate, the effect of temperature on the imidation reaction was examined. It was found that the imidation reaction was best performed at 30 °C. When the temperature was decreased to 20 °C, the reaction time needs to be extended to at least 6 hours to obtain a good yield of **2**. When the reaction temperature was increased to 65 °C, the yield of **2** decreased to 40–50%.

In this work, the N-imidation of aromatic nitrogen heterocycles with phenyl(tosylimino)iodinane as imidation reagents was conducted in dichloromethane at 30 °C, in the presence of trace amounts of [Ru(II)(TTP)(CO)] catalyst, and the corresponding hydrazine derivatives were obtained. Several aromatic nitrogen heterocycle derivatives have been employed to demonstrate universality of the intermolecular ruthenium(II)–porphyrin-catalyzed imidation reactions.

In summary, we have demonstrated an efficient procedure for imidation catalyzed by a ruthenium(II)–porphyrin to form the corresponding (tosylimino)pyridinium ylides using phenyl(tosylimino)iodinane as nitrene precursors. The method has advantages, such as the requirement for only trace amounts of catalyst, mild conditions, simple work-

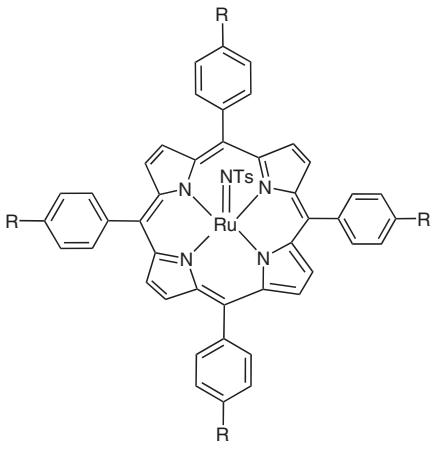


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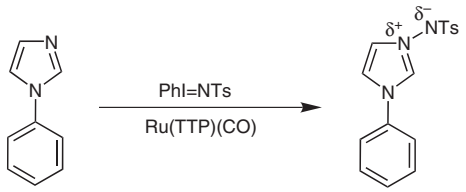
Figure 1

Table 3 Optimization of Solvents



4 **5**

Entry	Solvent	Yield[a] (%)
1	MeCN	58
2	toluene	20
3	DCE	85
4	CH_2Cl_2	91

[a] Reactions were performed at 30 °C for 4 h.

flow, moderate to high yields, and easy preparation of the nitrene precursors. The reaction proceeds in a highly selective manner, generating exclusively the products of the imidation reaction of the sp^2 nitrogen.

All catalyses were performed under N_2 and argon atmosphere. Silica gel F254 plates were used for TLC and spots were examined under UV light at 254 nm and developed by I_2 vapor. Flash chromatography was performed on silica gel H. Solvents were purified according to standard procedures. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-E 200 MHz Varian Mercury 400 MHz and Bruker Avance 600 MHz spectrometer, using $CDCl_3$ as the solvent. The mass spectra (ESI/HRMS) were recorded on a Bruker Daltonics Data analysis 3.2 mass spectrometer.

N-Imidation of Aromatic Nitrogen Heterocycles; Typical Procedure

A reaction flask was charged with substrate (1 mmol), phenyl(tosylimino)iodinane (1.5 mmol), catalyst (0.5 mmol%), 4 Å molecular sieves, and CH_2Cl_2. The mixture was stirred at 30 °C under an N_2 atmosphere for 2–6 h. After cooling to r.t., the resulting mixture was filtered; the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2–acetone, 4:1) to afford the product of N-imidation.

Pyridinium *N*-Tosylimide (6)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.58–7.59 (m, 4 H), 7.97 (t, *J* = 7.6 Hz, 1 H), 8.47 (d, *J* = 6.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 126.7, 127.0, 129.2, 138.5, 138.6, 141.6, 145.1.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{12}N_2NaO_2S$: 271.0512; found: 271.0514.

2-Methylpyridinium *N*-Tosylimide (7)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 2.43 (s, 3 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 7.46 (td, *J* = 1.2, 7.6 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.87 (td, *J* = 1.2, 7.6 Hz, 1 H), 8.60 (dd, *J* = 1.2, 6.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 21.3, 124.1, 126.4, 128.2, 129.4, 138.5, 140.7, 141.4, 146.4, 156.2.

HRMS (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{15}N_2NaO_2$: 263.0849; found: 263.0841.

4-Methylpyridinium *N*-Tosylimide (8)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 2.52 (s, 3 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.39 (d, *J* = 6.8 Hz, 2 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 8.25 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 21.5, 127.1, 127.3, 129.2, 136.9, 141.4, 144.6, 144.6, 152.4.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{14}N_2NaO_2S$: 285.0668; found: 285.0683.

2-Bromo-4-methylpyridinium *N*-Tosylimide (9)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 2.50 (s, 3 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.38 (dd, *J* = 2.0, 6.4 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 2.0 Hz, 1 H), 8.81 (d, *J* = 6.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 21.4, 125.9, 126.9, 129.3, 132.6, 139.2, 140.2, 141.6, 147.5, 151.7.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{13}BrN_2NaO_2S$: 362.9773; found: 362.9793.

4-(Dimethylamino)pyridinium *N*-Tosylimide (2)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 3.07 (s, 6 H), 6.44 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.69 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 39.6, 106.3, 126.6, 126.7, 139.3, 140.6, 144.1, 153.9.

HRMS (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{18}N_3O_2S$: 292.1114; found: 292.1115.

1-Methyl-1*H*-benzimidazol-3-ium *N*-Tosylimide (10)

^1H NMR (600 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 4.12 (s, 3 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 7.27–7.36 (m, 2 H), 7.43–7.49 (m, 2 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 9.22 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.3, 33.2, 113.2, 114.0, 125.5, 126.1, 126.8, 129.3, 130.7, 132.6, 140.5, 142.1, 142.3.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{15}N_3NaO_2S$: 324.0777; found: 324.0769.

1,2-Dimethyl-1*H*-benzimidazol-3-ium *N*-Tosylimide (11)

^1H NMR (600 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 2.74 (s, 3 H), 3.87 (s, 3 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.2 Hz, 1 H), 7.15 (td, *J* = 1.0, 8.2 Hz, 1 H), 7.35 (td, *J* = 1.0, 8.2 Hz, 1 H), 7.39 (d, *J* = 8.2 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 10.6, 21.3, 31.6, 110.5, 114.7, 124.9, 125.5, 126.7, 129.0, 129.7, 132.7, 140.8, 142.1, 151.4.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{17}N_3NaO_2S$: 338.0934; found: 338.0926.

Quinolinium *N*-Tosylimide (12)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.63 (q, 1 H), 7.68–7.75 (m, 2 H), 7.96–7.98 (m, 1 H), 8.44 (d, *J* = 8.4 Hz, 1 H), 8.60–8.63 (m, 1 H), 9.09 (dd, *J* = 1.2, 5.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 76.4, 77.0, 77.6, 120.6, 121.0, 126.0, 126.4, 129.4, 130.0, 133.2, 139.3, 139.6, 141.1, 141.2, 146.7.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{14}N_2NaO_2S$: 321.0668; found: 321.0672.

Isoquinolinium *N*-Tosylimide (13)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.81–7.86 (m, 2 H), 7.95–7.98 (m, 2 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 8.13 (d, *J* = 6.0 Hz, 1 H), 9.29 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 124.6, 126.8, 127.2, 128.1, 128.6, 129.3, 130.5, 134.2, 134.5, 137.8, 129.2, 140.5, 146.9.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{14}N_2NaO_2S$: 321.0668; found: 321.0665.

4-(1,3-Dioxolan-2-yl)pyridinium *N*-Tosylimide (14)

^1H NMR (600 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 3.96–4.10 (m, 4 H), 5.88 (s, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.69 (d, *J* = 5.8 Hz, 2 H), 8.47 (d, *J* = 5.8 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.4, 65.7, 100.2, 124.2, 127.1, 129.3, 138.7, 141.7, 144.9, 150.1.

HRMS (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{16}N_2NaO_4S$: 343.0723; found: 343.0721.

2-(1,3-Dioxolan-2-yl)pyridinium *N*-Tosylimide (15)

^1H NMR (600 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 3.97–4.03 (m, 4 H), 6.19 (s, 1 H), 7.18 (d, *J* = 8.2 Hz, 2 H), 7.55 (m, 1 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 7.83 (dd, *J* = 1.6, 7.9 Hz, 1 H), 7.91 (t, *J* = 7.7 Hz, 1 H), 8.83 (d, *J* = 6.3 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.4, 65.7, 125.0, 126.3, 126.3, 126.8, 129.3, 129.6, 137.6, 139.8, 141.6, 145.6, 152.3.

HRMS (ESI+): *m/z* $[M + H]^+$ calcd for $C_{15}H_{17}N_2O_4S$: 321.0904; found: 321.0902.

1-Phenyl-1*H*-imidazol-3-ium *N*-Tosylimide (5)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.41 (t, 1 H, *J* = 1.6 Hz), 8.04 (t, 1 H, *J* = 2.0 Hz), 7.72 (d, 2 H, *J* = 8.0 Hz), 7.62–7.57 (m, 2 H), 7.54–7.50 (m, 3 H), 7.34 (t, 1 H, *J* = 1.7 Hz), 7.24 (d, 2 H, *J* = 7.9 Hz), 2.34 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8, 140.4, 135.4, 133.1, 131.0, 130.5, 129.5, 127.6, 126.2, 122.3, 117.9, 21.8.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{15}N_3O_2S$: 313.0885; found: 313.0880.

Anal. Calcd for $C_{16}H_{15}N_3O_2S$: C, 61.32; H, 4.82; N, 13.41. Found: C, 61.07; H, 4.83; N, 13.28.

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