

## A simple and efficient method for the synthesis of 4-tosyloxazoles from tosylmethyl isocyanide with $\alpha$ -ketoimidoyl chlorides

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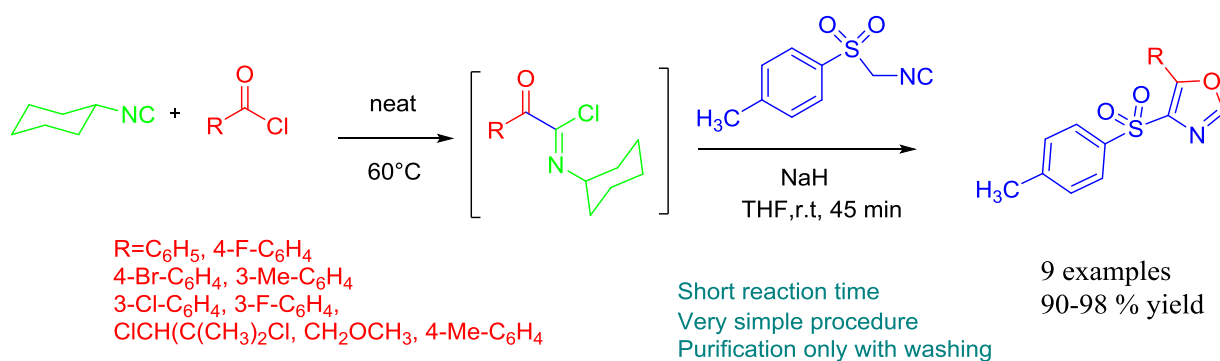
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### Abstract

An efficient one-pot method for the synthesis of potentially biologically active 4-tosyloxazole derivatives is described *via* reaction of imidoyl chloride adducts generated *in situ* from the reaction of isocyanide and acyl chlorides with *p*-toluenesulfonylmethyl isocyanide (TosMIC). This reaction was carried out in the presence of sodium hydride as a base and in THF to produce 4-tosyloxazoles in excellent yield.



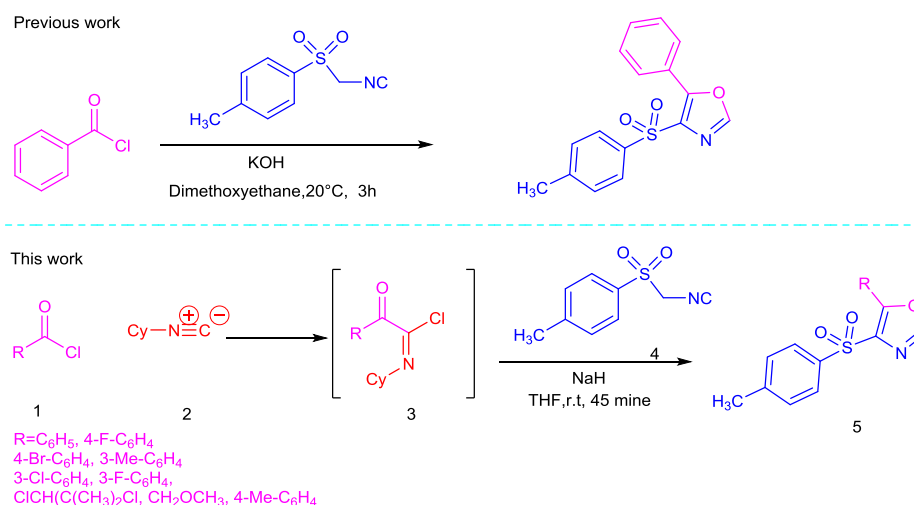
**Keywords:** 4-Tosyloxazoles,  $\alpha$ -ketoimidoyl chloride, tosylmethyl isocyanide, oxazole

## Introduction

Oxazole compounds have attracted much attention due to their emergence as subunits of interesting biological and pharmacological compounds with anticancer<sup>1,2</sup>, antibacterial<sup>3,4</sup>, anti-inflammatory<sup>5,6</sup> and antitubercular activities.<sup>7-10</sup> Also, these compounds are used as valuable precursors in many useful synthetic transformations.<sup>11-13</sup> Oxazoles are commonly synthesized using the Hantzsch reaction<sup>14,15</sup> or by cyclodehydration of ketoamides.<sup>16-19</sup> Synthesis *via* dehydration of 2-acylaminoketones is an important method for the preparation of a wide range of 2,5-disubstituted and 2,4,5-trisubstituted oxazole derivatives.<sup>20,21</sup> Alkyl isocyanoacetates, methyl isocyanoacetate were exploited by different groups towards the synthesis of 5-substituted oxazole derivatives as well as 5-(aminomethyl) oxazoles.<sup>22-26</sup> Sasaki prepared bisoxazole derivatives which were substituted at the 4-position and dioxazolo metacyclophane derivatives using TosMIC.<sup>27</sup> Oxazole derivatives with substitution at the 5-position were synthesized by cyclocondensation of aldehydes with monosubstituted tosylmethyl isocyanide in moderate yield<sup>28-39</sup> and by reaction of aryl aldehydes with TosMIC and also metalated methyl isocyanides.<sup>40-44</sup> Although there are many methods for the synthesis of oxazoles,<sup>45-48</sup> few approaches are available for the preparation of 4,5-disubstituted oxazoles.<sup>28-39</sup> Reaction of  $\alpha$ -diazo- $\beta$ -keto- carboxylates and -phosphonates with arene carboxamides gives 2-aryloxazole-4-carboxylates and 4-phosphonates by carbene N-H insertion, followed by cyclodehydration results in the formation of oxazole-5-carboxylates and 5-phosphonates.<sup>49</sup> NIS-mediated iodocyclization of N-sulfonyl propargylamides is developed for the synthesis of various oxazolidines and iodoalkylidenedihydrooxazoles *via* a 5-exo-dig process.<sup>46</sup> According to this investigation and literature reports<sup>50,29</sup> reactions directly arising from acid chlorides are useful and high yielding methods for synthesis of functionalized oxazoles.

## Results and Discussion

A literature search revealed that only 5-phenyl-4-tosyloxazole has been synthesized from reaction of benzoyl chloride and TosMIC in the presence of  $K_2CO_3$  as base in dimethoxyethane at 20 °C, but the yield of this reaction is low (50-55%)<sup>39</sup> (Scheme 1).

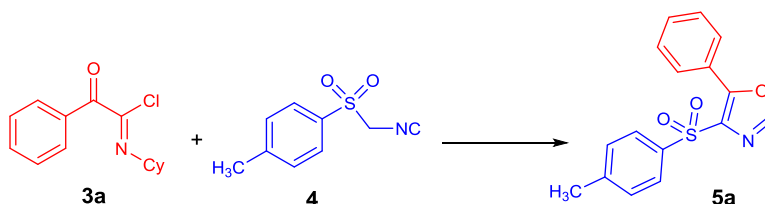


**Scheme 1.** Methods for the synthesis of 4-tosyloxazoles.

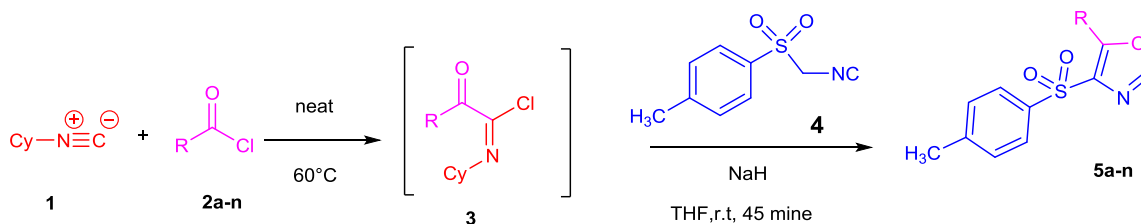
Due to the importance of oxazoles in medicinal chemistry and drug discovery, and also, in continuation of our work to develop syntheses of heterocyclic compounds from imidoyl chlorides,<sup>48</sup> we were looking to synthesize 4-tosyloxazole derivatives by condensation of aromatic and aliphatic  $\alpha$ -ketoimidoyl chlorides with cyclohexyl isocyanide. In this work, we report a simple method for the synthesis of 4-tosyloxazole derivatives by condensation of aromatic and aliphatic  $\alpha$ -ketoimidoyl chlorides with TosMIC in THF as solvent in excellent yields without using any catalyst. The Nef isocyanide adducts **3** obtained from addition of isocyanide **1** with aromatic or aliphatic acyl chloride **2** was reacted at ambient temperature with TosMIC to afford 5-phenyl-4-tosyloxazole (**5a**, Scheme 2).

In search for selective and efficient conditions, different solvent such as THF, CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> (at room temperature and reflux conditions) and also a variety of bases, including K<sub>2</sub>CO<sub>3</sub>, NaH, and Et<sub>3</sub>N were studied. As mentioned in Table 1, in the presence of Et<sub>3</sub>N or K<sub>2</sub>CO<sub>3</sub> (in THF solvent at room temperature and reflux conditions) and also in the presence of K<sub>2</sub>CO<sub>3</sub> (in CH<sub>2</sub>Cl<sub>2</sub> solvent at room temperature), we did not obtain any products (Table 1, entries 1–5). But when NaH was used as a base in THF or CH<sub>3</sub>CN at room temperature, the corresponding product was produced in excellent yields (entry 6-7). Therefore, all of the reactions were performed in THF in the presence of NaH at room temperature. To extend the scope of the reaction, the optimized protocol was applied for the synthesis of 4-tosyloxazoles by reaction with different imidoyl chlorides (Table 2).  $\alpha$ -Ketoimidoyl chlorides **1a-i** bearing various electron-donating functional groups at various positions reacted with TosMIC (**2**) smoothly and the corresponding compounds (**5a-i**) were obtained in excellent yield (Table 2). But  $\alpha$ -ketoimidoyl chlorides with electron-withdrawing functional groups such as 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, pyridin-4-yl, EtO<sub>2</sub>CCO and MeO<sub>2</sub>CCO in the same reaction conditions, did not produce any products. The results are summarized in Table 2.

**Table 1.** Model reaction, conditions and yields

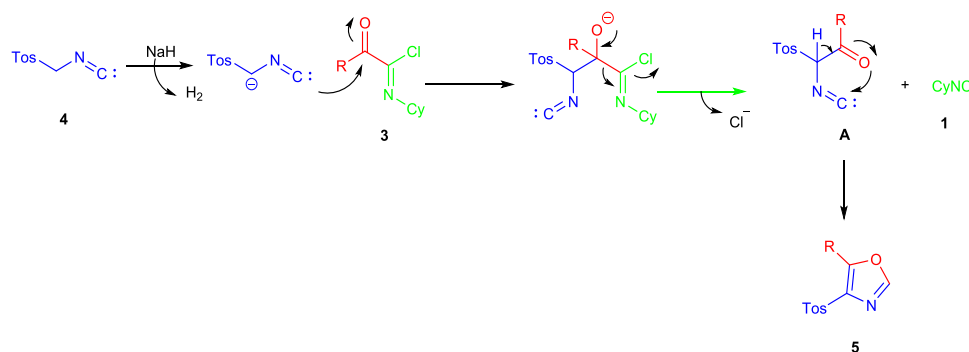


Entry	Solvent	Base	Conditions	Yield (%)
1	THF	NEt <sub>3</sub>	25 °C, 24 h	-
4	THF	K <sub>2</sub> CO <sub>3</sub>	Reflux, 24 h	-
5	CH <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	25 °C, 24 h	-
-				
6	THF	NaH	25 °C, 45min	90
7	CH <sub>3</sub> CN	NaH	25 °C, 45min	89

**Table 2.** Synthesis of 4-tosyloxazole derivatives from tosylmethyl isocyanide and  $\alpha$ - ketoimidoyl chlorides

Entry	R	Product	Melting point (°C)	Isolated Yield (%)
1	C <sub>6</sub> H <sub>5</sub>	<b>5a</b>	134-135	90
2	4-BrC <sub>6</sub> H <sub>4</sub>	<b>5b</b>	153-155	98
3	4-FC <sub>6</sub> H <sub>4</sub>	<b>5c</b>	214-216	96
4	3-FC <sub>6</sub> H <sub>4</sub>	<b>5d</b>	193-195	96
5	3-ClC <sub>6</sub> H <sub>4</sub>	<b>5e</b>	260-262	97
6	4-MeC <sub>6</sub> H <sub>4</sub>	<b>5f</b>	281-282	96
7	3-MeC <sub>6</sub> H <sub>4</sub>	<b>5g</b>	270-272	95
8	CH <sub>3</sub> OCH <sub>2</sub>	<b>5h</b>	200-212	98
9	Cl(CH <sub>3</sub> ) <sub>2</sub> CCHCl	<b>5i</b>	180-182	98
10	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> ,	<b>5j</b>	-	-
11	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	<b>5k</b>	-	-
12	pyridin-4-yl	<b>5l</b>	-	-
13	EtO <sub>2</sub> CCO	<b>5m</b>	-	-
14	MeO <sub>2</sub> CCO	<b>5n</b>	-	-

A possible mechanism is proposed in Scheme 2. The formation of 4-tosyloxazole **5** by reaction of cyclohexyl isocyanide, acyl chloride and TosMIC can be rationalized by initial formation of the ketoimidoyl chloride adducts **3** by the reaction of cyclohexyl isocyanide **1** with acyl chlorides **2**. Then, the intermediate **3** is attacked by TosMIC **4** to form the intermediate **A**, which then undergoes an intramolecular cyclization reaction to afford product **5** (Scheme 2).

**Scheme 2.** Plausible mechanism for the synthesis of 4-tosyloxazole.

According to the mechanism reaction, the second step (intramolecular cyclization reaction of intermediate **A** to product **5**) is suggested to be very important. So, the electron-donating groups on the  $\alpha$ -

ketoimidoyl chlorides increase the reaction rate and the electron-withdrawing groups on the  $\alpha$ -ketoimidoyl chlorides decrease the reaction rate. The structures of compounds **5a-i** were deduced by the IR, NMR spectral and elemental analytical data. For example the  $^1\text{H-NMR}$  spectrum of **5a** exhibited a singlet at  $\delta = 8.90$  due to the oxazole proton. Multiplet at  $\delta = 7.89-7.91$ , doublet at  $\delta = 7.84$ ,  $^3J_{\text{HH}} = 8.0$  Hz, multiplet at  $\delta = 7.59-7.61$  and doublets at  $\delta = 7.46$ ,  $^3J_{\text{HH}} = 8.2$  Hz correspond to nine aromatic protons present in the molecule. The signal at  $\delta = 2.41$  was assigned to the methyl protons. The  $^{13}\text{C-NMR}$  spectrum of **5a** displayed a downfield signal at  $\delta = 152.22$  for the carbon C2 of the oxazole ring and at  $\delta = 21.60$  for methyl carbon.

## Conclusions

In summary, the reaction of ketoimidoyl chlorides with TosMIC in THF in the presence of sodium hydride (NaH) as base at room temperature provides a facile and efficient route for the synthesis of 4-tosyloxazole derivatives in excellent yields. The advantages of this method are high yield, readily available starting materials, simple procedure and a straightforward purification of the products.

## Experimental Section

**General.**  $^1\text{H-NMR}$  spectra were recorded in  $\text{DMSO-}d_6$  on a Bruker model DRX-400 AVANCE spectrometer (400 MHz) with TMS as internal standard.  $^{13}\text{C-NMR}$  spectra were taken by a Bruker model DRX-400 AVANCE (100 MHz) spectrometer. Chemical shifts are given in ppm relative to TMS, the coupling constants  $J$  are given in Hz. Melting points were determined on a Melt-Tem II melting point apparatus and are uncorrected. IR spectra were obtained on a Thermo scientific, Nicolet is10 FT-IR spectrometer. Peaks are reported in wave numbers ( $\text{cm}^{-1}$ ). Element analyses (CHN) were performed with a EUROVECTOR EuroEA3000 CHNSO analyzer.

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### General procedure for the synthesis of compounds **5a-i**

In a typical experimental procedure, a dry, two-necked, 50 mL round bottomed flask was charged with 1.0 mmol of acyl chloride derivatives and 1.0 mmol of cyclohexyl isocyanide and heated at  $60^\circ\text{C}$  for 1 h. Then a mixture of TosMIC (1.0 mmol) and sodium hydride (60% w/w) (1.0 mmol) in THF (10 ml) was added. The mixture was stirred at room temperature for 45 min. After completion of the reaction, as indicated by TLC (ethyl acetate : n-hexane = 1 : 3), the solvent was evaporated at reduced pressure; the precipitate was washed with diethyl ether (10 ml) and was recrystallized from 95% ethanol to afford pure products **5a-i**.

**5-Phenyl-4-tosyloxazole (5a).** Light yellow solid, mp  $134-135^\circ\text{C}$  (Yield: 98%). IR (KBr) ( $\bar{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ ); 1595 (C=N), 1314, 1144 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.41 (3H, s,  $\text{CH}_3$ ), 7.46 (2H, d,  $^3J_{\text{HH}} = 8.1$  Hz, HAr), 7.59-7.61 (3H, m, HAr), 7.84 (2H, d,  $^3J_{\text{HH}} = 8.1$  Hz, HAr), 7.89-7.91 (2H, m, HAr), 8.90 (1H, s, oxazole proton).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 21.60 ( $\text{CH}_3$ ), 125.74, 125.98, 128.53, 128.71, 129.16, 129.42, 130.55, 131.49, 137.19, 145.56, 152.22 (C=N). Calcd. For ( $\text{C}_{16}\text{H}_{13}\text{NO}_3\text{S}$ ): C, 64.18; H, 4.39; N, 4.69; S, 10.70%. Found: C, 64.20; H, 4.38; N, 4.68; S, 10.71%.

**5-(4-Bromophenyl)-4-tosyloxazole (5b).** Colorless crystals, mp  $153-155^\circ\text{C}$  (Yield: 90%). IR (KBr)  $\bar{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ ; 1594 (C=N), 1332, 1149 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.40 (3H, s,  $\text{CH}_3$ ), 7.47 (2H, d,  $^3J_{\text{HH}} = 8.1$  Hz, HAr), 7.83-7.85 (6H, m, HAr), 8.68 (1H, s, oxazole proton).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 21.60 ( $\text{CH}_3$ ), 124.95, 125.24, 128.32, 130.58, 131.39, 132.25, 135.45, 136.98, 145.68, 151.29, 152.44 (C=N). Calcd. for ( $\text{C}_{16}\text{H}_{12}\text{BrNO}_3\text{S}$ ): C, 50.83; H, 30.19; N, 3.71; S, 8.49%. Found: C, 50.81; H, 30.20; N, 3.70; S, 8.48%.

**5-(4-Fluorophenyl)-4-tosyloxazole (5c).** Yellow solid, mp 214 -216°C (Yield: 98%). IR (KBr) ( $\bar{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ); 1609 (C=N) 1329, 1149 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.41 (3H, s,  $\text{CH}_3$ ), 7.43-7.48 (4H, m, HAr), 7.84 (2H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr), 7.96 (2H, dd,  $^3J_{\text{HF}}$  8.2 Hz,  $^3J_{\text{HH}}$  4 Hz, HAr), 8.66 (1H, s, oxazole proton);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 21.59 ( $\text{CH}_3$ ), 116.36 (d,  $^2J_{\text{CF}}$  22.0 Hz), 122.31, 128.27, 130.55, 132.10 (d,  $^3J_{\text{CF}}$  9.1 Hz), 134.94, 137.10, 145.60, 151.50, 152.22 (C=N), 162.75 (d  $^1J_{\text{CF}}$  248 Hz) Calcd. For ( $\text{C}_{16}\text{H}_{12}\text{FNO}_3\text{S}$ ): C, 60.55; H, 3.83; N, 4.40; S, 10.12%. Found: C, 60.56; H, 3.81; N, 4.41; S, 10.10%.

**5-(3-Fluorophenyl)-4-tosyloxazole (5d).** Light yellow solid, mp 193-195 °C (Yield: 98%). IR (KBr) ( $\bar{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ); 1590 (C=N) 1330, 1150 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.41(3H, s,  $\text{CH}_3$ ), 7.47-7.48 (3H, m, HAr), 7.66 (1H, dd,  $^3J_{\text{HF}}$  12.1 Hz,  $^3J_{\text{HH}}$  8.0 Hz, HAr), 7.76-7.77 (2H, m, HAr), 7.85 (2H, d,  $^3J_{\text{HH}}$  8.0 Hz, HAr), 8.70 (1H, s, oxazole proton).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 21.60 ( $\text{CH}_3$ ), 116.25 (d,  $^2J_{\text{CF}}$  24 Hz), 118.44 (d,  $^2J_{\text{CF}}$  20 Hz), 125.71, 127.69 (d,  $^3J_{\text{CF}}$  8.0 Hz), 128.34, 130.59, 131.43 (d  $^3J_{\text{CF}}$  8.0 Hz), 135.77, 136.92, 145.73, 150.76, 152.50 (C=N), 162.14 (d,  $^1J_{\text{CF}}$  242.0 Hz). Calcd. For ( $\text{C}_{16}\text{H}_{12}\text{FNO}_3\text{S}$ ): C, 60.55; H, 3.83; N, 4.40; S, 10.12%. Found: C, 60.56; H, 3.81; N, 4.41; S, 10.10%.

**5-(3-Chlorophenyl)-4-tosyloxazole (5e).** Colorless crystals, mp 260-262 °C (Yield: 90%). IR (KBr)  $\bar{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ; 1609 (C=N) 1329, 1149 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.40 (3H, s,  $\text{CH}_3$ ), 7.42 (2H, d,  $^3J_{\text{HH}}$  8.0 Hz, HAr), 7.44-7.47 (3H, m, HAr), 7.60 (1H, s, HAr), 7.84 (2H, d,  $^3J_{\text{HH}}$  8.0 Hz, HAr), 8.60 (1H, s, oxazole proton).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 21.26 ( $\text{CH}_3$ ), 124.79 125.97, 127.94, 128.55, 128.74, 129.24, 129.52, 132.52, 137.04, 138.12, 143.55, 146.15, 157.71 (C=N) Calcd. for ( $\text{C}_{16}\text{H}_{12}\text{ClNO}_3\text{S}$ ): C, 57.56; H, 3.06; N, 4.19; S, 9.60%. Found: C, 57.57; H, 3.06; N, 4.20; S, 9.61%.

**5-(*p*-Tolyl)-4-tosyloxazole (5f).** Dark brown solid, mp 281-282°C (Yield: 98%). IR (KBr) ( $\bar{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ); 1597 (C=N) 1316, 1146 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.40, 2.41(6H, s, 2 $\text{CH}_3$ ), 7.40 (2H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr), 7.46 (2H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr), 7.78-7.83 (4H, m, HAr), 8.84 (1H, s, oxazole proton);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ) 21.38, 21.57 (2 $\text{CH}_3$ ), 125.67, 126.65, 128.25, 129.04, 129.67, 130.52, 132.11, 135.00, 137.25, 138.45, 145.51, 152.07, 152.44 (C=N). Calcd. For ( $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{S}$ ): C, 65.15; H, 4.82; N, 4.49; S, 10.25%. Found: C, 65.16; H, 4.82; N, 4.47; S, 10.23%.

**5-(*m*-Tolyl)-4-tosyloxazole (5g).** Dark brown solid, mp 270-272°C (Yield: 98%). IR (KBr) ( $\bar{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ); 1594 (C=N) 1313, 1143 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.40 (6H, s, 2 $\text{CH}_3$ ), 7.40 (1H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr), 7.45-7.47 (3H, m, HAr), 7.68 (1H, s, HAr), 7.71 (1H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr), 7.84 (2H, d,  $^3J_{\text{HH}}$  8.0 Hz, HAr), 8.64 (1H, s, oxazole proton).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 21.38, 21.57 (2 $\text{CH}_3$ ), 125.67, 126.65, 128.25, 129.04, 129.67, 130.52, 132.11, 135.00, 137.25, 138.45, 145.51, 152.07, 152.44 (C=N). Calcd. For ( $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{S}$ ): C, 65.14; H, 4.84; N, 4.48; S, 10.20%. Found: C, 65.16; H, 4.82; N, 4.47; S, 10.23%.

**5-(Methoxymethyl)-4-tosyloxazole (5h).** Brown powder, mp 200-202 °C (Yield: 98%). IR (KBr) ( $\bar{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ); 1595 (C=N) 1334, 1152 (S=O).  $^1\text{H-NMR}$  (400 MHz  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 2.41 (3H, s,  $\text{CH}_3$ ), 3.33 (3H, s,  $\text{OCH}_3$ ), 4.82 (3H, s,  $\text{OCH}_2$ ), 7.48 (2H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr), 7.87 (2H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr) 8.61 (1H, s, oxazole proton).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 21.58 ( $\text{CH}_3$ ), 58.59 ( $\text{OCH}_3$ ), 62.60 ( $\text{OCH}_2$ ), 128.23, 128.60, 130.64, 137.58, 145.71, 152.18, 153.39 (C=N). Calcd. For ( $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$ ): C, 53.90; H, 4.91; N, 5.26; S, 11.99%. Found: C, 53.92; H, 4.90; N, 5.24; S, 12.00%.

**5-(1,2-Dichloro-2-methylpropyl)-4-tosyloxazole (5i).** Light brown powder, mp 180-182 °C (Yield: 98%). IR (KBr) ( $\bar{\nu}_{\max}$ ,  $\text{cm}^{-1}$ ); 1595 (C=N) 1326, 1148 (S=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 1.21, 1.49, (6H, s, 2 $\text{CH}_3$ ), 2.49, (3H, s,  $\text{CH}_3$ ), 4.40 (1H, s, CH), 7.50 (2H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr), 7.90 (2H, d,  $^3J_{\text{HH}}$  8.1 Hz, HAr) 8.57 (1H, s, oxazole proton);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 19.41, 21.61, 24.05 (3 $\text{CH}_3$ ), 55.26, 62.64, 128.21, 130.71, 136.90, 138.24, 145.81, 151.30, 152.95 (C=N). Calcd. For ( $\text{C}_{14}\text{H}_{15}\text{Cl}_2\text{NO}_3\text{S}$ ): C, 48.29; H, 4.32; N, 4.01; S, 9.23%. Found: C, 48.28; H, 4.34; N, 4.02; S, 9.21%.

## Acknowledgements

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## Supplementary Material

Copies of FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectras for compounds **5a-l**.

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