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A Metal-Free Protocol for Aminofunctionalization of Olefins Using $TsNBr_2$

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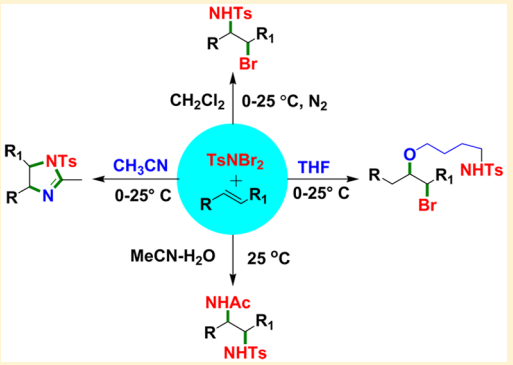
Supporting Information

ABSTRACT: *N,N*-Dibromo-*p*-toluene sulfonamide ($TsNBr_2$) has been found to be an effective reagent for various aminofunctionalization reactions. This reagent behaves both as an electrophilic bromine source as well as amine to react with olefins under different conditions to yield aminoether, imidazoline, diamine and amino bromine. The reaction proceeds rapidly under mild conditions with high regioselectivity. Olefins react with $TsNBr_2$ in moist THF to form δ-amino ether at room temperature. Treatment of $TsNBr_2$ with olefin in MeCN at room temperature produced imidazoline in high yield. Further modification of the reaction condition resulted in the development of a one-step procedure for the synthesis of *N*-acetyl,*N*′-tosyl diamine derivatives directly from olefin. When the olefin was treated with 2.4 mol equiv of $TsNBr_2$ in the presence of K_2CO_3, *N,N*′-ditosyl diamine derivative was obtained in moderate yield. Instantaneous formation of aminobromine was observed when an olefin was treated with the reagent in dry CH_2Cl_2 at room temperature.



INTRODUCTION

Carbon−nitrogen bond formation reaction is an important tool in organic chemistry for the construction of nitrogen-containing natural products, materials and many bioactive molecules with high medicinal value. Among them, haloamines, diamines, amidines and imidazolines are of great interest as they are the structural unit found in different natural products and alkaloids and also responsible for the biological activity of various organic compounds.[1]

For example, 4,5-dihydro-6′-deoxybromotopsentin (Figure 1, **I**) is a natural product isolated from sponge that is found to have potent cytotoxicity.[2] 2-Amino-β-glycosylamines (Figure 1, **II**) moieties are found in the central core of *N*-linked glycoproteins and glycopeptides, which play key role in cell-recognition and signal transduction processes.[3] Oseltamivir (Figure 1, **III**)[4] is employed for the treatment and prophylaxis of influenza virus A and B infections. Besides biological activities, these particular compounds can be used as organocatalysts, ligand in coordination chemistry, and chiral auxiliaries in several important chemical transformation reactions.[5] Direct amino functionalization of alkenes is a potential route for accessing these systems. During the past few years, several protocols have been developed for direct aminofunctionalization of olefins under different conditions.[6] However, development of a metal-free protocol for such transformations with a broader substrate scope and high selectivity is greatly desirable. Recently, we have established that *N,N*-Dibromo-*p*-toluene sulfonamide ($TsNBr_2$)[7] is a very powerful and efficient reagent for various organic transformations.[8] In continuation of our work[8] on different organic transformations using $TsNBr_2$, we wish to report herein the synthesis of various amino functionalized products from olefins under a very mild conditions (Scheme 1). This work clearly addresses the dual behavior of $TsNBr_2$ as a source of electrophilic bromonium ion as well as a nucleophilc amine counterpart.

RESULTS AND DISCUSSION

During our investigation on various organic transformations using $TsNBr_2$, we found that this reagent is an excellent source of bromonium ion.[8c,d] In presence of olefin, it readily forms cyclic bromonium ion which can further be opened in situ by a suitable nucleophile added to the reaction system to produce corresponding *vicinal* bromofunctionalized product.[8c,d] To begin our venture, we intended to investigate the reaction of olefin with $TsNBr_2$ in the presence of a cyclic oxygen nucleophile, THF. We envisioned that THF will act a nucleophile for opening of the cyclic bromonium ion to yield an oxonium ion, which in turn should be trapped by the NHTs group generated in situ to produce corresponding amino ethers.[9−12] There are few reports in the literature for opening of cyclic ethers in the presence of a bromine source.[9−12] Thomas et al. developed a strategy for the synthesis of dibromo bicyclic ethers via bromine assisted ring expansion of unsaturated epoxide.[9] A similar strategy was developed by Jamison et al. to construct some polycyclic ether compound.[10] They used NBS for generation of bromonium ion, which assisted epoxide ring opening to produce the desired product. Braddock et al. reported an intramolecular bromonium ion assisted epoxide ring-

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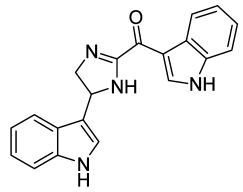
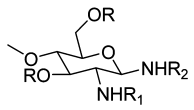
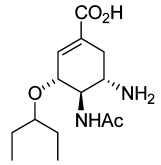


4, 5-Dihydro-6'-deoxybromotopsentin (**I**)



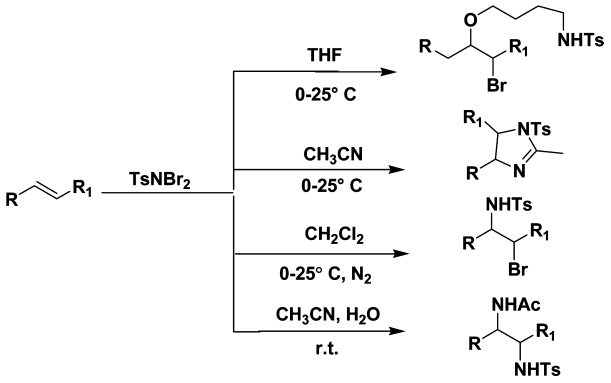
2-Amino-β-glycosylamines (**II**)



Oseltamivir (**III**)

Figure 1. Some biologically active amino compounds.

Scheme 1. Aminofunctionalization of Olefins Using $TsNBr_2$



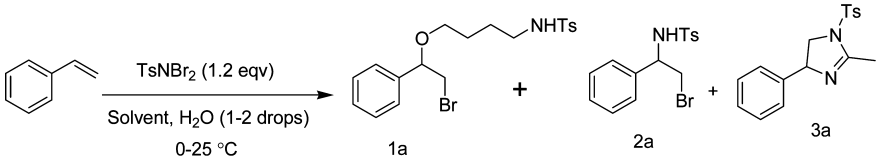
expansions where in situ formed oxonium ion was captured with externally added nucleophile.[11] On the basis of this concept, Yeung et al. developed a method for aminoalkoxylation of olefin using NBS and $TsNH_2$ in the presence of cyclic ethers.[12]

To begin our investigation we have taken styrene as a model substrate to find out the optimum reaction condition. Results are summarized in Table 1. A reaction was carried out by adding $TsNBr_2$ (1 mmol) to a stirred solution of styrene (1 mmol) in THF (5 mL) at room temperature. After 2 h of reaction (TLC), the desired aminoether was isolated in 70% yield along with bromoamine as byproduct with the product ratio of 70:20 (Table 1, entry 1). Diminishing effect was observed when lesser amount of THF was used. The formation of bromoamine is due to the competitive attack of the NHTs group at bromonium ion of original olefin. So in order to increase the yield of the desired product, the NHTs group must attack at oxonium intermediate. Next, the reaction was examined by adding $TsNBr_2$ under ice cold condition and reaction was continued at room temperature. In this case, a marginal improvement in yield was observed as it prevented the formation of byproduct (**2a**) to some extent. Thereafter, the reaction was studied by adding 1−2 drops of water to the reaction mixture. Interestingly, this could produce excellent result with 81% yield of aminoether (**1a**) within a short span of time. Increasing the amount of $TsNBr_2$ under similar condition (Table 1, entry 5) produced a better result with 87% yield. When dichloromethane (dry) was used as a solvent, instantaneous formation of bromoamine (**2a**) was observed as the exclusive product (Table 1, entry 6, 87%).

After optimizing the condition for alkoxyamination reaction, the reaction was extended to a variety of olefins. Results are summarized in the Table 2. From the table it can be seen that the reaction proceeds well with almost all kind of olefins. The reaction is very efficient as it occurs readily under mild conditions with high yield. In the reaction system, $TsNBr_2$ itself act as a bromine source as well as nitrogen source. Unlike other methods reported in the literature,[11,12] this protocol does not require any external amine for alkoxyamination reaction.

Next, we have examined the scope of aminobromination reaction using $TsNBr_2$. Vicinal haloamino moieties are considered as versatile building blocks in organic synthesis because of their synthetic potential for further manipulation by replacement of halogen with diverse nucleophiles. They are synthetic intermediates for functional materials and biologically

Table 1. Optimization of Reaction Conditions[a]



entry	solvent	$TsNBr_2$ (mmol)	time (h)	temp. (°C)	yield[b] of **1a** (%)	yield[b] of **2a** (%)	yield[b] of **3a** (%)
1	THF (5 mL)	1	2	RT	70	20	–
2	THF (2 mL)	1	2.5	RT	60	30	–
3	THF (5 mL)	1	2	0−25	75	15	–
4	THF (5 mL), 1−2 drops water	1	1	0−25	81	trace	–
5	THF (5 mL), 1−2 drops water	1.2	1	0−25	87	trace	–
6	CH_2Cl_2 (2 mL)	1.2	instantaneous	0−25	–	87	–
7	$CHCl_3$ (2 mL)	1.2	30 (min)	0−25	–	78	–
8	DMF (2 mL)	1.2	30 (min)	0−25	–	NR	–
9	CH_3CN (5 mL)	1	3	RT		30	60
10	CH_3CN (5 mL)	1	3	0−25	–	trace	71
11	CH_3CN (5 mL)	1.2	3	0−25	–	trace	76

[a]Reaction condition: Styrene 1 mmol. [b]Isolated yield.

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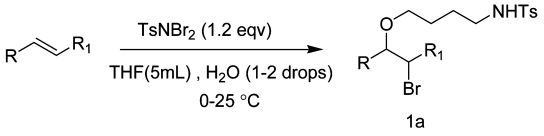
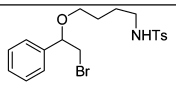
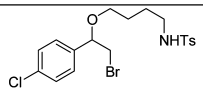
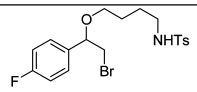
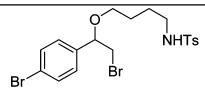
Table 2. Synthesis of Alkoxyamine from Various Olefins[a]

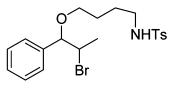


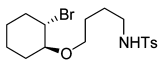

1a, 1h,87%

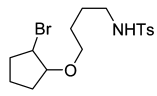

1b, 1h, 84%

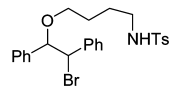

1c, 1h, 82%

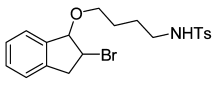

1d, 1h, 84%

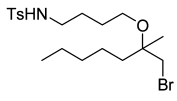

1e, 1h, 89%


1f, 1.2h, 81%


1g, 1.2h, 81%

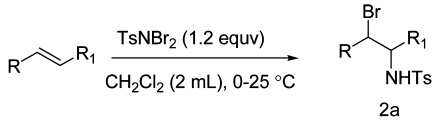

1h, 1.2h, 80%

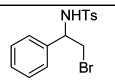

1i, 1.2h, 83%

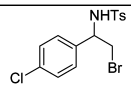

1j, 2h, 79%

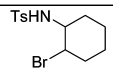
[a]Reaction condition: $TsNBr_2$ (1.2 mmol), olefin (1 mmol), THF (5 mL), water (1−2 drops), 0−25 °C; yields reported refers the isolated yields after chromatographic purification

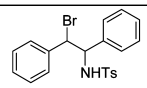
Table 3. Synthesis of Aminobromine with Different Olefins[a,b]

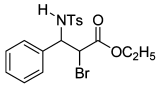


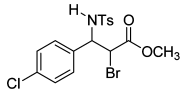

2a, 87%

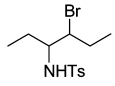

2b, 90%

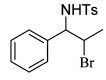

2c, 78%

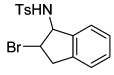

2d, 77%

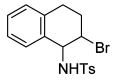

2e, 79%

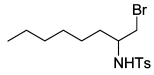

2f, 80%

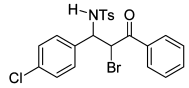

2g, 79%

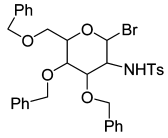

2h, 82%

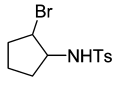

2i, 86%


2j, 90%


2k, 88%


2l, 83%


2m, 80%


2n, 88%

[a]Reaction condition: Olefin (1 mmol), $TsNBr_2$ (1.2 mmol), CH_2Cl_2 (2 mL), 0−25 °C, 10 min. [b]Isolated yield.

active compounds.[1a,13] In the past several decades, a number of procedures have been developed for vicinal aminobromination using various combinations of reagents and catalysts, which includes important examples such as *N,N*-dihalo sulphonamides,[7] *N,N*-dihalo carbamates,[14] *N*-halo carbamates,[13,15] *N*-bromoacetamide,[16] *N,N*-dibromo phosphoramidate,[17] *S,S*-dimethyl-*N*-(*p*-toluenesulfonyl)-sulfilimine/NBS,[18] $TsNBr_2$/$TsNH_2$,[19] *N*-methyl-*p*-toluenesulfonamide/NBS[20] and cyanamide/NBS,[21] KI-NBS-$TsNH_2$[22] and others.[23−28] Very recently, Yeung and his co-workers reported a catalyst and metal free protocol for the bromoamidation of unactivated olefins using 4-(trifluoromethyl)benzenesulfonamide and *N*-bromosuccinimide

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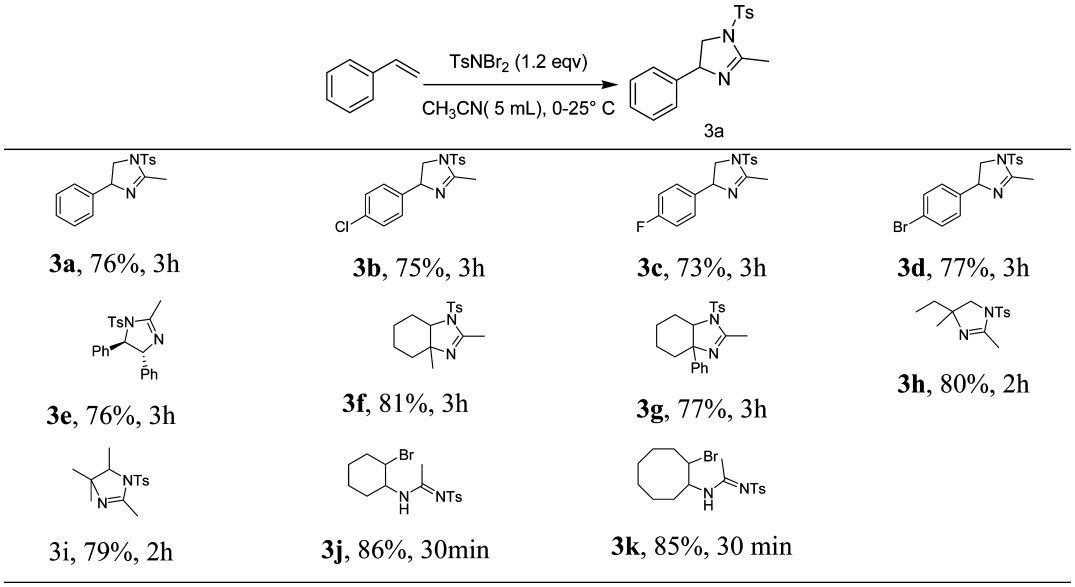
Table 4. Synthesis of Imidazoline and Bromoamidine from Different Olefins[a,b]



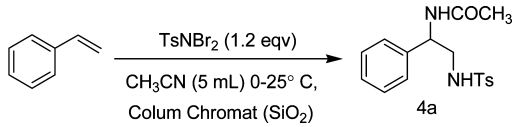
[a]Reaction condition: $TsNBr_2$ (1.2 mmol), styrene (1 mmol), CH_3CN (5 mL), 0–25 °C. [b]Isolated yields.

as nitrogen and bromine source.[29] In contrast, we have developed a much simpler protocol for the synthesis of aminobromine using a single reagent (Table 1, entry 6). The scope of this methodology was examined by using various types of olefins like substituted styrenes, α,β unsaturated cinnamic esters, chalcone, aliphatic olefin, cyclohexene, stilbene etc. (Table 3). From the table, it can be seen that all kind of olefins could be transformed into the desired aminobromines with high yields. The reaction was found to be completely stereo- and regioselective. The reaction proceeds via a three-membered cyclic bromonium ion intermediate due to electrophilic addition of the Br^+ ion (generated from $TsNBr_2$) onto the olefin.[8c,d] This intermediate undergoes ring opening by the amine nucleophile via a S_N2 pathway, which results in the *anti*-selectivity of the aminobromine adduct. Nucleophilic opening of the cyclic bromonium intermediate is most likely from the more positive β-position.[8c,d]

While examining the reactions of $TsNBr_2$, we found that olefins, when treated with $TsNBr_2$ in acetonitrile, produce imidazolines (Table 1, entry 9–11). Imidazolines are another important class of compounds that exhibits high therapeutic importance. Several methods have been reported for the synthesis of imidazolines.[30] [3 + 2] Cycloaddition of *N*-tosylaziridines with nitriles in the presence of several Lewis acids has been found to be the most efficient methods reported so far.[31] Ritter reaction with nitrile is another important methodology for the synthesis of imidazolines.[31d,32] We found that the treatment of styrene with $TsNBr_2$ in acetonitrile results in the formation of imidazoline as the major product (Table 1, Entry 9). In this instance also, we have isolated corresponding aminobromine as a side product. Addition of $TsNBr_2$ to an ice cold solution of styrene in moist acetonitrile and continuation of the reaction at room temperature could improve the yield of desired imidazoline up to 71% with trace amount of the side product. One important observation we made is that the use of dry acetonitrile increases the formation of bromoamine which has also been noticed in case of aminoether formation reaction. Further increase of the amount of $TsNBr_2$ from 1 to 1.2 mmol could bring up the yield of imidazoline to 76% (Table 1, Entry 11). After obtaining the optimized reaction condition, the process was extended for different olefins and the results are shown in Table 4. In this case, CH_3CN acts as a nucleophile to form an intermediate nitronium ion, which further reacts with in situ generated NHTs group to produce the desired product via the formation of a bromoamidine.[32]

Interestingly, when the reaction was carried out with cyclohexene and cyclooctene, intermediate bromoamidine was isolated as the sole product. However, in all other cases, imidazolines were isolated as the lone product. During the purification of imidazoline, we observed that column chromatography over silicagel results in the formation of a mixture of imidazoline and *N*-(1-phenyl-2-(tosylamino)ethyl)acetamide. However, if the reaction mixture is kept over silicagel (in the column) for 24 h, corresponding diamine derivative forms as the single product (Scheme 2).

Scheme 2. Formation *N*-Acetyl, *N*′-Tosyl Diamine from Styrene



Hence, in this case, chromatographic purification was performed over silicagel by adding little amount of diethyl amine to the eluting solvent to isolate imidazolines exclusively. Hydrolytic disintegration of imidazolines to corresponding diamine is known in the literature.[33] 1,2-Diamino compounds have received significant interest as they are present in numbers of natural products with profound biological activity. 1,2-Diamines can also be used as ligand as well as an organocatalysts in many reactions. Efforts were made to design and synthesis of this particular substrate during the past few years. Kumar and Ramesh had developed a procedure for diamination of glycals with chloramine-T in the presence of iodine as catalyst at 0 °C to afford 2-amino-*b*-glycosylamine derivatives.[34] This procedure is restricted to glycals only. Usually, the transformation of olefin to

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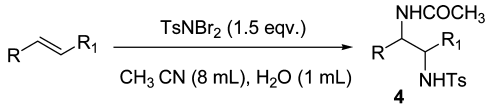
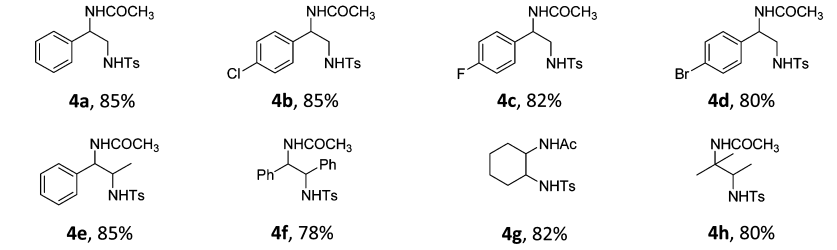
Table 5. Synthesis of Diamine Derivative from Various Olefins[a]



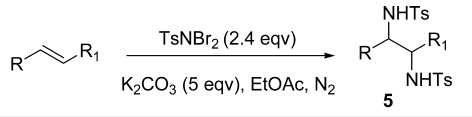


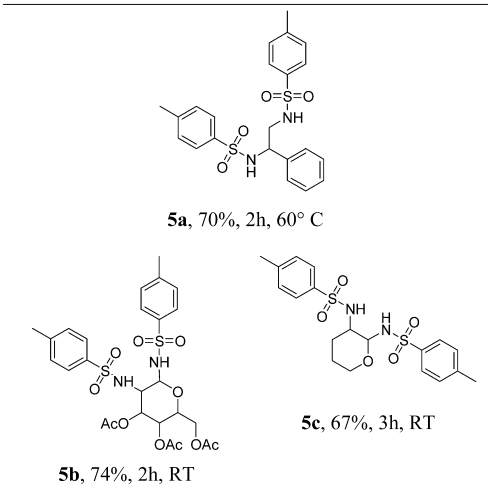
[a]Reaction condition: $TsNBr_2$ (1.5 mmol), olefin (1 mmol), CH_3CN (8 mL), H_2O (1 mL); isolated yield.

diamine is carried out with the aid of a metal catalyst.[35] This protocol has also been extended for intramolecular diamination reaction to produce some interesting heterocycles.[35] Muñiz et al. synthesized some diamino compounds from internal alkenes using Pd as a catalyst using two different amine sources.[36] They utilized a combination of a ditosyl amine and saccarine or phthalimide in the presence of a hypervalent iodine oxidant to achieve the transformation. Later, the same group had utilized iodine(III) reagent for similar transformations.[37] Thus, one pot synthesis of 1,2-diamine derivatives from olefin is highly desirable. To look for the possibilities for a direct one pot conversion of olefin to corresponding *N*-acetyl,*N*′-tosyl diamine, we examined the reaction of styrene at higher temperature. The reaction was carried out at 80 °C in the presence of HCl, H_2SO_4 and K_2CO_3 as additive (3 mol equiv). None of these efforts could produce the expected diamine derivative. After, extensive study of the reaction under varied conditions, it was finally found that when olefin (1 mmol) is treated with $TsNBr_2$ (1.5 mmol) in the presence of CH_3CN (8 mL) and H_2O (1 mL) produced the corresponding diamine derivative with reasonably high yield. Best result was found when the reaction was stirred for 3 h at room temperature. However, in case of cyclohexene, it is necessary to carry out the reaction at 80 °C to achieve the best results. The results are summarized in Table 5.

Thus, this procedure could produce *N*-acetyl,*N*′-tosyl diamine derivatives directly from olefin under a very mild reaction condition. In general, the reaction efficiently produced corresponding diamines at room temperature with high yield. Formation of diamine via the ring opening of in situ generated aziridine is known in the literature.[34a] Earlier, we have reported an efficient protocol for the synthesis of aziridine from olefin by treating with $TsNBr_2$ in the presence of potassium carbonate under mild reaction conditions.[8e] We believed that nucleophilic NHTs-group generated in situ from $TsNBr_2$ should take part in ring opening of aziridine to provide 1,2-diamines. Hence, the reaction was further investigated to explore the possibility of synthesis of *N*,*N*′-ditosyl diamine derivatives. Accordingly, under a similar reaction condition that holds for aziridination, styrene was treated with two molar equivalent of $TsNBr_2$ in the presence of K_2CO_3. In a typical reaction, a solution of styrene (1 mmol) and K_2CO_3 (5 mmol) in ethyl acetate (10 mL) was treated with $TsNBr_2$ (2 mmol) under nitrogen atmosphere at room temperature. The result was not found to be encouraging in this case, even after 12h of reaction. However, diamine was isolated in 60% yield when the reaction was carried out at 60 °C using the same concentration of the reagents. Further increase of $TsNBr_2$ amount to 2.4 equiv could improve the yield of the product and the reaction was found to complete within 2 h. However, the yields of the products were found to be low. Interestingly, sugar molecules showed better reactivity profile and corresponding product could be produced at room temperature with moderate yield. Few representative examples for the synthesis of *N*,*N*′-ditosyl diamine derivatives are included in Table 6. The reaction is believed to proceed through an initial formation of aziridine,[8e] which undergoes ring opening via a nucleophilic attack by NTs group.[34a]

Table 6. Synthesis of Diamines with Various Olefins[a]





[a]Reaction condition: $TsNBr_2$ (1.5 mmol), olefin (1 mmol), EtOAc (10 mL); isolated yield.

CONCLUSION

In summary, we have developed an efficient methodology for the synthesis of variety of compounds via amino functionalization of olefins using $TsNBr_2$. Under different reaction conditions aminoether, amino bromine, imidazoline and diamine could be synthesized using this reagent. The reactions are very simple, which can be carried out under mild conditions. The yields of respective products are also high. The reagent $TsNBr_2$ itself acts

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as an electrophilic bromine source as well as the source of nucleophilic nitrogen. No external amine is required for this aminofunctionalization reaction.

EXPERIMENTAL SECTION

General Remarks. All reagents and starting materials were purchased from commercial sources. Chemical shifts in NMR spectral data are given in δ units relative to the tetramethylsilane (TMS) signal as an internal reference in $CDCl_3$. Coupling constants (J) are reported in hertz. Chromatographic purification was performed using flash chromatography over a manually packed column containing silica gel (230−400 mesh).

General Procedure for the Synthesis of Alkoxyamine Using Various Olefins (1a−1j). To a solution of olefin (1 mmol) in THF (5 mL) and water (1−2 drops), $TsNBr_2$ (1.2 mmol) was added in small proportions over a period of 20 min under ice cold condition and the reaction was continued at room temperature for appropriate time (TLC). The excess solvent was removed in rotary evaporator and sodium thiosulfate (100 mg approx.) was added followed by the addition of water (5 mL). The reaction mixture was stirred for another 5 min and extracted with ethyl acetate (3 × 10 mL). The combined organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (230−400 mesh) with petroleum ether/ethyl acetate as eluent to obtain pure alkoxyamine product.

*4-(2-Bromo-1-phenylethoxy)-N-tosylbutan-1-amine (**1a**).* Colorless gum (370 mg, 87% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (d, J = 7.8 Hz, 2H), 7.41−7.23 (m, 7H), 5.11 (t, J = 6 Hz, 1H), 4.45−4.37 (m, 1H), 3.51−3.39 (m, 2H), 3.36−3.26 (m, 2H), 3.02−2.88 (m, 2H), 2.41(s, 3H), 1.65−1.53 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 139.4, 137.0, 129.7, 128.7, 128.5, 127.1, 126.7, 82.0, 68.9, 42.9, 36.5, 26.7, 26.5, 21.5; HRMS (QTOF-ESI+) calcd for $C_{19}H_{24}BrNO_3S$ [M + Na]$^+$ 448.0552, found 448.0574.

*4-(2-Bromo-1-(4-chlorophenyl)ethoxy)-N-tosylbutan-1-amine (**1b**).* Yellow gum (387 mg, 84%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 8.4, 2H), 7.33−7.25 (m, 4H), 7.20 (d, J = 8.4 Hz), 5.36−5.20 (m, 1H), 4.43−4.32 (m, 1H), 3.50−3.33 (m, 2H), 3.31−3.21 (m, 2H), 2.99−2.85 (m, 2H), 2.39 (s, 3H), 1.66−1.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.1, 137.7, 136.7, 133.9, 129.5, 128.6, 127.9, 126.9, 80.8, 68.7, 42.7, 35.9, 26.3, 26.2, 21.3; HRMS (QTOF-ESI+) calcd for $C_{19}H_{23}BrClNO_3S$ [M + Na]$^+$ 482.0168, found 482.0165.

*4-(2-Bromo-1-(4-fluorophenyl)ethoxy)-N-tosylbutan-1-amine (**1c**).* Yellow gum.(364 mg, 82%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (d, J = 8.1 Hz, 2H), 7.36- 7.21 (m, 4H), 7.05 (d, J = 8.1, 2H), 5.08−4.98 (m, 1H), 4.46−4.36 (m, 1H), 3.52- 3.36 (m, 2H), 3.35−3.28 (m, 2H), 3.06−2.83 (m, 2H), 2.41(s, 3H), 1.74−1.47(m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.6 ($^1J_{CF}$ = 245.5 Hz), 143.2, 136.9, 135.0 ($^4J_{CF}$ = 3.3 Hz), 129.6, 128.3 ($^3J_{CF}$ = 7.6 Hz), 127.0, 115.6 ($^2J_{CF}$ = 21.3 Hz), 81.2, 68.8, 42.8, 36.2, 26.6, 26.4, 21.4; HRMS (QTOF-ESI+) calcd for $C_{19}H_{23}BrFNO_3S$ [M + Na]$^+$ 466.0458, found 466.0458.

*4-(2-Bromo-1-(4-bromophenyl)ethoxy)-N-tosylbutan-1-amine (**1d**).* Colorless gum.(424 mg, 84%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 5.14−4.84 (m, 1H), 4.46−4.31 (m, 1H), 3.52−3.24 (m, 4H), 3.02−2.85 (m, 2H), 2.42 (s, 3H), 1.68−1.49 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.2, 138.3, 136.9, 131.8, 129.6, 128.4, 127.0, 122.4, 81.2, 68.9, 42.8, 35.9, 26.6, 26.5, 21.5; HRMS (QTOF-ESI+) calcd for $C_{19}H_{23}Br_2NO_3S$ [M + Na]$^+$ 527.9643, found 527.9638.

*4-(2-Bromo-1-phenylpropoxy)-N-tosylbutan-1-amine (**1e**).* Colorless gum (391 mg, 89%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (d, J = 7.8 Hz, 2H), 7.49 7.20 (m, 7H), 5.19−4.97 (m, 1H), 4.52−4.34 (m, 1H), 4.19 (t, J = 6 Hz, 1H), 3.54−3.22 (m, 2H), 3.15−2.87 (m, 2H), 2.41 (s, 3H), 1.79−1.51 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.2, 138.7, 136.9, 129.6, 128.2, 128.0, 127.2, 127.0, 85.5, 69.1, 52.6, 42.8, 26.6, 26.4, 21.4, 20.3; HRMS (QTOF-ESI+) calcd for $C_{20}H_{26}BrNO_3S$ [M + Na]$^+$ 462.0709, found 462.0709.

*4-((1S,2S)-2-Bromocyclohexyloxy)-N-tosylbutan-1-amine (**1f**).*[12] Light yellow gum (327 mg, 81%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.09−4.96 (m, 1H), 3.95−3.81 (m, 1H), 3.63−3.39 (m, 2H), 3.29−3.17 (m, 1H), 3.04−2.89 (m, 2H), 2.42 (s, 3H), 2.35−2.23 (m, 1H), 2.16−2.04 (m, 1H), 1.79−1.52(m, 7H), 1.34−1.20 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.1, 136.9, 129.6, 127.0, 82.1, 68.9, 55.9, 42.9, 35.9, 30.9, 27.0, 26.5, 25.6, 23.4, 21.5.

*4-(2-Bromocyclopentyloxy)-N-tosylbutan-1-amine (**1g**).* Light yellow gum (316 mg, 81%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72(d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 5.28 (t, J = 5.4 Hz, 1H), 4.16−4.07 (m, 1H), 4.00−3.90 (m, 1H), 3.47−3.28 (m, 2H), 2.97−2.83 (m, 2H), 2.40 (s, 3H), 2.31−1.86 (m, 4H), 1.83−1.63 (m, 2H), 1.59−1.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.1, 136.8, 129.5, 126.9, 87.9, 68.8, 54.0, 42.8, 34.5, 29.7, 26.7, 26.6, 21.5, 21.4. HRMS (QTOF-APCI+) calcd for $C_{16}H_{24}BrNO_3S$ [M + H]$^+$ 390.0739, found 390.0745.

*4-(2-Bromo-1,2-diphenylethoxy)-N-tosylbutan-1-amine (**1h**).* White solid (402 mg, 80%); mp (92−94 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (d, J = 7.8 Hz, 2H), 7.47−7.16 (m, 12H), 4.97 (d, J = 7.2 Hz, 1H), 4.65 (d, J = 6.6 Hz, 1H), 4.60−4.39 (m, 1H), 3.36−3.08 (m, 2H), 2.89−2.72 (m, 2H), 2.43 (s, 3H), 1.45−1.24 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.2, 138.9, 138.7, 136.9, 129.6, 128.7, 128.3, 128.1, 128.1, 127.7, 127.0, 85.7, 68.9, 56.8, 42.7, 26.3, 26.1, 21.5. HRMS (QTOF-ESI+) calcd for $C_{25}H_{28}BrNO_3S$ [M + Na]$^+$ 524.0871, found 524.0861.

*4-(1-Bromo-2,3-dihydro-1H-inden-2-yloxy)-N-tosylbutan-1-amine (**1i**).* Yellow gum (364 mg, 83%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (d, J = 8.4 Hz, 2H), 7.39−7.17 (m, 6H), 5.04−4.87 (m, 2H), 4.45-4.32 (m, 1H), 3.84−3.71 (m, 1H), 3.67−3.61 (m, 2H), 3.20 (dd, J = 16.5, 5.4 Hz, 1H), 2.99−2.89 (m, 2H), 2.41 (s, 3H), 1.67−1.55 (m, 4H); ^{13} C NMR ($CDCl_3$, 75 MHz) δ 143.3, 140.4, 140.1, 136.9, 129.7, 129.2, 127.3, 127.0, 125.1, 124.8, 90.5, 69.7, 51.3, 42.9, 41.3, 27.1, 26.6, 21.5. HRMS (QTOF-ESI+) calcd for $C_{20}H_{24}BrNO_3S$ [M + Na]$^+$ 460.0558, found 460.0561.

*4-(1-Bromo-2-methylheptan-2-yloxy)-N-tosylbutan-1-amine (**1j**).* Yellow gum (343 mg, 79%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.07 (t, J = 5.4 Hz, 1H), 3.40−3.33 (m, 2H), 3.32−3.24 (m, 2H), 2.94 (t, J = 6 Hz, 2H), 2.41 (s, 3H), 1.64−1.48 (m, 6H), 1.34−1.24 (m, 6H), 1.20 (s, 3H), 0.88 (t, J = 6 Hz, 3H); ^{13} C NMR ($CDCl_3$, 75 MHz) δ 143.1, 137.0, 129.6, 127.0, 75.5, 60.7, 43.0, 39.6, 36.4, 32.0, 27.1, 26.7, 23.0, 22.5, 22.0, 21.5, 14.0; HRMS (QTOF-ESI+) calcd for $C_{19}H_{32}BrNO_3S$ [M + Na]$^+$ 456.1184, found 456.1195.

General Procedure for Synthesis of Aminobromine (2a−2n). To a solution of olefin (1 mmol) in dichloromethane (2 mL), $TsNBr_2$ (1.2 mmol) were added in portions under nitrogen atmosphere and ice cold conditions. Instantaneous reaction took place. Reaction was stirred for another 10 min at room temperature. After completion of the reaction sodium thiosulfate was added and the reaction mixture was stirred for 15 min. The reaction mixture was taken up in ethyl acetate, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by flash chromatography on silica gel (230−400 mesh) with petroleum ether/ethyl acetate as eluent.

*2-Bromo-1-phenyl-N-tosylethanamine (**2a**).*[38] White solid (307 mg, 87%); mp (167−168 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, J = 8.1 Hz, 2H), 7.31−7.18 (m, 5H), 7.17−7.09 (m, 2H), 5.31 (d, J = 6.6 Hz, 1H), 4.66−4.48 (m,1H,), 3.66−3.50 (m, 2H) 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.6, 137.6, 136.8, 129.5, 128.6, 128.3, 127.2, 126.7, 57.9, 36.7, 21.5.

*2-Bromo-1-(4-chlorophenyl)-N-tosylethanamine (**2b**).*[39] White solid (349 mg, 90%); mp (147−148 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61 (d, J = 7.8 Hz, 2H), 7.28−7.16 (m, 4H), 7.05 (d, J = 8.4 Hz), 5.52 (d, J = 6.3 Hz, 1H), 4.59−4.54 (m, 1H), 3.53 (d, J = 5.7 Hz, 2 H) 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 136.6, 136.1, 134.2, 129.6, 128.7, 128.1, 127.1, 57.3, 36.3, 21.5.

*2-Bromo-N-tosylcyclohexanamine (**2c**).*[38] White solid (258 mg, 78%); mp (115−116 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1, 2H), 5.55 (d, J = 5.1 Hz, 1H), 3.90−3.85 (m, 1H), 3.23−3.19 (m, 1 H) 2.40 (s, 3H), 2.31−2.20 (m, 1H), 2.20−2.05 (m, 1H), 1.83−1.69 (m, 1H), 1.67−1.55 (m, 2H), 1.32−1.25 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 137.2, 129.5, 127.1, 58.3, 54.8, 35.4, 32.4, 24.9, 23.2, 21.4.

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*2-Bromo-1,2-diphenyl-N-tosylethanamine (**2d**).*[38] White solid (331 mg, 77%); mp (158−159 °C);^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45 (d, J = 6.3 Hz, 2H), 7.26−7.01 (m, 10 H), 6.90 (d, J = 7.5 Hz, 1H), 5.50 (d, J = 7.8 Hz, 1H), 5.16 (d, J = 6.3 Hz, 1H), 4.83−4.78 (m, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.1, 136.9, 136.3, 129.2, 129.1, 128.7, 128.6, 128.4, 128.0, 127.7, 127.6, 127.0, 63.1, 58.1, 21.4.

*Ethyl-2-bromo-3-phenyl-3-(tosylamino)propanoate (**2e**).*[38] White solid (336 mg, 79%); mp (174−176 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 (d, J = 7.8 Hz, 2H), 7.33−7.22 (m, 7 H), 5.24 (d, J = 9.9 Hz, 1H), 5.14 (d, J = 6.3 Hz, 1H), 4.49−4.43 (m, 1 H), 4.02−3.88 (m, 2H), 2.41 (s, 3H), 1.11 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.6, 143.8, 136.4, 136.2, 129.6, 129.1, 128.3, 127.3, 62.4, 61.8, 51.7, 21.5, 13.8.

*Methyl-2-bromo-3-(4-chlorophenyl)-3-(tosylamino)propanoate (**2f**).*[39,40] White solid (355 mg, 80%); mp (111−112 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, J = 7.8 Hz, 2H), 7.27−7.19 (m, 6H), 5.67 (d, J = 7.8 Hz, 1H), 5.01 (d, J = 8.4 Hz, 1H), 4.45 (t, J = 9.3 Hz, 1H), 3.56 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.6, 143.9, 136.1, 134.9, 134.8, 132.2, 129.5, 128.7, 127.1, 61.6, 52.8, 50.0, 21.5.

*4-Bromo-N-tosylhexan-3-amine (**2g**).*[41] White solid (263 mg, 79%); mp (99−100 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 4.59 (d, J = 8.8 Hz, 1H), 3.64 (m,1H,), 2.97 (t, J = 9.6 Hz, 1H), 2.24 (s, 3H), 1.58−1.54 (m, 2H), 1.36−1.34 (m, 2H), 0.76 (t, J = 7.2 Hz, 3H), 0.61 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 138.6, 130.1, 127.4, 65.6, 59.3, 29.7, 23.5, 21.9, 13.1, 10.5.

*2-Bromo-1-phenyl-N-tosylpropane-1-amine (**2h**).*[25] White solid (301 mg, 82%); mp (133−135 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, J = 8.4 Hz, 2H), 7.23−7.13 (m, 3H), 7.12−7.05 (m, 4H), 5.46 (d, J = 7.8 Hz, 1H), 4.51−4.37 (m, 2H), 2.34 (s, 3H), 1.53 (d, J = 6.3 Hz, 3H,); ^{13}C NMR $CDCl_3$, 100 MHz) δ 143.7, 137.4, 136.3, 129.7, 128.4, 128.2, 127.4, 62.7, 54.5, 54.3, 22.6, 21.8.

*1-Bromo-2,3-dihydro-N-tosyl-1H-indane-2-amine (**2i**).*[38] White solid (314 mg, 86%); mp (167−168 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, J = 8 Hz, 2H), 7.29 (d, J = 8 Hz, 2H), 7.20−7.18 (m, 1H), 7.17−7.11 (m, 2H), 7.03 (d, J = 8 Hz, 1H), 4.87−4.83 (m, 1H), 4.67 (d, J = 7.6 Hz, 1H), 4.27−4.22 (m, 1H), 3.51 (dd, J = 16.4, 7.2, Hz, 1H), 3.12 (dd, J = 16.8, 5.6 Hz 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 140.4, 139.4, 137.5, 130.0, 129.5, 128.0, 127.6, 125.0, 124.8, 67.3, 51.9, 41.3, 21.8.

*2-Bromo-1,2,3,4-tetrahydro-N-tosylnaphthalen-1-amine (**2j**).*[42] White solid (342 mg, 90%); mp (135−137 °C) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.33- 6.95 (m, 3H), 6.47 (d, J = 7.5 Hz, 1H), 4.83 (d, J = 4.2 Hz, 1H), 4.79−4.65 (m, 1H), 4.56−4.40 (m,1H), 3.19−2.99 (m, 1H), 2.88- 2.68 (m, 1H), 2.50 (s, 3H), 2.46−2.32 (m,1H), 2.21−2.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 136.7, 135.6, 131.3, 130.0, 129.6, 129.2, 128.5, 127.3, 126.8, 57.0, 51.0, 24.7, 24.5, 21.7.

*1-Bromo-N-tosyloctan-2-amine (**2k**).*[41] Colorless gum (318 mg, 88%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 5.04−4.86 (m, 1H), 4.06−3.88 (m, 1H), 3.43−3.34 (m, 1H), 3.30−3.02 (m, 1H), 2.43 (s, 3H), 1.84−1.65 (m, 2H), 1.37−1.04 (m, 8H), 0.84 (t, J = 9.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.7, 136.8, 129.8, 127.0, 55.5, 49.5, 36.0, 31.5, 28.4, 27.1, 25.2, 22.5, 21.5, 14.0.

*2-Bromo-3-(4-chlorophenyl)-1-phenyl-3-(tosylamino)propan-1-one (**2l**).*[43] White solid (408 mg, 83%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1 H), 7.56−7.38 (m, 4 H), 7.27−7.11 (m, 4H), 7.01 (d, J = 7.8 Hz, 2H), 5.70 (d, J = 9.9 Hz, 1 H), 5.49 (t, J = 8.4 Hz, 1H), 5.04 (d, J = 8.6 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.7, 143.7, 136.5, 135.1, 135.0, 134.9, 134.3, 129.8, 129.4, 128.9, 128.7, 128.6, 126.9, 60.3, 50.2, 21.4.

*4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)-2-bromo-tetrahydro-N-tosyl-2H-pyran-3-amine (**2m**).* Semi solid (532 mg, 80%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, J = 8.1 Hz, 2H), 7.38−7.19 (m, 17H), 5.62 (d, J = 9.3 Hz, 1H), 4.99−4.77 (m, 4H), 4.57−4.31 (m, 3H), 3.75−3.60 (m, 4H), 3.47−3.39 (m, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 138.2, 137.6, 129.6, 129.2, 128.3, 128, 127.9, 127.8, 127.7, 127.3, 125.9, 85.8, 84.8, 78.4, 76.4, 76,74.9, 73.4, 70.9, 67.9, 51.8, 21.4; LCMS (ESI) calcd for $C_{34}H_{36}$ BrN O_6S $[M + Na]^+$ 688.1344, found 688.8. Anal. Calcd (%) for $C_{34}H_{36}BrNO_6S$: C, 61.26; H, 5.44; N, 2.10; Found: C, 61.37; H, 5.30; N, 2.01.

*2-Bromo-N-tosylcyclopentanamine (**2n**).*[27] White solid (279 mg, 88%); mp (72−75 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.25 (d, J = 5.7 Hz, 1H), 4.16- 4.07 (m, 1H), 3.76−3.62 (m, 1H), 2.44 (s, 3H), 2.30−2.10 (m, 2H), 2.01−1.91 (m, 1H), 1.85−1.71 (m, 2H), 1.50−1.34 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 136.8, 129.8, 127.3, 62.9, 54.3, 34.0, 30.6, 21.6, 21.3.

General Procedure for the Synthesis Imidazoline and Bromoamidine (3a−3k). To a solution of olefin (1 mmol) in CH_3CN (5 mL), $TsNBr_2$ (1.2 mmol) was added in small proportions over a period of 20 min under ice cold condition and the reaction was continued at room temperature for appropriate time (TLC). The excess solvent was removed in rotary evaporator and sodium thiosulfate (200 mg approx) was added followed by the addition of water (5 mL). The reaction mixture was stirred for another 5 min and extracted with ethyl acetate followed by dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (230−400 mesh) with a mixture of petroleum ether and ethyl acetate (with a few drops of diethyl amine) as eluent to obtain the pure product.

*4,5-Dihydro-2-methyl-4-phenyl-1-tosyl-1H-imidazole (**3a**).*[44] White solid (238 mg, 76%); mp (100−102 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.30−7.20 (m, 3H), 7.10−6.98 (m, 2H), 4.97 (t, J = 9 Hz, 1H), 4.17 (t, J = 9.9 Hz, 1H), 3.62 (t, J = 7.8 Hz, 1H), 2.45 (s, 3H), 2.39 (d, J = 1.5 Hz, 3H); ^{13} C NMR ($CDCl_3$, 75 MHz) δ 156.3, 144.7, 141.4, 134.9, 130.0, 128.7, 128.6, 127.5, 127.1, 126.3, 66.5, 55.4, 21.5, 16.7.

*4-(4-Chlorophenyl)-4,5-dihydro-2-methyl-1-tosyl-1H-imidazole (**3b**).*[44] White solid (261 mg, 75%) mp (170−172 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz. 2H), 7.23 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 4.96 (t, J = 8.7 Hz, 1H), 4.16 (t, J = 9.9 Hz, 1H), 3.61−3.47 (m, 1H), 2.48 (s, 3H), 2.39 (s, 3H) ; ^{13} C NMR ($CDCl_3$, 75 MHz) δ 156.8, 144.8, 140.1, 135.0, 133.3, 130.1, 128.7, 127.7, 127.1, 65.8, 55.3, 21.5, 16.7.

*4-(4-Fluorophenyl)-4,5-dihydro-2-methyl-1-tosyl-1H-imidazole (**3c**).*[45] Colorless gum (242 mg, 73%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.01−6.89 (m, 4H), 4.96 (t, J = 8.1 Hz, 1H), 4.15 (t, J = 10.2 Hz, 1H), 3.58 (t, J = 8.1 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H); ^{13} C NMR ($CDCl_3$, 75 MHz) δ 162.2 ($^1J_{CF}$ = 244.4 Hz), 156.6, 144.8, 137.4 ($^4J_{CF}$ = 3.3 Hz), 135.0, 130.1, 128.0 ($^3J_{CF}$ = 8.3 Hz), 127.1, 126.9, 115.5 ($^2J_{CF}$ = 21.3 Hz), 65.8, 55.5, 21.5, 16.8.

*4-(4-Bromophenyl)-4,5-dihydro-2-methyl-1-tosyl-1H-imidazole (**3d**).*[31d] Colorless gum (298 mg, 77%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 8.4 Hz, 2H), 7.44−7.30 (m, 4H), 6.92 (d, J = 8.4 Hz, 2H), 4.95 (t, J = 8.7 Hz, 1H), 4.17 (t, J = 9.6 Hz, 1H), 3.57 (t, J = 8.1 Hz, 1H), 2.46 (s, 3H), 2.40 (s, 3H).

*(4R,5R)-4,5-Dihydro-2-methyl-4,5-diphenyl-1-tosyl-1H-imidazole (**3e**).*[46] White sticky solid (296 mg, 76%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53−7.42 (m, 2H), 7.39−7.31 (m, 3H), 7.29−7.19 (m, 6H), 7.12−6.99 (m, 1H), 6.96−6.83 (m, 2H), 4.99−4.84 (m, 2H), 2.53 (s, 3H), 2.42 (s, 3H) ; ^{13} C NMR ($CDCl_3$, 75 MHz) δ 156.7, 144.5, 141.4 135.8, 129.7, 128.9, 128.7, 128.1, 127.7, 127.3, 126.5, 126.0, 77.1, 71.9, 21.5, 17.2.

*3a,4,5,6,7,7a-Hexahydro-2,3a-dimethyl-1-tosyl-1H-benzo[d]-imidazole (**3f**).*[32] Light yellow gum (247 mg, 81%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 3.61 (t, J = 6 Hz, 1H), 2.43 (s, 3H), 2.26 (s, 3H), 2.02−1.84 (m, 1H), 1.79−1.63 (m, 2H), 1.56−1.28 (m, 5H), 0.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3, 144.3, 136.2, 129.9, 127.1, 66.4, 65.9, 32.7, 28.5, 27.6, 21.5, 18.9, 18.0, 17.4.

*3a,4,5,6,7,7a-Hexahydro-2-methyl-3a-phenyl-1-tosyl-1H-benzo-[d]imidazole (**3g**).*[32] Light yellow gum (282 mg, 77%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36 (d, J = 8.4 Hz, 2H), 7.14−7.08 (m, 3H), 7.08−6.96 (m, 4H), 4.24 (t, J = 5.4 Hz,1H), 2.40 (s, 3H), 2.31(s, 3H), 2.19−2.16 (m, 1H), 1.94−1.86 (m, 2H), 1.65−1.41 (m, 5H); ^{13} C NMR ($CDCl_3$, 75 MHz) δ 155.9, 143.9, 135.8, 129.5, 128.0, 126.5, 124.8, 71.9, 66.9, 33.7, 28.0, 21.4, 18.4, 17.2, 16.8.

*4-Ethyl-4,5-dihydro-2,4-dimethyl-1-tosyl-1H-imidazole (**3h**).*[32] White solid (224 mg, 80%); mp (114−116 °C); ^{1}H NMR ($CDCl_3$,

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300 MHz) δ 7.73 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 3.53 (d, J = 9.3 Hz, 1H), 3.39 (d, J = 9.3 Hz, 1H), 2.45 (s, 3H), 2.30 (s, 3H), 1.52−1.39 (m, 2H), 1.11 (s, 3H), 0.72 (t, J = 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.4, 144.5, 135.1, 128.9, 128.2, 67.4, 57.3, 33.5, 27.4, 22.5, 17.5, 8.8.

4,5-Dihydro-2,4,4,5-tetramethyl-1-tosyl-1H-imidazole (**3i**).[32] White solid (221 mg, 79%), mp (102 °C-104 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 3.68 (q, J = 6.9 Hz, 1H), 2.41 (s, 3H), 2.25 (s, 3H), 1.28 (d, J = 6.6 Hz, 3H), 1.31 (s, 3H), 0.72 (s, 3H).

N-(2-Bromocyclohexyl)-N′-tosylacetamidine (**3j**).[32] White solid (321 mg, 86%); mp (130−132 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84−7.77 (m, 2H), 7.29−7.23 (m, 2H), 6.24 (b, 1H), 4.19−4.05 (m, 1H), 3.94−3.78 (m, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 2.23−2.14 (m, 2H), 1.84−1.67 (m, 3H), 1.37−1.21 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.5, 142.1, 140.4, 129.2, 126.4, 56.9, 53.8, 36.8, 32.1, 26.3, 23.9, 21.4, 21.2.

N-(2-Bromocyclooctyl)-N′-tosylacetamidine (**3k**).[32] White solid (341 mg, 85%); mp (141−142 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (d, J = 7.8 Hz, 2H), 7.28−7.25 (m, 2H), 5.66 (d, J = 7.2 Hz, 1H), 4.44−4.32 (m, 1H), 4.10−3.97 (m, 1H), 2.41 (s, 3H), 2.35 (s, 3H), 2.23-2.08 (m, 4H), 1.76−1.44 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.1, 142.2, 140.5, 129.2, 126.3, 56.0, 51.5, 34.8, 33.1, 29.6, 28.9, 24.0, 23.1, 21.5, 20.8.

Synthesis of Diamine Derivative (4a−4h). To a solution of styrene (1 mmol) in CH_3CN (8 mL) and H_2O (1 mL), $TsNBr_2$ (1.5 mmol) was added and the reaction was continued at room temperature (in case of cyclohexene, 80 °C) for almost 3 h. The excess solvent was removed in rotary evaporator and sodium thiosulfate (200 mg approx.) was added followed by the addition of water (5 mL). The reaction mixture was stirred for another 5 min and extracted with ethyl acetate followed by dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Further purification of the crude product using petroleum ether/ethyl acetate as eluent led to isolation of corresponding diamine derivative in pure form.

N-(1-Phenyl-2-(tosylamino)ethyl)acetamide (**4a**). White solid (282 mg, 85%); mp (110−115 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (d, J = 8.1 Hz, 2H), 7.42- 7.17 (m, 7H), 6.45 (d, J = 7.5 Hz, 1H), 5.14 (t, J = 6.3 Hz, 1H), 5.10−4.99 (m, 1H), 3.35−3.20 (m, 2H), 2.42 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.5, 143.7, 138.5, 136.6, 129.8, 128.9, 128.0, 126.9, 126.4, 52.7, 48.0, 23.2, 21.4; ESI-MS for $(M+Na)^+$ 355.1092, found 355.23. Anal. Calcd (%) for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43; Found: C, 61.47; H, 6.13; N, 8.36.

N-(1-(4-Chlorophenyl)-2-(4-methylphenylsulfonamido)ethyl)-acetamide (**4b**). White solid (312 mg, 85%); mp (122−124 °C); ^{1}H NMR (DMSO, 300 MHz) δ 8.27 (d, J = 8.1 Hz, 1H),7.70−7.66 (m, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.34(d, J = 8.1 Hz, 4H), 7.23(d, J = 8.1 Hz, 2H), 4.85 (t, J = 6.9 Hz, 1H), 2.91 (t, J = 6.6 Hz, 2H), 2.35 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (DMSO, 125 MHz) δ 169.1, 143.1, 140.0, 137.6, 132.1, 129.9, 129.2, 128.5, 126.8, 52.1, 47.5, 23.0, 21.3; HRMS (QTOF-ESI+) calcd for $C_{17}H_{19}ClN_2O_3S$ $[M+H]^+$ 367.0883, found 367.0817.

N-(1-(4-Fluorophenyl)-2-(4-methylphenylsulfonamido)ethyl)-acetamide (**4c**). White solid (287 mg, 82%); mp (138−140 °C); ^{1}H NMR (DMSO, 300 MHz) δ 8.25 (d, J = 8.1 Hz, 1H), 7.64−7.65 (m,1H),7.60 (d, J = 7.8 Hz, 2H),7.35(d, J = 7.5 Hz, 2H),7.30−7.21(m, 2H), 7.17−7.06 (m, 2H), 4.87 (d, J = 7.2 Hz, 1H), 2.96−2.84 (m, 2H), 2.36 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (DMSO, 100 MHz) δ 168.7, 142.7, 137.1 ($^4J_{CF}$ = 35.5 Hz), 129.6, 128.9 ($^3J_{CF}$ = 8.4 Hz), 126.5, 115.0 ($^2J_{CF}$ = 21.2 Hz), 51.6, 47.4, 22.7, 21.0; HRMS (QTOF-ESI+) calcd for $C_{17}H_{19}FN_2O_3S$ $[M+H]^+$ 351.1179, found 351.1179.

N-(1-(4-Bromophenyl)-2-(4-methylphenylsulfonamido)ethyl)-acetamide (**4d**). White solid (329 mg, 80%); mp (141−143 °C); ^{1}H NMR (DMSO, 300 MHz) δ 8.27 (d, J = 8.4 Hz, 1H), 7.677 (t, J = 6 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.34(d, J = 7.8 Hz, 2H), 7.17(d, J = 8.4 Hz, 2H), 4.82 (d, J = 7.8 Hz, 1H), 2.91 (t, J = 6.3 Hz, 2H), 2.36 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (DMSO, 125 MHz) δ 169.3, 143.1, 140.4, 137.5, 131.4, 129.9, 129.6, 126.8, 120.7, 52.2, 47.4, 23.0, 21.3; HRMS (QTOF-ESI+) calcd for $C_{17}H_{19}BrN_2O_3S$ $[M+H]^+$ 411.0378, found 411.0367.

N-(2-(4-Methylphenylsulfonamido)-1-phenylpropyl)acetamide (**4e**). White solid (294 mg, 85%); mp (144−145 °C); ^{1}H NMR($CDCl_3$, 300 MHz):δ 7.74 (d, J = 7.8 Hz, 2H), 7.34−7.23 (m, 6H), 6.49 (d, J = 7.5 Hz, 1H), 5.61 (d, J = 8.1 Hz, 1H), 4.78 (t, J = 8.1 Hz, 1H), 3.68−3.48 (m, 1H), 2.42 (s, 3H),1.95 (s, 3H), 0.914 (d, J = 6.9 Hz, 3H); ^{13}CNMR-($CDCl_3$,75 MHz) δ 170.9, 143.3, 139.3, 138.2, 129.7, 128.9, 128.0, 127.2, 126.8, 58.8, 54.7,23.3,21.5,19.4; ESI-MS for $(M+Na)^+$ 369.1249, found 369.27. Anal. Calcd (%) for $C_{18}H_{22}N_2O_3S$: C, 62.40; H, 6.40; N, 8.09. Found: C, 62.51; H, 6.49; N, 8.16.

N-(2-(4-Methylphenylsulfonamido)-1,2-diphenylethyl)acetamide (**4f**).[5c] White solid (318 mg, 78%); mp (158−160 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7..46 (d, J = 8.4 Hz, 2H), 7.33−7.25 (m, 1H), 7.23−7.12 (m, 3H), 7.10−6.99 (m, 6H), 6.83 (d, J = 7.2 Hz, 2H), 6.50−6.39 (m, 1H), 5.19 (t, J = 10.2 Hz, 1H), 4.57 (t, J = 9.9 Hz, 1H), 2.31(s, 3H), 2.67(s, 3H); ^{13}C NMR (DMSO, 125 MHz) δ 169.1, 142.1, 140.3, 139.3, 138.7, 129.2, 128.1, 127.8, 127.5, 127.1, 126.9, 126.4, 62.5, 57.7, 23.0, 21.2; HRMS (QTOF-ESI+) calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$ 409.1586, found 409.1592.

N-(2-(Tosylamino)cyclohexyl)acetamide (**4g**).[47] White solid (254 mg, 82%); mp (158−160 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.25 (d, J = 7.8 Hz, 1H), 5.61 (d, J = 8.1 Hz, 1H), 3.99−3.72 (m, 1H), 3.41 (d, J = 3.6 Hz, 1H), 2.41 (s, 3H), 1.90 (s, 3H), 1.73−1.54 (m, 2H), 1.51−1.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1, 143.7, 136.9, 129.8, 127.1, 52.7, 49.4, 29.6, 27.5, 23.4, 23.3, 21.5, 19.9.

N-(2-Methyl-3-(4-methylphenylsulfonamido)butan-2-yl)-acetamide (**4h**). (238 mg, 80%); ^{1}H NMR ($CDCl_3$, 300 MHz) 7.73 (d, J = 8.1 Hz, 2H), 7.27−7.24 (m, 2H), 6.27 (d, J = 9 Hz, 1H), 5.74−5.70 (m, 1H), 3.36−3.30 (m, 1H), 2.39 (s, 3H), 1.90 (s, 3H), 1.26−1.19 (m, 6H), 0.89−0.87 (m, 3H); ^{13}CNMR($CDCl_3$,75 MHz):δ170.8, 143.0, 138.2, 129.6, 126.9, 57.0, 56.7, 24.4, 24.2, 24.1, 21.2, 16.5; HRMS (QTOF-ESI+) calcd for $C_{14}H_{22}N_2O_3S$ $[M+H]^+$ 299.1429, found 299.1412.

General Procedure for Synthesis of Diamines (5a−5c). To a solution of olefin (1 mmol) and K_2CO_3 (5 mmol), in dry ethyl acetate (10 mL), $TsNBr_2$ (2.5 mmol) was added under nitrogen atmosphere. The reaction was stirred at specific temperature (depending upon the type of substrate; RT for 1,2-dihydro pyran and their derivatives and 60 °C in case of styrene) for appropriate time. Progress of the reaction was monitored by TLC. After completion of the reaction, an aqueous solution of 10% sodium thiosulfate (10 mL) was added and the organic layer separated. The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with water and finally with brine solution. Combined organic part was dried over anhydrous sodium sulfate and concentrated. The crude product was purified by flash chromatography on silica gel (230−400 mesh) with petroleum ether/ethyl acetate as eluent.

1-Phenyl-N^1,N^2-ditosylethane-1,2-diamine (**5a**).[48] White sticky solid (310 mg, 70%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.34−7.29 (m, 2H), 7.20−7.18 (m, 4H), 6.99−6.96 (m, 2H), 5.37 (bs, 1H), 4.82 (d, J = 6 Hz, 1H), 4.33−4.27 (m, 1H), 3.22−3.15 (m, 2H), 2.43 (s, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 143.6, 137.4, 136.6, 136.4, 129.8, 129.5, 128.9, 128.3, 127.2, 127.1, 126.5, 57.1, 48.2, 21.5; HRMS (QTOF-APCI+) calcd for $C_{22}H_{25}N_2O_4S_2$ $[M+H]^+$ 445.1256, found 445.1243.

3,4,6-Tri-O-acetyl-1,2-dideoxy-1,2-di(p-toluenesulfonamido)-β-D-galactopyranose (**5b**).[34] White solid (464 mg, 74%); mp (110−112 °C); (1:1.25 diastereomeric mixture); ^{1}H NMR ($CDCl_3$, 300 MHz, for major diastereomer) δ 7.85−7.70 (m, 4H), 7.34−7.29 (m, 4H), 6.39 (d, J = 9 Hz, 1 H), 5.31 (d, J = 6 Hz, 1H), 5.17−5.07 (m, 1H), 4.99−4.92 (m, 2 H), 4.16−3.95 (m, 2H), 3.73−3.37 (m, 2H), 2.43(s, 3H), 2.42(s, 3H), 2.18 (s, 3H), 2.06−2.04 (m, 3H), 1.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.0, 171.1, 170.6, 169.4, 143.7, 137.9, 137.5, 137.3, 137.0, 129.9, 129.6, 129.4, 127.3, 127.0, 83.5, 80.7, 72.8, 70.2, 68.1, 67.7, 67.4, 61.7, 60.7, 56.6, 54.5, 21.5, 20.7, 20.6, 20.0; HRMS (QTOF-ESI+) calcd for $C_{26}H_{36}N_2O_{11}S_2$ $[M+NH_4]^+$ 630.1791, found 630.1774.

Tetrahydro-N^2,N^3-ditosyl-2H-pyran-2,3-diamine (**5c**).[34] White solid (284 mg, 67%); mp (117−119 °C); (1:1 diastereomeric mixture); ^{1}H NMR ($CDCl_3$, 300 MHz, for one diastereomer) δ 7.83−7.74 (m,

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4H), 7.3−7.23 (m, 4H), 5.98 (d, J = 6 Hz, 1H), 5.46 (d, J = 9 Hz, 1H), 4.47 (t, J = 9 Hz, 1H), 3.73−3.61 (m, 1H), 3.38−3.35 (m, 1H), 2.97−2.95 (m, 1H), 2.41(s, 3H), 2.39 (s, 3H), 2.17−2.07 (m, 1H), 1.52−1.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 144, 143.8, 143.5, 143.4, 139.1, 138.4, 138.1, 137.3, 137.2, 129.9, 129.7, 129.5, 129.4, 127.1, 127, 126.4, 85, 82.1, 66.3, 65.2, 53.4, 53.0, 51.4, 30.4, 29.6, 27.6, 24.5, 21.5, 20.2; HRMS (ESI) calcd for $C_{19}H_{24}N_2O_5S_2$ $[M + Na]^+$ 447.1024, found 447.1022.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00785.

^{1}H NMR, ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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