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Lewis Acid Mediated Intramolecular C−C Bond Formation of Alkyne-Epoxide Leading to Six-Membered Nitrogen and Oxygen Heterocycles

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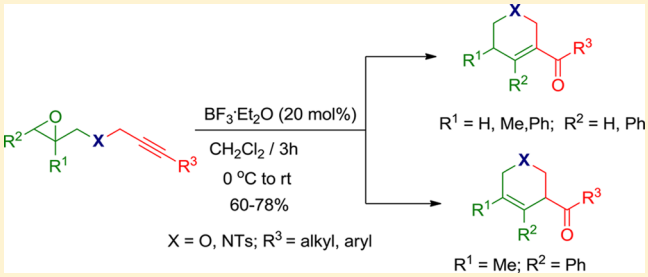
Supporting Information

ABSTRACT: Intramolecular C−C bond formation of oxygen- and nitrogen-tethered alkynes and epoxide mediated by Lewis acid under ambient conditions is described. A simple procedure for the synthesis of 3,6- and 5,6-dihydropyrans and 3,4-dehydropiperidines from acyclic building blocks in good yields without using any transition metal is shown.



Cyclic ethers have undoubtedly attracted the interest of synthetic chemists due to their occurrence in many natural products exhibiting several important biological activities.[1] Similarly, nitrogen heterocyclic compounds are important in synthetic chemistry because of their presence in many biologically active natural products and pharmaceuticals.[2] Cyclic ethers are prepared in high yield by either C−C[3] or C−O[4] bond formation. Numerous synthetic approaches have been proposed and used for the preparation of five- and six-membered oxygen and nitrogen rings, and strategies such as carbocyclization of enynes promoted by various transition metal catalysts such as Cu,[5] Pd,[6] Pt,[7] and Au,[8] reductive coupling of alkyne and epoxide using Ni,[9] and intramolecular alkene-epoxide cyclization[10] have been well explored. In this paper intramolecular C−C bond formation of oxygen- and nitrogen-tethered alkynes and epoxides mediated by Lewis acid under ambient conditions is described.

In continuation of our interest in oxygen and nitrogen heterocycles,[11] we were in search of methods for synthesizing multifunctional oxygen and nitrogen heterocyclic frameworks. Literature reports revealed that cyclization of enyne is one of the best method for achieving such goals.[7b,8] Di- and tetrahydropyrans can also be synthesized using epoxides and homoallylic alcohols under Prins cyclization conditions.[12] Taking clues from these we envisioned that functionalized oxygen and nitrogen heterocyclic compounds could be prepared from O- and N-tethered alkyne-epoxide substrates mediated by Lewis acid. Although there are reports for the synthesis of O- and N-heterocyclic compounds from alkyne-epoxide coupling via intramolecular alkyne−azide cycloadditions[13] and nickel-catalyzed reductive coupling of alkyne-epoxide,[14] to our knowledge the synthetic potential of the use of a Lewis acid for the synthesis of such rings using substrates with an epoxide and an alkyne has not been examined so far. To start with, alkyne-epoxide **1a** was treated with $BF_3{\cdot}Et_2O$ in dichloromethane at room temperature, and the reaction proceeded smoothly to afford **2a** in 68% yield, the structure of which was determined by NMR and X-ray analysis.[15] Oxygen-tethered[16] and nitrogen-tethered[17] alkyne-epoxide substrates were prepared using previously described methods.

In order to optimize the reaction conditions alkyne-epoxide **1a** was subjected to reaction with several Lewis and Bronsted acids (Table 1). It was observed that apart from $BF_3{\cdot}Et_2O$, $InCl_3$ and $Bi(OTf)_3$ also resulted in the desired product in good yields. $Zn(OTf)_2$ and $In(OTf)_3$ gave 28% and 20% yield, respectively. Brønsted acid CSA gave low yield, but TfOH gave moderate yield. $FeCl_3$ yielded only 25% of the desired product. However, reaction using TMSOTf was unsuccessful, and decomposed product was observed. $BF_3{\cdot}Et_2O$ at 0.2 equiv was found to be the best reagent for the reaction. Survey of the various solvents revealed that THF and dioxane gave relatively lower yields, and no progress in the reaction was noticed in toluene and acetonitrile. Dichloromethane (DCM) proved to be better than all other solvents. The reaction was also performed at −20 °C in CH_2Cl_2 for 10 h but gave only 50% yield.

Having obtained the optimized conditions, we further examined the scope of the reaction with variety of substrates (Table 2). During the course of this study, we noticed that varying the substitution of methyl and phenyl groups on the epoxide ring resulted in the products with different dihydropyrans and 3,4-dehydropiperidines along with some decomposed products. It was observed from Table 2 that 1,2-disubstituted (entries 1−3, 6, 7, 10) and terminal epoxides (entries 4 and 5) gave dihydropyrans in good yields. Substrates **1a**, **1b**, **1d−g**, and **1j** (entries 1, 2, 4−7, 10) gave 5,6-

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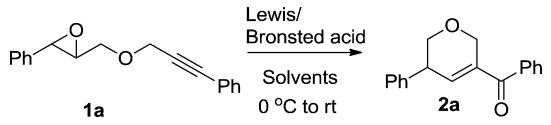
Table 1. Optimization of the Reaction



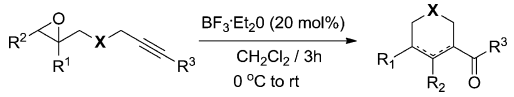
entry	Lewis/Brønsted acid (equiv)	time (h)	solvent	% yield[a]
1	$BF_3{\cdot}Et_2O$ (1)	3	CH_2Cl_2	68
2	$InCl_3$ (1)	3	CH_2Cl_2	65
3	$Bi(OTf)_3$ (0.5)	3	CH_2Cl_2	63
4	TMSOTf (0.5)	8	CH_2Cl_2	trace
5	$BF_3{\cdot}Et_2O$ (0.5)	3	CH_2Cl_2	68
6	**$BF_3{\cdot}Et_2O$ (0.2)**	**3**	**CH_2Cl_2**	**68**
7	$BF_3{\cdot}Et_2O$ (0.2)	3	THF	d
8	$BF_3{\cdot}Et_2O$ (0.2)	3	Toluene	d
9	$BF_3{\cdot}Et_2O$ (0.2)	8	CH_3CN	d
10	$Zn(OTf)_2$ (1)	10	CH_2Cl_2	28
11	CSA (1)	8	CH_2Cl_2	32
12	TfOH (1)	5	CH_2Cl_2	50
13	$FeCl_3$ (1)	10	CH_2Cl_2	25
14	$In(OTf)_3$ (1)	8	CH_2Cl_2	20

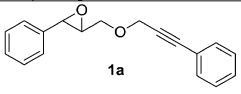
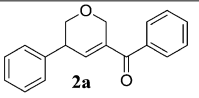
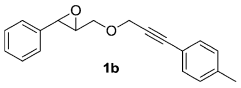
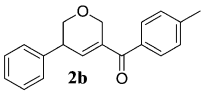
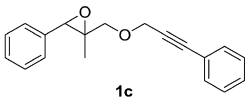
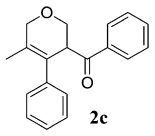
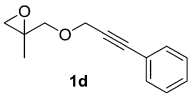
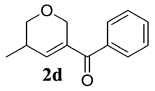
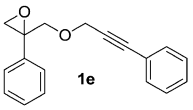
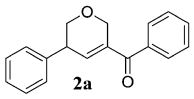
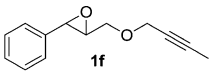
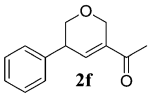
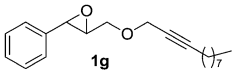
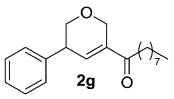
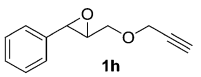
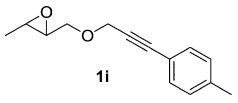
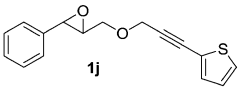
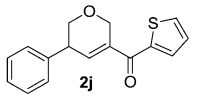
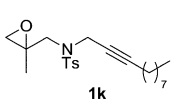
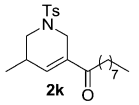
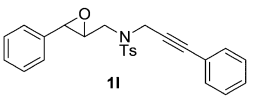
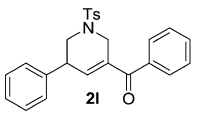
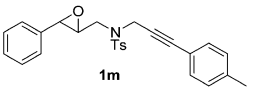
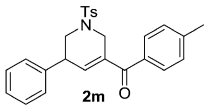
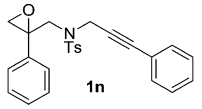
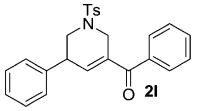
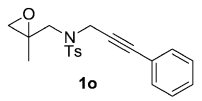
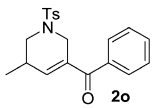
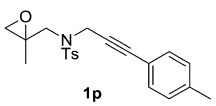
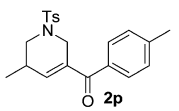
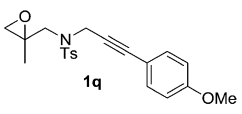
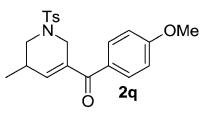
[a]Yields refer to isolated yield. The compounds were characterized by IR, NMR, and mass spectrometry. d = decomposed product.

dihydropyrans, whereas substrate **1c** (entry 3) gave 3,6-dihydropyran **2c**. The formation of **2c** might be due to higher stability of the conjugated enone 3,6-dihydropyran compared to 5,6-dihydropyran. Unsubstituted alkyne **1h** (entry 8) was found to be unreactive under the same reaction conditions. Similarly, terminal methyl-substituted alkyl-epoxide **1i** (entry 9) did not give any product. This is attributed to the lower stability of the carbocation **A** (Scheme 1), formed from methyl-substituted epoxide compared to the aryl-substituted epoxide.[12] Alkyl-substituted alkyne-epoxide **1f** and **1g** (entries 6 and 7) gave 74% and 76% yields, respectively. Thiophene-substituted alkyne-epoxide **1j** (entry 10) also worked well, giving 60% yield. Similarly, N-tethered epoxides **1k–q** (entries 11–17) having alkyl and aryl substituents gave 3,4-dehydropiperidines **2k–q** in good yields.

The mechanism of the reaction can be explained as follows. The epoxide **1** in the presence of $BF_3{\cdot}Et_2O$ opens up to generate carbocation **A**, which after rearrangement gives most stable oxocarbenium ions **B** and **F** via phenyl and hydrogen migration, respectively.[18] The oxocarbenium ions **B** and **F** are then attacked by alkyne group, via a 6-*exo*-*trig* cyclization to give carbocations **C** and **G**, respectively. The intermediates **C** and **G** are then trapped by water to give enols **D** and **H**, which

Table 2. $BF_3{\cdot}Et_2O$-Mediated Intramolecular C–C Bond Formation of Alkyne and Epoxide



Entry	Alkyne-Epoxide **1**	Product **2**	% Yield[a]
1			68
2			71
3			62
4			65
5			67
6			74
7			76
8		---	d
9		---	d
10			60
11			77
12			60
13			61
14			69
15			78
16			75
17			73

[a]Yield refers to isolated yield. The compounds are characterized by IR, ^1H, ^{13}C NMR and mass spectrometry. d = Decomposed product.

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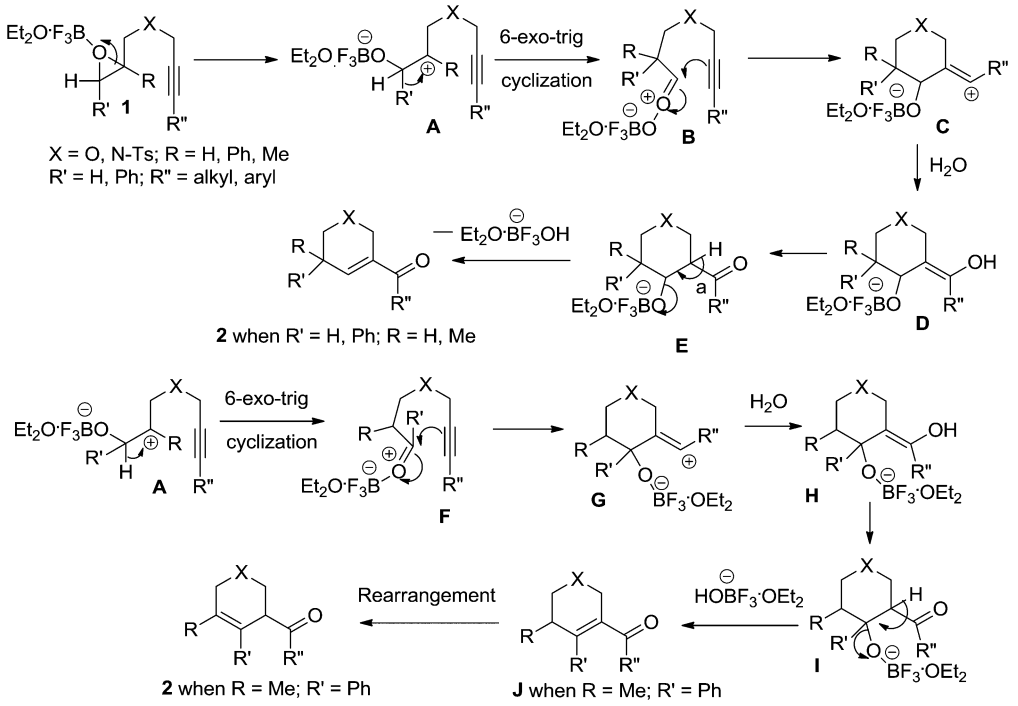
Scheme 1. Mechanism of the Reaction



after rearrangement give ketones **E** and **I**. The ketone **E** after elimination gives the final compound **2** (Scheme 1). On the other hand, ketone **I** initially forms compound **J** and then rearranges to give more stable compound **2**.

Conclusion. In conclusion, we have developed a mild and an efficient method for the synthesis of six-membered oxygen and nitrogen heterocyclic compounds by intramolecular C−C bond formation of alkyne-epoxide mediated by boron trifluoride etherate. The method is highly substrate-specific and works well for alkyl- and aryl-substituted alkyne-epoxide substrates.

EXPERIMENTAL SECTION

General Experimental Section. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on 600, 400, 300 and 150, 100, 75 MHz NMR spectrometers, respectively, using TMS as internal standard. HRMS spectra were recorded using a TOF mass spectrometer. Compounds **1a** and **1h** are known and were prepared according to the literature procedure.[13,15] Their IR, NMR, and HRMS data agreed well with the reported data. The same procedure was used to prepare compounds **1b**−**1g**, **1i**, and **1j**.[13,15] N-Tethered compounds **1k**−**1q** were prepared as per the literature procedures.[13,15,16]

General Procedure for Preparation of O-Tethered Compounds. In an oven-dried round-bottom flask was taken NaH (1.5 equiv), and dry THF (20 mL) was added to it. To this a solution of propargyl alcohol (1 equiv) or its derivatives was added slowly. The reaction mixture was stirred for 0.5 h at 0 °C. Allyl bromide (1 equiv) was added to the reaction mixture dropwise. The reaction was monitored by thin layer chromatography, and after completion of the reaction THF was removed by evaporation. The residue was extracted with ethyl acetate (30 mL) and washed with water and brine solution (20 mL × 2). The organic layer was dried over anhydrous Na_2SO_4, and solvent was evaporated using a rotary evaporator to give crude product. The crude product was purified on silica gel column chromatography using ethyl acetate and hexane as eluents. The ether (1.0 equiv) thus obtained was treated with metachloroperbenzoic acid (1.5 equiv) in dichloromethane (15 mL) at 0 °C. The reaction mixture was brought to room temperature and stirred for a specific time. After completion of the reaction as determined by TLC, a saturated aqueous solution of Na_2SO_3 was added to quench excess *m*CPBA. Dichloromethane was added to the reaction mixture, washed with saturated sodium bicarbonate and brine solution, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by neutral alumina using ethyl acetate and hexane as eluents.

*2-Phenyl-3-(((3-(p-tolyl)prop-2-yn-1-yl)oxy)methyl)oxirane (**1b**).* Colorless oil; R_f (hexane/EtOAc 9:1) 0.60; yield 242 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.26 (m, 7 H), 7.11 (d, J = 8 Hz, 2 H), 4.47 (s, 2 H), 3.97 (dd, J = 11.6 and 3.6 Hz, 1 H), 3.84 (d, J = 1.6 Hz, 1 H), 3.76 (dd, J = 11.6 and 4.8 Hz, 1 H), 3.29−3.26 (m, 1 H), 2.34 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 136.6, 131.6, 128.5, 128.4, 128.2, 125.5, 119.2, 86.8, 83.7, 69.3, 60.9, 59.3, 55.9, 21.4. IR (KBr, neat) 2922, 2851, 1256, 1098, 1073, 749, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}O_2$ (M + H)$^+$ 279.1385, found 279.1387.

*2-Methyl-3-phenyl-2-(((3-phenylprop-2-yn-1-yl)oxy)methyl)-oxirane (**1c**).* Colorless oil; R_f (hexane/EtOAc 9:1) 0.50; yield 242 mg, 87%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47- 7.26 (m, 10 H), 4.49 (s, 2 H), 4.23 (s, 1 H), 3.79 (d, J = 10.8 Hz, 1 H), 3.75 (d, J = 10.8 Hz, 1 H), 1.15 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.8, 132.0, 128.6, 128.5, 128.3, 127.9, 126.6, 122.7, 86.9, 85.0, 73.9, 62.1, 61.5, 59.2, 20.3; IR (KBr, neat) 2926, 2853, 1490, 1255, 1092, 1027, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}O_2$ (M + H)$^+$ 279.1385, found 279.1386.

*2-Methyl-2-(((3-phenylprop-2-yn-1-yl)oxy)methyl)oxirane (**1d**).* Colorless oil; R_f (hexane/EtOAc 9:1) 0.60; Yield 186 mg, 92%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45- 7.31 (m, 5 H), 4.43 (d, J = 2.4 Hz, 2 H), 3.69 (d, J = 11.2 Hz, 1 H), 3.58 (d, J = 11.2 Hz, 1 H), 2.81 (d, J = 4.8 Hz, 1 H), 2.64 (d, J = 4.8 Hz, 1 H), 1.42 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 131.9, 128.7, 128.5, 122.7, 86.7, 84.9, 73.2, 59.4, 56.0, 51.8, 18.7; IR (KBr, neat) 2916, 2848, 1255, 1095, 757 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2$ (M + H)$^+$ 203.1072, found 203.1069.

*2-Phenyl-2-(((3-phenylprop-2-yn-1-yl)oxy)methyl)oxirane (**1e**).* Colorless oil; R_f (hexane/EtOAc 9:1): 0.50; Yield 248 mg, 94%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58−7.15 (m, 10 H), 4.47 (s, 2 H), 4.20 (d, J = 11.4 Hz, 1 H), 3.95 (d, J = 11.4 Hz, 1 H), 3.20 (d, J = 5.4 Hz, 1 H), 2.83 (d, J = 5.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 131.7, 128.5, 128.4, 128.3, 127.4, 126.2, 122.4, 86.6, 84.6, 71.4, 59.3, 58.8, 53.3; IR (KBr, neat) 2925, 2854, 1490, 1256, 1098, 1027, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{17}O_2$ (M + H)$^+$ 265.1229, found 265.1228.

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*2-((But-2-yn-1-yloxy)methyl)-3-phenyloxirane (**1f**).* Colorless oil; R_f (hexane/EtOAc 9:1): 0.50; Yield 213 mg, 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.26 (m, 5 H), 4.21 (s, 2 H), 3.87 (dd, J = 11.6 and 3.2 Hz, 1 H), 3.82 (brs, 1 H), 3.67 (dd, J = 11.6 and 4.8 Hz, 1 H), 3.24 (t, J = 2.4 Hz, 1 H), 1.85 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.5, 128.3, 125.7, 83.0, 74.8, 69.2, 60.8, 59.1, 55.9, 3.6; IR (KBr, neat) 2920, 1497, 1461, 1357, 1139, 1095, 1023, 698 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{13}H_{14}O_2$ (M + Na)$^+$ 225.0886, found 225.0885.

*2-Phenyl-3-((undec-2-yn-1-yloxy)methyl)oxirane (**1g**).* Colorless oil; R_f (hexane/EtOAc 9:1): 0.60; Yield 276 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.25 (m, 5 H), 4.23 (s, 2 H), 3.87 (d, J = 11.2 Hz, 1 H), 3.81 (s, 1 H), 3.68 (dd, J = 11.2 and 5.2 Hz, 1 H), 3.23 (d, J = 1.6 Hz, 1 H), 2.21 (t, J = 5.6 Hz, 2 H), 1.54−1.47 (m, 2 H), 1.41−1.20 (m, 10 H), 0.87 (t, J = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 128.6, 128.3, 125.8, 87.8, 75.5, 69.2, 60.9, 59.2, 56.1, 31.9, 29.5, 29.2, 29.0, 28.7, 22.8, 18.9, 14. 2; IR (KBr, neat) 2927, 2855, 1461, 1357,1137, 1095, 750, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{29}O_2$ (M + H)$^+$ 301.2162, found 301.2158.

*2-Methyl-3-(((3-(p-tolyl)prop-2-yn-1-yl)oxy)methyl)oxirane (**1i**).* Colorless oil; R_f (hexane/EtOAc 9:1) 0.50; yield 194 mg, 90%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 4.41 (d, J = 9.6 Hz, 2 H), 3.80 (dd, J = 10.8 and 3.0 Hz, 1 H), 3.60 (dd, J = 11.4 and 5.4 Hz, 1 H), 2.93−2.97 (m, 2 H), 2.34 (s, 3 H), 1.33 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.7, 131.7, 129.1, 119.4, 86.8, 83.9, 69.9, 59.3, 57.6, 52.3, 21.5, 17.3; IR (KBr, neat) 2924, 2855, 1510, 1356, 1258, 1120, 1091, 817, 753 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{17}O_2$ (M + H)$^+$ 217.1229, found 217.1227.

*2-Phenyl-3-(((3-(thiophen-2-yl)prop-2-yn-1-yl)oxy)methyl)-oxirane (**1j**).* Colorless oil; R_f (hexane/EtOAc 9:1) 0.50; yield 238 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.22 (m, 7 H), 6.99−6.96 (dd, J = 4.8 and 3.6 Hz, 1 H), 4.50 (s, 2 H), 3.97 (dd, J = 11.2 and 3.2 Hz, 1 H), 3.85 (d, J = 1.6 Hz, 1 H), 3.75 (dd, J = 11.2 and 4.8 Hz, 1 H), 3.29−3.26 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.7, 128.6, 128.4, 127.6, 127.1, 125.8, 122.4, 88.8, 80.1, 69.5, 60.9, 59.5, 56.0; IR (KBr, neat) 2923, 2854, 1674, 1463, 1359, 1190, 1098, 848, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{15}O_2S$ (M + H)$^+$ 271.0787, found 271.0789.

General Procedure for the Synthesis of N-Tethered Compounds. To an oven-dried round-bottom flask with magnetic stir bar were added allyl bromide (1.1 equiv), 4-methylbenzenesulfonamide (1 equiv), K_2CO_3 (2 equiv), and acetone (20 mL). The round-bottom flask was heated at 60 °C. Upon completion of the reaction (16 h), the solution was cooled to room temperature, filtered through a short plug of Celite, and washed with EtOAc, and solvent was removed in vacuo to afford a crude product. Purification of the resulting crude residue via silica gel flash column chromatography afforded the desired *N*-toysl allylic amine. In an oven-dried round-bottom flask was taken NaH (1.5 equiv), and dry THF (20 mL) was added to it. To this a solution of *N*-tosyl allylic amine (1 equiv) or its derivatives was added slowly. The reaction mixture was stirred for 0.5 h at 0 °C. Propargyl bromide (1 equiv) was added to the reaction mixture dropwise. The reaction was monitored by thin layer chromatography, and after completion of the reaction THF was removed by evaporation. The residue was extracted with ethyl acetate (30 mL) and washed with water and brine solution (20 mL × 2). The organic layer was dried over anhydrous Na_2SO_4, and solvent was evaporated using a rotary evaporator to obtain crude product. The crude product was purified by silica gel column chromatography using ethyl acetate and hexane as eluents to give the N-tethered product. The product (1.0 equiv) thus obtained was treated with *m*-chloroperbenzoic acid (1.5 equiv) in dichloromethane at 0 °C. The reaction mixture was brought to room temperature and stirred for a specific time. After completion of the reaction as determined by TLC, a saturated aqueous solution of Na_2SO_3 was added to quench excess *m*CPBA. Dichloromethane (30 mL) was added to the reaction mixture, washed with saturated sodium bicarbonate and brine solution, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified by neutral alumina using ethyl acetate and hexane as eluents.

*4-Methyl-N-((2-methyloxiran-2-yl)methyl)-N-(undec-2-yn-1-yl)-benzenesulfonamide (**1k**).* Colorless oil; R_f (hexane/EtOAc 9:1) 0.45; yield 352 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.2 Hz, 2 H), 7.26 (d, J = 7.2 Hz, 2 H), 4.23 (d, J = 18.4 Hz, 1 H), 4.12 (d, J = 18.4 Hz, 1 H), 3.28 (s, 2 H), 2.75 (d, J = 4.4 Hz, 1 H), 2.62 (d, J = 3.6 Hz, 1 H), 2.39 (s, 3 H), 1.82 (t, J = 6.0 Hz, 2 H), 1.39 (s, 3 H), 1.28−1.14 (m, 12 H), 0.87 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.2, 129.5, 128.0, 86.7, 72.3, 55.7, 51.9, 50.9, 38.4, 32.0, 29.3, 29.2, 28.9, 28.4, 22.8, 21.6, 19.0, 18.6, 14.3; IR (KBr, neat) 2927, 2856, 1442, 1351, 1164, 1090, 1047, 658 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{34}NO_3S$ (M + H)$^+$ 392.2254, found 392.2261.

*4-Methyl-N-((3-phenyloxiran-2-yl)methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1l**).* Colorless oil; R_f (hexane/EtOAc 4:1) 0.40; yield 342 mg, 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2 H), 7.35−7.21 (m, 10 H), 7.06 (d, J = 7.2 Hz, 2 H), 4.52 (d, J = 18.6 Hz, 1 H), 4.44 (d, J = 18.6 Hz, 1 H), 3.74 (d, J = 2.4 Hz, 1 H), 3.58 (d, J = 3.6 Hz, 2 H), 3.26 (dt, J = 4.8 and 4.2 Hz, 1 H), 2.34 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.8, 136.3, 135.8, 131.5, 129.6, 128.6, 128.5, 128.4, 128.2, 127.8, 125.7, 122.0, 86.0, 81.7, 60.5, 57.0, 48.0, 39.0, 21.4; IR (KBr, neat) 2922, 2851, 1643, 1447, 1383, 1265 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{24}NO_3S$ (M + H)$^+$ 418.1477, found 418.1474.

*4-Methyl-N-((3-phenyloxiran-2-yl)methyl)-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (**1m**).* Colorless oil; R_f (hexane/EtOAc 4:1) 0.45; yield 357 mg, 83%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2 H), 7.27−7.11 (m, 7 H), 6.96 (d, J = 8.4 Hz, 2 H), 6.88 (d, J = 8.4 Hz, 2 H), 4.44 (d, J = 18.0 Hz, 1 H), 4.34 (d, J = 18.0 Hz, 1 H), 3.74 (d, J = 1.2 Hz, 1 H), 3.50 (dd, J = 12.0 and 4.8 Hz, 2 H), 3.17 (dt, J = 5.4 and 4.2 Hz, 1 H), 2.27 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9, 138.9, 136.5, 131.6, 129.8, 129.1, 128.7, 128.6, 127.6, 127.5, 125.8, 119.2, 86.3, 81.2, 60.6, 57.3, 48.2, 39.2, 21.7 (2C); IR (KBr, neat) 2922, 2851, 1462, 1349, 1163, 1090, 843, 744 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{26}NO_3S$ (M + H)$^+$ 432.1633, found 432.1639.

*4-Methyl-N-((2-phenyloxiran-2-yl)methyl)-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (**1n**).* Colorless oil; R_f (hexane/EtOAc 4:1) 0.50; yield 371 mg, 89%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2 H), 7.48 (d, J = 8.4 Hz, 2 H), 7.38 (t, J = 8.4 Hz, 3 H), 7.25- 7.19 (m, 5 H), 7.00 (d, J = 8.4 Hz, 2 H), 4.38 (brs, 2 H), 3.97 (d, J = 15 Hz, 1 H), 3.74 (d, J = 15.0 Hz, 1 H), 3.27 (d, J = 5.4 Hz, 1 H), 2.83 (d, J = 5.4 Hz, 1 H), 2.32 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9, 137.6, 136.2, 131.7, 129.8, 128.7, 128.6, 128.4, 128.3, 128.1, 126.5, 122.4, 86.0, 82.0, 59.4, 53.3, 49.5, 39.2, 21.6; IR (KBr, neat) 2923, 2853, 1447, 1350, 1161, 1027, 757, 696 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{24}NO_3S$ (M + H)$^+$ 418.1477, found 418.1476.

*4-Methyl-N-((2-methyloxiran-2-yl)methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1o**).* Colorless oil; R_f (hexane/EtOAc 4:1) 0.50; yield 298 mg, 84%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2 H), 7.34- 7.20 (m, 5 H), 7.00 (d, J = 8.1 Hz, 2 H), 4.48 (d, J = 18.6 Hz, 2 H), 4.40 (d, J = 18.6 Hz, 1 H), 3.39 (d,, J = 13.2 Hz, 2 H), 2.82 (d, J = 4.8 Hz, 1 H), 2.67 (d, J = 4.8 Hz, 1 H), 2.33 (s, 3 H), 1.45 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 135.8, 131.4, 129.5, 128.4, 128.0, 127.7, 122.0, 85.8, 81.5, 55.7, 51.6, 50.9, 38.6, 21.4, 18.9. IR (KBr, neat) 2923, 2853, 1491, 1349, 1162, 1090, 1027, 757 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{22}NO_3S$ (M + H)$^+$ 356.1320, found 356.1315.

*4-Methyl-N-((2-methyloxiran-2-yl)methyl-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (**1p**).* Colorless oil; R_f (hexane/EtOAc 4:1) 0.50; yield 306 mg, 83%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H), 7.02 (d, J = 8.0 Hz, 2 H), 6.91 (d, J = 8.0 Hz, 2 H), 4.47 (d, J = 18.6 Hz, 1 H), 4.39 (d, J = 18.6 Hz, 1 H), 3.39 (s, 2 H), 2.81 (d, J = 4.2 Hz, 1 H), 2.66 (d, J = 4.8 Hz, 1 H), 2.33 (s, 3 H), 2.32 (s, 3 H), 1.43 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 138.6, 136.0, 131.4, 129.6, 128.8, 127.8, 119.0, 86.0, 80.9, 55.7, 51.7, 51.0, 38.7, 21.4 (2C), 19.0; IR (KBr, neat) 2921, 2851, 1348, 1162, 1090, 1039, 844, 743 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{24}NO_3S$ (M + H)$^+$ 370.1477, found 370.1476.

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*N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-N-((2-methyloxiran-2-yl)methyl)benzenesulfonamide (**1q**).* Colorless oil; R_f (hexane/EtOAc 4:1) 0.50; yield 315 mg, 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H), 6.96 (d, J = 8.4 Hz, 2 H), 6.75 (d, J = 8.4 Hz, 2 H), 4.46 (d, J = 18.6 Hz, 1 H), 4.37 (d, J = 18.6 Hz, 1 H), 3.78 (s, 3 H), 3.38 (s, 2 H), 2.82 (d, J = 4.8 Hz, 1 H), 2.66 (d, J = 4.8 Hz, 1 H), 2.34 (s, 3 H), 1.44 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 143.8, 136.2, 133.1, 130.1, 129.7, 114.4, 113.9, 85.9, 80.4, 55.9, 55.5, 51.9, 51.2, 38.9, 21.6, 19.1; IR (KBr, neat) 2923, 2850, 1606, 1509, 1348, 1248, 1162, 1031, 750 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{24}NO_4S$ $(M + H)^+$ 386.1426, found 386.1422.

General Procedure for Lewis Acid Catalyzed Intramolecular C−C Bond Formation of Alkyne-Epoxide. To a corresponding alkyne-epoxide substrates (1.0 equiv) in CH_2Cl_2 (5 mL) at 0 °C was added $BF_3{\cdot}Et_2O$ (0.2 equiv) dropwise, and the reaction mixture was brought to room temperature. The reaction was continued for a specified time and monitored by TLC. After completion of the reaction, the reaction mixture was treated with saturated sodium bicarbonate solution (5 mL). The product was extracted with CH_2Cl_2 (2 × 10 mL) and washed with brine. Organic layer was separated and dried over anhydrous Na_2SO_4 and evaporated using rotary evaporator to obtain the crude product. The crude product was purified by silica gel column chromatography using ethyl acetate and hexane as eluents to afford the cyclic compounds **2**.

*Phenyl(4-phenyl-3,6-dihydro-2H-pyran-3-yl)methanone (**2a**).* Colorless solid; mp 111−112 °C; R_f (hexane/EtOAc 9:1) 0.50; Yield 179 mg, 68%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 7.6 Hz, 1 H), 7.51 (t, J = 7.8 Hz, 1 H), 7.43−7.40 (m, 3 H), 7.34−7.31 (m, 3 H), 7.27 (t, J = 7.8 Hz, 1 H), 7.22 (d, J = 7.8 Hz, 1 H), 6.73 (dd, J = 1.8 and 1.2 Hz, 1 H), 4.63 (dd, J = 2.4 and 1.8 Hz, 2 H), 4.12 (dd, J = 11.4 and 5.4 Hz, 1 H), 3.78−3.74 (m, 1 H), 3.63 (dd, J = 11.4 and 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 143.0, 140.1, 137.7, 137.5, 132.2, 129.3, 129.0, 128.5, 128.3, 127.5, 70.6, 65.4, 42.1; IR (KBr, neat) 2923, 2852, 1640, 1447, 1265, 1105, 1047, 742, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{17}O_2$ $(M + H)^+$ 265.1229 found 265.1229.

*(4-Phenyl-3,6-dihydro-2H-pyran-3-yl)(p-tolyl)methanone (**2b**).* Yellow oil; R_f (hexane/EtOAc 9:1) 0.50; yield 197 mg, 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1 H), 7.35- 7.21 (m, 8 H), 6.71 (dd, J = 2.8 and 1.6 Hz,1 H), 4.62 (dd, J = 2.8 and 2.0 Hz, 2 H), 4.12 (dd, J = 11.2 and 5.6 Hz, 1 H), 3.78−3.74 (m, 1 H), 3.63 (dd, J = 11.2 and 7.2 Hz, 1 H), 2.38 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 142.1, 140.3, 137.9, 134.8, 130.6, 129.6, 129.4, 129.2, 128.4, 127.5, 70.7, 65.5, 42.1, 21.7; IR (KBr, neat) 2924, 2852, 1641, 1454, 1264, 1106, 759, 7001 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}O_2$ $(M + H)^+$ 279.1385, found 279.1384.

*(5-Methyl-4-phenyl-3,6-dihydro-2H-pyran-3-yl)(phenyl)-methanone (**2c**).* Yellow oil; R_f (hexane/EtOAc 9:1) 0.50; yield 172 mg, 62%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.4 Hz, 1 H), 7.59−7.26 (m, 9 H), 4.48−4.38 (m, 2 H), 4.07 (dd, J = 11.2 and 4.4 Hz, 1 H), 3.87 (dd, J = 11.2 and 4.0 Hz, 1 H), 3.33 (brs, 1 H), 1.45 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 141.4, 137.3, 135.5, 133.8, 133.7, 129.4, 129.1, 128.9, 128.8, 127.3, 71.4, 66.9, 46.5, 19.7; IR (KBr, neat) 2923, 2852, 1641, 1447, 1265, 1105, 1047, 742, 701 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}O_2$ $(M + H)^+$ 279.1385, found 279.1383.

*(5-Methyl-5,6-dihydro-2H-pyran-3-yl)(phenyl)methanone (**2d**).* Yellow oil; R_f (hexane/EtOAc 9:1) 0.50; yield 131 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.65 (m, 2 H), 7.56−7.52 (m, 1 H), 7.47−7.43 (m, 2 H), 6.54 (brs, 1 H), 4.49 (dd, J = 12.0 and 2.0 Hz, 2 H), 3.95 (dd, J = 10.8 and 5.6 Hz, 1 H), 3.34 (dd, J = 10.8 and 7.2 Hz, 1 H), 2.63−2.58 (m, 1 H), 1.06 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 146.0, 137.8, 136.9, 132.0, 129.3, 128.4, 70.1, 65.3, 30.3, 16.7; IR (KBr, neat) 2924, 2852, 1641, 1447, 1264, 1111, 1024, 820, 711 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2$ $(M + H)^+$ 203.1072, found 203.1074.

*1-(5-Phenyl-5,6-dihydro-2H-pyran-3-yl)ethanone (**2f**).* Yellow oil; R_f (hexane/EtOAc 9:1) 0.40; yield 166 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.387.34 (m, 2 H), 7.32−7.29 (m, 1 H), 7.26−7.22 (m, 2 H), 6.98 (brs, 1 H), 4.48 (d, J = 16.8 Hz, 1 H), 4.42 (d, J = 16.8 Hz, 1 H), 4.06 (dd, J = 11.6 and 5.2 Hz, 1 H), 3.74−3.69 (m, 1 H), 3.56 (dd, J = 10.8 and 7.6 Hz, 1 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 140.5, 140.1, 138.6, 129.0, 128.3, 127.5, 70.2, 64.6, 41.9, 25.2; IR (KBr, neat) 2922, 2850, 1667, 1389, 1239, 1107, 701 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{14}O_2$ $(M + Na)^+$ 225.0886, found 225.0871.

*1-(5-Phenyl-5,6-dihydro-2H-pyran-3-yl)nonan-1-one (**2g**).* Yellow oil; R_f (hexane/EtOAc 9:1) 0.50; yield 228 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.33 (m, 2 H), 7.30−7.27 (m, 1 H), 7.23−7.20 (m, 2 H), 6.97 (brs, 1 H), 4.47 (d, J = 16.4 Hz, 1 H), 4.39 (d, J = 16.4 Hz, 1 H), 4.04 (dd, J = 13.6 and 5.6 Hz, 1 H), 3.74−3.66 (m, 1 H), 3.53 (dd, J = 10.8 and 7.2 Hz, 1 H), 2.65 (t, J = 16.4 Hz, 2 H), 1.65−1.58 (m, 2 H), 1.32−1.20 (m, 10 H), 0.87 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 140.2, 139.2, 138.2, 129.0, 128.3, 127.5, 70.4, 64.8, 41.9, 37.2, 32.0, 29.5, 29.4, 29.3, 24.7, 22.8, 14.3; IR (KBr, neat) 2925, 2854, 1667, 1454, 1108, 1024, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{29}O_2$ $(M + H)^+$ 301.2162, found 301.2168.

*(5-Phenyl-5,6-dihydro-2H-pyran-3-yl)(thiophen-2-yl)methanone (**2j**).* Pale yellow oil; R_f (hexane/EtOAc 9:1) 0.40; yield 163 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.64 (m, 2 H), 7.41−7.34 (m, 2 H), 7.31−7.27 (m, 3 H), 7.11 (t, J = 3.6 Hz, 1 H), 6.95 (brs, 1 H), 4.60 (brs, 2 H), 4.13 (dd, J = 11.2 Hz, 1 H), 3.82−3.75 (m, 1 H), 3.64 (dd, J = 11.2 and 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 142.7, 140.3, 139.8, 138.2, 133.9, 133.6, 129.1, 128.4, 128.1, 127.6, 70.7, 65.4, 42.0; IR (KBr, neat) 2957, 2824, 1621, 1414, 1121, 1052, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{15}O_2S$ $(M + H)^+$ 271.0787, found 271.0790.

*1-(5-Methyl-1-tosyl-3,4-dehydropiperidin-3-yl)nonan-1-one (**2k**).* Yellow oil; R_f (hexane/EtOAc 9:1) 0.40; yield 301 mg, 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2 H), 7.31 (d, J = 7.6 Hz, 2 H), 6.70 (brs, 1 H), 3.90 (d, J = 16.8 Hz, 1 H), 3.48 (d, J = 18.0 Hz, 1 H), 3.43 (dd, J = 11.6 and 4.4 Hz, 1 H), 2.72−2.64 (m, 1 H), 2.58 (t, J = 6.8 Hz, 2 H), 2.49 (dd, J = 11.2 and 7.6 Hz, 1 H), 2.41 (s, 3 H), 1.58−1.50 (m, 2 H), 1.30−1.18 (m, 10 H), 1.11 (d, J = 7.2 Hz, 3 H), 0.86 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 143.8, 142.3, 134.8, 133.1, 129.9, 127.8, 48.7, 43.8, 36.9, 31.8, 31.2, 29.4, 29.3, 29.2, 24.5, 22.7, 21.6, 17.7, 14.1; IR (KBr, neat) 2925, 2854, 1667, 1459, 1348, 1166, 1025, 657 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{34}NO_3S$ $(M + H)^+$ 392.2254, found 392.2258.

*Phenyl(4-phenyl-1-tosyl-3,4- dehydropiperidin-3-yl)methanone (**2l**).* Yellow oil; (hexane/EtOAc 4:1) 0.30; yield 250 mg, 60%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2 H), 7.62 (d, J = 7.8 Hz, 2 H), 7.42−7.27 (m, 8 H), 7.15 (d, J = 7.8 Hz, 2 H), 6.63 (s, 1 H), 4.35 (dd, J = 18.0 and 1.8 Hz, 1 H), 3.95−3.89 (m, 2 H), 3.75 (d, J = 16.8 Hz, 1 H), 2.67 (dd, J = 10.8 and 7.2 Hz, 1 H), 2.43 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.4, 143.9, 139.3, 137.1, 135.3, 132.2, 130.9, 129.9, 129.4, 128.5, 127.9, 127.7, 127.3, 124.4, 114.1, 49.6, 44.5, 42.8, 21.5; IR (KBr, neat) 2922, 2852, 1643, 1163, 1090, 1039, 1026, 761, 670 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{24}NO_3S$ $(M + H)^+$ 418.1477, found 418.1477.

*(4-Phenyl-1-tosyl-3,4-dehydropiperidin-3-yl)(p-tolyl)methanone (**2m**).* Yellow oil; R_f (hexane/EtOAc 4:1) 0.35; yield 263 mg, 61%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.36−7.27 (m, 5 H), 7.20 (d, J = 8.4 Hz, 2 H), 7.15 (d, J = 8.4 Hz, 2 H), 6.60 (brs, 1 H), 4.34 (dd, J = 16.8 and 1.8 Hz, 1 H), 3.95−3.88 (m, 2 H), 3.74(d, J = 16.8 Hz, 1 H), 2.64 (dd, J = 12.0 and 7.2 Hz, 1 H), 2.43 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 144.1, 143.3, 142.7, 139.5, 135.6, 134.6, 130.1, 129.6, 129.5, 129.3, 129.2, 128.2, 128.0, 114.3, 49.9, 44.8, 42.9, 22.8 (2C); IR (KBr, neat) 2923, 2853, 1642, 1454, 1348, 1166, 1091, 701 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{26}NO_3S$ $(M + H)^+$ 432.1633, found 432.1632.

*(5-Methyl-1-tosyl-3,4-dehydropiperidin-3-yl)(phenyl)methanone (**2o**).* Yellow oil; R_f (hexane/EtOAc 4:1) 0.50; yield 277 mg, 78%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 7.8 Hz, 2 H), 7.53 (t, J = 7.2 Hz, 1 H), 7.43 (t, J = 7.8 Hz, 2 H), 7.35 (d, J = 7.8 Hz, 2 H), 6.45 (d, J = 4.2 Hz, 1 H), 4.09 (d, J = 16.2 Hz, 1 H), 3.74 (dt, J = 16.8 and 2.4 Hz, 1 H), 3.53 (dd, J = 11.4 and 5.4 Hz, 1 H), 2.71−2.76 (m,1 H), 2.58 (dd, J = 11.4 and 7.8 Hz, 1 H), 2.44 (s, 3

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H), 1.10 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 146.3, 143.7, 137.2, 132.8, 131.4, 129.9, 129.6, 128.7, 128.0, 127.5, 48.7, 44.3, 31.1, 21.5, 17.5; IR (KBr, neat) 2964, 2926, 1644, 1346, 1167, 1091, 713 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{22}NO_3S$ $(M + H)^+$ 356.1320, found 356.1314.

*(5-Methyl-1-tosyl-3,4-dehydropiperidin-3-yl)(p-tolyl)methanone (**2p**).* Yellow oil; R_f (hexane/EtOAc 4:1) 0.4; yield 278 mg, 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2 H), 7.51 (d, J = 8.4 Hz, 2 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.23 (d, J = 8.4 Hz, 2 H), 6.42 (d, J = 3.0 Hz, 1 H), 4.08 (d, J = 16.8 Hz, 1 H), 3.74 (dt, J = 16.8 and 2.4 Hz, 1 H), 3.53 (dd, J = 11.4 and 5.4 Hz, 1 H), 2.70−2.78 (m, 1 H), 2.57 (dd, J = 11.4 and 7.2 Hz, 1 H), 2.43 (s, 3 H), 2.41 (s, 3 H), 1.09 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.4, 145.6, 144.0, 143.1, 134.8, 134.2, 133.4, 130.0, 129.6, 129.2, 128.0, 49.0, 44.7, 31.4, 21.8, 21.7, 17.9; IR (KBr, neat) 2925, 2854, 1727, 1643, 1605, 1347, 1167, 1091, 745 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{24}NO_3S$ $(M + H)^+$ 370.1477, found 370.1477.

*(4-Methoxyphenyl)(5-methyl-1-tosyl-3,4-dehydropiperidin-3-yl)-methanone (**2q**).* Yellow oil; R_f (hexane/EtOAc 4:1) 0.35; yield 281 mg, 73%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2 H), 7.64 (d, J = 8.1 Hz, 2 H), 7.34 (d, J = 7.8 Hz, 2 H), 6.91 (d, J = 8.1 Hz, 2 H), 6.38 (d, J = 3.6 Hz, 1 H), 4.07 (d, J = 16.2 Hz, 1 H), 3.87 (s, 3 H), 3.67 (dt, J = 16.8 and 2.4 Hz, 1 H), 3.54 (dd, J = 11.4 and 5.4 Hz, 1 H), 2.70−76 (m, 1 H), 2.56 (dd, J = 11.4 and 7.2 Hz, 1 H), 2.43 (s, 3 H), 1.10 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.4, 163.3, 144.3, 144.0, 134.2, 133.4, 131.8, 130.0, 129.9, 128.0, 113.8, 55.7, 49.1, 44.9, 31.3, 21 0.7, 17.9; IR (KBr, neat) 2918, 2849, 1640, 1598, 1256, 1165, 1091, 1028, 842, 746 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{24}NO_4S$ $(M + H)^+$ 386.1426, found 386.1421.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR and HRMS spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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