Supporting information

***tert*-Butyl (phenylsulfonyl)alkyl-*N*-hydroxycarbamates : The First Class of *N*-(Boc) Nitron Equivalents**

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Tools, Reagents, Solvents and Procedures

^1H NMR-Spectra (200 or 300 MHz), and **^{13}C NMR-spectra** (75.5 MHz) spectra were recorded on either a Brüker AC200 or an Advance300 spectrometers. Chemical shifts are given in ppm (δ) and were referenced to the internal solvent signal or to TMS used as an internal standard. Multiplicities are declared as follow: *s* (singlet), *br s* (broad singlet), *d* (doublet), *t* (triplet), *q* (quadruplet), *quint* (quintuplet), *sept* (septet), *dd* (doublet of doublet), *ddd* (doublet of doublet of doublet), *dt* (doublet of triplet), *m* (multiplet). Coupling constants *J* are given in Hz.

Infrared spectra (IR) were obtained either as neat films on sodium chloride discs or in potassium bromide plates. All IR spectra were recorded on a Nicolet Impact-400 Fourier transform infrared spectrometer (FTIR) and the data are reported in reciprocal centimetres (cm^{-1}).

Melting points were determined with a Büchi B35 apparatus or a Kofler bank and were uncorrected.

Mass spectra (LRMS) were recorded on a Brüker Esquire 3000 plus (ESI) or a ThermoFinnigan PolarisQ ion-trap spectrometer, using DCI (ammonia/isobutane 63/37). Exact Mass spectra (HRMS) were recorded at the “Service Central d’Analyses du CNRS”, Vernaison, France or at the “Centre Régional de Mesures Physiques de l’Ouest”, Rennes, France.

Elemental analyses were performed at the “Service Central d’Analyses du CNRS”, Vernaison, France.

Reactions were performed using oven dried glasswares under an atmosphere of dry argon. They were monitored by thin layer chromatography (TLC) using commercial aluminium-backed silica gel plates (Merck, Kieselgel 60 PF_{254}). TLC spots were viewed under ultraviolet light and by heating the plate after treatment with an appropriate revelatory (ninhydrin, KMnO_4 , TTC).

Chromatography purifications were performed by gravity column chromatography using Macherey-Nagel Silica Gel 60 (70-230 mesh).

Solvents: Tetrahydrofuran and diethyl ether were refluxed on sodium-benzophenone and then distilled. Dichloromethane and methanol were dried by refluxing on CaH_2 and then distilled. Unless otherwise noted, all reagent-grade chemicals and solvents were obtained from commercial suppliers (Sigma-Aldrich, Acros Organics and Avocado) and were used as received.

Preparation of *tert*-butyl (phenylsulfonyl)alkyl-*N*-hydroxycarbamates 1

General procedure

Sodium benzenesulfinate (3.08 g, 18.8 mmol) was dissolved into 22.5 mL of a mixture of water/methanol (2/1) (except when mentioned, reaction was carried out in THF/water 1/1). To this solution was added sequentially *tert*-butyl-*N*-hydroxycarbamate (1 g, 7.52 mmol), the appropriate aldehyde (15.04 mmol) and then formic acid (0.57 mL, 15.04 mmol). This solution was stirred for 20 hours at room temperature. The resulting white precipitate was collected by filtration and washed with water and pentane. The obtained white solid was then dried under reduce pressure and used either without further purification or after recrystallisation.

- *tert*-Butyl (phenylsulfonyl)methyl-*N*-hydroxycarbamate 1^a

Prepared according to the above procedure from a solution of 230 mg (610 mg solution 37% wt in water, 7.52 mmol) of formaldehyde, 500 mg (3.76 mmol) of *tert*-butyl-*N*-hydroxycarbamate, 1.54 g (9.40 mmol) of sodium benzenesulfinate, and 190 mg (4.51 mmol) of formic acid in 3.7 mL of methanol and 7.4 mL of water. After filtration, the sulfone was collected as a white solid (960 mg, 3.35 mmol) and recrystallized from hexane/EtOAc (3:1).

Yield: 89%. **Mp:** 120 °C. **IR (KBr):** 3360, 3011, 2981, 2928, 2909, 1714, 1471, 1449, 1399, 1365, 1312, 1289, 1225, 1157, 1096, 1081, 902, 751 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 1.31 (s, 9H, C(CH₃)₃), 4.90 (s, 2H, CH₂), 7.50-7.75 (m, 3H, H arom.), 7.82 (br s, 1H, OH), 7.90-8.05 (m, 2H, H arom.). **¹³C NMR (acetone, 75.5 MHz):** δ= 28.0 (C(CH₃)₃), 72.3 (CH₂), 82.3 (C(CH₃)₃), 129.6 (CH arom.), 130.0 (CH arom.), 134.6 (CH arom.), 140.3 (C arom.), 155.1 (C=O). **LRMS (ESI):** m/z= 288 [(M+H)⁺]. **Anal. Calcd for C₁₂H₁₇NO₅S:** C, 50.17; H, 5.97; N, 4.88. **Found:** C, 50.03; H, 6.17; N, 4.80.

- ***tert*-Butyl 1-(phenylsulfonyl)ethyl-*N*-hydroxycarbamate 1b**

Prepared according to the above procedure from 660 mg (15.04 mmol) of acetaldehyde. Reaction was carried out in THF/H₂O. After filtration, the sulfone was collected as a white solid (1.69 g, 5.64 mmol) and recrystallized from EtOAc.

Yield: 75%. **Mp:** 124 °C. **IR (KBr):** 3334, 2983, 2935, 1711, 1474, 1445, 1364, 1293, 1250, 1146, 1127, 1046, 866 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 1.33 (s, 9H, C(CH₃)₃), 1.68 (d, *J*= 7.1 Hz, 3H, CH₃), 5.31 (q, *J*= 6.8 Hz, 1H, CHN), 6.92 (br s, 1H, OH), 7.50-7.60 (m, 2H, H arom.), 7.62-7.70 (m, 1H, CH arom.), 7.90-8.00 (m, 2H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 10.6 (CH₃), 27.9 (C(CH₃)₃), 83.4 (C(CH₃)₃), 124.9 (CHN), 129.0 (CH arom.), 129.1 (CH arom.), 129.4 (CH arom.), 134.0 (CH arom.), 137.2 (C arom.), 154.6 (C=O). **LRMS (ESI):** *m/z*= 324 [(M+Na)⁺], 341 [(nitron dimer+Na)⁺]. **Anal. Calcd for C₁₃H₁₉NO₅S:** C, 51.82; H, 6.36; N, 4.65. **Found:** C, 51.56; H, 6.55; N, 4.62.

- ***tert*-Butyl 1-(phenylsulfonyl)propyl-*N*-hydroxycarbamate 1c**

Prepared according to the above procedure from 872 mg (15.04 mmol) of propionaldehyde. After filtration, the sulfone was collected as a white solid (1.893 g, 6.00 mmol) and recrystallized from EtOAc.

Yield: 80%. **Mp:** 92-93 °C. **IR (KBr):** 3367, 3063, 2972, 1673, 1454, 1395, 1305, 1273, 1092, 1072, 852 cm⁻¹. **¹H RMN (CDCl₃, 300 MHz):** δ= 1.01 (t, *J*= 7.3 Hz, 3H, CH₃), 1.32 (s, 9H, C(CH₃)₃), 2.05-2.25 (m, 2H, CH₂), 4.90-5.15 (m, 1H, CHN), 7.45-7.60 (m, 2H, H arom.), 7.60-7.70 (m, 1H, H arom.), 7.90-8.00 (m, 2H, H arom.). **¹³C RMN (CDCl₃, 75.5 MHz):** δ= 10.5 (CH₃), 18.0 (CH₂), 28.3 (C(CH₃)₃), 83.8 (C(CH₃)₃), 125.3 (CHN), 129.3 (CH arom.), 129.4 (CH arom.), 129.7 (CH arom.), 134.3 (CH arom.), 138.0 (C arom.), 155.8 (C=O). **LRMS (ESI):** *m/z*= 653 [(dimer+Na)⁺], 369 [(nitron dimer+Na)⁺], 338 [(M+Na)⁺], 196 [(Nitron+Na)⁺]. **Anal. calcd for C₁₄H₂₁NO₅S:** C, 53.32; H, 6.71; N, 4.44. **Found:** C, 53.25; H, 6.54; N, 4.29.

- ***tert*-Butyl 3-methyl-1-(phenylsulfonyl)butyl-*N*-hydroxycarbamate 1d**

Prepared according to the above procedure from 1.293 g (1.61 mL, 15.04 mmol) of isovaleraldehyde. After filtration, the sulfone was collected as a white solid (2.55 g, 7.42 mmol) and recrystallized from EtOAc. When the reaction was performed with 1 equiv of aldehyde and 1.2 equiv of sodium benzenesulfinate, the yield decreased to 69%.

Yield: 99%. **Mp:** 102 °C. **IR (KBr):** 3347, 2959, 2934, 2869, 1667, 1434, 1395, 1369, 1318, 1260, 1150, 1085, 852, 755 cm⁻¹. **¹H RMN (CDCl₃, 300 MHz):** δ= 0.88 (d, *J*= 6.4 Hz, 3H, CH₃), 0.98 (d, *J*= 6.4 Hz, 3H, CH₃), 1.28 (s, 9H, C(CH₃)₃), 1.65-1.85 (m, 2H, CH₂), 2.12-2.32 (m, 1H, CHMe₂), 5.05-5.30 (m, 1H, CHN), 6.95 (br s, 1H, OH), 7.50-7.60 (m, 2H, H arom.), 7.60-7.68 (m, 1H, H arom.), 7.90-8.00 (m, 2H, H arom.). **¹³C RMN (CDCl₃, 75.5 MHz):** δ= 20.7 (CH₃), 23.1 (CH₃), 24.7 (CH), 27.8 (C(CH₃)₃), 31.7 (CH₂), 83.3 (C(CH₃)₃), 124.9 (CHN), 129.0 (CH arom.), 129.1 (CH arom.), 129.3 (CH arom.), 133.9 (CH arom.), 137.6 (C arom.), 154.5 (C=O). **LRMS (ESI):** *m/z*= 344 [(M+H)⁺], 318, 272. **HRMS (ESI) calcd for C₁₆H₂₅NO₅NaS:** 366.1351. **Found:** 366.1356 [(M+Na)⁺]. **Anal. Calcd for C₁₆H₂₅NO₅S:** C, 55.96; H, 7.34; N, 4.08. **Found:** C, 55.95; H, 7.42; N, 3.91.

- ***tert*-Butyl 3-phenyl-1-(phenylsulfonyl)propyl-*N*-hydroxycarbamate 1e**

Prepared according to the above procedure from 2.02 g (2.0 mL, 15.04 mmol) of 3-phenylpropionaldehyde. After filtration, the sulfone was collected as a white solid (2.21 g, 5.65 mmol) and recrystallized from EtOAc.

Yield: 75 %. **Mp:** 142 °C. **IR (KBr):** 3360, 3045, 2980, 2956, 2932, 1712, 1445, 1365, 1300, 1252, 1139, 1106 cm⁻¹. **¹H RMN (CDCl₃, 300 MHz):** 1.23 (s, 9H, C(CH₃)₃), 2.22-2.72 (m, 3H, H of CH₂), 2.72-3.00 (m, 1H, H of CH₂), 4.85-5.25 (m, 1H, CHN), 7.05-7.40 (m, 5H, H arom.), 7.40-7.75 (m, 3H, H arom.), 7.75-8.00 (m, 2H, H arom.). **¹³C RMN (CDCl₃, 75.5 MHz):** δ= 25.4 (CH₂), 27.7 (C(CH₃)₃), 31.2 (CH₂), 83.5 (C(CH₃)₃), 124.8 (CHN), 126.3 (CH arom.), 128.3 (CH arom.), 128.4 (CH arom.), 128.5 (CH arom.), 129.0 (CH arom.), 129.3 (CH arom.), 133.9 (CH arom.), 137.5 (C arom.), 139.5 (C arom.), 155.0 (C=O). **LRMS (ESI):** *m/z*= 414 [(M+Na)⁺], 318, 272. **HRMS (ESI) calcd for C₂₀H₂₅NO₅NaS:** 414.1351. **Found:** 414.1342 [(M+Na)⁺].

- ***tert*-Butyl 1-cyclohexyl-1-(phenylsulfonyl)methyl-*N*-hydroxycarbamate 1f**

Prepared according to the above procedure from 1.69 g (15.04 mmol) of cyclohexanecarboxaldehyde. Reaction was carried out in THF/H₂O. After filtration, the sulfone was collected as a white solid (2.45 g, 6.64 mmol) and recrystallized from EtOAc.

Yield: 91 %. **Mp:** 124 °C. **IR (KBr):** 3320, 3069, 2980, 2924, 2851, 1664, 1454, 1389, 1308, 1147, 1082, 847 cm⁻¹. **¹H NMR (acetone, 300 MHz):** δ= 1.29 (s, 9H, C(CH₃)₃), 1.40-1.50 (m, 3H, CH and CH₂), 1.55-1.65 (m, 4H, CH₂), 1.70-1.83 (m, 2H, CH₂), 2.20-2.40 (m, 2H, CH₂), 4.95-5.25 (m, 1H, CHN), 7.50-7.65 (m, 2H, H arom.), 7.65-7.78 (m, 1H, H arom.), 7.95-8.05 (m, 2H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 25.4 (CH₂), 25.6 (CH₂), 25.9 (CH₂), 27.9 (C(CH₃)₃), 29.7 (CH₂), 30.2 (CH₂), 35.6 (CH), 83.6 (C(CH₃)₃), 124.9 (CHN), 129.0 (CH arom.), 131.8 (CH arom.), 133.7 (CH arom.), 154.8 (C=O). **LRMS (ESI, MeOH):** m/z= 455 [(M-PhSO₂H dimer+H)⁺], 228 [(nitron+H)⁺]. **Anal. Calcd for C₁₈H₂₇NO₅S:** C, 58.51; H, 7.37; N, 3.79. **Found:** C, 58.53; H, 7.51; N, 3.80.

- ***tert*-Butyl 2-*N'*-(*tert*-butoxycarbonyl)amino-1-(phenylsulfonyl)ethyl-*N*-hydroxycarbamate 1g**

Prepared according to the above procedure from 1.18 g (7.52 mmol) of *N*-Boc aminoacetaldehyde. The reaction was performed during 48h. After filtration, the sulfone was collected as a white solid (1.02 g, 2.45 mmol) and engaged rapidly in following reaction.

Yield: 33 %. **Mp:** 123.5-124.5 °C. **IR (KBr):** 3360, 2988, 2932, 1712, 1672, 1526, 1373, 1324, 1155, 1114 cm⁻¹. **¹H RMN (CDCl₃, 300 MHz):** δ= 1.29 (s, 9H, C(CH₃)₃), 1.39 and 1.42 (2s, 9H, C(CH₃)₃), 3.65-4.05 (m, 2H, CH₂), 5.05-5.20 (m, 1H, CHN), 5.20-5.45 (m, 1H, NHBoc), 7.50-7.60 (m, 2H, H arom.), 7.60-7.70 (m, 1H, H arom.), 7.95-8.05 (m, 2H, H arom.). **¹³C RMN (CDCl₃, 75.5 MHz):** δ= 27.9 (C(CH₃)₃), 28.1 (C(CH₃)₃), 35.3 (CH₂), 81.2 (C(CH₃)₃), 82.4 (C(CH₃)₃), 124.8 (CHN), 129.0 (CH arom.), 129.4 (CH arom.), 134.1 (CH arom.), 137.4 (C arom.), 157.5 (C=O). **LRMS (ESI, 1% LiCl):** m/z= 423 [(M+Li)⁺], 839 [(dimer+Li)⁺]. **HRMS (EI) calcd for C₈H₁₄N₂O₅:** 218.0903. **Found:** 218.0879 [(M-PhSO₂H-*t*-Bu+H)⁺].

- ***tert*-Butyl 1-phenyl-1-(phenylsulfonyl)methyl-*N*-hydroxycarbamate 1h**

Prepared according to the above procedure from 1.60 g (15.04 mmol) of benzaldehyde. After filtration, the sulfone was collected as a white solid (660 mg, 1.12 mmol).

Yield: 25%. **Mp:** 132 °C. **IR (KBr):** 3339, 3068, 2985, 2946, 1666, 1422, 1391, 1370, 1311, 1148, 1116, 1085, 845 cm⁻¹. **¹H NMR (CDCl₃, 200 MHz):** δ= 1.42 (s, 9H, C(CH₃)₃), 6.28 (s, 1H, CHN), 7.30-7.50 (m, 5H, C₆H₅), 7.55-7.67 (m, 3H, SO₂C₆H₅), 7.70-7.81 (m, 2H, SO₂C₆H₅). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 27.9 (C(CH₃)₃), 84.2 (C(CH₃)₃), 124.9 (CHN), 128.5 (CH arom.), 128.8 (CH arom.), 129.0 (CH arom.), 129.1 (C arom.), 129.5 (CH arom.), 129.8 (CH arom.), 130.3 (CH arom.), 131.9 (CH arom.), 133.9 (CH arom.), 137.6 (C arom.), 155.2 (C=O). **LRMS (ESI, MeOH):** m/z= 276 [(*tert*-Butyl 1-phenyl-1-(methoxy)methyl-*N*-hydroxycarbamate+Na)⁺]. **HRMS (EI) calcd for C₁₂H₁₅NO₃:** 221.1052. **Found:** 221.1055 [(M-PhSO₂H+H)⁺].

- ***tert*-Butyl 3,7-dimethyl-1-(phenylsulfonyl)oct-6-enyl-*N*-hydroxycarbamate 1i**

Prepared according to the above procedure from a solution of 695 mg (0.82 mL, 4.51 mmol, 1.2 equiv) of *S*-citronellal, 500 mg (3.76 mmol) of *t*-butyl-*N*-hydroxycarbamate, 1.54 g (9.40 mmol) of sodium benzenesulfinate, and 190 mg (4.51 mmol) of formic acid in 3.7 mL of methanol and 7.4 mL of water. After filtration, the sulfone was collected as a white solid (1.18 g, 2.87 mmol).

Yield: 76%. **Mp:** 83.0-84.0 °C. **IR (KBr):** 3354, 2972, 2934, 1719, 1454, 1369, 1305, 1285, 1143, 1085, 756 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 0.86 and 0.96 (d, *J* = 6.5 Hz, 3H, CH₃), 1.00-1.20 (m, 1H, CH), 1.28 (s, 9H, C(CH₃)₃), 1.50-1.80 (m, 1H, H of CH₂), 1.56 (s, 3H, CH₃), 1.66 (s, 3H, CH₃), 1.60-2.10 (m, 2H, CH₂), 2.10-2.40 (m, 1H, CH), 4.95-5.10 (m, 1H, CH vinyl), 5.10-5.30 (m, 1H, CHN), 6.30 (br s, 1H, OH), 7.45-7.60 (m, 2H, CH arom.), 7.60-7.70 (m, 1H, CH arom.), 7.90-8.00 (m, 2H, CH arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 17.6 (CH₃), 18.3 (CH₃), 19.7 (CH₃), 25.3 (CH₂), 25.6 (CH), 27.8 (C(CH₃)₃), 29.0 and 29.2 (CH), 35.1 (CH₂), 37.5 (CH₂), 83.3 (C(CH₃)₃), 124.1 and 124.2 (CHN), 124.7 (CH vinyl), 129.1 (CH arom.), 129.2 (CH arom.), 131.5 (Cq), 133.9 (CH arom.), 137.6 (C arom.), 154.5 (C=O). **LRMS (ESI):** m/z= 561 [(nitron dimer+Na)⁺], 434 [(M+Na)⁺], 292 [(nitron+Na)⁺]. **HRMS (ESI) calcd for C₂₁H₃₃NO₅NaS:** 434.1977. **Found:** 434.1974 [(M+Na)⁺]. **Anal. Calcd for C₂₁H₃₃NO₅S:** C, 61.29; H, 8.09; N, 3.41. **Found:** C, 60.96; H, 8.08; N, 3.28.

Test of 1,3-dipolar cycloaddition

- **2-(*tert*-Butoxycarbonyl)-3-isobutyl-4,5-dimethyldicarboxylate-2,3-dihydro-isoxazole 3**

Sulfone **1d** (200 mg, 0.583 mmol) was dissolved into 5 mL of THF under argon. Dimethylacetylene dicarboxylate (828 mg, 5.583, 10 equiv) and dry potassium carbonate (402 mg, 2.915 mmol) were added, and the crude mixture was warmed to 50 °C during 2 h. It was then cooled, filtered onto celite and evaporated. The brown residue was triturated with pentane two times and pentane was evaporated. The obtained oil was purified by column chromatography (eluent: Et₂O/Pentane 1/9), affording 130 mg (0.38 mmol) of product **3**.

Yield: 65%. **IR (film):** 2959, 2872, 1760, 1726, 1666, 1438, 1370, 1303, 1280, 1232, 1157, 1108, 1067, 1026 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 0.94 (d, *J* = 6.5 Hz, 3H, CH₃), 1.00 (d, *J* = 6.5 Hz, 3H, CH₃), 1.45-1.70 (m, 2H), 1.52 (s, 9H, C(CH₃)₃), 1.70-1.95 (m, 1H), 3.77 (s, 3H, CH₃), 3.91 (s, 3H, CH₃), 5.19 (dd, *J* = 4.1 and 8.7 Hz, 1H, CHN). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 21.3 (CH₃), 23.4 (CH₃), 24.5 (CH), 28.1 (C(CH₃)₃), 43.3 (CH₂), 52.1 (CH₃), 53.2 (CH₃), 64.8 (CHN), 84.0 (C(CH₃)₃), 111.7 (Cq), 150.9 (Cq), 157.0 (Cq), 158.2 (Cq), 161.7 (Cq). **LRMS (DCI):** *m/z* = 361 [(M+NH₄)⁺].

Addition of 1-alkynyllithiums

General procedure

1-alkyne was dissolved in dry THF and the resulting solution was cooled at -78 °C. *n*-Butyllithium was then added dropwise, and after 10 minutes, a solution of sulfone in dry THF was added via syringe. The resulting mixture was stirred 30 minutes at -78 °C and then allowed to run at 0 °C for 2 hours. Aqueous NH₄Cl was then added and the solution was allowed to reach room temperature. The reaction mixture was then extracted two times by EtOAc. The combined organic layers were washed with brine, dried over anhydrous MgSO₄ and filtered. After the removal of the solvent, the obtained propargylic hydroxylamine was purified by column chromatography (eluent : CH₂Cl₂).

- *tert*-Butyl 1-methyl-3-phenylprop-2-ynyl-*N*-hydroxycarbamate **6a**

Prepared according to the above procedure from 100 mg (0.33 mmol) of the sulfone **1b** into 0.6 mL of THF, 70 mg (0.68 mmol) of phenylacetylene in 0.6 mL of THF and 0.44 mL of *n*-BuLi (0.78 mmol, 1.5 M solution in THF). The product was collected as a pale yellow oil (72 mg, 0.28 mmol).

Yield: 83%. **IR (film):** 3294, 2981, 2930, 2869, 1698, 1491, 1443, 1395, 1370, 1319, 1300, 1255, 1165, 1120, 1069 cm⁻¹. **¹H RMN (CDCl₃, 300 MHz):** δ= 1.52 (s, 9H, C(CH₃)₃), 1.57 (d, *J*=6.9 Hz, 3H, CH₃), 5.04 (q, *J*= 6.9 Hz, 1H, CHN), 6.19 (br s, 1H, OH), 7.23-7.33 (m, 3H, H arom.), 7.35-7.50 (m, 2H, H arom.). **¹³C RMN (CDCl₃, 75.5 MHz):** δ= 18.9 (CH₃), 28.2 (C(CH₃)₃), 48.7 (CHN), 82.8 (C(CH₃)₃), 83.4 (Cq), 86.9 (Cq), 122.6 (C arom.), 128.12 (CH arom.), 128.3 (CH arom.), 131.8 (CH arom.), 157.3 (C=O). **LRMS (ESI + 1% LiCl):** *m/z*= 268 [(M+Li)⁺], 529 [(dimer+Li)⁺]. **Anal. Calcd for C₁₅H₁₉NO₃:** C, 68.95; H, 7.33; N, 5.36. **Found:** C, 68.68; H, 7.44; N, 5.38.

- ***tert*-Butyl 1-methyl-4,4-(diethoxy)but-2-ynyl-*N*-hydroxycarbamate 6b**

Prepared according to the above procedure from 450 mg (1.5 mmol) of the sulfone **1b** into 3 mL of THF, 384 mg (3.07 mmol) of propiolaldehyde diethylacetal in 3 mL of THF and 2.0 mL of *n*-BuLi (0.78 mmol, 1.5 M solution in THF). The product was collected as a pale yellow oil (370 mg, 1.29 mmol).

Yield: 86%. **IR (film):** 3318, 2979, 2935, 2886, 1697, 1478, 1451, 1391, 1369, 1319, 1254, 1117, 1095, 1046, 1002 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 1.22 (dt, *J*= 0.6 and 7.0 Hz, 6H, 2 CH₃), 1.49 (s, 9H, C(CH₃)₃), 3.52-3.63 (m, 2H, CH₂ ether), 3.68-3.78 (m, 2H, CH₂ ether), 4.91 (dq, *J*= 1.3 and 7.0 Hz, 1H, CHN), 5.28 (d, *J*= 1.4 Hz, 1H, CH(OEt)₂), 6.80 (s, 1H, OH). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 14.9 (CH₃), 18.4 (CH₃), 28.1 (C(CH₃)₃), 47.6 (CHN), 60.7 (CH₂), 60.8 (CH₂), 78.3 (Cq), 82.5 (C(CH₃)₃), 83.5 (Cq), 91.1 (CH(OEt)₂), 156.7 (C=O). **LRMS (ESI, 1% LiCl):** *m/z*= 294 [(M+Li)⁺], 310 [(M+Na)⁺]. **HRMS (ESI) calcd for C₁₄H₂₅NO₅Na:** 310.1630. **Found:** 310.1634 [(M+Na)⁺].

- ***tert*-Butyl 1-ethyl-3-phenylprop-2-ynyl-*N*-hydroxycarbamate 6c**

Prepared according to the above procedure from 161 mg (0.51 mmol) of the sulfone **1c** into 1 mL of THF, 107 mg (1.05 mmol) of phenylacetylene in 1 mL of THF and 0.68 mL of *n*-BuLi (1.02 mmol, 1.5 M solution in THF). The product was collected as a colourless oil (119 mg, 0.43 mmol).

Yield: 85%. **IR (film):** 3333, 2974, 2932, 1697, 1492, 1395, 1363, 1325, 1255, 1168, 1127, 1095 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 1.05 (t, *J*= 7.3 Hz, 3H, CH₃), 1.51 (s, 9H, C(CH₃)₃), 1.85-2.05 (m, 2H, CH₂), 4.81 (t, *J*= 7.7 Hz, 1H, CHN), 6.37 (s, 1H, OH), 7.25-7.33 (m, 3H, H arom.), 7.38-7.44 (m, 2H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 10.8 (CH₃), 26.2 (CH₂), 28.2 (C(CH₃)₃), 54.5 (CHN), 82.6 (C(CH₃)₃), 84.0 (Cq), 86.2 (Cq), 122.7 (C arom.), 128.2 (CH arom.), 128.3 (CH arom.), 131.8 (CH arom.), 157.4 (C=O). **LRMS (ESI, 1% LiCl):** *m/z*= 282 [M+Li]⁺. **Anal. Calcd for C₁₆H₂₁NO₃:** C, 69.80; H, 7.69; N, 5.09. **Found:** C, 69.69; H, 7.62; N, 5.09.

- ***tert*-Butyl 1-(ethyl)hept-2-ynyl-*N*-hydroxycarbamate 6d**

Prepared according to the above procedure from 288 mg (0.87 mmol) of the sulfone **1c** into 1.7 mL of THF, 147 mg (1.79 mmol) of hexyne in 1.7 mL of THF and 1.2 mL of *n*-BuLi (1.79 mmol, 1.5 M solution in THF). The product was collected as a colourless oil (132 mg, 0.49 mmol).

Yield: 56%. **IR (film):** 3263, 2972, 2940, 2875, 1696, 1454, 1373, 1324, 1252, 1147, 1114 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.90 (t, J = 7.3 Hz, 3H, CH_3), 0.97 (t, J = 7.3 Hz, 3H, CH_3), 1.30-1.55 (m, 4H, 2 CH_2), 1.50 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.70-1.90 (m, 2H, CH_2), 2.19 (dt, J = 2.0 and 6.9 Hz, 2H, CH_2), 4.55 (tt, J = 2.0 and 7.7 Hz, 1H, CHN), 6.40 (s, 1H, OH). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 10.9 (CH_3), 13.7 (CH_3), 18.5 (CH_2), 22.0 (CH_2), 26.6 (CH_2), 28.4 ($\text{C}(\text{CH}_3)_3$), 31.0 (CH_2), 54.3 (CHN), 77.7 (Cq), 82.4 ($\text{C}(\text{CH}_3)_3$), 84.7 (Cq), 157.6 (C=O). **LRMS (ESI):** m/z = 278 $[(\text{M}+\text{Na})^+]$. **HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_3\text{Na}$:** 278.1732 **Found:** 278.1723 $[(\text{M}+\text{Na})^+]$.

- ***tert*-Butyl 1-isobutyl-3-phenylprop-2-ynyl-*N*-hydroxycarbamate 6e**

Prepared according to the above procedure from 200 mg (0.58 mmol) of the sulfone **1d** into 1 mL of THF, 122 mg (1.20 mmol) of phenylacetylene in 1 mL of THF and 0.78 mL of *n*-BuLi (1.16 mmol, 1.5 M solution in THF). The product was collected as an oil (150 mg, 0.49 mmol).

Yield: 85%. **IR (film):** 3244, 2959, 2934, 2869, 1699, 1492, 1395, 1369, 1169, 1137, 1098, 755 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.90-1.05 (m, 6H, CH_3), 1.50 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.65-1.90 (m, 3H, CH_2 and CH), 4.97 (dd, J = 6.2 and 7.2 Hz, 1H, CHN), 6.30 (s, 1H, OH), 7.15-7.30 (m, 3H, H arom.), 7.30-7.45 (m, 2H, H arom.). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 22.2 (CH_3), 22.3 (CH_3), 24.8 (CH), 28.2 ($\text{C}(\text{CH}_3)_3$), 41.5 (CH_2), 51.3 (CHN), 82.6 ($\text{C}(\text{CH}_3)_3$), 84.0 (Cq), 86.3 (Cq), 122.7 (C arom.), 128.2 (CH arom.), 128.3 (CH arom.), 131.8 (CH arom.), 157.2 (C=O). **LRMS (ESI):** m/z = 326 $[(\text{M}+\text{Na})^+]$. **HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_3$:** 304.1913. **Found:** 304.1918 $[(\text{M}+\text{H})^+]$. **Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_3$:** C, 71.26; H, 8.31; N, 4.62. **Found:** C, 71.21; H, 8.33; N, 4.50.

- ***tert*-Butyl 1-isobutylhept-2-ynyl-*N*-hydroxycarbamate **6f****

Prepared according to the above procedure from 300 mg (0.87 mmol) of the sulfone **1d** into 1.6 mL of THF, 147 mg (1.80 mmol) of hexyne in 1.6 mL of THF and 1.2 mL of *n*-BuLi (1.79 mmol, 1.5 M solution in THF). The product was collected as an oil (150 mg, 0.53 mmol).

Yield: 61%. **IR (film):** 3244, 2959, 2934, 2863, 1699, 1473, 1454, 1395, 1370, 1324, 1260, 1175, 1130, 1091 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.87-0.97 (m, 9H, 3 CH_3), 1.35-1.50 (m, 6H, 3 CH_2), 1.49 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.55-1.80 (m, 3H, CH and CH_2), 2.19 (dt, J = 2.1 and 6.9 Hz, 2H, CH_2), 4.73 (tt, J = 2.1 and 7.7 Hz, 1H, CHN), 6.10 (s, 1H, OH). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 13.5 (CH_3), 18.3 (CH_2), 21.8 (CH_2), 22.2 (CH_3), 22.3 (CH_3), 24.7 (CH), 28.2 ($\text{C}(\text{CH}_3)_3$), 30.8 (CH_2), 41.7 (CH_2), 51.0 (CHN), 76.9 (Cq), 82.3 ($\text{C}(\text{CH}_3)_3$), 84.5 (Cq), 157.3 (C=O). **LRMS (ESI):** m/z = 282 [M-H]. **HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{29}\text{NO}_3\text{Na}$:** 306.2045. **Found:** 306.2030 [M+Na] $^+$.

- ***tert*-Butyl 1-isobutyl-4-methoxybut-2-ynyl-*N*-hydroxycarbamate **6g****

Prepared according to the above procedure from 500 mg (1.46 mmol) of the sulfone **1d** into 3 mL of THF, 210 mg (3.0 mmol) of methylpropargylether in 3 mL of THF and 1.93 mL of *n*-BuLi (3.0 mmol, 1.5 M solution in THF). The product was collected as an oil (340 mg, 1.25 mmol).

Yield: 86%. **IR (film):** 3289, 2959, 2934, 2869, 2824, 1699, 1473, 1454, 1395, 1369, 1324, 1169, 1098 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.92 (d, J = 6.2 Hz, 3H, CH_3), 0.95 (d, J = 6.4 Hz, 3H, CH_3), 1.50 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.60-1.83 (m, 3H, CH_2 and CH), 3.37 (s, 3H, OCH_3), 4.12 (d, J = 1.7 Hz, 2H, CH_2), 4.82 (tt, J = 1.7 and 7.2 Hz, 1H, CHN), 6.58 (s, 1H, OH). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 22.1 (CH_3), 22.3 (CH_3), 24.7 (CH), 28.2 ($\text{C}(\text{CH}_3)_3$), 41.3 (CH_2), 50.5 (CHN), 57.4 (OCH_3), 59.9 (CH_2), 79.4 (Cq), 82.5 ($\text{C}(\text{CH}_3)_3$), 83.8 (Cq), 156.9 (C=O). **LRMS (ESI):** m/z = 270 [M-H]. **Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_4$:** C, 61.97; H, 9.29; N, 5.17. **Found:** C, 61.44; H, 9.67; N, 5.31.

- ***tert*-Butyl 1-isobutyl-3-cyclohexen-1'-yl-prop-2-ynyl-*N*-hydroxycarbamate 6h**

Prepared according to the above procedure from 300 mg (0.874 mmol) of the sulfone **1d** into 1.6 mL of THF, 190 mg (1.79 mmol, 0.21 mL) of 1-ethynylcyclohexene in 1.6 mL of THF and 1.2 mL of *n*-BuLi (1.79 mmol, 1.5 M solution in THF). The product was collected as an oil (200 mg, 0.65 mmol).

Yield: 75%. **IR (film):** 3242, 2959, 2935, 2869, 2833, 1696, 1456, 1390, 1366, 1323, 1257, 1173, 1131, 1089, 842 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 0.93 (d, *J* = 6.3 Hz, 3H, CH₃), 0.94 (d, *J* = 6.3 Hz, 3H, CH₃), 1.50 (s, 9H, C(CH₃)₃), 1.53-1.83 (m, 7H, CH and 3 CH₂), 2.02-2.15 (m, 4H, 2 CH₂), 4.86 (t, *J* = 7.4 Hz, 1H, CHN), 5.94 (s, 1H, OH), 6.06-6.11 (m, 1H, H vinyl). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 21.4 (CH₂), 22.18 (CH₃), 22.23 (CH₃), 22.3 (CH₂), 24.8 (CH), 25.6 (CH₂), 28.2 (C(CH₃)₃), 29.3 (CH₂), 41.6 (CH₂), 51.4 (CHN), 82.4 (C(CH₃)₃), 83.3 (Cq), 85.9 (Cq), 120.1 (C vinyl), 135.2 (CH vinyl), 157.2 (C=O). **LRMS (ESI):** *m/z* = 306 [M-H].

- ***tert*-Butyl 1-isobutyl-3-trimethylsilylprop-2-ynyl-*N*-hydroxycarbamate 6i**

Prepared according to the above procedure from 250 mg (0.73 mmol) of the sulfone **1d** into 1.5 mL of THF, 147 mg (1.49 mmol) of trimethylsilylacetylene in 1.5 mL of THF and 0.97 mL of *n*-BuLi (1.46 mmol, 1.5 M solution in THF). The product was collected as an oil (136 mg, 0.46 mmol).

Yield: 62%. **IR (film):** 3239, 2957, 2863, 1697, 1456, 1368, 2321, 1250, 1174, 1127, 1091, 838 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 0.14 (s, 9H, SiMe₃), 0.91 (d, *J* = 6.3 Hz, 3H, CH₃), 0.92 (d, *J* = 6.4 Hz, 3H, CH₃), 1.48 (s, 9H, C(CH₃)₃), 1.55-1.80 (m, 3H, CH and CH₂), 4.72 (dd, *J* = 7.1 and 8.1 Hz, 1H, CHN), 6.28 (s, 1H, OH). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = -0.1 (Me₃Si), 22.0 (CH₃), 22.4 (CH₃), 24.7 (CH), 28.2 (C(CH₃)₃), 41.3 (CH₂), 51.5 (CHN), 82.4 (C(CH₃)₃), 88.4 (Cq), 102.7 (Cq), 157.2 (C=O). **LRMS (ESI):** *m/z* = 298 [M-H]. **HRMS (ESI) calcd for C₁₅H₂₉NO₃NaSi:** 322.1814. **Found:** 322.1812 [M+Na]⁺.

- ***tert*-Butyl 1-isobutyl-4,4-diethoxybut-2-ynyl-*N*-hydroxycarbamate 6j**

Prepared according to the above procedure from 300 mg (0.87 mmol) of the sulfone **1d** into 1.6 mL of THF, 230 mg (1.79 mmol, 0.26 mL) of propiolaldehyde diethyl acetal in 1.6 mL of THF and 1.2 mL of *n*-BuLi (1.79 mmol). The product was collected as an oil (200 mg, 0.61 mmol).

Yield: 70%. **IR (film):** 3291, 2975, 2956, 2929, 2898, 2872, 1697, 1470, 1458, 1393, 1370, 1324, 1162, 1085, 1054, 1008 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 0.93 (d, *J* = 6.2 Hz, 6H, 2 CH₃), 1.22 (t, *J* = 7.2 Hz, 6H, 2 CH₃ ether), 1.49 (s, 9H, C(CH₃)₃), 1.55-1.85 (m, 3H, CH and CH₂), 3.50-3.65 (m, 2H, CH₂ ether), 3.65-3.80 (m, 2H, CH₂ ether), 4.84 (dt, *J* = 1.3 and 6.9 Hz, 1H, CHN), 5.28 (d, *J* = 1.3 Hz, 1H, CH(OEt)₂), 6.37 (s, 1H, OH). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 15.0 (CH₃), 22.0 (CH₃), 22.3 (CH₃), 24.6 (CH), 28.2 (C(CH₃)₃), 41.1 (CH₂), 50.3 (CHN), 60.78 (CH₂), 60.84 (CH₂), 79.1 (Cq), 82.5 (C(CH₃)₃), 82.8 (Cq), 91.2 (CH(OEt)₂), 156.7 (C=O). **LRMS (ESI):** *m/z* = 352 [(M+Na)⁺], 329 [(M+Li)⁺]. **HRMS (ESI) calcd for C₁₇H₃₁NO₅Na:** 352.2100. **Found:** 352.2097 [(M+Na)⁺].

- ***tert*-Butyl 1-phenethyl-3-phenylprop-2-ynyl-*N*-hydroxycarbamate 6k**

Prepared according to the above procedure from 200 mg (0.51 mmol) of the sulfone **1e** into 1 mL of THF, 107 mg (1.05 mmol, 0.12 mL) of phenylacetylene in 1 mL of THF and 0.68 mL of *n*-BuLi (1.02 mmol, 1.5 M solution in THF). The product was collected as an oil (144 mg, 0.41 mmol).

Yield: 80%. **IR (film):** 3250, 2972, 2934, 1686, 1492, 1395, 1369, 1163, 1104, 755 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 1.48 (s, 9H, C(CH₃)₃), 2.14-2.40 (m, 2H, CH₂), 2.81 (t, *J* = 7.4 Hz, 2H, CH₂), 4.85 (t, *J* = 7.4 Hz, 1H, CHN), 6.14 (s, 1H, OH), 7.10-7.35 (m, 8H, H arom.), 7.35-7.50 (m, 2H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 28.1 (C(CH₃)₃), 32.1 (CH₂), 34.3 (CH₂), 52.0 (CHN), 82.6 (C(CH₃)₃), 84.2 (Cq), 86.1 (Cq), 122.6 (C arom.), 126.0 (CH arom.), 128.15 (CH arom.), 128.24 (CH arom.), 128.4 (CH arom.), 128.5 (CH arom.), 131.8 (CH arom.), 141.0 (C arom.), 157.4 (C=O). **LRMS (ESI, 1% LiCl):** *m/z* = 358 [(M+Li)⁺]. **HRMS (ESI) calcd for C₂₂H₂₅NO₃Na:** 374.1732. **Found:** 374.1723 [M+Na⁺]

- ***tert*-Butyl 1-phenethylhept-2-ynyl-*N*-hydroxycarbamate **6l****

Prepared according to the above procedure from 150 mg (0.39 mmol) of the sulfone **1e** into 1 mL of THF, 80 mg (0.78 mmol) of hexyne in 1 mL of THF and 0.52 mL of *n*-BuLi (0.78 mmol, 1.5 M solution in THF). The product was collected as an oil (80 mg, 0.24 mmol).

Yield: 63%. **IR (film):** 3263, 2959, 2934, 2869, 1699, 1369, 1163, 1105 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 0.90 (t, *J*= 7.2 Hz, 3H, CH₃), 1.30-1.55 (m, 4H, 2 CH₂), 1.46 (s, 9H, C(CH₃)₃), 2.00-2.25 (m, 2H, CH₂), 2.15-2.25 (m, 2H, CH₂), 2.74 (t, *J*= 8.1 Hz, 2H, CH₂), 4.60 (tt, *J*= 2.1 and 7.0 Hz, 1H, CHN), 5.70 (s, 1H, OH), 7.15-7.35 (m, 5H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 13.5 (CH₃), 18.3 (CH₂), 21.8 (CH₂), 28.1 (C(CH₃)₃), 30.7 (CH₂), 32.2 (CH₂), 34.6 (CH₂), 52.1 (CHN), 76.4 (Cq), 82.5 (C(CH₃)₃), 85.1 (Cq), 125.9 (CH arom.), 128.3 (CH arom.), 128.4 (CH arom.), 128.5 (CH arom.), 141.2 (C arom.), 157.5 (C=O). **LRMS (ESI):** *m/z*= 354 [(M+Na)⁺]. **HRMS (ESI) calcd for C₂₀H₂₉NO₃Na:** 354.2045. **Found:** 354.2074 [(M+Na)⁺].

- ***tert*-butyl 1-phenethyl-3-cyclohexen-1'-ylprop-2-ynyl-*N*-hydroxycarbamate **6m****

Prepared according to the above procedure from 150 mg (0.39 mmol) of the sulfone **1e** into 1 mL of THF, 105 mg (0.98 mmol) of 1-ethynylcyclohexene in 1 mL of THF and 0.52 mL of *n*-BuLi (0.78 mmol, 1.5 M solution in THF). The product was collected as a yellow oil (102 mg, 0.28 mmol).

Yield: 75%. **IR (film):** 3250, 2979, 2934, 2869, 1699, 1369, 1156, 1105 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 1.38 (s, 9H, C(CH₃)₃), 1.45-1.60 (m, 4H, 2 CH₂), 1.90-2.20 (m, 6H, 3 CH₂), 2.67 (t, *J*= 7.4 Hz, 2H, CH₂Ph), 4.66 (t, *J*= 7.5 Hz, 1H, CHN), 5.95-6.05 (m, 1H, CH vinyl), 6.39 (s, 1H, OH), 7.05-7.25 (m, 5H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 21.4 (CH₂), 22.2 (CH₂), 25.5 (CH₂), 28.1 (C(CH₃)₃), 29.2 (CH₂), 32.1 (CH₂), 34.4 (CH₂), 52.2 (CHN), 82.4 (C(CH₃)₃), 83.0 (Cq), 86.2 (Cq), 120.0 (C vinyl), 125.9 (CH arom.), 128.3 (CH arom.), 128.36 (CH arom.), 128.42 (CH arom.), 128.5 (CH arom.), 135.2 (CH vinyl), 141.1 (C arom.), 157.4 (C=O). **LRMS (ESI):** *m/z*= 354 [(M-H)]. **HRMS (ESI) calcd for C₂₂H₂₉NO₃Na:** 378.2045. **Found:** 378.2049 [(M+Na)⁺].

- ***tert*-Butyl 1-cyclohexyl-3-phenylprop-2-ynyl-*N*-hydroxycarbamate 6n**

Prepared according to the above procedure from 276 mg (0.75 mmol) of the sulfone **1f** into 1.3 mL of THF, 153 mg (1.5 mmol) of phenylacetylene diethyl acetal in 1.3 mL of THF and 0.97 mL of *n*-BuLi (1.5 mmol, 1.55 M solution in THF). The product was collected as an oil (226 mg, 0.69 mmol).

Yield: 92%. **IR (film):** 3232, 2973, 2929, 2851, 1696, 1494, 1489, 1450, 1397, 1253, 1171, 1139, 1102 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 0.90-1.40 (m, 6H, 3 CH₂), 1.51 (s, 9H, (C(CH₃)₃)), 1.60-2.20 (m, 5H, CH and 2 CH₂), 4.60 (d, *J*= 9.7 Hz, 1H, CHN), 6.00 (s, 1H, OH), 7.25-7.35 (m, 3H, H arom.), 7.38-7.47 (m, 2H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 25.7 (CH₂), 25.9 (CH₂), 26.3 (CH₂), 28.3 (C(CH₃)₃), 29.6 (CH₂), 30.4 (CH₂), 40.0 (CH), 58.1 (CHN), 82.4 (C(CH₃)₃), 84.7 (Cq), 85.7 (Cq), 122.8 (C arom.), 128.16 (CH arom.), 128.20 (CH arom.), 131.8 (CH arom.), 157.3 (C=O). **LRMS (ESI):** *m/z*= 336 [(M+Li)⁺], 352 [(M+Na)⁺], 368 [(M+K)⁺], 665 [(dimer+Li)⁺], 681 [(dimer+Na)⁺]. **Anal. Calcd for C₂₀H₂₇NO₃:** C, 72.92; H, 8.27; N, 4.26. **Found:** C, 72.85; H, 8.46; N, 4.35.

- ***tert*-Butyl 1-cyclohexyl-4,4-(diethoxy)but-2-ynyl-*N*-hydroxycarbamate 6o**

Prepared according to the above procedure from 276 mg (0.75 mmol) of the sulfone **1f** into 1.3 mL of THF, 192 mg (1.5 mmol) of propiolaldehyde diethyl acetal in 1.3 mL of THF and 0.97 mL of *n*-BuLi (1.5 mmol, 1.55 M solution in THF). The product was collected as an oil (187 mg, 0.53 mmol).

Yield: 71%. **IR (film):** 3289, 2979, 2934, 2856, 1706, 1454, 1395, 1369, 1331, 1176, 1143, 1092, 1053 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 1.85-1.10 (m, 2H, CH₂), 1.10-1.35 (m, 4H, 2 CH₂), 1.22 (t, *J*= 7.2 Hz, 6H, 2 CH₃), 1.49 (s, 9H, (C(CH₃)₃)), 1.55-2.10 (m, 7H, CH and 3 CH₂), 3.52-3.65 (m, 2H, CH₂ ether), 3.66-3.79 (m, 2H, CH₂ ether), 4.47 (dd, *J*= 1.2 and 9.6 Hz, 1H, CHN), 5.29 (d, *J*= 1.2 Hz, 1H, CH(OEt)₂), 6.57 (s, 1H, OH). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 15.0 (CH₃), 25.6 (CH₂), 25.8 (CH₂), 26.2 (CH₂), 28.2 (C(CH₃)₃), 29.4 (CH₂), 30.2 (CH₂), 39.7 (CH), 57.2 (CHN), 60.8 (CH₂O), 60.9 (CH₂O), 80.0 (Cq), 82.0 (Cq), 82.3 (C(CH₃)₃), 91.3 (CH(OEt)₂), 156.8 (C=O). **LRMS (ESI):** *m/z*= 378 [(M+Na)⁺]. **HRMS (ESI) calcd for C₁₉H₃₃NO₅Na:** 378.2256. **Found:** 378.2265 [(M+Na)⁺].

- ***tert*-Butyl 1-[(*tert*-butoxycarbonyl)aminomethyl]-3-phenylprop-2-ynyl-*N*-hydroxycarbamate 6p**

Prepared according to the above procedure from 75 mg (0.18 mmol) of the sulfone **1g** into 0.6 mL of THF, 52 mg (0.55 mmol) of phenylacetylene in 0.6 mL of THF and 0.36 mL of *n*-BuLi (0.55 mmol). The product was collected as an oil (59 mg, 0.16 mmol).

Yield: 89%. **IR (film):** 3346, 2977, 2933, 1698, 1520, 1393, 1367, 1323, 1287, 1254 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 1.44 (s, 9H, C(CH₃)₃), 1.50 (s, 9H, C(CH₃)₃), 3.28-3.42 (m, 1H, H of CH₂), 3.70-3.85 (m, 1H, H of CH₂), 5.06 (dd, J = 4.5 and 10.9 Hz, 1H, CHN), 5.13 (t, J = 6.0 Hz, 1H, NHBoc), 7.25-7.31 (m, 3H, H arom.), 7.38-7.45 (m, 2H, H arom.). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 28.3 (2 C(CH₃)₃), 41.7 (CH₂), 52.2 (CHN), 80.7 (Cq), 80.9 (Cq), 83.8 (Cq), 84.9 (Cq), 122.4 (C arom.), 128.2 (CH arom.), 128.4 (CH arom.), 131.9 (CH arom.), 157.6 (C=O). **LRMS (ESI, 1% LiCl):** m/z = 383 [(M+Li)⁺], 759 [(dimer+Li)⁺]. **HRMS (ESI) calcd for C₂₀H₂₈N₂O₅Na:** 399.1896. **Found:** 399.1900 [(M+Na)⁺].

- ***tert*-Butyl 1-[(*tert*-butoxycarbonyl)aminomethyl]-4,4-(diethoxy)but-2-ynyl-*N*-hydroxycarbamate 6q**

Prepared according to the above procedure from 75 mg (0.18 mmol) of the sulfone **1g** into 0.6 mL of THF, 71 mg (0.55 mmol) of propionaldehyde diethyl acetal in 0.6 mL of THF and 0.36 mL of *n*-BuLi (0.55 mmol). The product was collected as an oil (60 mg, 0.15 mmol).

Yield: 83%. **IR (film):** 3346, 2976, 2933, 2885, 1699, 1518, 1455, 1393, 1369, 1325, 1290, 1256, 1172, 1051, 1004 cm^{-1} . **^1H RMN (CDCl_3 , 300 MHz):** δ = 1.22 (dt, J = 0.6 and 7.1 Hz, 6H, 2 CH₃), 1.43 (s, 9H, C(CH₃)₃), 1.48 (s, 9H, C(CH₃)₃), 3.20-3.35 (m, 1H, H of CH₂), 3.51-3.69 (m, 2H, CH₂ ether), 3.65-3.80 (m, 3H, CH₂ ether and 1H of CH₂), 4.90 (ddd, J = 1.2, 4.3 and 10.9 Hz, 1H, CHN), 5.14 (t, J = 6.2 Hz, 1H, NHBoc), 5.26 (d, J = 1.2 Hz, 1H, CH(OEt)₂), 7.71 (s, 1H, OH). **^{13}C RMN (CDCl_3 , 75.5 MHz):** δ = 15.0 (CH₃), 28.19 (C(CH₃)₃), 28.23 (C(CH₃)₃), 41.4 (CH₂), 51.3 (CHN), 60.9 (CH₂), 80.15 (Cq), 80.22 (Cq), 80.5 (Cq), 81.9 (Cq), 91.2 (CH(OEt)₂), 156.1 (C=O), 157.4 (C=O). **LRMS (ESI, 1% LiCl):** m/z = 409 [(M+Li)⁺], 811 [(dimer+Li)⁺]. **HRMS (ESI) calcd for C₁₉H₃₄N₂O₇Na:** 425.2264. **Found:** 425.2256 [(M+Na)⁺].

- ***tert*-Butyl 1-(2',6'-dimethylhept-5'-enyl)-3-phenylprop-2-ynyl-*N*-hydroxycarbamate 6r**

Prepared according to the above procedure from 150 mg (0.37 mmol) of the sulfone **1i** into 0.6 mL of THF, 76 mg (0.75 mmol) of phenylacetylene in 0.6 mL of THF and 0.5 mL of *n*-BuLi (0.75 mmol, 1.5 M solution in THF). The product was collected as a pale yellow oil (113 mg, 0.31 mmol).

Yield: 84%. **IR (film):** 3243, 2966, 2920, 2875, 2854, 1695, 1488, 1437, 1393, 1368, 1323, 1166, 1108, 756 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 0.97 (d, *J* = 6.4 Hz, 3H, CH₃), 1.15-1.30 (m, 1H, H of CH₂), 1.33-1.48 (m, 1H, H of CH₂), 1.51 (s, 9H, C(CH₃)₃), 1.60 (s, 3H, CH₃), 1.67 (s, 3H, CH₃), 1.60-1.78 (m, 2H, CH₂), 1.90-2.10 (m, 3H, CH and CH₂), 4.94-5.05 (m, 1H, CHN), 5.11 (t, *J* = 7.0 Hz, 1H, CH vinyl), 6.1 and 6.16 (2 s, 1H, OH), 7.20-7.35 (m, 3H, H arom.), 7.35-7.45 (m, 2H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 17.7 (CH₃), 19.2 and 19.3 (CH₃), 25.3 and 25.4 (CH₂), 25.6 (CH), 28.2 (C(CH₃)₃), 29.2 and 29.4 (CH₃), 36.78 and 36.83 (CH₂), 39.6 and 39.7 (CH₂), 51.0 and 51.5 (CHN), 82.6 (C(CH₃)₃), 83.9 and 84.2 (Cq), 86.1 and 86.5 (Cq), 122.7 (C arom.), 124.57 and 124.60 (CH vinyl), 128.2 and 128.3 (CH arom.), 131.29 and 131.32 (C vinyl), 131.79 and 131.81 (CH arom.), 157.1 (C=O). **LRMS (ESI):** *m/z* = 394 [(M+Na)⁺]. **HRMS (ESI) calcd for C₂₃H₃₃NO₃Na:** 394.2358. **Found:** 394.2355 [(M+Na)⁺].

- ***tert*-Butyl 1-(2',6'-dimethylhept-5'-enyl)-4-methoxybut-2-ynyl-*N*-hydroxycarbamate 6s**

Prepared according to the above procedure from 150 mg (0.37 mmol) of the sulfone **1i** into 0.6 mL of THF, 52 mg (0.75 mmol) of methylpropargylether in 0.6 mL of THF and 0.5 mL of *n*-BuLi (0.75 mmol, 1.5 M solution in THF). The product was collected as a pale yellow oil (78 mg, 0.23 mmol).

Yield: 62%. **IR (film):** 3267, 2965, 2927, 2853, 1697, 1455, 1393, 1368, 1318, 1256, 1166, 1099 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 0.92 (d, *J* = 6.2 Hz, 3H, CH₃), 1.10-1.50 (m, 3H, CH and CH₂), 1.49 (s, 9H, C(CH₃)₃), 1.52-1.70 (m, 1H, H of CH₂), 1.60 (s, 3H, CH₃), 1.67 (s, 3H, CH₃), 1.80-2.10 (m, 3H, CH₂ and CH), 3.37 (s, 3H, OMe), 4.11 (d, *J* = 1.4 Hz, 2H, CH₂), 4.80-4.89 (m, 1H, CH vinyl), 5.03-5.13 (tt, *J* = 1.4 and 8.4 Hz, 1H, CHN), 6.40 and 6.47 (2 s, 1H, OH). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 17.6 (CH₃), 19.1 and 19.2 (CH₃), 25.2 and 25.3 (CH₂), 25.6 (CH), 28.2 (C(CH₃)₃), 29.0 and 29.3 (CH₃), 36.7 and 36.8 (CH₂), 39.5 and 39.6 (CH₂), 50.1 and 50.6 (CHN), 57.36 and 57.41 (OCH₃), 59.8 (CH₂), 79.3 and 79.6 (Cq), 82.5 (C(CH₃)₃), 83.6 and 84.0 (Cq), 124.5 and 124.6 (CH vinyl), 131.2 and 131.3 (C vinyl), 156.8 and 156.9 (C=O). **LRMS (ESI):** *m/z* = 362 [(M+Na)⁺]. **HRMS (ESI) calcd for C₁₉H₃₃NO₄Na:** 362.2307. **Found:** 362.2303 [(M+Na)⁺].

Transformations and valorisations of propargylic *N*-hydroxylamines 6

- 2-(*tert*-Butoxycarbonyl)-3-isobutyl-5-phenyl-2,3-dihydro-isoxazole **7**

To a solution of the propargylic *N*-hydroxylamine **6e** (177 mg, 0.58 mmol) in 1 mL of a mixture of THF-MeCN (1/1) was added Pd(OAc)₂ (13 mg, 0.058 mmol) and Et₃N (0.09 mL, 0.64 mmol). The reaction mixture was stirred at room temperature overnight. It was then filtered through a short pad of silica gel, which was rinsed twice by EtOAc. The filtrate was evaporated. Purification of the obtained oil by column chromatography (eluent: CH₂Cl₂) yielded pure 2,3-dihydro-isoxazole **7** (151 mg, 0.496 mmol) as a pale oil.

Yield: 85%. **IR (film):** 2957, 2929, 2870, 1743, 1715, 1659, 1492, 1370, 1328, 1165, 1064, 1029, 904, 848 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ = 0.96 (d, *J* = 6.5 Hz, 3H, CH₃), 0.98 (d, *J* = 6.5 Hz, 3H, CH₃), 1.35-1.45 (m, 1H, H of CH₂), 1.53 (s, 9H, (C(CH₃)₃), 1.55-1.68 (m, 1H, H of CH₂), 1.85 (hep., *J* = 6.5 Hz, 1H, CH), 5.04 (ddd, *J* = 2.6, 5.5 and 8.1 Hz, 1H, CHN), 5.37 (d, *J* = 2.6 Hz, 1H, CH vinyl), 7.25-7.40 (m, 3H, H arom.), 7.55-7.65 (m, 2H, H arom.). **¹³C NMR (CDCl₃, 75.5 MHz):** δ = 22.5 (CH₃), 22.9 (CH₃), 24.9 (CH), 28.2 (C(CH₃)₃), 45.4 (CH₂), 65.0 (CHN), 82.3 (C(CH₃)₃), 97.0 (CH vinyl), 125.5 (CH arom.), 127.8 (C arom.), 128.4 (CH arom.), 129.2 (CH arom.), 153.3 (Cq), 157.9 (C=O). **LRMS (DCI):** *m/z* = 304 [(M+H)⁺]. **HRMS (ESI) calcd for C₁₈H₂₅NO₃Na:** 326.1732. **Found:** 326.1732 [(M+Na)⁺].

- 1-isobutyl-4-methoxybut-2-ynyl-*N*-hydroxylamine **8**

A cold solution of hydrochloric acid was prepared at 0 °C by adding 0.37 mL (0.4 g, 5.16 mmol) of freshly distilled acetyl chloride to 1.2 mL of dry methanol. The solution was stirred for 15 minutes at 0 °C. A solution of the protected propargylic *N*-hydroxylamine **6g** (0.10 g, 0.37 mmol) in 1 mL of methanol was then added to the resulting HCl solution at 0 °C. The resulting mixture was stirred for an additional hour. Methanol was then slowly evaporated under vacuum. The crude product was dissolved into dichloromethane and a saturated aqueous solution of sodium hydrogenocarbonate was added. Aqueous layer was then extracted twice by EtOAc. The combined organic phases were then washed by brine and dried over anhydrous MgSO₄. After the removal of the solvent, the product was obtained as an oil (64 mg, 0.37 mmol).

Yield: 100%. **IR (film):** 3388, 3258, 2961, 2927, 2873, 2821, 1472, 1354, 1309, 1188, 1100, 1010, 904 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.92 (d, J = 6.5 Hz, 3H, CH_3), 0.96 (d, J = 6.7 Hz, 3H, CH_3), 1.52 (t, J = 7.4 Hz, 2H, CH_2), 1.86 (hep, J = 6.8 Hz, 1H, CH), 3.38 (s, 3H, CH_3O), 3.81 (tt, J = 1.6 and 7.4 Hz, 1H, CHN), 4.13 (d, J = 1.6 Hz, 2H, CH_2), 5.0-6.0 (br s, 2H, NH and OH). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 21.9 (CH_3), 23.1 (CH_3), 25.2 (CH), 41.1 (CH_2), 53.3 (CHN), 57.5 (OCH_3), 59.9 (CH_2), 79.9 (Cq), 85.8 (Cq). **LRMS (ESI):** m/z = 172 $[(\text{M}+\text{H})^+]$, 156 $[(\text{M}-\text{OH})^+]$.

- ***tert*-Butyl 1-isobutyl-4-methoxybut-2-ynylcarbamate 9**

N-Hydroxylamine **6g** (100 mg, 0.37 mmol) was dissolved into 3 mL of THF under inert atmosphere. The resulting solution was cooled to 0 °C and then 8 equiv of ungazed water (0.053 mL, 2.96 mmol) were added followed by 2.75 equiv of a SmI_2 solution in THF (1.02 mmol, 10.2 mL). The resulting mixture was stirred at 0 °C during 2 hours. It was then quenched by air, and then by adding a saturated aqueous solution of sodium thiosulfate. The resulting aqueous mixture was extracted three times by EtOAc. The combined organics layers were washed with brine and dried over anhydrous MgSO_4 . After the removal of the solvent, the residue was purified by column chromatography (eluent: CH_2Cl_2). Product **9** was obtained as a colorless oil (68 mg, 0.27 mmol).

Yield: 73%. **IR (film):** 3336, 2957, 2931, 2872, 2361, 2335, 1701, 1517, 1368, 1249, 1161, 1104 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.93 (d, J = 6.6 Hz, 3H, CH_3), 0.94 (d, J = 6.6 Hz, 3H, CH_3), 1.45 (s, 9H, $(\text{C}(\text{CH}_3)_3)$), 1.52 (t, J = 7.4 Hz, 2H, CH_2), 1.79 (hep., J = 6.8 Hz, 1H, CH), 3.36 (s, 3H, CH_3O), 4.09 (d, J = 1.8 Hz, 2H, CH_2), 4.49 (br s, 1H, CHN), 4.65 (br s, 1H, NHBoc). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 21.9 (CH_3), 22.7 (CH_3), 25.0 (CH), 28.3 ($(\text{C}(\text{CH}_3)_3)$), 41.7 (CHN), 45.4 (CH_2), 57.4 (OCH_3), 59.9 (CH_2), 78.3 (Cq), 79.7 ($(\text{C}(\text{CH}_3)_3)$), 86.4 (Cq), 154.8 (C=O). **LRMS (ESI, 1% LiCl):** m/z = 262 $[(\text{M}+\text{Li})^+]$, 278 $[(\text{M}+\text{Na})^+]$, 294 $[(\text{M}+\text{K})^+]$. **Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{NO}_3$:** C, 65.85; H, 9.87; N, 5.49. **Found:** C, 66.01; H, 9.94; N, 5.49.

- ***tert*-Butyl 1-isobutyl-4-methoxybut-2-(*Z*)-enylcarbamate 10**

N-Hydroxylamine **6g** (76 mg, 0.28 mmol) was dissolved into 2 mL of THF under inert atmosphere. The resulting solution was cooled to 0 °C and then 5 equiv of a SmI_2 solution in THF (1.40 mmol, 14 mL) were added, immediately followed by 20 equiv of ungazed water (0.1 mL, 5.6 mmol). The reaction was allowed to reach room temperature overnight. It was then quenched by air, and then by adding a saturated aqueous solution of sodium thiosulfate. The resulting aqueous mixture was extracted three times by EtOAc. The combined

organics layers were washed with brine and dried over anhydrous MgSO_4 . After the removal of the solvent, the residue was purified by column chromatography (eluent: CH_2Cl_2). Product **10** was obtained as a colorless oil (41 mg, 0.16 mmol).

Yield: 57%. **IR (film):** 3337, 2958, 2928, 2868, 2818, 1706, 1522, 1393, 1369, 1253, 1176, 1100, 1040, 1013, 950, 870 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.91 (d, J = 6.4 Hz, 3H, CH_3), 0.93 (d, J = 6.4 Hz, 3H, CH_3), 1.15-1.32 (m, 2H, CH_2), 1.43 (s, 9H, $(\text{C}(\text{CH}_3)_3)$), 1.35-1.70 (m, 3H, CH and CH_2), 3.34 (s, 3H, CH_3O), 4.09 (d, J = 6.1 Hz, 2H, CH_2), 4.30-4.60 (m, 2H, CHN and NHBoc), 5.25-5.40 (m, 1H, H vinyl), 5.58 (dt, J = 6.5 and 10.9 Hz, 1H, H vinyl). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 22.5 (2 CH_3), 24.6 (CH), 28.4 ($\text{C}(\text{CH}_3)_3$), 45.1 (CH_2), 46.5 (CHN), 58.0 (OCH_3), 68.4 (CH_2), 79.2 ($\text{C}(\text{CH}_3)_3$), 127.9 (CH vinyl), 134.0 (CH vinyl), 155.0 (C=O). **LRMS (DCI):** m/z = 158 [(M-Boc+H) $^+$], 258 [(M+H) $^+$]. **Anal. Calcd for $\text{C}_{14}\text{H}_{27}\text{NO}_3$:** C, 65.34; H, 10.58; N, 5.45. **Found:** C, 65.38; H, 10.77; N, 5.44.

Additions of vinyl- and allyl magnesium bromides

- *tert*-Butyl 1-isobutylprop-2-enyl-*N*-hydroxycarbamate **13a**

To a solution of sulfone **1d** (100 mg, 0.29 mmol) in dry toluene (3 mL) was added 0.58 mL of vinylmagnesium bromide (1M solution in THF, 0.58 mmol). The resulting solution was stirred at room temperature during 45 min before being quenched by a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted twice by EtOAc. The combined organic layers were washed by brine, dried over anhydrous MgSO_4 and the solvents were evaporated. Purification by column chromatography (eluent: CH_2Cl_2) of the crude product yielded the pure allylic *N*-hydroxylamine **13a** (55 mg, 0.24 mmol).

Yield: 83%. **IR (film):** 3215, 2957, 2933, 2871, 1690, 1470, 1455, 1393, 1367, 1325, 1232, 1177, 1152, 1133, 1095, 993, 921, 869 cm^{-1} . **^1H NMR (CDCl_3 , 300 MHz):** δ = 0.91 (d, J = 6.5 Hz, 3H, CH_3), 0.92 (d, J = 6.5 Hz, 3H, CH_3), 1.25-1.38 (m, 1H, CH), 1.47 (s, 9H, $(\text{C}(\text{CH}_3)_3)$), 1.60-1.72 (m, 1H, H of CH_2), 1.72-1.84 (m, 1H, H of CH_2), 4.42-4.52 (m, 1H, CHN), 5.12 (dt, J = 1.4 and 10.1 Hz, 1H, CH vinyl Z), 5.16 (dt, J = 1.4 and 18.4 Hz, 1H, CH vinyl E), 5.89 (ddd, J = 6.9, 10.1 and 18.4 Hz, 1H, CH vinyl), 7.35 (s, 1H, OH). **^{13}C NMR (CDCl_3 , 75.5 MHz):** δ = 21.9 (CH_3), 22.9 (CH_3), 24.4 (CH), 28.3 ($\text{C}(\text{CH}_3)_3$), 40.1 (CH_2), 59.5 (CHN), 81.6 ($\text{C}(\text{CH}_3)_3$), 115.9 (CH_2 vinyl), 136.5 (CH vinyl), 157.2 (C=O). **LRMS (ESI, 1% LiCl):** m/z = 236 [(M+Li) $^+$], 465 [(dimer+Li) $^+$]. **Anal. Calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_3$:** C, 62.86; H, 10.11; N, 6.11. **Found:** C, 62.52; H, 10.12; N, 5.82.

- ***tert*-Butyl 1-[(*tert*-butoxycarbonyl)aminomethyl]-prop-2-enyl-*N*-hydroxycarbamate **13b****

To a solution of the sulfone **1g** (100 mg, 0.24 mmol) in dry toluene (5 mL) was added 0.72 mL of vinylmagnesium bromide (1M solution in THF, 0.72 mmol). The resulting solution was stirred at room temperature during 45 min before being quenched by a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted twice by EtOAc. The combined organic layers were washed by brine, dried over anhydrous MgSO₄ and the solvents were evaporated. Purification by column chromatography (eluant: CH₂Cl₂) of the crude product yielded the pure allylic hydroxylamine **13b** (50 mg, 0.17 mmol).

Yield: 71%. **IR (film):** 3340, 2979, 2933, 1702, 1520, 1394, 1360, 1285, 1255, 1173, 1104, 923 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 1.44 (s, 9H, C(CH₃)₃), 1.47 (s, 9H, C(CH₃)₃), 3.00-3.18 (m, 1H, H of CH₂), 3.45-3.65 (m, 1H, H of CH₂), 4.50-4.63 (m, 1H, CHN), 5.11 (t, *J*= 5.6 Hz, 1H, NHBoc), 5.22 (dt, *J*= 1.3 and 10.2 Hz, 1H, CH vinyl *Z*), 5.26 (dt, *J*= 1.3 and 16.9 Hz, 1H, CH vinyl *E*), 5.86 (ddd, *J*= 6.4, 10.2 and 16.9 Hz, 1H, CH vinyl), 7.85 (s, 1H, OH). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 28.30 (C(CH₃)₃), 28.34 (C(CH₃)₃), 40.9 (CH₂), 61.1 (CHN), 80.3 and 81.2 (C(CH₃)₃), 117.9 (CH₂ vinyl), 133.0 (CH vinyl), 156.7 (C=O), 157.7 (C=O). **LRMS (ESI, 1% LiCl):** *m/z*= 309 [(M+Li)⁺], 325 [(M+Na)⁺], 611 [(dimer+Li)⁺]. **Anal. Calcd for C₁₄H₂₆N₂O₅:** C, 55.62; H, 8.67; N, 9.27. **Found:** C, 55.66; H, 8.86; N, 8.97.

- ***tert*-Butyl 1-isobutylbut-3-enyl-*N*-hydroxycarbamate **14****

To a solution of the sulfone **1d** (100 mg, 0.29 mmol) in dry toluene (5 mL) was added 0.90 mL of allylmagnesium bromide (1M solution in diethyl ether, 0.90 mmol). The resulting solution was stirred at room temperature overnight before being quenched by a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted twice by EtOAc. The combined organic layers were washed by brine, dried over anhydrous MgSO₄ and the solvents were evaporated. Purification by column chromatography (eluent: CH₂Cl₂) of the crude product yielded the pure homoallylic *N*-hydroxylamine **14** (35 mg, 0.15 mmol).

Yield: 50%. **IR (film):** 3204, 2958, 2928, 2871, 1686, 1399, 1246, 1180, 1150, 1100, 920 cm⁻¹. **¹H NMR (CDCl₃, 300 MHz):** δ= 0.89 (d, *J*= 6.5 Hz, 3H, CH₃), 0.90 (d, *J*= 6.5 Hz, 3H, CH₃), 1.06-1.18 (m, 1H, CH), 1.46 (s, 9H, C(CH₃)₃), 1.58-1.80 (m, 2H, CH₂), 2.07-2.20 (m, 1H, CH), 2.37-2.50 (m, 1H, CH), 4.02-4.15 (m, 1H, CHN), 4.97-5.15 (m, 2H, CH₂ vinyl), 5.70-5.87 (m, 1H, CH vinyl), 7.10 (s, 1H, OH). **¹³C NMR (CDCl₃, 75.5 MHz):** δ= 21.7 (CH₃), 23.3 (CH₃), 24.6 (CH), 28.3 (C(CH₃)₃), 36.9 (CH₂), 40.7 (CH₂), 56.5 (CHN), 81.3 (C(CH₃)₃), 116.9 (CH₂ vinyl), 135.4 (CH vinyl), 156.8 (C=O). **LRMS (ESI):** *m/z*= 250 [(M+Li)⁺], 266 [(M+Na)⁺], 493 [(dimer+Li)⁺]. **Anal. Calcd for C₁₃H₂₅NO₃:** C, 64.16; H, 10.36; N, 5.76. **Found:** C, 63.89; H, 10.19; N, 5.67.