Supporting Information

Chemoselective Intramolecular Allylic C–H Amination versus C=C Aziridination through Co(II)-Based Metalloradical Catalysis

Hongjian Lu, Huiling Jiang, Yang Hu, Lukasz Wojtas, and X. Peter Zhang*

Department of Chemistry, University of South Florida, Tampa, Florida 33620-5250

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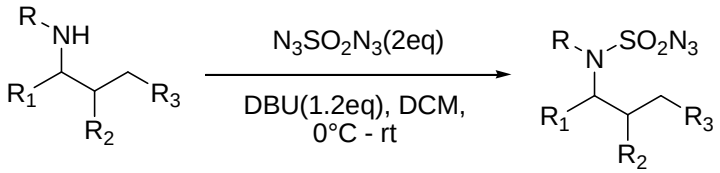
General Considerations. All C-H amination reactions were performed under nitrogen in oven-dried glassware following standard Schlenk techniques. 4 Å molecular sieves were dried in a vacuum oven prior to use. Anhydrous benzene was purchased from Sigma-Aldrich and used without further purification. [Co(**P1**)] was prepared by following the literature.[1] Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 μm). ^{1}H NMR and ^{13}C NMR were recorded on a Varian Inova400 (400 MHz) or a Bruker250 (250 MHz) instrument with chemical shifts reported relative to residual solvent. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. HRMS data was obtained on an Agilent 1100 LC/MS/TOF mass spectrometer.

General Experimental Procedures for Preparation of Sulfamoyl Azides



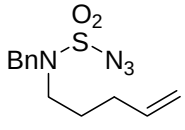
Sulphuryl Azide ($N_3SO_2N_3$)[2]. To a solution of sodium azide (2.6 g, 40 mmol) and pyridine (1.58 g, 20 mmol) in acetonitrile (50 ml) at 0 ^{o}C, sulphuryl chloride (1.34 g, 10 mmol) was added dropwise for 20 min. Then the reaction mixture was stirred for a further 1 h at room temperature. After addition of 30 ml DCM, the mixture was poured into ice-cold water and extracted with DCM (3 x 20 mL) The combined organic layer was washed with hydrochloric acid (1 mol/L in H_2O), water, potassium hydroxide (1 mol/L in H_2O), hydrochloric acid (1 mol/L in H_2O), and water. After drying (Na_2SO_4), the sulphuryl azide solution was used directly for the subsequent reaction. This solution can be stored in the refrigerator for at least two months without significant decomposition.

To a solution of $N_3SO_2N_3$ (2 eq, 0.25 mol/L in DCM) at 0 °C, a mixture of amine (1 eq) and DBU (1.2 eq) in DCM was added dropwise via syringe. The reaction showed almost complete consumption of the starting amine after 5 min to 3 hours when monitored by TLC, then the majority of the solvent was removed under reduced pressure at room temperature. Purification of this mixture by chromatography on silica gel (as given below) afforded the sulfamoyl azide. Note: Some azides could be explosive and should be handled carefully. Based on DSC experiments (see Page S15, DSC spectrogram of azide **1a**), this type of azide is stable under the temperature of the reaction conditions used.

General Procedure for C–H Amination of Sulfamoyl Azides

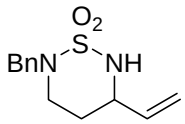
An oven dried Schlenk tube was charged with catalyst (0.002 mmol) and 4Å MS (50 mg), then evacuated and back filled with nitrogen. The Teflon screw cap was replaced with a rubber septum and then an approximately 0.5 ml portion of benzene was added, then azide (0.1 mmol), followed by the remaining benzene (total 1 mL). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced

with a Teflon screw cap. The Schlenk tube was then placed in an oil bath for the desired time and temperature. After completion of the reaction, the reaction mixture was purified by flash column chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the target compound.



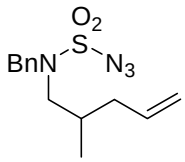
1a

Yield: 85%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.61 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.31 (m, 5H), 5.73-5.62 (m, 1H), 4.99-4.94 (m, 2H), 4.44 (s, 2H), 3.21 (t, *J* = 7.6 Hz, 2H), 1.98 (q, *J* = 7.2 Hz, 2H), 1.68-1.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 134.7, 128.8, 128.5, 128.4, 115.6, 52.6, 48.2, 30.4, 26.4. IR (neat, cm^{-1}): 2123, 1380, 1205, 1166, 1122, 918, 783, 735, 698.



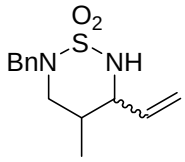
2a

Yield: 99%. Purified by chromatography on silica gel (gradient elution: 4:1-2:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.56 (2:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.34-7.29 (m, 5H), 5.88-5.73 (m, 1H), 5.30-5.17 (m, 2H), 4.50, 3.94 (AB q, *J* = 14.0 Hz, each 1H), 4.28-4.16 (m, 1H), 4.06 (d, *J* = 9.5 Hz, 1H), 3.39-3.26 (m, 1H), 3.15-3.06 (m, 1H), 1.72-1.59 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 135.9, 135.3, 128.8, 128.7, 128.0, 116.6, 57.6, 51.7, 47.3, 28.6. IR (neat, cm^{-1}): 2922, 1628, 1414, 1342, 1163, 1093, 837, 771, 743, 691. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{12}H_{17}N_2O_2S$ 253.1005, Found 253.1007.



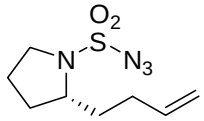
1b

Yield: 82%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.56 (10:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.34 (s, 5H), 5.69-5.52 (m, 1H), 4.99-4.91 (m, 2H), 4.49, 4.40 (AB q, *J* = 15.0 Hz, each 1H), 3.18-2.95 (m, 2H), 2.09-1.98 (m, 1H), 1.87-1.70 (m, 2H), 0.84 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 135.6, 134.5, 128.8, 128.7, 128.4, 116.8, 54.6, 53.4, 38.3, 31.2, 17.0. IR (neat, cm^{-1}): 2123, 1379, 1205, 1164, 1018, 781, 736, 699.



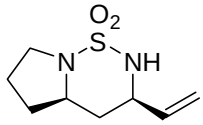
2b

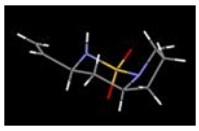
Yield: 99%. Purified by chromatography on silica gel (gradient elution: 3:1-2:1 hexanes/EtOAc), white solid, TLC R_f = 0.56 (1:1 hexanes/EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.28-7.25 (m, 5H), 5.73-5.58 (m, 1H), 5.30-5.14 (m, 2H), 4.70, 3.57 (AB q, *J* = 13.8 Hz, each 0.25H), 4.40, 3.96 (AB q, *J* = 13.8 Hz, each 0.75H), 4.35 (brs, 0.5H), 4.13 (d, *J* = 8.0 Hz, 0.75H), 3.79-3.68 (m, 0.75H), 3.22-2.74 (m, 2H), 1.81-1.63 (m, 1H), 0.81 (t, *J* = 7.3 Hz, 0.75H), 0.74 (t, *J* = 6.8 Hz, 0.75H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 135.4, 135.2, 134.6, 128.7, 128.6, 128.5, 127.9, 119.2, 116.1, 64.0, 60.2, 54.2, 53.8, 52.0, 51.5, 32.4, 31.9, 14.2, 10.2. IR (neat, cm^{-1}): 1310, 1155, 1076, 1015, 997, 926, 768, 749, 697. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{19}N_2O_2S$ 267.1162, Found 267.1160.



1c

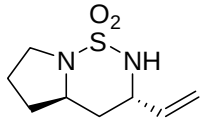
Yield: 70%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.36 (10:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.86-5.68 (m, 1H), 5.07-4.92 (m, 2H), 3.80-3.70 (m, 1H), 3.42 (t, *J* = 6.5 Hz, 2H), 2.12-1.80 (m, 6H), 1.78-1.66 (m, 1H), 1.60-1.45 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 137.3, 115.1, 61.7, 50.1, 34.2, 30.7, 30.1, 24.2. IR (neat, cm^{-1}): 2122, 1381, 1203, 1165, 1058, 998, 731.



≡ 

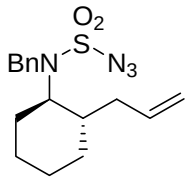
cis-**2c**

Yield: 75%. Purified by chromatography on silica gel (gradient elution: 3:1-2:1 hexanes/EtOAc), white solid, TLC R_f = 0.36 (2:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.86-5.72 (m, 1H), 5.28-5.14 (m, 2H), 4.13-4.04 (m, 2H), 3.58-3.46 (m, 1H), 3.38-3.27 (m, 1H), 3.23-3.12 (m, 1H), 2.16-2.05 (m, 1H), 1.93-1.79 (m, 3H), 1.64-1.49 (m, 1H), 1.35-1.19 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 135.8, 116.4, 60.5, 57.2, 45.6, 34.3, 31.2, 20.6. IR (neat, cm^{-1}): 1418, 1336, 1158, 1098, 1070, 1013, 942, 907, 776, 747. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_8H_{14}N_2O_2SNa$ 225.0668, Found 225.0674.



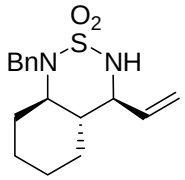
trans-**2c**

Yield: 25%. Purified by chromatography on silica gel (gradient elution: 3:1-2:1 hexanes/EtOAc), white solid, TLC R_f = 0.27 (2:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.24-6.10 (m, 1H), 5.26-5.21 (m, 1H), 5.18 (d, *J* = 1.5 Hz, 1H), 4.43 (d, *J* = 5.8 Hz, 1H), 4.17-4.08 (m, 1H), 3.70-3.58 (m, 1H), 3.47-3.36 (m, 1H), 3.26-3.18 (m, 1H), 2.18-1.56 (m, 6H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 136.5, 116.4, 58.0, 56.0, 46.1, 32.8, 31.4, 21.2. IR (neat, cm^{-1}): 1464, 1420, 1410, 1342, 1287, 1154, 1100, 1000, 926, 717. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_8H_{15}N_2O_2S$ 203.0849, Found 203.0854.



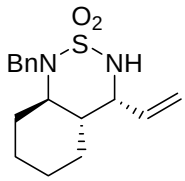
1d

Yield: 75% (purity ≈ 95%). Purified by chromatography on silica gel (30:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.48 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.29 (m, 5H), 5.39-5.29 (m, 1H), 4.90-4.80 (m, 2H), 4.49, 4.36 (AB q, *J* = 15.2 Hz, each 1H), 3.39 (brs, 1H), 2.32-2.26 (m, 1H), 1.95-1.76 (m, 3H), 1.63-1.52 (m, 3H), 1.40-1.23 (m, 2H), 1.06-1.01 (m, 1H), 0.85-0.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 128.9, 128.7, 128.3, 116.4, 40.2, 37.1, 31.6, 30.7, 26.0, 25.3. IR (neat, cm^{-1}): 2121, 1376, 1204, 1171, 1206, 855, 780, 737, 699.



trans,trans-**2d**

Yield: 59%. Major one Purified by chromatography on silica gel (4:1 hexanes/EtOAc), white solid, TLC R_f = 0.32 (4/1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.67 (ddd, J = 8.0, 10.4, 17.2 Hz, 1H), 5.30 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.46, 4.20 (AB q, *J* = 16.8 Hz, each 1H), 4.06 (d, *J* = 4.8 Hz, 1H), 3.09-3.73 (m, 2H), 1.86-1.81 (m, 1H), 1.72-1.66 (m, 3H), 1.42 (dq, *J* = 3.6, 10.8 Hz, 1H), 1.26-1.06 (m, 3H), 0.97-0.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 135.2, 128.3, 127.2, 127.0, 119.8, 63.9, 63.6, 48.5, 39.6, 31.2, 27.6, 25.4, 25.0. IR (neat, cm^{-1}): 1388, 1176, 1158, 932, 901, 794, 733, 696. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{16}H_{22}N_2O_2SNa$ 329.1294, Found 329.1290.



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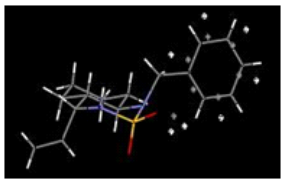
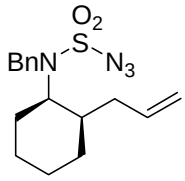


trans,cis-**2d**

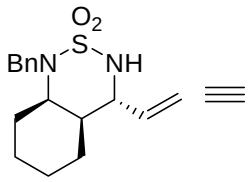
Yield: 32%. Minor one Purified by chromatography on silica gel (4:1 hexanes/EtOAc),

white solid, TLC R_f = 0.26 (4:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 6.8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.36 (dq, J = 10.0, 16.8 Hz, 1H), 5.23 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.16 (d, *J* = 17.6 Hz, 1H), 4.43, 4.31 (AB q, *J* = 16.4 Hz, each 1H), 4.43 (d, *J* = 3.6 Hz, 1H), 3.79-3.71 (m, 2H), 2.08-2.02 (m, 1H), 1.79-1.74 (m, 1H), 1.69-1.65 (m, 2H), 1.52-1.47 (m, 1H), 1.26-0.98 (m, 4H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 134.7, 128.4, 127.3, 127.1, 119.3, 63.0, 60.4, 49.0, 37.3, 31.4, 28.6, 25.2, 24.8. IR (neat, cm^{-1}): 1463, 1367, 1150, 944, 727, 681. HRMS (ESI) ($[M+Na]^+$) Calcd. $C_{16}H_{22}N_2O_2SNa$ 329.1294, Found 329.1287.



1e

Yield: 23%. Purified by chromatography on silica gel (gradient elution: 50:1-30:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.54 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.30-7.24 (m, 1H), 5.72-5.61 (m, 1H), 5.05-5.00 (m, 2H), 4.64, 4.39 (AB q, *J* = 16.8 Hz, each 1H), 3.98 (dt, *J* = 12.4, 4.0 Hz, 1H), 2.24-2.14 (m, 3H), 1.79-1.58 (m, 4H), 1.36-1.23 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.7, 128.6, 127.7, 127.2, 116.4, 63.9, 51.2, 37.9, 29.8, 27.4, 26.4, 25.8, 19.0. IR (neat, cm^{-1}): 2122, 1377, 1204, 1168, 909, 731, 609.



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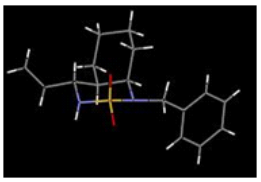
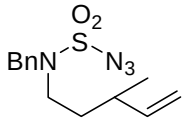


cis,trans-**2e**

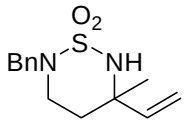
Yield: 92%. Purified by chromatography on silica gel (4:1 hexanes/EtOAc), white solid, TLC R_f = 0.36 (4:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 5H), 5.68 (ddd, J = 7.6, 10.0, 17.6 Hz, 1H), 5.38-5.27 (m, 2H), 4.56, 4.19 (AB *q*, *J* = 14.8 Hz, each 1H), 4.38-4.36 (m, 1H), 3.90 (d, *J* = 16.4 Hz, 1H), 3.13 (dq, *J* = 12.8, 4.0 Hz, 1H), 2.25 (dq, *J* = 4.0, 13.2 Hz, 1H), 1.93-1.77 (m, 4H), 1.39-0.88 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 134.6, 128.7, 128.4, 127.8, 119.3, 59.7, 56.8, 49.8, 39.2, 27.0, 25.6, 24.3, 20.4. IR (neat, cm^{-1}): 1306, 1161, 1144, 1089, 1047, 1022, 946, 799, 766, 736, 701. HRMS (ESI) ($[M+Na]^+$) Calcd. $C_{16}H_{22}N_2O_2SNa$ 329.1294, Found 329.1291.



1f

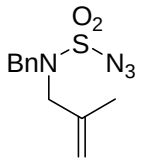
Yield: 81%. Purified by chromatography on silica gel (20:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.52 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.41-7.29 (m, 5H), 5.59-5.49 (m, 1H), 4.93-4.88 (m, 2H), 4.45, 4.41 (AB q, J = 14.8 Hz, each 1H), 3.25-3.12 (m, 2H), 2.09-1.98 (m, 1H), 1.61-1.45 (m, 2H), 0.93 (d, J = 6.8 Hz, 3H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 134.8, 128.8, 128.5, 128.4, 113.9, 52.6, 47.1, 35.4, 33.7, 20.1. IR (neat, cm^{-1}): 2123, 1380, 1205, 1165, 911, 784, 734, 698.



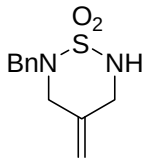
2f

Yield: 92%. Purified by chromatography on silica gel (4:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.27 (4:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.28 (m, 5H), 6.02 (dd, J = 10.8, 17.6 Hz, 1H), 5.15 (d, J = 10.8 Hz, 1H), 5.14 (d, J = 18.0 Hz, 1H), 4.23, 4.17 (AB q, J = 14.0 Hz, each 1H), 4.22 (brs, 1H), 3.20 (t, J = 6.0 Hz, 2H), 1.90-1.82 (m, 1H), 1.67-1.60 (m, 1H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 135.4, 128.8, 128.6, 127.9, 113.3, 60.1, 51.6, 44.7, 32.9, 27.4. IR (neat, cm^{-1}): 1403, 1336, 1178, 1171, 1152, 1103, 1087, 922, 911, 764, 725, 696. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{19}N_2O_2S$ 267.1162, Found 267.1153.



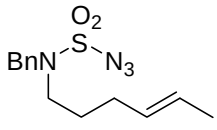
1g

Yield: 86%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.56 (10:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.36 (s, 5H), 5.04 (s, 1H), 4.97 (s, 1H), 4.45 (s, 2H), 3.80 (s, 2H), 1.76 (s, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 138.6, 134.2, 128.8, 128.6, 128.2, 115.8, 53.7, 51.3, 19.7. IR (neat, cm^{-1}): 2124, 1378, 1205, 1165, 1093, 1016, 904, 789, 738, 700.



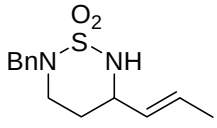
2g

Yield: 96%. Purified by chromatography on silica gel (gradient elution: 4:1-2:1 hexanes/EtOAc hexanes/EtOAc), white solid, TLC R_f = 0.32 (2:1 hexanes/EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.32 (s, 5H), 5.11 (s, 1H), 4.92 (s, 1H), 4.42 (t, J = 7.0 Hz, 1H), 4.19 (s, 2H), 3.96 (d, J = 7.0 Hz, 2H), 3.74 (s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 134.9, 133.8, 128.8, 128.7, 128.0, 116.7, 53.3, 51.8, 50.4. IR (neat, cm^{-1}): 1413, 1339, 1330, 1161, 1078, 1020, 894, 770, 737, 695. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{11}H_{14}N_2O_2SNa$ 261.0668, Found 261.0666.



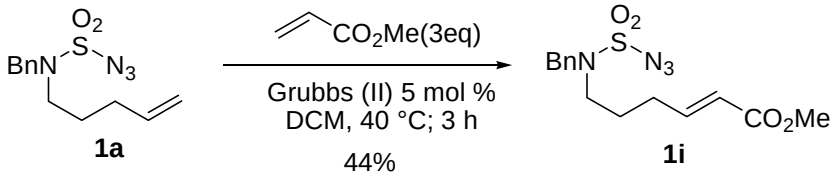
1h

Yield: 80%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.50 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.30 (m, 5H), 5.42-5.22 (m, 2H), 4.43 (s, 2H), 3.22-3.15 (m, 2H), 1.93-1.86 (m, 2H), 1.62-1.56 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 129.3, 128.8, 128.5, 128.3, 126.2, 52.4, 48.1, 29.3, 26.9, 17.8. IR (neat, cm^{-1}): 2122, 1380, 1206, 1165, 967, 786, 735, 698.



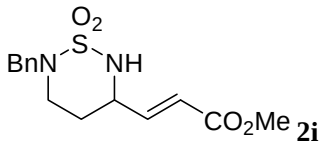
2h

Yield: 99%. Purified by chromatography on silica gel (4:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.32 (4:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.26 (m, 5H), 5.76-5.66 (m, 1H), 5.44-5.37 (m, 1H), 4.47, 3.95 (AB q, J = 13.6 Hz, each 1H), 4.20-4.12 (m, 1H), 4.00-3.96 (m, 1H), 3.35-3.27 (m, 1H), 3.08 (dt, J = 12.8, 3.6 Hz, 1H), 1.68 (d, J = 6.8 Hz, 3H), 1.66-1.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 129.1, 128.7, 128.6, 128.5, 127.9, 57.5, 51.7, 47.3, 28.9, 17.7. IR (neat, cm^{-1}): 1327, 1162, 1103, 967, 856, 767, 727, 697. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{13}H_{19}N_2O_2S$ 267.1162, Found 267.1159.



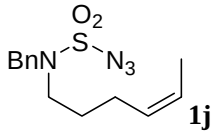
1a **1i**

An oven dried Schlenk tube was charged with Grubbs (II) catalyst (34.0 mg, 0.04 mmol) in CH_2Cl_2 solution (8 mL). With stirring, the solution was added azide **1a** (224 mg, 0.8 mmol) and methyl acrylate (206 mg, 2.4 mmol) through a syringe. The reaction was heated to 40 ^{0}C under nitrogen. After 3 h, CH_2Cl_2 was removed by rotary evaporation. The residue was purified directly by flash column chromatography on silica gel (gradient elution: 10:1-4:1 hexanes/EtOAc) to azide **1i** (120 mg, 44 % yield) as colorless liquid, TLC R_f = 0.25 (4:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.36-7.28 (m, 5H), 6.78 (dt, J = 15.6, 6.8 Hz, 1H), 5.73 (dt, J = 15.6, 1.5 Hz, 1H), 4.42 (s, 2H), 3.69 (s, 3H), 3.21 (t, J = 7.5 Hz, 2H), 2.14-2.04 (m, 2H), 1.71-1.57 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 166.6, 147.1, 134.4, 128.9, 128.5, 128.4, 121.8, 52.8, 51.4, 48.2, 28.8, 25.8. IR (neat, cm^{-1}): 2125, 1721, 1379, 1207, 1164, 1020, 736, 699.



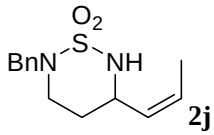
2i

Yield: 97%. Purified by chromatography on silica gel (gradient elution: 4:1-2:1 hexanes/EtOAc), white solid, TLC R_f = 0.38 (2:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.31 (s, 5H), 6.84 (dd, *J* = 4.5, 15.8 Hz, 1H), 6.00 (dd, *J* = 1.5, 15.8 Hz, 1H), 4.48, 3.96 (AB q, *J* = 13.8 Hz, each 1H), 4.44-4.31 (m, 2H), 3.73 (s, 3H), 3.41-3.29 (m, 1H), 3.17-3.08 (m, 1H), 1.78-1.61 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 166.1, 144.4, 135.0, 128.7, 128.1, 121.8, 56.4, 52.0, 51.7, 47.1, 28.3. IR (neat, cm^{-1}): 1719, 1340, 1317, 1268, 1194, 1181, 1160, 1090, 978, 832, 771, 745. 698. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{19}N_2O_4S$ 311.1060, Found 311.1060.



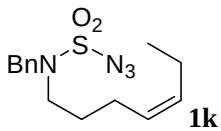
1j

Yield: 98%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.51 (10:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (m, 5H), 5.49-5.40 (m, 1H), 5.28-5.20 (m, 1H), 4.44 (s, 2H), 3.20 (t, *J* = 8.0 Hz, 2H), 1.96 (q, *J* = 7.2 Hz, 2H), 1.64-1.56 (m, 2H), 1.54 (dt, *J* = 6.8, 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 128.8, 128.5, 128.4, 125.2, 52.5, 48.3, 27.1, 23.7, 12.7. IR (neat, cm^{-1}): 2123, 1380, 1206, 1165, 1010, 756, 735, 697.



2j

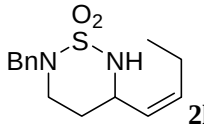
Yield: 91%. Purified by chromatography on silica gel (4:1 hexanes/EtOAc), white solid, TLC R_f = 0.32 (4:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (m, 5H), 5.69-5.60 (m, 1H), 5.26-5.20 (m, 1H), 4.54-4.45 (m, 1H), 4.46, 3.99 (AB q, *J* = 14.0 Hz, each 1H), 4.01 (d, *J* = 8.0 Hz, 1H), 3.37 (dt, *J* = 13.2, 3.2 Hz, 1H), 3.11-3.05 (m, 1H), 1.70 (d, *J* = 6.8 Hz, 3H), 1.68-1.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 129.6, 128.8, 128.6, 128.0, 127.9, 53.3, 51.8, 47.4, 28.9, 13.5. IR (neat, cm^{-1}): 1420, 1334, 1316, 1148, 1089, 933, 861, 762, 732, 695. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{19}N_2O_2S$ 267.1162, Found 267.1163.



1k

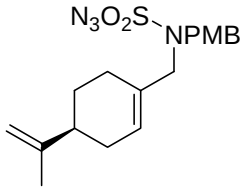
Yield: 90%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.50 (10:1 hexanes/EtOAc). ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.38-7.32 (m, 5H), 5.41-5.33 (m, 1H), 5.22-5.15 (m, 1H), 4.44 (s, 2H), 3.23-3.18 (m, 2H), 1.98-1.91 (m, 4H), 1.64-1.55 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 133.0, 128.8, 128.5, 128.4, 126.9, 52.5, 48.3, 27.3, 24.0, 20.5, 14.1. IR (neat, cm^{-1}): 2123, 1382, 1207, 1166, 910, 731, 698.



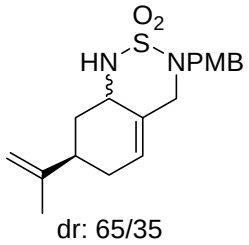
2k

Yield: 91%. Purified by chromatography on silica gel (6:1 hexanes/EtOAc), white solid, TLC R_f = 0.33 (4:1 hexanes/EtOAc). Major one: ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (m, 5H), 5.56 (dt, *J* = 14.8, 1.2 Hz, 1H), 5.35-5.14 (m, 1H), 4.50-4.44 (m, 1H), 4.46, 3.99 (AB q, *J* = 14.0 Hz, each 1H), 3.99 (brs, 1H), 3.36 (dt, *J* = 2.8, 13.2 Hz, 1H), 3.08 (dq, *J* = 13.2, 2.4 Hz, 1H), 2.19-2.05 (m, 2H), 1.69-1.59 (m, 1H), 1.51 (dq, *J* = 17.2, 2.8 Hz, 1H), 0.97 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 135.5, 128.7, 128.6, 127.9, 126.4, 53.5, 51.8, 47.4, 29.2, 21.3, 14.0. IR (neat, cm^{-1}): 1334, 1156, 1095, 849, 765, 726, 697. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{21}N_2O_2S$ 281.1318, Found 281.1312.



1l

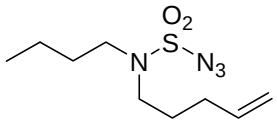
Yield: 70%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.36 (10:1 hexanes/EtOAc). ^1H NMR (250 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.65 (brs, 1H), 4.73-4.71 (m, 1H), 4.68 (d, *J* = 0.8 Hz, 1H), 4.33 (s, 2H), 3.79 (s, 3H), 3.73 (s, 2H), 2.17-1.88 (m, 5H), 1.81-1.74 (m, 1H), 1.71 (s, 3H), 1.42-1.28 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 159.5, 149.2, 131.2, 130.4, 127.8, 126.6, 114.0, 108.9, 55.2, 54.3, 51.0, 40.6, 30.6, 27.1, 26.4, 20.7. IR (neat, cm^{-1}): 2124, 1513, 1377, 1250, 1206, 1164, 1035, 902, 822, 778.



2l

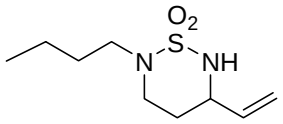
Yield: 99%. Purified by chromatography on silica gel (gradient elution: 4:1-3:1 hexanes/EtOAc), white solid, TLC R_f = 0.24 (4:1 hexanes/EtOAc). ^1H NMR (250 MHz, $CDCl_3$): δ. 7.22 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.68 (brs, 0.65H),

5.60 (brs, 0.35H), 4.78-4.65 (m, 2H), 4.24-3.91 (m, 5H), 3.79 (s, 3H), 3.64-3.24 (m, 1H), 2.32-1.91 (m, 4H), 1.73 (s, 1.95H), 1.71 (s, 1.05H), 1.75-1.63 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 159.4, 147.5, 146.5, 130.3, 128.7, 128.3, 127.1, 127.0, 126.9, 126.8, 114.1, 110.4, 110.0, 55.3, 55.2, 53.3, 53.2, 52.3, 51.4, 51.2, 39.7, 36.9, 34.3, 32.7, 30.9, 29.9, 21.3, 20.7. IR (neat, cm^{-1}): 2925, 1514, 1141, 1343, 1256, 1163, 1035, 906, 746. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{25}N_2O_3S$ 349.1580, Found 349.1579.



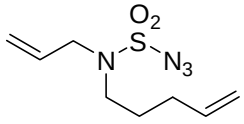
1m

Yield: 81%. Purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.56 (10:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.84-5.69 (m, 1H), 5.08-4.94 (m, 2H), 3.27-3.20 (m, 4H), 2.12-2.00 (m, 2H), 1.77-1.50 (m, 4H), 1.38-1.28 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 136.8, 115.6, 49.0, 48.6, 30.5, 29.8, 26.9, 19.7, 13.5. IR (neat, cm^{-1}): 2120, 1382, 1206, 1158, 917, 731.



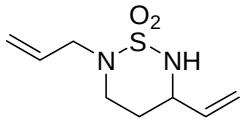
2m

Yield: 94%. Purified by chromatography on silica gel (gradient elution: 3:1-2:1 hexanes/EtOAc), white solid, TLC R_f = 0.52 (1:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.86-5.72 (m, 1H), 5.29-5.16 (m, 2H), 4.22-4.12 (m, 1H), 3.87 (d, J = 9.0 Hz, 1H), 3.52-3.39 (m, 1H), 3.30-3.09 (m, 2H), 3.00-2.88 (m, 1H), 1.76-1.89 (m, 6H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 136.1, 116.5, 57.5, 48.3, 48.2, 29.6, 28.5, 19.9, 13.7. IR (neat, cm^{-1}): 2925, 1325, 1301, 1164, 1113, 1074, 910, 859, 761, 733. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_9H_{18}N_2O_2SNa$ 241.0981, Found 241.0978.



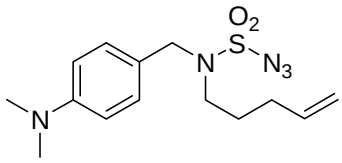
1n

Yield: >65%. Purified by chromatography on silica gel (20:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.53 (10:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.92-5.60 (m, 2H), 5.36-5.27 (m, 2H), 5.07-4.97 (m, 2H), 3.88 (d, J = 6.5 Hz, 2H), 3.24 (t, J = 7.5 Hz, 2H), 2.09-2.02 (m, 2H), 1.76-1.63 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 136.9, 131.5, 120.2, 115.6, 51.5, 47.9, 30.4, 26.7. IR (neat, cm^{-1}): 2123, 1383, 1206, 1169, 990, 923, 780, 734.



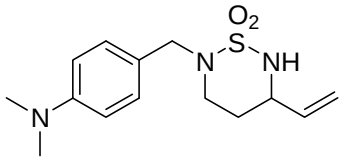
2n

Yield: 95%. Purified by chromatography on silica gel (4:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.14 (4:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85-5.73 (m, 2H), 5.29-5.19 (m, 4H), 4.21 (brs, 1H), 3.88-3.81 (m, 2H), 3.54 (dd, *J* = 6.4, 14.4 Hz, 1H), 3.39-3.25 (m, 2H), 1.79-1.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 132.5, 119.6, 116.6, 57.6, 51.1, 47.4, 28.7. IR (neat, cm^{-1}): 1419, 1331, 1162, 1096, 989, 928, 849, 759. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_8H_{15}N_2O_2S$ 203.0849, Found 203.0846.



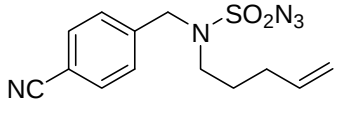
1o

Yield: 75%. Purified by chromatography on silica gel (2/1 Hexane/EtOAc), colorless liquid, TLC R_f = 0.39 (1/1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 5.75-5.65 (m, 1H), 5.01-4.94 (m, 2H), 4.35 (s, 2H), 3.17 (t, *J* = 7.6Hz, 2H), 3.95 (s, 6H), 1.99 (q, *J* = 7.6 Hz, 2H), 1.68-1.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 137.0, 129.8, 121.4, 115.5, 112.3, 52.0, 47.3, 40.4, 30.5, 26.3. IR (neat, cm^{-1}): 2120, 1614, 1524, 1376, 1190, 1163, 913, 809, 776, 732.



2o

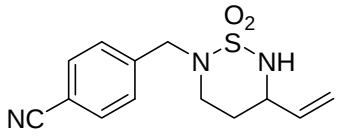
Yield: 90%. Purified by chromatography on silica gel (2/1 Hexane/EtOAc), white solid, TLC R_f = 0.37 (1/1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.14 (m, 2H), 6.70-6.65 (m, 2H), 5.79 (ddd, *J* = 17.6, 10.8, 5.2 Hz, 1H), 5.27-5.17 (m, 2H), 4.39, 3.84 (AB q, *J* = 13.6 Hz, each 1H), 4.25-4.17 (m, 1H), 4.00 (d, *J* = 9.2 Hz, 1H), 3.24 (dt, *J* = 3.2, 12.8 Hz, 1H), 3.15-3.06 (m, 1H), 2.93 (s, 6H), 1.70-1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 136.1, 130.0, 122.4, 116.4, 112.4, 57.6, 51.3, 46.7, 40.5, 28.5. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{14}H_{22}N_3O_2S$ 296.1427, Found 296.1430. IR (neat, cm^{-1}): 1616, 1525, 1344, 1330, 1158, 1136, 1104, 984, 918, 844, 807, 758.



1p

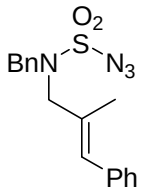
Yield: 75%. Purified by chromatography on silica gel (gradient elution: 10/1-6/1 Hexane/EtOAc), colorless liquid, TLC R_f = 0.25 (4/1 hexane/EtOAc). ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.71-5.60 (m, 1H), 4.98-4.92 (m, 2H), 4.46 (s, 2H), 3.21 (t, *J* = 8.0 Hz, 2H), 1.98 (q, *J* = 7.2 Hz, 2H), 1.66-1.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 136.4, 132.5, 128.7, 118.2, 115.8, 112.2, 52.1, 48.9, 30.3, 26.4. IR (neat, cm^{-1}): 2125, 1379, 1201, 1164, 914, 777, 736.



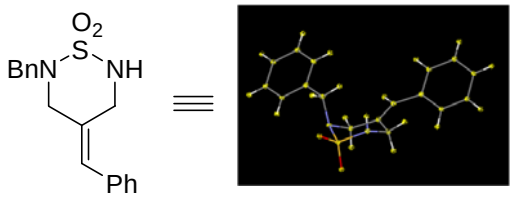
2p

Yield: 94%. Purified by chromatography on silica gel (4:1 DCM/EtOAc), white solid, TLC R_f = 0.59 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.00 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.85-5.76 (m, 1H), 5.30-5.21 (m, 2H), 4.51, 4.03 (AB q, *J* = 14.8 Hz, each 1H), 4.28-4.20 (m, 1H), 4.06 (d, *J* = 10.4 Hz, 1H), 3.41 (dt, *J* = 2.8, 12.8 Hz, 1H), 3.05 (ddd, *J* = 13.2, 4.4, 2.8 Hz, 1H), 1.78-1.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 135.7, 132.5, 129.1, 118.5, 116.9, 111.9, 57.6, 51.6, 48.2, 28.7. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{16}N_3O_2S$ 278.0958, Found 278.0957. IR (neat, cm^{-1}): 1423, 1324, 1287, 1164, 1145, 1106, 998, 935, 857, 840, 820, 776, 745.



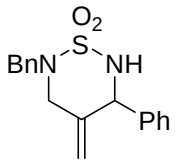
1q

Yield: 90%. Purified by chromatography on silica gel (gradient elution: 10:1-8:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.21 (10:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.34-7.14 (m, 10H), 6.35 (s, 1H), 4.45 (s, 2H), 3.92 (s, 2H), 1.80 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 136.6, 134.5, 131.5, 130.6, 129.0, 128.8, 128.7, 128.4, 128.2, 127.0, 56.9, 51.7, 15.7. IR (neat, cm^{-1}): 2125, 1379, 1204, 1165, 781, 736, 697.



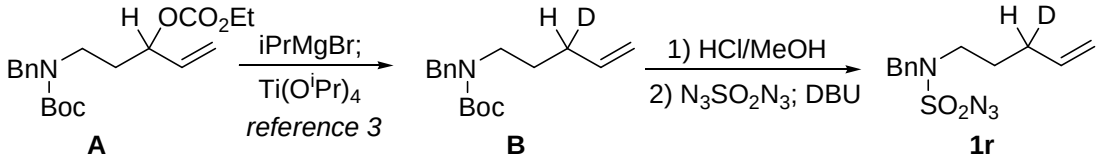
2q

Yield: 90%. Purified by chromatography on silica gel (gradient elution: 10:1–5:1 hexanes/EtOAc), white solid, TLC R_f = 0.60 (10:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.40-7.29 (m, 8H), 7.14-7.10 (m, 2H), 6.42 (s, 1H), 4.25-4.15 (m, 5H), 3.88 (d, *J* = 1.0 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 135.0, 134.8, 131.0, 128.9, 128.8, 128.7, 128.6, 128.1, 127.9, 126.7, 55.1, 52.0, 45.1. IR (neat, cm^{-1}): 1414, 1340, 1265, 1156, 1079, 1019, 764, 733, 697. HRMS (ESI) ($[M+K]^+$) Calcd. $C_{17}H_{18}N_2O_2SK$ for 353.0721, Found 353.0722.

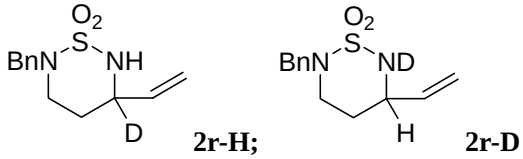


2q'

Yield: 9%. Purified by chromatography on silica gel (gradient elution: 4:1-2:1 hexanes/EtOAc), white solid, TLC R_f = 0.65 (5:1 hexanes/EtOAc). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.42-7.29 (m, 10H), 5.02 (d, *J* = 4.3 Hz, 1H), 4.99 (s, 1H), 4.59-4.51 (m, 2H), 4.38-4.29 (m, 2H), 4.08 (d, *J* = 13.5 Hz, 1H), 3.54 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 136.8, 135.0, 129.0, 128.9, 128.7, 128.1, 118.8, 63.4, 53.7, 52.2. IR (neat, cm^{-1}): 2924, 1458, 1351, 1165, 1076, 1027, 802, 777, 696. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{19}N_2O_2S$ 315.1162, Found 315.1155.



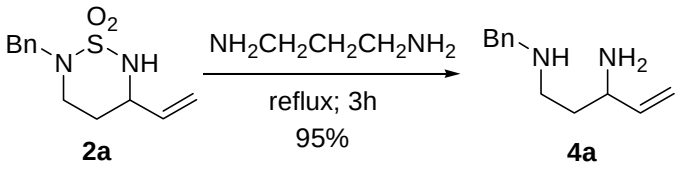
Corresponding mono-deuterated material **B** was synthesized in around 40% yield through a known procedure.[3] Deuterium Azide **1r** was synthesized in 72% yield from compound **B** through the general procedure, and purified by chromatography on silica gel (gradient elution: 20:1-10:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.61 (10:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.31 (m, 4H), 5.73-5.66 (m, 1H), 5.02-4.97 (m, 2H), 4.47 (s, 2H), 3.24 (t, *J* = 7.5Hz, 2H), 2.02-1.96 (m, 1H), 1.68-1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 134.6, 128.8, 128.5, 128.4, 115.6, 52.5, 48.1, 30.1 (t, *J* = 19.3 Hz), 26.3. IR (neat, cm^{-1}): 2122, 1379, 1205, 1165, 916, 775, 734, 698.



2r-H; **2r-D**

Purified by chromatography on silica gel (gradient elution: 4:1-2:1 hexanes/EtOAc), colorless liquid, TLC R_f = 0.56 (2:1 hexanes/EtOAc). **2r-H** (major one): ^{1}H NMR(500 MHz, $CDCl_3$): δ 7.38-7.30 (m, 5H), 5.84 (dd, *J* = 10.5, 17.0 Hz, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 4.54, 3.98 (AB q, *J* = 14.0 Hz, each 1H), 3.92 (s, 1H), 3.36 (dt, *J* = 3.0, 13.0 Hz, 1H), 3.14 (ddd, *J* = 13.5, 4.5, 2.5 Hz, 1H), 1.76-1.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.9, 135.4, 128.8, 128.7, 128.0, 116.7, 57.3 (t, *J* = 21.6 Hz), 51.8, 47.3, 28.6. **2r-D** (minor one)**:** ^{1}H NMR and ^{13}C NMR are very similar as the compound **2a,** and was confirmed by the ^{1}H NMR and ^{13}C NMR of mixture **2r-H** and **2r-D**(see supporting information-2). IR: 1397, 1329, 1162, 1095, 1007, 936, 926, 817, 769, 739. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_{16}DN_2O_2S$ 254.1068, Found 254.1092.

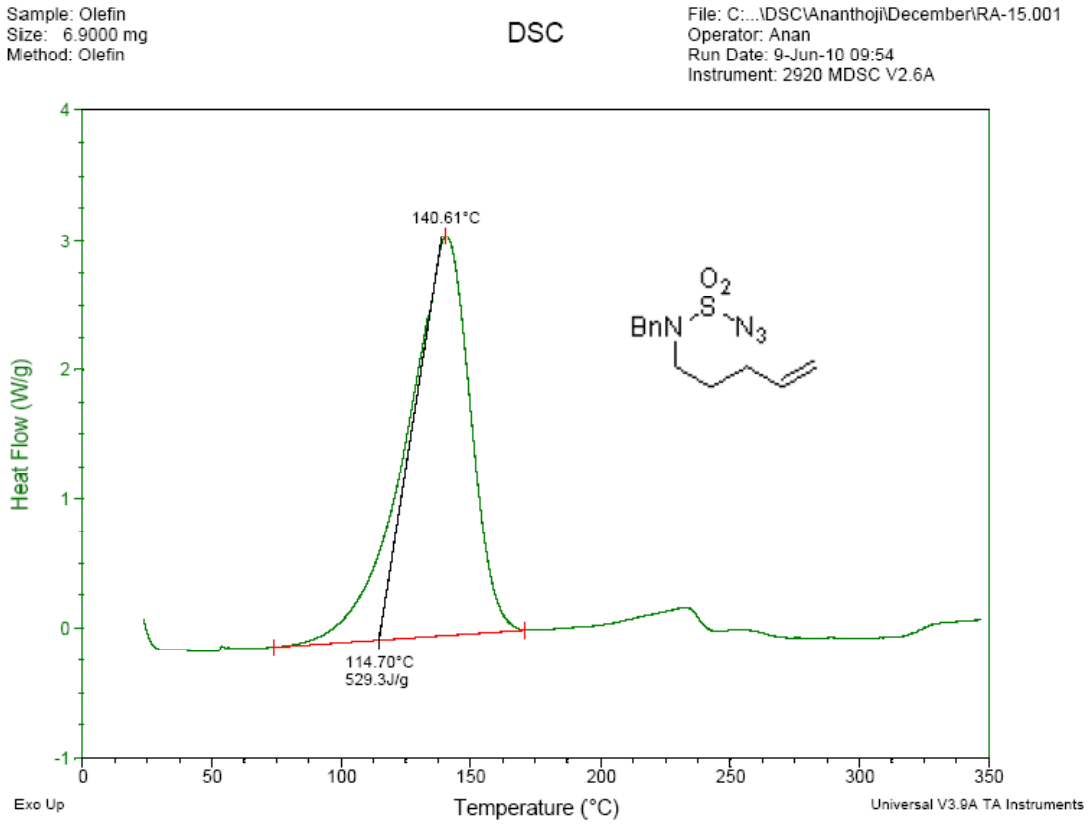
General Procedure for Deprotection of Sulfone Group



2a **4a**

An oven dried Schlenk tube was charged with 0.1 mmol of Sulfamoyl amide **2a** in 0.3 mL of dry 1,3-diaminopropane. The Teflon screw cap was replaced with a rubber septum. The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The mixture was heated on an oil bath at 145 ^{o}C and refluxed for 3 h. After cooling down to room temperature, the mixture was diluted with 5 mL of CH_2Cl_2 and 5 mL of water. After extraction of the water layer with 4 x 5 mL of CH_2Cl_2, the combined organic layers were dried over Na_2SO_4. The product **4a** was obtained as a colorless oil in high yield after removal of the solvent under reduced pressure. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.32-7.19 (m, 5H), 5.85-5.71 (m, 1H), 5.12-4.95 (m, 2H), 3.76 (s, 2H), 3.39 (q, *J* = 6.5 Hz, 1H), 2.69 (t, J = 7.0 Hz, 2H), 1.70-1.50 (m, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 143.3, 140.3, 128.4, 128.1, 126.9, 113.3, 54.1, 53.2, 46.6, 37.4. IR (neat, cm^{-1}): 2930, 1563, 1494, 1466, 1411, 1269, 918, 813, 735, 698. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_{19}N_2$ 191.1543 Found 191.1539.

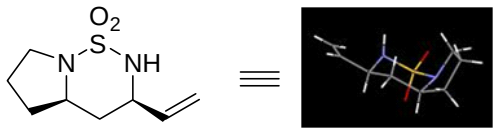
DSC of Azide **1a**



X-ray Crystallography

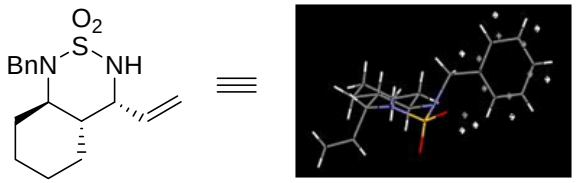
The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2* [1]. Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2 [1] and WinGX v1.70.01 [4,5,6,7] programs packages. Structure *cis*-**2c**: All non-hydrogen atoms were refined anisotropically. H2n hydrogen atom was located from the difference Fourier map and refined using riding model and Uiso(H)=1.5eq(N). The remaining hydrogen atoms were located geometrically and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(C). Crystal data and refinement conditions are shown in Table 1. Structure *trans,cis*-**2d**: All non-hydrogen atoms, except atoms of disordered benzyl group, were refined anisotropically. The benzyl group is disordered over two positions with refined occupancies of 0.65 and 0.35. One of the disordered parts of the molecule was refined using geometrical restraints. H1n hydrogen atom was located from the difference Fourier map and refined using riding model (Uiso(H)=1.5eq(N)). The remaining hydrogen atoms were located geometrically and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(C). Crystal data and refinement conditions are shown in Table 2. Structure *cis,trans*-**2e**: All non-hydrogen atoms were refined anisotropically. H2 hydrogen atom was located from the difference Fourier map and freely refined with isotropic thermal parameter - Uiso(H)=1.5eq(N). The remaining hydrogen atoms were located geometrically and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(C). Crystal data and refinement conditions are shown in Table 3. Structure **2o:** All non-hydrogen atoms were refined anisotropically. H2n hydrogen atom was located from the difference Fourier map and freely refined with isotropic thermal parameter. The remaining hydrogen atoms were located geometrically and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(C). Crystal data and refinement conditions are shown in Table 4.

[1] Bruker (2010). *APEX2*). Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Bruker (2009). SAINT. Data Reduction Software. Bruker AXS Inc., Madison, Wisconsin, USA.
[3] Sheldrick, G. M. (2008). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.
[4] Farrugia L.J. Appl. Cryst. (1999). 32, 837±838
[5] Sheldrick, G.M. (1997) SHELXL-97. Program for the Refinement of Crystal
[6] Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473
[7] Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.



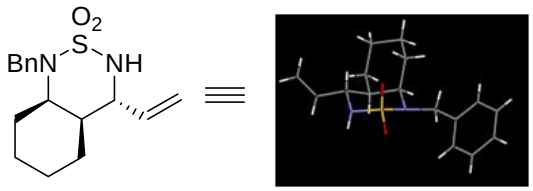
cis-**2c**

Table 1. Crystal data and structure refinement for compound *cis*-**2c**	
Empirical formula	C8 H14 N2 O2 S
Formula weight	202.27
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, P212121
Unit cell dimensions	a = 5.20710(10) A alpha = 90 deg. b = 12.8881(3) A beta = 90 deg. c = 14.6972(4) A gamma = 90 deg.
Volume	986.32(4) A^3
Z, Calculated density	4, 1.362 Mg/m^3
Absorption coefficient	2.698 mm^-1
F(000)	432
Crystal size	0.40 x 0.11 x 0.05 mm
Theta range for data collection	4.56 to 67.64 deg.
Limiting indices	-5<=h<=6, -14<=k<=15, -17<=l<=17
Reflections collected / unique	8608 / 1742 [R(int) = 0.0382]
Completeness to theta = 67.64	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8769 and 0.4117
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1742 / 0 / 119
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0986
R indices (all data)	R1 = 0.0344, wR2 = 0.0997
Absolute structure parameter	0.04(2)
Extinction coefficient	0.0028(6)
Largest diff. peak and hole	0.245 and -0.239 e.A^-3



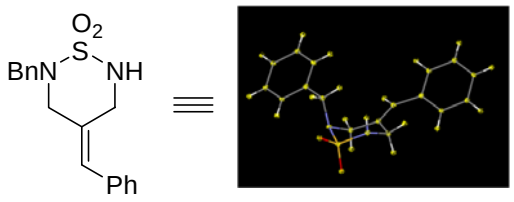
trans,cis-**2d**

Table 2. Crystal data and structure refinement for compound *trans,cis*-**2d**	
Empirical formula	C16 H22 N2 O2 S
Formula weight	306.42
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 14.5628(4) A alpha = 90 deg. b = 6.4095(2) A beta = 102.174(2) deg. c = 16.6818(4) A gamma = 90 deg.
Volume	1522.07(7) A^3
Z, Calculated density	4, 1.337 Mg/m^3
Absorption coefficient	1.939 mm^-1
F(000)	656
Crystal size	0.15 x 0.05 x 0.02 mm
Theta range for data collection	3.10 to 65.97 deg.
Limiting indices	-16<=h<=16, -6<=k<=7, -19<=l<=19
Reflections collected / unique	12157 / 2598 [R(int) = 0.0370]
Completeness to theta = 65.94	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9623 and 0.7597
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2598 / 6 / 194
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0996
R indices (all data)	R1 = 0.0474, wR2 = 0.1050
Largest diff. peak and hole	0.240 and -0.388 e.A^-3



cis,trans-**2e**

Table 3. Crystal data and structure refinement for compound *cis,trans*-**2e**	
Empirical formula	C16 H22 N2 O2 S
Formula weight	306.42
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 12.3076(3) A alpha = 90 deg. b = 9.7760(3) A beta = 90 deg. c = 26.6952(7) A gamma = 90 deg.
Volume	3211.94(15) A^3
Z, Calculated density	8, 1.267 Mg/m^3
Absorption coefficient	1.837 mm^-1
F(000)	1312
Crystal size	0.12 x 0.05 x 0.04 mm
Theta range for data collection	3.31 to 67.12 deg.
Limiting indices	-14<=h<=14, -11<=k<=11, -31<=l<=31
Reflections collected / unique	32841 / 2859 [R(int) = 0.0679]
Completeness to theta = 65.94	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9301 and 0.8096
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2859 / 0 / 193
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1041
R indices (all data)	R1 = 0.0504, wR2 = 0.1110
Largest diff. peak and hole	0.333 and -0.329 e.A^-3



2q

Table 4. Crystal data and structure refinement for compound **2q**	
Empirical formula	C17 H18 N2 O2 S
Formula weight	314.39
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 34.0823(7) A alpha = 90 deg. b = 5.4014(1) A beta = 102.680(1) deg. c = 16.6312(3) A gamma = 90 deg.
Volume	2987.0(1) A^3
Z, Calculated density	8, 1.398 Mg/m^3
Absorption coefficient	1.999 mm^-1
F(000)	1328
Crystal size	0.15 x 0.08 x 0.05 mm
Theta range for data collection	5.32 to 65.94 deg.
Limiting indices	-39<=h<=39, -6<=k<=5, -19<=l<=19
Reflections collected / unique	11857 / 2549 [R(int) = 0.0387]
Completeness to theta = 65.94	97.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9067 and 0.7536
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2549 / 0 / 203
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0869
R indices (all data)	R1 = 0.0385, wR2 = 0.0900
Largest diff. peak and hole	0.255 and -0.409 e.A^-3

Reference

(1) Lu, H. J.; Tao, J. R.; Jones, J. E.; Wojtas, L.; Zhang, X. P. *Org. Lett.* **2010**, *12*, 1248.

(2) Nojima, M. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 1811.

(3) S. Matsuda, D. K. An, S. Okamoto and F. Sato, *Tetrahedron Lett.*, 1998, **39**, 7513-7516