Supporting Information

Catalytic One-Pot Synthesis of Cyclic Amidines by Virtue of Tandem Reactions Involving Intramolecular Hydroamination under Mild Conditions

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General Methods. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F₂₅₄ plates. Visualization on TLC was achieved by use of UV light (254 nm) and treatment with phosphomolybdic acid and anisaldehyde stain followed by heating. Flash column chromatography was undertaken on silica gel (60 F₂₅₄ 400-630 mesh). ¹H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). ¹³C NMR was recorded on FT AM 400 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell. Frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbance is reported. High resolution mass spectra were recorded using FAB method.

Experimental Procedures for the Synthesis of Aminoalkyne Substrates

1-(*N*-Benzylamino)-4-pentyne (*Table 2*, entries 1–3).¹ 4-Pentynoic acid (520 mg, 5.3 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.44 g, 8.0 mmol) and 4-dimethylaminopyridine (24.4 mg, 0.20 mmol) were placed in a round bottom flask (100 mL), and then the mixture was flushed with nitrogen three times followed by the addition of 40 mL

¹ Overman, L. E.; Sarkar, A. K., *Tetrahedron Lett.* **1992**, *33*, 4103–4106.

of dichloromethane. To this solution, benzylamine (804 mg, 7.5 mmol) was added dropwise and then was stirred for 12 h at room temperature. The reaction mixture was quenched with HCl solution (1 N, 10 mL) and extracted with dichloromethane (30 mL x 3). The combined organic layer was dried (MgSO₄), filtered, and evaporated followed by a silica gel column chromatography (EtOAc/Hx, 1:2) to afford *N*-benzyl-4-pentynoylamide (946 mg, 92%).

In a two-neck round bottom flask (100 mL), a solution of lithium aluminum hydride in diethyl ether (1.0 M, 18.5 mL) was added and it was diluted with 20 mL of diethyl ether. To this, a solution of *N*-benzyl-4-pentynoylamide (864 mg, 4.6 mmol) in diethyl ether (10 mL) was added dropwise at 0 °C and then stirred under reflux for 4 h. The reaction mixture was cooled to room temperature and water (2 mL) was added slowly to quench the reaction, followed by the same amount of aqueous NaOH solution (1 N, 10 mL). The resulting white slurry was stirred for further 30 min, and filtered through a pad of celite. The filtrate was condensed and purified by a silica gel column chromatography (dichloromethane/MeOH, 10:1) to give 1-(*N*-benzylamino)-4-pentyne (771 mg, 97%) as orange liquid; ¹H-NMR (400 MHz, CDCl₃) δ 7.33-7.21 (m, 5H), 3.80 (s, 2H), 2.75 (t, *J* = 6.9 Hz, 2H), 2.30-2.25 (m, 2H), 1.94 (t, *J* = 2.7 Hz, 1H), 1.78-1.69 (m, 2H), 1.26 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 128.4, 128.0, 126.9, 84.1, 68.5, 53.9, 48.2, 28.7, 16.3; IR (KBr) 3300, 3027, 2937, 2862, 2116, 1495, 1454, 1121 cm⁻¹.

1-(*N*-Benzylamino)-2,2-diphenyl-4-pentyne (*Table 2*, entry 4). To a suspension of NaH (264 mg, 11 mmol) in THF (10 mL) was slowly added a solution of diphenylacetonitrile (1.93 g, 10.0 mmol) in THF (3 mL) at 0 °C. After stirring for 1 h at room temperature, propargyl

bromide (1.31 g, 11 mmol) was slowly added at 0 °C and the reaction mixture was stirred at room temperature for 12 h. The mixture was diluted with diethyl ether (60 mL) and water (20 mL) was added to quench the reaction. The layers were separated washing with brine, dried (MgSO₄), filtered, evaporated, and purified by flash chromatography on silica gel (EtOAc/Hx, 1:10) to give 2,2-diphenylpent-4-ynenitrile (2.24 g, 97%).

To a solution of the above obtained nitrile (925 mg, 4.0 mmol) in diethyl ether (5 mL) was slowly added a solution of lithium aluminum hydride (8 mL, 1.0 M in diethyl ether) at 0 °C. After stirring the reaction mixture for 5 h at room temperature, water (5 mL) and 1N NaOH solution (5 mL) were carefully added. The resulting white slurry was further stirred for 30 min and then filtered through a pad of celite. The solvent was removed under reduced pressure. To a solution of the obtained crude amine in dichloromethane (10 mL) was added benzoyl chloride (760 μ L, 6.5 mmol) at 0 °C. After stirring the reaction mixture for 0.5 h at 0 °C, it was quenched with aqueous NaHCO₃ solution (20 mL). After extraction with dichloromethane (20 mL x 3), the organic layer was dried (MgSO₄), filtered, evaporated, and then chromatographed on silica gel (EtOAc/Hx, 1:5) to give N-(2,2-diphenylpent-4-ynyl)benzamide (950 mg, 70% in two steps).

In a two-neck round bottom flask (50 mL), a solution of lithium aluminum hydride in diethyl ether (1.0 M, 5.6 mL) was added and it was diluted with 10 mL of diethyl ether. To this, a solution of above benzamide derivative (950 mg, 2.8 mmol) in diethyl ether (5 mL) was added dropwise and then stirred for 12 h at room temperature. Water (2 mL) and 1N NaOH (2 mL) were added slowly, and then the resulting white slurry was stirred for additional 30 min followed by filtration through a pad of celite. The filtrate was condensed and purified by a silica gel column chromatography (EtOAc/Hx, 1:10) to give 1-(*N*-benzylamino)-2,2-diphenyl-4-pentyne (464 mg, 51%) as a yellowish oil; ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.16 (m, 15H),

3.76 (s, 2H), 3.36 (s, 2H), 3.19 (d, $J = 2.6$ Hz, 2H), 1.83 (t, $J = 2.6$ Hz, 1H), 1.24 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 128.2, 128.0, 127.9, 127.8, 126.7, 126.3, 81.8, 71.1, 55.8, 54.0, 50.2, 28.3; IR (KBr) 3229, 3026, 2921, 2850, 2117, 1495, 1446, 1171 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{24}\text{H}_{24}\text{N}$ $[M+H]^+$: 326.1909, found: 326.1910.

1-[N-(4-Methoxybenzyl)amino]-5-hexyne (*Table 2*, entry 5) was prepared using the same procedure as for 1-(*N*-benzylamino)-4-pentyne with 91% yield in two steps; ^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, $J = 11.5$ Hz, 2H), 6.81 (dd, $J = 8.8, 2.6$ Hz, 2H), 3.76 (s, 3H), 3.69 (s, 2H), 2.60 (t, $J = 9.0$ Hz, 2H), 2.20-2.14 (m, 2H), 1.91 (t, $J = 3.6$ Hz, 1H), 1.60-1.53 (m, 4H), 1.43 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 132.5, 129.2, 113.7, 84.3, 68.3, 55.1, 53.3, 48.6, 29.0, 26.2, 18.2; IR (KBr) 3294, 3000, 2935, 2115, 1612, 1512, 1461, 1247 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{NO}$ $[M+H]^+$: 218.1545, found: 218.1546.

1-[(*R*)-N-(1-Phenylethyl)amino]-5-hexyne (*Table 2*, entry 6) was prepared using the same procedure as for 1-(*N*-benzylamino)-4-pentyne with 93% yield in two steps; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.28 (m, 4H), 7.24-7.20 (m, 1H), 3.74 (q, $J = 6.6$ Hz, 1H), 2.53-2.43 (m, 2H), 2.16-2.12 (m, 2H), 1.90 (t, $J = 2.6$ Hz, 1H), 1.56 (br, 1H), 1.53 (m, 4H), 1.33 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 128.3, 126.8, 126.4, 84.3, 68.3, 58.3, 47.1, 29.2, 26.2, 24.2, 18.2; IR (KBr) 3302, 3026, 2935, 2116, 1493, 1452, 1131 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{N}$ $[M+H]^+$: 202.1596, found: 202.1598.

1-(N-Benzylamino)-5-hexyne (**7**, *Table 1* and entry 7 of *Table 2*)² was prepared using the same procedure as for 1-(N-benzylamino)-4-pentyne with 89% yield in two steps; ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.24 (m, 5H), 3.77 (s, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.19-2.18 (m, 2H), 1.91 (t, *J* = 2.7 Hz, 1H), 1.60-1.58 (m, 4H), 1.53 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.3, 128.4, 128.1, 126.9, 84.4, 68.4, 54.0, 48.8, 29.1, 26.2, 18.3; IR (KBr) 3300, 3027, 2937, 2862, 2116, 1495, 1454, 1121 cm⁻¹.

1-(N-Benzylaminomethyl)-1-(2-propynyl)cyclohexane (*Table 2*, entry 8). To a solution of diisopropylamine (364 mg, 3.6 mmol) in THF (5 mL) was added dropwise *n*-BuLi (1.8 mL, 2.0 M solution in cyclohexane) at 0 °C under N₂ atmosphere. The resulting solution was stirred for 15 min before cooling to -78 °C. To this freshly prepared LDA solution, a solution of cyanocyclohexane (327 mg, 3.0 mmol) was added dropwise at -78 °C and stirred for 1 h at -78 °C followed by the addition of propargyl bromide (368 μL, 80 wt% solution in toluene). The reaction mixture was stirred for 1 h at -78 °C and then warmed to room temperature. Saturated aq NH₄Cl solution (10 mL) was added followed by diethyl ether (30 mL), and extracted with diethyl ether (30 mL x 3). The organic layer was dried (MgSO₄), filtered, evaporated, purified by a silica gel chromatography (EtOAc/Hx, 1:50) to afford propargylated cyclohexanenitrile (252 mg, 57%).

To a solution of the above obtained nitrile (234 mg, 1.6 mmol) in diethyl ether (13 mL) was added dropwise diisobutylaluminum hydride (3.2 mL, 1.0 M solution in toluene) under N₂

² Overman, L. E.; Rodriguez-Campos, I. M. *Synlett* **1992**, 995–996.

atmosphere at -78 °C. After stirring for 3 h at the same temperature, MeOH (2.1 mL) was added followed by benzylamine (437 μ L, 4.0 mmol). The reaction mixture was warmed to room temperature while stirring for additional 2 h, after which time the formation of white precipitate was observed. Rubber septum was removed and sodium borohydride (121 mg, 3.2 mmol) was added. The reaction mixture was stirred for overnight at room temperature. The organic solvent was removed under reduced pressure and the crude residue was re-dissolved in dichloromethane (20 mL). The resulting slurry was washed with saturated aqueous sodium bicarbonate solution, water and brine. The organic layer was dried over anhydrous MgSO₄ and filtered. The solvent was removed and then the residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:4 with 1-5% of Et₃N) to give the desired product (192 mg, 50%); ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.21 (m, 5H), 3.80 (s, 2H), 2.56 (s, 2H), 2.27 (s, 2H), 1.93 (s, 1H), 1.40 (m, 10H), 1.24 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 128.2, 127.9, 126.7, 82.3, 69.9, 54.7, 39.1, 36.7, 33.3, 26.1, 26.0, 21.6; IR (KBr) 3327, 3031, 2927, 2110, 1489, 1452, 1119 cm⁻¹; HRMS (FAB), m/z calcd. for C₁₇H₂₄N [M+H]⁺: 242.1909, found: 242.1909.

1-(N-Benzylaminomethyl)-2-(2-propynyl)benzene (*Table 2*, entry 9). To a solution of 3-isochromanone (740 mg, 5.0 mmol) in CH₂Cl₂ (20 mL) was added diisobutylaluminum hydride (5.5 mL, 1.0 M solution in toluene) under N₂ at -78 °C. After stirring at -78 °C for 2 h, the reaction mixture was quenched by the addition of aqueous HCl solution (1 N) and then diluted with dichloromethane (20 mL). The aqueous layer was extracted with dichloromethane (20 mL x 2), dried over MgSO₄ and filtered. The solvent was removed under the reduced pressure to give crude 3-isochroman-1-ol, which was used in the following step without further

purifications. To a solution of diisopropylamine (1.6 mL, 11.4 mmol) in THF (15 mL) was added dropwise *n*-BuLi (5.7 mL, 2.0 M solution in cyclohexane) at 0 °C under N₂ atmosphere. The resulting solution was stirred for 15 min before cooling to -78 °C. To this freshly prepared LDA solution, a solution of trimethylsilyldiazomethane in diethyl ether (2.9 mL, 2.0 M solution in diethyl ether, 5.8 mmol) was added dropwise at -78 °C. Upon the completion of the addition, the color of solution turned into orange and stirring was continued for additional 30 min at -78 °C. To this solution, a solution of the above obtained crude 3-isochroman-3-ol (662 mg, 4.4 mmol) in THF (3 mL) was added dropwise. After stirring at -78 °C for 30 min, the reaction mixture was slowly warmed to room temperature (during this process, the vigorous evolution of gas bubble was observed). Saturated aqueous NH₄Cl (20 mL) was added to quench the reaction and diethyl ether (100 mL) was added to dilute the reaction mixture. The organic layers were separated and the resulting aqueous layer was further extracted with diethyl ether (50 mL x 3). The combined organic layers were dried (MgSO₄), filtered, evaporated to provide crude 2-(2-propynyl)benzyl alcohol which was further purified by a silica gel column chromatography (EtOAc/Hx, 1:5) leading to analytically pure compound (299 mg, 41% in two steps).

To a solution of the above obtained benzyl alcohol derivative (265 mg, 1.8 mmol) in dichloromethane (10 mL) was added a mixture of pyridiniumchlorochromate (PCC, 1.16 g, 5.4 mmol) and celite (1.74 g) in one portion and the resulting brown slurry was stirred for 6 h at room temperature. The resulting slurry was filtered through a pad of celite and then through a pad of silica gel. The solvent was removed under the reduced pressure and the resulting residue was further purified on silica gel (EtOAc/Hx, 1:20) to give 2-(2-propynyl)benzaldehyde (169 mg, 65%).

To a solution of the obtained benzaldehyde derivative (164 mg, 1.14 mmol) in methanol (4 mL) was added benzylamine (131 μ L, 1.2 mmol). The reaction mixture was then stirred for 5 h

room temperature. To this solution was added sodium borobhdride NaBH₄ (65 mg, 1.7 mmol) was added carefully. The reaction mixture was stirred for 2 h at room temperature and the organic solvent was removed under reduced pressure. The resulting mixture was dissolved in dichloromethane (20 mL) and water was added to quench the excessive sodium borohydride. The layers were separated and the aqueous layer was further extracted with dichloromethane (20 mL x 2). The combined organic layers were dried (MgSO₄), filtered, evaporated, and finally purified by a silica gel column chromatography (EtOAc/Hx, 1:2) to give the desired product (214 mg, 80%); ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.32 (m, 9H), 3.90 (s, 4H), 3.79 (s, 2H), 2.26 (t, *J* = 2.7 Hz, 1H), 1.62 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 128.2, 127.9, 126.7, 82.3, 69.9, 54.7, 36.7, 33.3, 26.1, 21.6; IR (KBr) 3295, 3063, 3027, 2822, 2118, 1603, 1494, 1454, 1048. cm⁻¹; HRMS (FAB) *m/z* calcd. for C₁₇H₁₈N [*M*+*H*]⁺: 236.1439, found: 236.1440.

1-(*N*-Benzylamino)-3-(*tert*-butyldimethylsilyloxy)-5-hexyne (16, eq 3). To a solution of trimethylsilylacetylene (1.96 g, 20.0 mmol) in THF (40 mL) was added dropwise a solution of *n*-BuLi (10 mL, 2.0 M solution in cyclohexane) at -78 °C. After stirring the reaction mixture for 30 min at the same temperature, BF₃·Et₂O (2.86 g, 20 mmol) was added to the above solution and stirred for additional 30 min at -78 °C followed by a slow addition of a solution of epichlorohydrin (925 mg, 10 mmol) at the same temperature. The resulting solution was stirred for 4 h at -78 °C and quenched with saturated aqueous NH₄Cl solution followed by extraction with diethyl ether (30 mL x 3), dried (MgSO₄), filtered, and then evaporated to give

crude hydroxyl alkyne (1.91 g). To a stirred solution of the above obtained crude product in DMSO/H₂O (10:1, 44 mL) were added KCN (976 mg, 15 mmol) and NaI (2.99 g, 20 mmol). The mixture was stirred at 80 °C for 5 h, diluted with EtOAc (50 mL) and then extracted with EtOAc (50 mL x 4) washing with brine. The combined organic layer was dried over MgSO₄, filtered, evaporated, and then chromatographed on silica gel (EtOAc/Hx, 1:20) to give the analytically pure nitrile product (873 mg, 80% yield in two steps).

To a stirred solution of the above obtained hydroxyl nitrile (340 mg, 3.1 mmol) in DMF (10 mL) were added imidazole (306 mg, 4.5 mmol), *tert*-butylchlorodimethylsilane (678 mg, 4.5 mmol) at 0 °C. The mixture was stirred for 5 h at room temperature and then quenched with H₂O (15 mL) followed by extraction with dichloromethane (30 mL x 3). The combined organic layer was dried (MgSO₄), concentrated, purified by a silica gel column chromatography (EtOAc/Hx, 1:20) to give silyl-protected nitrile product (645 mg, 93%).

To a solution of the obtained silyl-protected nitrile (640 mg, 2.9 mmol) in dichloromethane (10 mL) was added dropwise diisobutylaluminum hydride (5.8 mL, 1.0 M solution in toluene) under N₂ at -78 °C. After stirring the mixture at the same temperature for 3 h and then quenched with EtOH (1 mL) and solvent was removed under reduced pressure. This was diluted with 1N aqueous HCl (5mL), and extracted with dichloromethane (20 mL x 3). The combined organic layers were washed with saturated brine-saturated aqueous NaHCO₃ (1:1). The organic layer was dried and concentrated in vacuo.

To a solution of the obtained crude aldehyde derivative (1.31 mg, 6.2 mmol) in methanol (20 mL) was added benzylamine (0.71 mL, 6.5 mmol). The reaction mixture was then stirred for 5 h room temperature. To this solution was added sodium borohydride NaBH₄ (351.8 mg, 9.3 mmol) was added carefully. The reaction mixture was stirred for 2 h at room temperature and the organic solvent was removed under reduced pressure. The resulting mixture was

dissolved in dichloromethane (20 mL) and water was added to quench the excessive sodium borohydride. The layers were separated and the aqueous layer was further extracted with dichloromethane (20 mL x 2). The combined organic layers were dried (MgSO₄), filtered, evaporated, and purified by a silica gel column chromatography (EtOAc/Hx, 1:10) to give the desired product (**16**, 1.4 g, 71 %); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.20 (m, 5H), 3.91-3.79 (m, 1H), 3.76 (s, 2H), 2.73-2.68 (m, 2H), 2.33-2.30 (m, 2H), 1.95 (t, *J* = 2.7, 1H), 1.94-1.85 (m, 1H), 1.76-1.72 (m, 2H), 0.84 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 128.4, 128.2, 126.9, 81.4, 70.1, 69.5, 54.1, 45.6, 36.5, 27.5, 25.8, 18.0, -4.5, -4.8; IR (KBr) 3311, 2956, 2931, 2320, 1472, 1257, 1110, 839 cm⁻¹; HRMS (FAB) *m/z* calcd. for C₁₉H₃₂NOSi [*M*+*H*]⁺: 318.2253, found:318.2253.

Experimental Procedure for the Optimization Studies (Table SI). To a solution of 1-(*N*-benzylamino)-5-hexyne (**7**, 37.5 mg, 0.20 mmol), an examined catalyst (5 mol %), and 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol) in the indicated solvent (2.0 mL) was added *p*-toluenesulfonyl azide (47.3 mg, 0.24 mmol) at room temperature. The reaction mixture was stirred for 12 h at the same temperature before quenching with saturated aqueous NH₄Cl solution (3 mL) and diluted with dichloromethane (5 mL). The crude products were extracted with dichloromethane (5 mL x 3), dried (MgSO₄), and evaporated under the reduced pressure. The yield and ratio of two products (**A** and **B**) in each reaction (**Table SI**) were determined by integration of ¹H NMR relative to an internal standard (1,1,2,2-tetrachloroethane).

Table S1. Optimization Experiments on Catalysts and Solvents

entry	catalyst	solvent	ratio (A/B) ^a	yield (%) ^b
1	—	THF	—	<5
2	CuI	THF	1.6:1	46
3	CuBr	THF	2.1:1	37
4	CuCl	THF	1:2.5	43
5	CuCl ₂	THF	1:1.5	22
6	PtCl ₂	THF	1.3:1	49
7	PdCl ₂	THF	3.7:1	35
8	Pd(OAc) ₂	THF	16:1	16
9	AuCl ₃	THF	18:1	31
10	Ru(acac) ₃	THF	—	<5
11	RuCl ₃ ·(H ₂ O) _n	THF	7.4:1	41
12	Ru ₃ (CO) ₁₂	THF	8.0:1	75
13	Ru ₃ (CO) ₁₂	CH ₃ CN	4.5:1	39
14	Ru ₃ (CO) ₁₂	CH ₂ Cl ₂	7.1:1	41
15	Ru ₃ (CO) ₁₂	Toluene	2.1:1	29
16	Ru ₃ (CO) ₁₂	DMF	5.3:1	41
17	Ru ₃ (CO) ₁₂	MeOH	>25:1	35

^a Determined by ¹H-NMR of crude reaction mixture. ^b NMR yield based on an internal standard (1,1,2,2-tetrachloroethane).

Representative Procedure for the Preparation of Cyclic Amidines (Table 1 and 2).

To a solution of 1-(*N*-benzylamino)-5-hexyne (**7**, 37.5 mg, 0.20 mmol) and Ru₃(CO)₁₂ (6.4 mg, 0.010 mmol) in THF (2.0 mL) was added *p*-toluenesulfonyl azide (47.3 mg, 0.24 mmol) at room temperature. The reaction mixture was stirred for 12 h at the same temperature before quenching with saturated aqueous NH₄Cl solution (3 mL) and diluted with dichloromethane (5 mL). The crude products were extracted with dichloromethane (5 mL x 3), dried (MgSO₄), and

evaporated under the reduced pressure. The ratio of two possible products was determined by integration of ^1H NMR peaks of the residue after removal of organic solvents. The residue was purified by a flash column chromatography on silica gel using EtOAc/Hx (normally 1:5) to afford the analytically pure cyclic amidines with indicated yields in Table 1 and 2. When Et_3N was used as an additive, 1.2 equiv relative to aminoalkyne substrates was employed at the start of each reaction under otherwise identical conditions.

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (4-toluene)sulfonylamide (8a, Table 1, entries 1 and 2, major product); ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 6.5$ Hz, 2H), 7.23 (m, 3H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.11 (m, 2H), 4.69 (d, $J = 14.5$ Hz, 1H), 4.50 (d, $J = 14.5$ Hz, 1H), 3.96 (m, 1H), 3.32-3.25 (m, 2H), 2.34 (s, 3H), 1.89-1.85 (m, 2H), 1.67-1.64 (m, 2H), 1.48 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 141.8, 141.4, 135.9, 128.9, 128.6, 127.9, 127.6, 125.9, 53.3, 48.2, 31.8, 26.4, 21.3, 19.8, 17.4; IR (KBr) 2920, 1548, 1494, 1451, 1269, 1136, 1086, 815 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ [$M+H$] $^+$: 357.1637, found: 357.1635.

Figure S1. ORTEP of 1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (4-toluene)sulfonylamide (8a, Table 1, entries 1 and 2, major product)

1-(*N*-Benzyl)-(2-piperidinylidene) (4-toluene)sulfonylamide (*Table 1*, entries 1 and 2, minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.28-18 (m, 7H), 4.67 (s, 2H), 3.28 (m, 2H), 3.16 (m, 2H), 2.36 (s, 3H), 1.75 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 141.7, 141.3, 135.7, 129.0, 128.7, 128.1, 127.8, 126.2, 53.3, 48.3, 29.7, 22.2, 21.4, 19.6; IR (KBr) 2931, 1578, 1481, 1287, 1136, 1092, 872 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$ [$M+H$] $^+$: 343.1480, found: 343.1480.

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) methanesulfonylamide (*Table 1*, entry 3); ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.19 (m, 5H), 4.74 (d, $J = 14.6$ Hz, 1H), 4.53 (d, $J = 14.6$ Hz, 1H), 3.83 (m, 1H), 3.32-3.25 (m, 2H), 2.93 (s, 3H), 1.96-1.87 (m, 2H), 1.71-1.64 (m, 2H), 1.47 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 136.1, 128.8, 127.7, 53.1, 48.2, 43.9, 31.9, 26.5, 19.8, 17.4; IR (KBr) 2945, 1551, 1495, 1362, 1268, 1168, 1114, 967, 819 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$ [$M+H$] $^+$: 281.1324, found: 281.1324.

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (2-pyridine)sulfonylamide (*Table 1*, entry 4); ^1H NMR (400 MHz, CDCl_3) δ 8.60 (d, $J = 5.4$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.74 (m, 1H), 7.33 (m, 1H), 7.17 (m, 3H), 7.07 (m, 2H), 4.58 (d, $J = 3.0$ Hz, 2H), 4.05 (m, 1H), 3.30-3.23 (m,

1H), 1.91-1.86 (m, 2H), 1.69-1.64 (m, 2H), 1.51 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 160.3, 149.2, 137.4, 135.6, 128.5, 127.9, 127.5, 125.4, 120.6, 53.4, 48.2, 32.1, 26.3, 20.3, 17.3; IR (KBr) 2951, 1549, 1494, 1278, 1168, 1107, 960, 818 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}_2\text{S}$ $[M+H]^+$: 344.1433, found: 344.1433.

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) benzoylamide (*Table 1*, entry 5); ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.6$ Hz, 2H), 7.43-7.23 (m, 8H), 4.93 (d, $J = 14.6$ Hz, 1H), 4.71 (d, $J = 14.6$ Hz, 1H), 3.85 (m, 1H), 3.31 (m, 2H), 1.95-1.88 (m, 2H), 1.72 (m, 1H), 1.55 (m, 1H), 1.16 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 169.4, 137.6, 136.7, 131.1, 129.3, 128.7, 127.8, 127.4, 53.2, 48.2, 29.9, 27.6, 20.0, 19.3; IR (KBr) 3018, 2931, 2866, 1631, 1572, 1481, 1263, 1187, 1130, 749 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}$ $[M+H]^+$: 307.1810, found: 307.1810.

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) (4-nitro)benzoylamide (*Table 1*, entry 6); ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 4H), 7.35-7.24 (m, 5H), 4.84 (q, $J = 32.5, 19.4$ Hz, 2H), 3.90 (m, 1H), 3.37 (m, 2H), 1.94 (m, 2H), 1.77 (m, 1H), 1.60 (m, 1H), 1.16 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 171.8, 149.3, 143.5, 136.0, 130.1, 128.8, 127.7, 127.5, 123.0, 53.6, 48.6, 30.1, 27.4, 20.0, 19.3; IR (KBr) 2938, 1623, 1551, 1495, 1342, 1319, 1286, 1087, 785, 727 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_3$ $[M+H]^+$: 352.1661, found: 352.1659.

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) (4-methyl)benzoylamidie (*Table 1*, entry 7); ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.1$ Hz, 2H), 7.35-7.27 (m, 5H), 7.13 (d, $J = 7.9$ Hz, 2H), 4.93 (d, $J = 14.6$ Hz, 1H), 4.48 (d, $J = 14.6$ Hz, 1H), 3.82 (m, 1H), 3.30 (m, 2H), 2.35 (s, 3H), 1.94-1.87 (m, 2H), 1.72 (m, 1H), 1.53 (m, 1H), 1.15 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.3, 168.8, 141.4, 136.8, 134.9, 129.3, 128.6, 128.5, 127.8, 127.3, 53.1, 48.2, 29.9, 27.7, 21.5, 19.9, 19.3; IR (KBr) 3029, 2937, 2866, 1551, 1495, 1376, 1282, 1187, 1140, 756 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}$ $[M+H]^+$: 321.1967, found: 321.1967.

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) diphenylphosphorylamide (*Table 1*, entry 8); ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.17 (m, 11H), 7.03-6.99 (m, 4H), 4.66 (d, $J = 14.5$ Hz, 1H), 4.39 (d, $J = 14.5$ Hz, 1H), 3.63 (m, 1H), 3.22-3.15 (m, 2H), 1.87-1.81 (m, 2H), 1.67-1.61 (m, 2H), 1.40 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 171.6, 152.1, 152.0, 151.9, 136.1, 129.3, 129.2, 128.6, 127.7, 127.4, 124.0, 123.9, 120.6, 120.6, 120.5, 52.6, 47.9, 47.9, 33.8, 33.7, 26.9, 19.8, 17.7; IR (KBr) 2952, 1567, 1489, 1250, 1202, 1008, 919, 765, 691 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_3\text{P}$ $[M+H]^+$: 435.1838, found: 435.1838.

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) (benzyloxycarbonyl)amidine (*Table 1*, entry 9);

^1H NMR (300 MHz, CDCl_3) δ 7.43-7.23 (m, 10H), 5.15 (q, J = 12.4 Hz, 2H), 4.75 (q, J = 14.7 Hz, 2H), 3.71 (m, 1H), 3.23-3.16 (m, 2H), 1.88-1.80 (m, 2H), 1.68-1.53 (m, 2H), 1.23 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 161.9, 137.3, 136.6, 128.5, 128.2, 128.1, 127.9, 127.6, 127.3, 67.1, 52.6, 47.8, 30.2, 27.5, 19.9, 18.7; IR (KBr) 3054, 2940, 1668, 1565, 1496, 1454, 1321, 1225, 1136, 1050, 1027, 733, 699 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_2$ $[M+H]^+$: 337.1916, found: 337.1916.

1-(*N*-Benzyl)-(2-pyrrolinyldiene) (4-toluene)sulfonylamide (3, Table 2, entry 1, major product); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.3 Hz, 2H), 7.79-7.16 (m, 7H), 4.56 (s, 2H), 3.30 (t, J = 7.3 Hz, 2H), 3.09 (t, J = 8.0 Hz, 2H), 2.38 (s, 3H), 1.97 (q, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.9, 140.8, 135.0, 129.1, 128.3, 128.1, 127.7, 126.4, 48.9, 48.6, 31.0, 21.4, 19.0; IR (KBr) 3060, 2924, 1571, 1494, 1454, 1283, 1145, 1093, 817, 704 cm^{-1} ; HRMS (FAB) m/z calcd. $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$ for $[M+H]^+$: 329.1324, found: 329.1320.

Figure S2. ORTEP of 1-(*N*-benzyl)-(2-pyrrolinyldiene) (4-toluene)sulfonylamide (3, Table 2, entry 1, major product)

1-(*N*-Benzyl)-3-methyl-(2-pyrrolinyldiene) (4-toluenesulfonyl)amide (4, Table 2, entry 1, minor product); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.3$ Hz, 2H), 7.28-7.13 (m, 5H), 7.12 (m, 2H), 4.52 (s, 2H), 3.80 (q, $J = 7.4$ Hz, 1H), 3.40 (m, 1H), 2.37 (s, 3H), 2.16 (m, 1H), 1.69 (m, 1H), 1.35 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 141.8, 135.2, 129.0, 128.9, 128.8, 128.7, 128.1, 126.2, 48.6, 46.9, 37.4, 28.1, 21.4, 17.7; IR (KBr) 2925, 1570, 1491, 1277, 1145, 1087, 872, 585 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 343.1480, found: 343.1486.

1-(*N*-Benzyl)-(2-pyrrolinyldiene) methanesulfonylamine (Table 2, entry 2, major product); ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.18 (m, 5H), 4.51 (s, 2H), 3.29 (t, $J = 7.4$ Hz, 2H), 3.10 (t, $J = 8.0$ Hz, 2H), 2.96 (s, 3H), 1.97 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 134.9, 128.6, 128.0, 127.8, 48.6, 48.3, 42.5, 30.8, 18.9; IR (KBr) 3061, 1589, 1455, 1321, 1165, 910, 773 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 253.1011, found: 253.1010.

1-(*N*-Benzyl)-3-methyl-(2-pyrrolinyldiene) methanesulfonylamine (Table 2, entry 2, minor product); ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.19 (m, 5H), 4.52 (s, 2H), 3.72 (m, 1H), 3.41 (m, 1H), 3.23 (t, $J = 9.4$ Hz, 1H), 3.00 (s, 3H), 2.17 (m, 1H), 1.67 (m, 1H), 1.36 (d, $J = 7.2$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 168.5, 135.3, 128.9, 127.9, 48.4, 46.8, 43.2, 37.4, 28.1, 17.8; IR (KBr) 2931, 1575, 1494, 1455, 1280, 1135, 1121, 873 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 267.1167, found: 267.1165.

1-(*N*-Benzyl)-(2-pyrrolinyldine) (2-pyridine)sulfonylamide (*Table 2*, entry 3); ^1H NMR (400 MHz, CDCl_3) δ 8.62 (m, 1H), 8.01 (d, $J = 7.8$ Hz, 1H), 7.81 (t, $J = 1.7$ Hz, 1H), 7.38 (m, 1H), 7.19 (m, 1H), 7.24-7.13 (m, 3H), 4.55 (s, 2H), 3.33 (m, 4H), 2.01 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 159.9, 149.3, 137.5, 134.7, 128.6, 128.2, 127.8, 125.7, 121.2, 49.0, 48.6, 31.7, 18.9; IR (KBr) 3262, 3061, 2889, 1576, 1561, 1369, 1217, 1087, 960 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_2\text{S}$ $[M+H]^+$: 316.1120, found: 316.1119.

1-(*N*-Benzyl)-4,4-diphenyl-(2-pyrrolinyldinene) (4-toluene)sulfonylamide (*Table 2*, entry 4); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.23-7.15 (m, 11H), 7.01-6.97 (m, 6H), 4.60 (s, 2H), 3.88 (s, 2H), 3.80 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.65, 144.4, 142.1, 140.3, 134.3, 129.1, 128.6, 128.5, 128.1, 127.8, 126.8, 126.4, 126.3, 59.6, 50.7, 48.4, 43.6, 21.4; IR (KBr) 3030, 1575, 1495, 1449, 1298, 1146, 1091, 898 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 481.1950, found: 481.1950.

1-[N-(4-Methoxybenzyl)]-3-methyl-(2-piperidinylidene) diphenylphosphorylamide (*Table 2*, entry 5); ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.18 (m, 8H), 7.03 (m, 2H), 6.92 (d, $J = 8.6$ Hz, 2H), 6.71 (d, $J = 6.7$ Hz, 2H), 4.55 (d, $J = 14.2$ Hz, 1H), 4.31 (d, $J = 14.2$ Hz, 1H), 3.74 (s, 3H), 3.59 (m, 1H), 3.18-3.10 (m, 2H), 1.83-1.76 (m, 2H), 1.62-1.53 (m, 2H), 1.37 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 171.2, 158.4, 151.9, 151.9, 151.8, 151.8, 129.1, 129.0, 129.0, 128.9, 128.0, 123.8, 123.7, 120.5, 120.4, 120.4, 120.3, 113.7, 55.0, 51.8, 47.5, 47.5, 33.6, 33.5, 26.7, 19.6, 17.4; IR (KBr) 2950, 1567, 1489, 1379, 1248, 1202, 1007, 919, 691 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_4\text{P}$ [$M+H$] $^+$: 465.1943, found: 465.1943.

3-Methyl-1-{N-[(R)-phenylethyl]}-(2-piperidinylidene) (benzyloxycarbonyl)amidine (*Table 2*, entry 6); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.3$ Hz, 2H), 7.33-7.23 (m, 8H), 6.40-6.30 (m, 1H), 5.17 (m, 2H), 3.71 (m, 1H), 3.01 (m, 1H), 2.77 (m, 1H), 1.84-1.79 (m, 2H), 1.57 (m, 1H), 1.47 (m, 4H), 1.22-1.16 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 170.0, 162.0, 161.7, 139.5, 129.5, 137.3, 137.3, 137.3, 128.3, 128.2, 128.2, 128.1, 127.6, 127.5, 127.2, 127.1, 127.1, 67.0, 66.9, 52.2, 52.1, 42.0, 41.6, 30.5, 30.4, 27.7, 20.5, 20.1, 19.6, 19.1, 14.9, 14.5; IR (KBr) 3031, 2871, 1663, 1556, 1455, 1377, 1139, 1049 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_2$ [$M+H$] $^+$: 351.2073, found: 351.2074.

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) [(1S)-menthylcarbonyl]amidine (*Table 2*, entry 7); ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.20 (m, 5H), 4.86 (t, $J = 14.6$ Hz, 1H), 4.59-4.51 (m, 2H), 3.66 (m, 1H), 3.16 (m, 2H), 2.05 (m, 2H), 1.84 (m, 2H), 1.62 (m, 3H), 1.43 (m, 2H), 1.27 (m, 3H), 1.02 (m, 2H), 0.87 (m, 6H), 0.77 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 169.2, 162.0, 161.9, 136.8, 128.5, 128.0, 127.9, 127.3, 127.2, 74.7, 74.6, 52.6, 52.5, 47.8, 47.7, 47.1, 46.9, 41.2, 41.1, 34.4, 31.4, 30.1, 27.6, 26.1, 25.8, 23.5, 23.2, 22.1, 20.8, 20.7, 19.9, 19.9, 18.8, 18.7, 16.3; IR (KBr) 2953, 2868, 1665, 1569, 1454, 1282, 1045 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_2$ $[M+H]^+$: 385.2855, found: 385.2858.

Cyclic amidine (*Table 2*, entry 8); ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.2$ Hz, 2H), 7.25 (m, 5H), 7.14 (m, 2H), 4.52 (s, 2H), 3.03 (s, 2H), 2.91 (s, 2H), 2.36 (s, 3H), 1.33 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 141.9, 140.6, 134.9, 129.0, 128.6, 128.7, 128.1, 127.8, 126.2, 59.5, 48.4, 43.4, 38.0, 36.2, 25.2, 22.6, 21.3; IR (KBr) 3030, 2927, 2855, 1575, 1484, 1277, 1146, 737 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 397.1950, found: 397.1949.

Cyclic amidine (*Table 2*, entry 9); ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 7.3$ Hz, 2H), 7.36-7.25 (m, 9H), 7.16 (m, 2H), 7.02 (d, $J = 7.4$ Hz, 1H), 5.21 (s, 2H), 5.04 (d, $J = 14.9$ Hz,

1H), 4.83 (d, $J = 14.9$ Hz, 1H), 4.73 (q, $J = 7.2$ Hz, 1H), 4.53 (d, $J = 16.0$ Hz, 1H), 4.18 (d, $J = 16.1$ Hz, 1H), 1.44 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 162.4, 137.4, 137.1, 136.1, 130.6, 128.7, 128.3, 128.1, 128.0, 127.7, 127.6, 126.7, 126.6, 125.1, 67.2, 52.3, 49.6, 38.0, 20.4; IR (KBr) 3031, 1670, 1560, 1491, 1376, 1220, 1028 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_2$ $[M+H]^+$: 385.1916, found: 385.1919.

1-(*N*-Benzyl)-4-(*tert*-butyldimethylsilyloxy)-(2-piperidinylidene) (4-toluene)sulfonylamide (17, eq 2); ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 8.2$ Hz, 2H), 7.25 (m, 4H), 7.18 (d, $J = 7.9$ Hz, 2H), 7.11 (m, 2H), 4.74 (d, $J = 14.5$ Hz, 1H), 4.43 (d, $J = 14.5$ Hz, 1H), 3.96 (m, 2H), 3.34 (m, 1H), 3.32 (m, 1H), 2.36 (s, 3H), 1.99 (m, 1H), 1.77 (m, 1H), 1.41 (d, $J = 6.8$ Hz, 3H), 0.86 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.3, 141.6, 135.7, 129.0, 128.7, 128.0, 127.8, 126.2, 126.1, 66.0, 52.8, 46.2, 39.1, 26.0, 25.7, 25.6, 21.4, 18.0, 12.5, -4.8, -4.9; IR (KBr) 2954, 2928, 2866, 1553, 1494, 1471, 1266, 1153, 1100, 837, 814, 684 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{26}\text{H}_{39}\text{N}_2\text{O}_3\text{SSi}$ $[M+H]^+$: 487.2451, found: 487.2451.

63% isolated yield (**A/B**, >25:1)

1-(*N*-Propyl)-3-methyl-(2-piperidinylidene) (4-toluene)sulfonylamide (Text, Ref 7, major product); ^1H NMR (400 MHz, CDCl_3) δ 7.76(d, $J = 8.2$ Hz, 2H), 7.18(d, $J = 8.1$ Hz, 2H), 3.81(m, 1H), 3.37-3.21(m, 4H), 2.34(s, 3H), 1.80(m, 1H), 1.65(m, 1H), 1.60(m, 1H), 1.55(m,

1H), 1.49(m, 2H), 1.40(d, $J = 7.2$ Hz 3H), 0.77(t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 142.1, 141.2, 128.8, 125.8, 52.3, 48.8, 31.6, 26.4, 21.3, 19.8, 19.5, 17.5, 11.1; IR (KBr) 2960, 1557, 1484, 1270, 1142, 822cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 309.1637, found: 309.1637.

Experimental Procedure of the *in situ* Trapping of Diazomethane. To a stirred solution of 1-(*N*-benzylamino)-4-pentyne (69 mg, 0.40 mmol), $\text{Ru}_3(\text{CO})_{12}$ (13 mg, 0.020 mmol), and 4-phenylbenzoic acid (40 mg, 0.20 mmol) in THF (4 mL) was added dropwise Et_3N (112 μL , 0.80 mmol) and *p*-toluenesulfonyl azide (118 mg, 0.6 mmol) at 0 $^\circ\text{C}$. The resulting dark red solution was stirred for 12 h at room temperature and the organic solvent was removed under reduced pressure. The residue was purified by a silica gel column chromatography (EtOAc/Hx, 1:5) to give cyclic amidines along with methyl 4-biphenylcarboxylate (20% based on the used 4-phenylbenzoic acid).

Experimental Procedure of the *in situ* Generation of Enamine followed by the Reaction with Sulfonyl Azide. To a solution of $\text{Cp}_2\text{Ti}(\text{Cl})(\text{CH}_2)\text{AlMe}_2$ (2.2 mL, 0.5 M

solution in toluene) was added THF (3 mL) at -78 °C followed by a slow addition of 1-benzyl-2-pyrrolidinone (175 mg, 1.0 mmol) at the same temperature. This solution was slowly warmed to room temperature and further stirred for 3 h. The reaction mixture was diluted with diethyl ether (15 mL) and then cooled to 0 °C. MeOH (3 mL) was added to the reaction mixture to quench the Tebbe reagent and then additional diethyl ether (5 mL) was added. This mixture was stirred for 1 h before filtration through a pad of Celite. The filtrate was concentrated in vacuo and re-dissolved in THF (5 mL). To this solution was added *p*-toluenesulfonyl azide (394 mg, 2.0 mmol) and then stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude residue was purified by a flash column chromatography on silica gel (EtOAc/Hx, 1:1) to afford cyclic amidines as a mixture of **C** and **D** (**C/D**, 2.7:1) in combined 40% yield. When the reaction was carried out in the presence of Ru₃(CO)₁₂ complex (32 mg, 0.05 mmol), the result was not changed leading to the same yield and ratio of two cyclic amidines **C** and **D**.

Experimental Procedure of the Isotope Studies. Deuterated aminoalkyne **7-d₂** was prepared by deprotonation of **7** using *n*-BuLi (2.2 equiv) at -78 °C followed by quenching with D₂O in 70% yield with >98% deuterium incorporation at both terminal alkynyl and amino sites. To a solution of **7-d₂** (43.5 mg, 0.23 mmol) and Ru₃(CO)₁₂ (7.7 mg, 0.012 mmol) in THF (3 mL) was slowly added benzyloxycarbonyl azide (50 mg, 0.28 mmol) and the reaction mixture was stirred at room temperature for 12 h. After evaporation of organic solvent, the residue was passed through a pad of silica gel, and the crude mixture was analyzed using ¹H-NMR

spectroscopy to determine the content of the deuterium incorporation. It was revealed that one deuterium was incorporated with 33% contents at the C-3 methyl site on the piperidinylidene ring product **8a** (that is CH₂D). In addition, it was observed that deuterium was incorporated with 25% contents at the C-3 methinyl site of **8a**.

Appendix I

Copies of ^1H , ^{13}C and ^{31}P NMR Spectra of New Compounds Obtained in this Study

1-(*N*-Benzylamino)-4-pentyne (Table 2, entries 1-3)

1-(*N*-Benzylamino)-2,2-diphenyl-4-pentyne (*Table 2*, entry 4)

1-[*N*-(4-Methoxybenzyl)amino]-5-hexyne (Table 2, entry 5)

1-[(*R*)-*N*-(1-Phenylethyl)amino]-5-hexyne (Table 2, entry 6)

1-(*N*-Benzylamino)-5-hexyne (*Table 1* and entry 7 of *Table 2*)

1-(*N*-Benzylaminomethyl)-1-(2-propynyl)cyclohexane (Table 2, entry 8).

1-(N-Benzylaminomethyl)-2-(2-propynyl)benzene (*Table 2*, entry 9)

1-(*N*-Benzylamino)-3-(*tert*-butyldimethylsilyloxy)-5-hexyne (eq 2)

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (4-toluene)sulfonylamide (8a, Table 1, entries 1-2, major product)

1-(*N*-Benzyl)-(2-piperidinylidene) (4-toluene)sulfonylamide (*Table 1*, entry 1, minor)

3)

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) (2-pyridine)sulfonylamide (Table 1, entry 4)

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) benzoylamide (*Table 1*, entry 5)

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (4-nitro)benzoylamdie (*Table 1*, entry 6)

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (4-methyl)benzoylamide (*Table 1*, entry 7)

1-(N-Benzyl)-3-methyl-(2-piperidinylidene) diphenylphosphorylamide (*Table 1*, entry 8)

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (benzyloxycarbonyl)amidine (Table 1, entry 9)

1-(*N*-Benzyl)-*N*-(2-pyrrolinyldine) (4-tolunene)sulfonylamide (3, *Table 2*, entry 1, major product)

1-(*N*-Benzyl)-3-methyl-(2-pyrrolinyldine) (4-toluene)sulfonylamide (*Table 2*, entry 1, minor product)

1-(*N*-Benzyl)-(2-pyrrolinylidene) methaneulfonamide (Table 2, entry 2, major product)

1-(*N*-Benzyl)-3-methyl-(2-pyrrolinyldine) methanesulfonylamide (*Table 2*, entry 2, minor)

1-(*N*-Benzyl)-(2-pyrrolidinylidene) (2-pyridine)sulfonylamide (*Table 2*, entry 3, major product)

1-(N-Benzyl)-4,4-diphenyl-(2-pyrrolinylidene) (4-toluene)sulfonylamide (Table 2, entry 4)

1-(*N*-4-methoxybenzyl)-3-methyl-(2-piperidinylidene) diphenylphosphorylamide
 (Table 2, entry 5)

3-Methyl-1- $\{N-[(R)\text{-phenylethyl}]\}$ -(2-piperidinylidene)(benzyloxycarbonyl)amidine
 (Table 2, entry 6, diastereomeric mixture)

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene)-[(1*S*)-menthylcarbonyl]amidine (Table 2, entry 7, diastereomeric mixture)

Cyclic amidine (Table 2, entry 8)

Cyclic amidine (Table 2, entry 9)

**1-(*N*-Benzyl)-4-(*tert*-butyldimethylsilyloxy)-(2-piperidinylidene) (4-toluene) sulfon-
ylamide (17, eq 2)**

NOE of 1-(*N*-benzyl)-4-(*tert*-butyldimethylsilyloxy)-(2-piperidinylidene) (4-toluene) sulfonamide (17)

1-(*N*-Propyl)-3-methyl-(2-piperidinylidene)-(4-toluene)sulfonylamide (Text, Ref 7, major product)

Deuterium Incorporation Experiments

Appendix II

X-Ray Crystallographic Data for

1-(*N*-Benzyl)-3-methyl-(2-piperidinylidene) (4-toluene)sulfonylamide (8a, Table 1, entry 1, major product)

1-(*N*-Benzyl)-(2-pyrrolinyldiene) (4-toluene)sulfonylamide (3, Table 2, entry 1, major product)

Table S1. Crystal data and structure refinement for **8a**.

Identification code	8a
Empirical formula	C ₂₀ H ₂₄ N ₂ O ₂ S
Formula weight	356.47
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.1543(14) Å alpha = 90 deg. b = 8.2699(9) Å beta = 110.089(2) deg. c = 17.976(2) Å gamma = 90 deg.
Volume	1836.5(3) Å ³
Z, Calculated density	4, 1.289 Mg/m ³
Absorption coefficient	0.192 mm ⁻¹
F(000)	760
Theta range for data collection	1.68 to 27.98 deg.
Limiting indices	-16 ≤ h ≤ 15, -10 ≤ k ≤ 6, -23 ≤ l ≤ 23
Reflections collected / unique	10525 / 4103 [R(int) = 0.0424]
Completeness to theta = 27.98	92.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4103 / 0 / 322
Goodness-of-fit on F ²	1.004
Final R indices [I > 2σ(I)]	R1 = 0.0476, wR2 = 0.0955
R indices (all data)	R1 = 0.0921, wR2 = 0.1053
Largest diff. peak and hole	0.224 and -0.307 e.Å ⁻³

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for **8a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	$U(\text{eq})$
S	0.46339(5)	0.62579(6)	0.15679(3)	0.05424(19)
O(1)	0.55665(13)	0.52258(15)	0.17492(10)	0.0751(5)
O(2)	0.37798(14)	0.59543(19)	0.08333(9)	0.0857(5)
C(1)	0.40948(15)	0.5981(2)	0.23335(12)	0.0467(5)
C(2)	0.4620(2)	0.6559(3)	0.30797(14)	0.0627(6)
C(3)	0.4232(2)	0.6214(3)	0.36797(16)	0.0713(7)
C(4)	0.33148(19)	0.5289(3)	0.35596(15)	0.0634(6)
C(5)	0.2786(2)	0.4752(3)	0.28028(17)	0.0679(7)
C(6)	0.31556(19)	0.5084(3)	0.21902(17)	0.0606(6)
C(7)	0.2924(4)	0.4891(7)	0.4228(3)	0.1027(12)
N(1)	0.49322(13)	0.81336(16)	0.16712(9)	0.0470(4)
C(8)	0.56968(15)	0.8858(2)	0.14833(10)	0.0406(5)
C(9)	0.64173(16)	0.8057(2)	0.10923(12)	0.0459(5)
C(10)	0.74541(18)	0.9007(3)	0.12063(16)	0.0570(6)
C(11)	0.7182(2)	1.0763(3)	0.09893(17)	0.0608(6)
C(12)	0.6669(2)	1.1484(2)	0.15444(15)	0.0547(6)
N(2)	0.58280(12)	1.04398(17)	0.16602(9)	0.0430(4)
C(13)	0.5780(3)	0.7697(4)	0.02227(15)	0.0658(7)
C(14)	0.51772(18)	1.1205(2)	0.20719(12)	0.0460(5)
C(15)	0.55570(16)	1.0909(2)	0.29506(12)	0.0441(5)
C(16)	0.65048(18)	1.0093(2)	0.33559(13)	0.0506(5)
C(17)	0.6831(2)	0.9889(3)	0.41700(15)	0.0634(7)
C(18)	0.6217(3)	1.0493(3)	0.45784(18)	0.0798(9)
C(19)	0.5271(3)	1.1296(4)	0.41867(18)	0.0823(8)
C(20)	0.4957(2)	1.1500(3)	0.33789(16)	0.0633(7)

Table S3. Bond lengths [Å] and angles [deg] for **8a**.

S-O(2)	1.4318(15)
S-O(1)	1.4369(15)
S-N(1)	1.5951(15)
S-C(1)	1.766(2)
C(1)-C(2)	1.367(3)
C(1)-C(6)	1.387(3)
C(2)-C(3)	1.372(3)
C(3)-C(4)	1.381(3)
C(4)-C(5)	1.372(3)
C(4)-C(7)	1.497(4)
C(5)-C(6)	1.376(3)
N(1)-C(8)	1.311(2)
C(8)-N(2)	1.344(2)
C(8)-C(9)	1.513(3)
C(9)-C(10)	1.526(3)
C(9)-C(13)	1.528(3)
C(10)-C(11)	1.514(3)
C(11)-C(12)	1.507(3)
C(12)-N(2)	1.473(2)
N(2)-C(14)	1.455(2)
C(14)-C(15)	1.504(3)
C(15)-C(20)	1.368(3)
C(15)-C(16)	1.385(3)
C(16)-C(17)	1.387(3)
C(17)-C(18)	1.360(4)
C(18)-C(19)	1.372(4)
C(19)-C(20)	1.377(3)
O(2)-S-O(1)	116.31(11)
O(2)-S-N(1)	111.20(9)
O(1)-S-N(1)	113.24(9)
O(2)-S-C(1)	107.34(10)
O(1)-S-C(1)	106.65(9)
N(1)-S-C(1)	100.59(9)

C(2)-C(1)-C(6)	119.1(2)
C(2)-C(1)-S	121.12(17)
C(6)-C(1)-S	119.67(18)
C(1)-C(2)-C(3)	120.0(2)
C(2)-C(3)-C(4)	122.2(3)
C(5)-C(4)-C(3)	116.9(2)
C(5)-C(4)-C(7)	121.9(3)
C(3)-C(4)-C(7)	121.2(3)
C(4)-C(5)-C(6)	122.1(2)
C(5)-C(6)-C(1)	119.7(2)
C(8)-N(1)-S	126.45(14)
N(1)-C(8)-N(2)	115.56(16)
N(1)-C(8)-C(9)	125.34(16)
N(2)-C(8)-C(9)	119.09(17)
C(8)-C(9)-C(10)	112.71(17)
C(8)-C(9)-C(13)	110.46(18)
C(10)-C(9)-C(13)	112.9(2)
C(11)-C(10)-C(9)	109.78(19)
C(12)-C(11)-C(10)	109.2(2)
N(2)-C(12)-C(11)	112.99(18)
C(8)-N(2)-C(14)	119.60(16)
C(8)-N(2)-C(12)	125.39(16)
C(14)-N(2)-C(12)	114.72(16)
N(2)-C(14)-C(15)	114.97(17)
C(20)-C(15)-C(16)	117.8(2)
C(20)-C(15)-C(14)	119.0(2)
C(16)-C(15)-C(14)	123.11(19)
C(15)-C(16)-C(17)	120.7(2)
C(18)-C(17)-C(16)	120.0(3)
C(17)-C(18)-C(19)	120.2(3)
C(18)-C(19)-C(20)	119.4(3)
C(15)-C(20)-C(19)	121.9(3)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2$) for **8a**. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S	0.0675(4)	0.0387(3)	0.0574(4)	-0.0089(2)	0.0225(3)	-0.0069(3)
O(1)	0.0946(12)	0.0359(8)	0.1162(14)	0.0058(8)	0.0637(11)	0.0122(8)
O(2)	0.1045(13)	0.0944(12)	0.0493(10)	-0.0219(9)	0.0150(10)	-0.0435(10)
C(1)	0.0471(12)	0.0392(11)	0.0501(13)	0.0005(9)	0.0120(10)	0.0002(9)
C(2)	0.0576(15)	0.0721(16)	0.0557(17)	-0.0093(12)	0.0159(13)	-0.0190(13)
C(3)	0.0718(18)	0.0877(18)	0.0492(17)	-0.0081(14)	0.0139(14)	-0.0136(14)
C(4)	0.0567(15)	0.0710(15)	0.0634(18)	0.0049(12)	0.0218(13)	0.0019(12)
C(5)	0.0525(15)	0.0716(16)	0.078(2)	0.0052(13)	0.0198(15)	-0.0127(13)
C(6)	0.0560(15)	0.0603(14)	0.0588(17)	-0.0060(12)	0.0113(13)	-0.0099(11)
C(7)	0.088(3)	0.149(4)	0.081(3)	0.012(2)	0.043(2)	-0.011(3)
N(1)	0.0507(10)	0.0325(8)	0.0567(12)	-0.0040(7)	0.0170(9)	-0.0017(7)
C(8)	0.0469(11)	0.0357(10)	0.0313(11)	0.0016(8)	0.0034(9)	0.0067(9)
C(9)	0.0572(13)	0.0389(11)	0.0415(13)	0.0029(9)	0.0167(10)	0.0100(10)
C(10)	0.0562(15)	0.0528(13)	0.0668(18)	0.0022(11)	0.0273(14)	0.0067(11)
C(11)	0.0601(16)	0.0527(14)	0.0741(19)	0.0047(12)	0.0288(15)	-0.0011(12)
C(12)	0.0625(15)	0.0404(12)	0.0608(16)	0.0005(11)	0.0208(13)	-0.0043(11)
N(2)	0.0519(10)	0.0339(8)	0.0411(10)	-0.0004(7)	0.0132(8)	0.0023(7)
C(13)	0.080(2)	0.0691(17)	0.0463(16)	-0.0075(13)	0.0191(14)	0.0087(16)
C(14)	0.0557(14)	0.0315(10)	0.0496(14)	-0.0020(9)	0.0168(11)	0.0047(10)
C(15)	0.0501(12)	0.0326(10)	0.0496(13)	-0.0063(9)	0.0170(10)	-0.0056(9)
C(16)	0.0600(14)	0.0396(11)	0.0487(15)	-0.0066(10)	0.0142(12)	-0.0047(10)
C(17)	0.0803(19)	0.0490(13)	0.0507(17)	-0.0008(11)	0.0094(15)	-0.0092(13)
C(18)	0.107(3)	0.0851(19)	0.0438(18)	0.0007(14)	0.0219(18)	-0.0237(17)
C(19)	0.089(2)	0.105(2)	0.065(2)	-0.0167(17)	0.0417(18)	-0.0113(18)
C(20)	0.0582(16)	0.0705(16)	0.0624(18)	-0.0075(13)	0.0221(14)	0.0011(13)

Table S5. Hydrogen coordinates and isotropic displacement parameters ($\text{\AA}^2$) for **8a**.

	x	y	z	U(eq)
H(2)	0.5247(16)	0.713(2)	0.3175(11)	0.058(6)
H(3)	0.4603(18)	0.659(3)	0.4186(15)	0.085(8)
H(5)	0.2120(16)	0.415(2)	0.2726(12)	0.064(6)
H(6)	0.2859(17)	0.467(2)	0.1685(13)	0.066(7)
H(7A)	0.348(3)	0.472(4)	0.466(2)	0.151(17)
H(7B)	0.241(3)	0.418(5)	0.414(2)	0.160(18)
H(7C)	0.260(3)	0.586(5)	0.432(3)	0.20(2)
H(9)	0.6584(13)	0.704(2)	0.1368(10)	0.039(5)
H(10A)	0.7857(15)	0.852(2)	0.0882(11)	0.054(6)
H(10B)	0.7936(17)	0.897(2)	0.1794(13)	0.072(7)
H(11A)	0.6663(18)	1.081(2)	0.0444(14)	0.072(7)
H(11B)	0.7841(16)	1.137(2)	0.1045(11)	0.053(6)
H(12A)	0.6282(15)	1.253(2)	0.1331(11)	0.057(6)
H(12B)	0.7229(16)	1.167(2)	0.2106(13)	0.067(7)
H(13A)	0.5574(18)	0.866(3)	−0.0063(14)	0.082(8)
H(13B)	0.6232(19)	0.712(3)	−0.0005(14)	0.087(8)
H(13C)	0.509(2)	0.710(3)	0.0158(14)	0.093(9)
H(14A)	0.4460(15)	1.082(2)	0.1841(10)	0.043(5)
H(14B)	0.5181(14)	1.235(2)	0.1960(10)	0.048(5)
H(16)	0.6943(14)	0.966(2)	0.3070(11)	0.046(5)
H(17)	0.7472(17)	0.931(3)	0.4437(13)	0.074(7)
H(18)	0.6419(18)	1.036(3)	0.5124(15)	0.081(8)
H(19)	0.4826(17)	1.168(2)	0.4442(14)	0.070(7)
H(20)	0.4336(15)	1.196(2)	0.3135(11)	0.048(6)

Table S6. Crystal data and structure refinement for **3**.

Identification code	3
Empirical formula	C ₁₈ H ₂₀ N ₂ O ₂ S
Formula weight	328.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.992(8) Å alpha = 90 deg. b = 20.362(15) Å beta = 113.707(19) deg. c = 8.962(7) Å gamma = 90 deg.
Volume	1670(2) Å ³
Z, Calculated density	4, 1.307 Mg/m ³
Absorption coefficient	0.205 mm ⁻¹
F(000)	696
Theta range for data collection	2.00 to 27.82 deg.
Limiting indices	-13 ≤ h ≤ 7, -18 ≤ k ≤ 25, -11 ≤ l ≤ 11
Reflections collected / unique	4506 / 3232 [R(int) = 0.0519]
Completeness to theta = 27.82	81.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3232 / 0 / 209
Goodness-of-fit on F ²	1.005
Final R indices [I > 2σ(I)]	R1 = 0.0770, wR2 = 0.1737
R indices (all data)	R1 = 0.1501, wR2 = 0.1989
Largest diff. peak and hole	1.330 and -0.488 e.Å ⁻³

Table S7. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for **3**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	$U(\text{eq})$
C(1)	0.1504(5)	0.3862(2)	0.0106(5)	0.0272(11)
C(2)	0.1781(5)	0.3246(2)	−0.0332(6)	0.0366(12)
C(3)	0.1260(5)	0.3064(2)	−0.1951(6)	0.0394(13)
C(4)	0.0479(5)	0.3511(3)	−0.3168(6)	0.0379(13)
C(5)	0.0218(5)	0.4132(2)	−0.2716(5)	0.0325(12)
C(6)	0.0734(5)	0.4315(2)	−0.1097(5)	0.0299(11)
C(7)	−0.0118(7)	0.3320(3)	−0.4960(6)	0.0625(17)
S(1)	0.20212(13)	0.40713(6)	0.21840(14)	0.0308(4)
O(1)	0.2840(4)	0.35204(16)	0.3141(4)	0.0513(10)
O(2)	0.0711(3)	0.42506(16)	0.2383(4)	0.0378(9)
N(1)	0.2967(4)	0.47325(18)	0.2515(4)	0.0287(9)
C(8)	0.4300(5)	0.4743(2)	0.2552(5)	0.0310(11)
C(9)	0.5179(6)	0.4204(3)	0.2220(6)	0.0520(16)
C(10)	0.6697(7)	0.4604(4)	0.2313(10)	0.112(3)
C(11)	0.6557(5)	0.5293(3)	0.2954(6)	0.0394(13)
N(2)	0.5062(4)	0.5306(2)	0.2913(4)	0.0309(10)
C(12)	0.4502(5)	0.5912(2)	0.3312(5)	0.0353(12)
C(13)	0.4000(5)	0.6408(2)	0.1913(5)	0.0299(11)
C(14)	0.2592(5)	0.6381(3)	0.0717(6)	0.0387(13)
C(15)	0.2148(6)	0.6823(3)	−0.0544(6)	0.0467(14)
C(16)	0.3086(6)	0.7297(3)	−0.0660(6)	0.0499(15)
C(17)	0.4493(6)	0.7336(3)	0.0528(6)	0.0467(14)
C(18)	0.4945(5)	0.6892(2)	0.1801(6)	0.0410(13)

Table S8. Bond lengths [Å] and angles [deg] for **3**.

C(1)–C(2)	1.376(6)
C(1)–C(6)	1.392(6)
C(1)–S(1)	1.772(5)
C(2)–C(3)	1.380(6)
C(3)–C(4)	1.393(6)
C(4)–C(5)	1.384(6)
C(4)–C(7)	1.522(7)
C(5)–C(6)	1.382(6)
S(1)–O(2)	1.438(3)
S(1)–O(1)	1.449(3)
S(1)–N(1)	1.603(4)
N(1)–C(8)	1.318(6)
C(8)–N(2)	1.342(6)
C(8)–C(9)	1.509(6)
C(9)–C(10)	1.694(9)
C(10)–C(11)	1.544(8)
C(11)–N(2)	1.479(6)
N(2)–C(12)	1.457(6)
C(12)–C(13)	1.529(6)
C(13)–C(14)	1.385(7)
C(13)–C(18)	1.396(6)
C(14)–C(15)	1.371(7)
C(15)–C(16)	1.378(7)
C(16)–C(17)	1.383(7)
C(17)–C(18)	1.383(7)
C(2)–C(1)–C(6)	119.6(4)
C(2)–C(1)–S(1)	120.8(4)
C(6)–C(1)–S(1)	119.5(3)
C(1)–C(2)–C(3)	120.7(4)
C(2)–C(3)–C(4)	120.2(5)
C(5)–C(4)–C(3)	118.6(4)

C(5)-C(4)-C(7)	120.1(5)
C(3)-C(4)-C(7)	121.2(5)
C(6)-C(5)-C(4)	121.3(4)
C(5)-C(6)-C(1)	119.4(4)
O(2)-S(1)-O(1)	116.6(2)
O(2)-S(1)-N(1)	105.2(2)
O(1)-S(1)-N(1)	113.0(2)
O(2)-S(1)-C(1)	107.2(2)
O(1)-S(1)-C(1)	107.0(2)
N(1)-S(1)-C(1)	107.3(2)
C(8)-N(1)-S(1)	122.2(3)
N(1)-C(8)-N(2)	119.3(4)
N(1)-C(8)-C(9)	130.2(5)
N(2)-C(8)-C(9)	110.5(4)
C(8)-C(9)-C(10)	102.8(4)
C(11)-C(10)-C(9)	104.0(5)
N(2)-C(11)-C(10)	104.4(4)
C(8)-N(2)-C(12)	123.1(4)
C(8)-N(2)-C(11)	117.4(4)
C(12)-N(2)-C(11)	119.5(4)
N(2)-C(12)-C(13)	113.0(3)
C(14)-C(13)-C(18)	118.6(5)
C(14)-C(13)-C(12)	120.3(4)
C(18)-C(13)-C(12)	121.1(4)
C(15)-C(14)-C(13)	120.2(5)
C(14)-C(15)-C(16)	121.1(5)
C(15)-C(16)-C(17)	119.6(5)
C(18)-C(17)-C(16)	119.4(5)
C(17)-C(18)-C(13)	121.0(5)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($\text{\AA}^2$) for **3**.. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	0.023(3)	0.031(3)	0.021(3)	-0.002(2)	0.002(2)	-0.005(2)
C(2)	0.037(3)	0.032(3)	0.029(3)	0.002(2)	0.001(2)	0.004(2)
C(3)	0.053(3)	0.028(3)	0.033(3)	-0.005(2)	0.013(3)	-0.002(3)
C(4)	0.041(3)	0.048(4)	0.027(3)	-0.003(2)	0.016(3)	-0.012(3)
C(5)	0.034(3)	0.039(3)	0.023(3)	0.013(2)	0.011(2)	0.008(2)
C(6)	0.035(3)	0.031(3)	0.024(3)	0.004(2)	0.012(2)	0.004(2)
C(7)	0.091(5)	0.056(4)	0.037(3)	-0.005(3)	0.022(3)	-0.012(4)
S(1)	0.0348(7)	0.0300(7)	0.0202(6)	0.0020(5)	0.0034(5)	-0.0032(6)
O(1)	0.067(3)	0.034(2)	0.030(2)	0.0025(16)	-0.0039(19)	0.0031(19)
O(2)	0.037(2)	0.048(2)	0.0284(19)	-0.0018(16)	0.0136(16)	-0.0106(16)
N(1)	0.026(2)	0.031(2)	0.024(2)	0.0015(17)	0.0058(18)	0.0002(18)
C(8)	0.034(3)	0.037(3)	0.015(2)	0.000(2)	0.003(2)	0.001(2)
C(9)	0.050(4)	0.069(4)	0.033(3)	-0.002(3)	0.013(3)	0.024(3)
C(10)	0.064(5)	0.132(7)	0.128(7)	-0.060(6)	0.027(5)	0.020(5)
C(11)	0.030(3)	0.050(4)	0.039(3)	-0.005(3)	0.015(2)	-0.005(2)
N(2)	0.029(2)	0.040(3)	0.022(2)	-0.0049(18)	0.0088(18)	-0.0036(19)
C(12)	0.038(3)	0.041(3)	0.026(3)	-0.012(2)	0.012(2)	-0.013(3)
C(13)	0.034(3)	0.032(3)	0.026(3)	-0.009(2)	0.014(2)	-0.003(2)
C(14)	0.031(3)	0.049(4)	0.036(3)	-0.006(3)	0.013(3)	-0.013(3)
C(15)	0.039(3)	0.053(4)	0.039(3)	0.006(3)	0.006(3)	-0.005(3)
C(16)	0.054(4)	0.047(4)	0.040(3)	0.012(3)	0.010(3)	-0.005(3)
C(17)	0.053(4)	0.038(4)	0.049(4)	0.004(3)	0.020(3)	-0.016(3)
C(18)	0.032(3)	0.043(4)	0.043(3)	-0.017(3)	0.009(3)	-0.010(3)

Table S10. Hydrogen coordinates and isotropic displacement parameters ($\text{\AA}^2$) for **3**.

	x	y	z	U(eq)
H(2)	0.2325	0.2949	0.0471	0.044
H(3)	0.1431	0.2642	−0.2230	0.047
H(5)	−0.0316	0.4431	−0.3518	0.039
H(6)	0.0569	0.4737	−0.0814	0.036
H(7A)	−0.1164	0.3293	−0.5382	0.094
H(7B)	0.0273	0.2901	−0.5071	0.094
H(7C)	0.0161	0.3645	−0.5556	0.094
H(9A)	0.4653	0.4011	0.1152	0.062
H(9B)	0.5422	0.3861	0.3040	0.062
H(10A)	0.7574	0.4384	0.3051	0.134
H(10B)	0.6722	0.4631	0.1244	0.134
H(11A)	0.7282	0.5356	0.4056	0.047
H(11B)	0.6678	0.5633	0.2261	0.047
H(12A)	0.5261	0.6111	0.4259	0.042
H(12B)	0.3686	0.5808	0.3595	0.042
H(14)	0.1946	0.6062	0.0769	0.046
H(15)	0.1197	0.6802	−0.1334	0.056
H(16)	0.2775	0.7588	−0.1533	0.060
H(17)	0.5129	0.7659	0.0470	0.056
H(18)	0.5893	0.6916	0.2596	0.049