Supporting Information

Highly Efficient One Pot Synthesis of *N*-Sulfonylamidines by Copper-Catalyzed Three-Component Coupling of Sulfonyl Azide, Alkyne, and Amine

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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 Merck precoated silica gel 60 F₂₅₄ plates. Visualization on TLC was achieved by use of UV light (254 nm) and treatment with ceric ammonium molybdate stain followed by heating. Flash column chromatography was undertaken on silica gel (Merck Kieselgel 60 F₂₅₄ 400-630 mesh). ¹H NMR was recorded on Bruker 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 TMSCl. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant, J was reported in Hertz unit (Hz). ¹³C NMR was recorded on Bruker FT AM 400 (100 MHz) and was fully decoupled by broad band 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 sodium chloride cells on Bruker EQUINOX 55. Frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbance are reported. High resolution mass spectra were recorded on a Jeol JMS-HX110/110A by using FAB method.

General Procedure for the Preparation of Amidine (Table 1). To a stirred mixture of azide (0.6 mmol), alkyne (0.5 mmol except a diyne being 0.25 mmol, entry 12), and CuI (0.05 mmol) in THF (1 mL) was slowly added amine nucleophile (0.6 mmol) at room temperature. under an N₂ atmosphere. Triethylamine (0.6 mmol) was added prior to the addition of nucleophiles, if necessary (entry 21-23 of Table 1 and eq. 3). After the reaction was completed, which was monitored with TLC, the reaction mixture was diluted by adding CH₂Cl₂ (2 mL) and aqueous NH₄Cl solution (3 mL). The mixture was stirred for an additional 30 min and two layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 mL x 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated in *vacuo*. The crude residue was purified by flash column chromatograph with an appropriate eluting solvent system.

Isotope experiment (eq. 1). To a stirred mixture of phenylacetylene-*d* (55 μ L, 0.5 mmol), *p*-toluenesulfonyl azide (99 mg, 0.5 mmol), and CuI (9.5 mg, 0.05 mmol) in THF (1 mL) was slowly added diisopropylamine (70 μ L, 0.5 mmol) at room temperature under an N₂ atmosphere. The usual work-up was applied and deuterium incorporation was analyzed by ¹H-NMR spectroscopy with crude mixture.

Cross scrambling experiment (eq. 2). Under the otherwise identical conditions compared to the above normal reaction conditions, 0.25 mmol of phenylacetylene-*d* (27 μ L) and 0.25 mmol of 4-ethynyl trifluorotoluene (41 μ L) were treated with diisopropylamine (85 μ L, 0.6 mmol) and the deuterium incorporation was analyzed by ¹H-NMR spectroscopy.

Scale-up experiment (eq. 3). To a stirred mixture of (*R*)-phenylalanine methyl ester hydrogen chloride salt (2.27 g, 10.5 mmol), phenylacetylene (1.1 mL, 10.0 mmol), and copper iodide (19 mg, 0.1 mmol) in THF (20 mL) was slowly added triethylamine (1.7 mL, 12.0 mmol) under N₂ at room temperature. After 15 min, a solution of *p*-toluenesulfonyl azide (2.17 g, 11.0 mmol) in THF (5 mL) was added dropwise. After overnight stirring, the reaction mixture was diluted by adding CH₂Cl₂ (20 mL) and aqueous NH₄Cl solution (50 mL). The mixture was stirred for an additional 30 min and two layers were separated. The aqueous layer was extracted with CH₂Cl₂ (50 mL x 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated in *vacuo*. The crude residue was purified by flash column chromatograph with EtOAc/hexane = 1/2 to give the desired product as a white solid (4.38 g, 97%); *R_f* 0.30 (EtOAc/hexane = 1/2); [α]_D²³ = + 44.5 (*c* = 2.2 in CHCl₃); mp: 125-126 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.1 Hz, 2H) 7.35-7.20 (m, 5H), 7.20-6.95 (m, 5H), 6.73 (d, *J* = 7.0 Hz, 2H), 5.63 (d, *J* = 6.2 Hz, 1H), 4.71 (q, *J* = 6.4 Hz, 1H), 4.30 (d, *J* = 17.5 Hz, 1H), 4.15 (d, *J* = 17.5 Hz, 1H), 3.59 (s, 2H), 3.05 (dd, *J* = 5.6, 13.9 Hz, 1H), 2.88 (dd, *J* = 5.6, 13.9 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 165.7, 142.6, 140.4, 134.8, 132.4, 130.0, 129.4, 129.2, 128.9, 128.7, 128.2, 127.2, 126.4, 54.9, 52.4, 39.5, 36.5, 21.5; IR (KBr) ν 3312, 2926, 1746, 1549, 1280, 1146, 1092, 698 cm⁻¹; HRMS (FAB) *m/z* calcd. for C₂₅H₂₇N₂O₄S [M+H]⁺: 451.1692, found: 451.1698; Chiralcel OD-H, hexane/*i*-PrOH (80/20), 0.7 mL/min, 20 °C, major 20.8 min (*R*-form), minor 18.0 min (*S*-form).

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (Table 1, entry 1):** white solid (89 %); *R_f* 0.42 (EtOAc/hexane = 1/2); mp: 147.5-148.5 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (dd, *J* = 1.7, 6.6 Hz, 2H), 7.30-7.10 (m, 7H), 4.38 (s, 2H), 3.98 (quintet, *J* = 6.6 Hz, 1H), 3.42 (quintet, *J* = 6.7 Hz, 1H), 2.36 (s, 3H), 1.36 (d, *J* = 6.7 Hz, 6H), 0.85 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 141.5, 134.9, 129.0, 128.8, 128.0, 126.7, 126.2, 50.4, 48.0, 38.7, 21.4, 19.8; IR (KBr) ν 2972, 1546, 1447, 1373, 1271, 1139, 1086, 754, 550 cm⁻¹; HRMS (FAB) *m/z* calcd. for C₂₁H₂₉N₂O₂S [M+H]⁺: 373.1950, found: 373.1949.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(4-trifluoromethylphenyl)acetamidine (Table 1, entry 2):** white solid (99 %); *R*_f 0.29 (EtOAc/hexane = 1/2); mp: 118-119 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.46 (s, 2H), 3.89 (quintet, *J* = 6.6 Hz, 1H), 3.47 (br. s, 1H), 2.37 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 6H), 0.90 (d, *J* = 6.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 141.8, 141.1, 139.0, 138.9, 129.2 (q, *J*₂ = 31.9 Hz), 129.0, 128.3, 126.1, 125.7 (q, *J*₃ = 3.4 Hz), 124.0 (q, *J*₁ = 270.2 Hz), 50.4, 48.2, 38.2, 21.3, 19.9, 19.8; IR (KBr) ν 2975, 1546, 1326, 1137, 1085, 819, 665, 550 cm⁻¹; HRMS (FAB) *m/z* calcd. for C₂₂H₂₈F₃N₂O₂S [*M*+*H*]⁺: 441.1824, found: 441.1821.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(4-methylphenyl)acetamidine (Table 1, entry 3):** white solid (90 %); *R*_f 0.58 (EtOAc/hexane = 1/2); mp: 190-192 °C, dec. (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.04 (m, 4H), 4.32 (s, 2H), 3.98 (quintet, *J* = 6.6 Hz, 1H), 3.42 (m, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 6H), 0.85 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 141.5, 141.5, 136.2, 131.7, 129.4, 129.0, 127.8, 126.2, 50.3, 47.9, 38.3, 21.4, 20.9, 19.8, 19.8; IR (KBr) ν 2972, 1542, 1268, 1138, 1085, 789, 549 cm⁻¹; HRMS (FAB) *m/z* calcd. for C₂₂H₃₁N₂O₂S [*M*+*H*]⁺: 387.2106, found: 387.2111.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(4-phenyloxyphenyl)acetamidine (Table 1, entry 4):** off-white solid (84 %); *R*_f 0.27 (EtOAc/hexane = 1/2); mp: 145-146 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.30 (dd, *J* = 7.5, 8.5 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.90-7.00 (m, 4H), 4.36 (s, 2H), 4.00 (quintet, *J* = 6.6 Hz, 1H), 3.43 (m, 1H), 2.37 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 6H), 0.89 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 157.2, 155.9, 141.6, 141.5, 129.8, 129.7, 129.4, 129.0, 126.2, 123.2, 119.4, 118.6, 50.3, 48.0, 38.1, 21.4, 19.8, 19.8; IR (KBr) ν 2973, 1540, 1489, 1240, 1138, 1085, 550 cm⁻¹; HRMS (FAB) *m/z* calcd. for C₂₇H₃₃N₂O₃S [*M*+*H*]⁺: 465.2212, found: 465.2217.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(pyridin-2-yl)acetamidine (Table 1, entry 5):** pale yellow solid (66 %); *R*_f 0.26 (EtOAc/hexane = 1/1); mp: 103-105 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.47 (d, *J* = 4.4 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.63 (dt, *J* = 1.7, 7.7 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.14 (m, 1H), 4.60 (s, 2H), 4.32 (quintet, *J* = 6.6 Hz, 1H), 3.44 (m, 1H), 2.38 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 155.6, 149.1, 141.6, 141.5, 137.0, 129.1, 126.2, 123.4, 121.9, 50.5, 48.1, 41.7, 21.4, 19.8, 19.8; IR (KBr) ν 2971, 1544, 1374, 1270, 1138, 1085, 549 cm⁻¹; HRMS (FAB) *m/z* calcd. for C₂₀H₂₈N₃O₂S [*M*+*H*]⁺: 374.1902, found: 374.1900.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(pyridin-3-yl)acetamidine (Table 1, entry 6):** pale

yellow solid (92 %); R_f 0.19 (EtOAc/hexane = 2/1); mp: 146.5-147.5 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.44 (m, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 7.9 Hz, 1H), 7.22 (m, 3H), 4.39 (s, 2H), 3.88 (quintet, J = 6.6 Hz, 1H), 3.44 (m, 1H), 2.36 (s, 3H), 1.34 (d, J = 6.8 Hz, 6H), 0.88 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 149.2, 148.2, 141.8, 141.1, 135.5, 130.9, 129.1, 126.1, 123.7, 50.4, 48.2, 35.9, 21.4, 19.9, 19.7; IR (KBr) ν 2974, 1548, 1373, 1270, 1139, 1085, 786, 550 cm⁻¹; HRMS (FAB) m/z calcd. for C₂₀H₂₈N₃O₂S [$M+H$]⁺: 374.1902, found: 374.1902.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(thien-3-yl)acetamidine (Table 1, entry 7):** off-white solid (86 %); R_f 0.24 (EtOAc/hexane = 1/3); mp: 149-150 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.1 Hz, 2H), 7.22 (m, 3H), 6.99 (m, 2H), 4.33 (s, 2H), 4.03 (quintet, J = 6.6 Hz, 1H), 3.43 (m, 1H), 2.36 (s, 3H), 1.34 (d, J = 6.8 Hz, 6H), 0.90 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 141.6, 141.4, 134.3, 129.0, 127.8, 126.1, 126.0, 121.9, 50.4, 48.0, 33.7, 21.4, 19.9, 19.8; IR (KBr) ν 2971, 1548, 1447, 1373, 1270, 1138, 1085, 779, 668, 549 cm⁻¹; HRMS (FAB) m/z calcd. for C₁₉H₂₇N₂O₂S₂ [$M+H$]⁺: 379.1514, found: 379.1511.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-hexanamidine (Table 1, entry 8):** white solid (90 %); R_f 0.43 (EtOAc/hexane = 1/2); mp: 113-114 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (dd, J = 1.6, 6.6 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 4.00 (quintet, J = 6.6 Hz, 1H), 3.48 (br. s, 1H), 2.84 (m, 2H), 2.36 (s, 3H), 1.60-1.50 (m, 2H), 1.40-1.30 (m, 4H), 1.29 (d, J = 6.8 Hz, 6H), 1.20 (d, J = 6.6 Hz, 6H), 0.88 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 141.9, 141.3, 128.9, 126.0, 49.8, 47.8, 32.7, 31.9, 27.0, 22.2, 21.4, 20.6, 20.0, 13.9; IR (KBr) ν 2966, 2932, 1539, 1372, 1264, 1132, 1080, 1051, 807, 788, 548 cm⁻¹; HRMS (FAB) m/z calcd. for C₁₉H₃₃N₂O₂S [$M+H$]⁺: 353.2263, found: 353.2263.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-(3,3-dimethyl)butanamidine (Table 1, entry 9):** white solid (79 %); R_f 0.45 (EtOAc/hexane = 1/2); mp: 97-99 °C (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 4.20 (quintet, J = 6.6 Hz, 1H), 3.46 (quintet, J = 6.8 Hz, 1H), 3.05 (br. s, 2H), 2.35 (s, 3H), 1.16 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 142.1, 141.0, 128.8, 126.0, 50.4, 47.9, 41.5, 32.3, 31.0, 21.4, 20.7, 20.4; IR (KBr) ν 2967, 1538, 1371, 1275, 1138, 1086, 782, 672, 550 cm⁻¹; HRMS (FAB) m/z calcd. for C₁₉H₃₃N₂O₂S [$M+H$]⁺: 353.2263, found: 353.2265.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-(5-hydroxy)pentanamidine (Table 1, entry 10):** white solid (78 %); R_f 0.23 (EtOAc/hexane = 2/1); mp: 123-124 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 4.06 (quintet, J = 6.6 Hz, 1H), 3.71 (t, J = 5.8 Hz, 2H), 3.50 (br. s, 1H), 2.89 (m, 2H), 2.53 (br. s, 1H), 2.37 (s, 3H), 1.90-1.70 (m, 2H), 1.70-1.50 (m, 2H), 1.29 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 141.6, 141.5, 129.0, 126.0, 60.4, 50.0, 48.0, 31.8, 31.7, 22.8, 21.4, 20.7, 20.0; IR (KBr) ν 3481, 2923, 1539,

1372, 1135, 1083, 549 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{18}\text{H}_{31}\text{N}_2\text{O}_3\text{S}$ $[M+H]^+$: 355.2055, found: 355.2053.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-(5-chloro)pentanamidine (Table 1, entry 11):** white solid (91 %); R_f 0.30 (EtOAc/hexane = 1/2); mp: 100-101 °C (CH_2Cl_2 /hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 4.03 (quintet, J = 6.6 Hz, 1H), 3.57 (t, J = 6.1 Hz, 2H), 3.49 (br. s, 1H), 2.90 (m, 2H), 2.36 (s, 3H), 1.90 (m, 2H), 1.80 (m, 2H), 1.28 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 141.7, 141.5, 129.0, 126.0, 50.0, 47.9, 44.4, 32.0, 31.7, 24.2, 21.4, 20.6, 19.9; IR (KBr) ν 2970, 1539, 1372, 1266, 1137, 1085, 807, 787, 549 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{18}\text{H}_{30}\text{ClN}_2\text{O}_2\text{S}$ $[M+H]^+$: 373.1717, found: 373.1720.

***N*¹,*N*¹,*N*³,*N*³-Tetraisopropyl-*N*²,*N*⁴-di(4-methylbenzensulfonyl)-octan-1,8-diamidine (Table 1, entry 12):** white solid (92 %); R_f 0.63 (EtOAc/hexane/ CH_2Cl_2 = 1/1/1); mp: 250-251, dec. °C (CH_2Cl_2 /hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.1 Hz, 4H), 7.20 (d, J = 8.1 Hz, 4H), 4.00 (quintet, J = 6.6 Hz, 2H), 3.47 (br. s, 2H), 2.85 (m, 4H), 2.35 (s, 6H), 1.65 (br. s, 4H), 1.46 (br. s, 4H), 1.27 (d, J = 6.8 Hz, 12H), 1.19 (d, J = 6.6 Hz, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 141.8, 141.3, 128.9, 125.9, 49.9, 47.8, 32.7, 29.0, 26.9, 21.3, 20.6, 20.0; IR (KBr) ν 2968, 1539, 1445, 1372, 1261, 1133, 1082, 808, 790, 550 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{34}\text{H}_{55}\text{N}_4\text{O}_4\text{S}_2$ $[M+H]^+$: 647.3665, found: 647.3661.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(trimethylsilyl)acetamidine (Table 1, entry 13):** white solid (85 %); R_f 0.49 (EtOAc/hexane = 1/2); mp: 99-101 °C (hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 4.01 (quintet, J = 6.6 Hz, 1H), 3.47 (m, 1H), 2.60 (s, 2H), 2.36 (s, 3H), 1.29 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.6 Hz, 6H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 142.0, 141.1, 128.9, 126.0, 49.8, 47.7, 24.4, 21.4, 20.6, 20.5, -0.3; IR (KBr) ν 2967, 1526, 1371, 1271, 1137, 1085, 854, 668, 548 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{18}\text{H}_{33}\text{N}_2\text{O}_2\text{SSi}$ $[M+H]^+$: 369.2032, found: 369.2037.

Ethyl 3-[[*N*¹,*N*¹-diisopropyl-*N*²-(4-methylbenzensulfonyl)amidino] propionate (Table 1, entry 14): white solid (94 %); R_f 0.22 (EtOAc/hexane = 1/2); mp: 121-122 °C (CH_2Cl_2 /hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dd, J = 1.7, 6.6 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 4.11 (m, 4H), 3.89 (quintet, J = 6.6 Hz, 1H), 3.59 (br. s, 1H), 2.36 (s, 3H), 1.34 (d, J = 6.8 Hz, 6H), 1.23 (t, J = 7.1 Hz, 3H), 1.19 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 157.9, 141.7, 141.1, 129.0, 126.2, 61.7, 48.4, 37.6, 21.4, 20.3, 19.9, 14.0; IR (KBr) ν 2976, 1739, 1556, 1373, 1275, 1139, 1086, 818, 669, 548 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{18}\text{H}_{29}\text{N}_2\text{O}_4\text{S}$ $[M+H]^+$: 369.1848, found: 369.1850.

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(cyclohexen-1-yl)acetamidine (Table 1, entry 15):**

off-white solid (90 %); R_f 0.36 (EtOAc/hexane = 1/2); mp: 101-102 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 5.19 (s, 1H), 3.91 (quintet, J = 6.6 Hz, 1H), 3.54 (s, 2H), 3.48 (br. s, 1H), 2.35 (s, 3H), 2.00-1.80 (m, 4H), 1.60-1.40 (m, 4H), 1.36 (d, J = 6.7 Hz, 6H), 1.11 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 141.7, 141.3, 131.2, 128.8, 126.2, 123.3, 50.2, 48.0, 39.7, 28.5, 25.1, 22.6, 21.9, 21.4, 20.2, 20.0; IR (KBr) ν 2929, 1539, 1274, 1139, 1086, 666, 550 cm⁻¹; HRMS (FAB) m/z calcd. for C₂₁H₃₃N₂O₂S [$M+H$]⁺: 377.2263, found: 377.2265.

Diethyl (3-propenyl) {3-[*N*¹,*N*¹-diisopropyl-*N*²-(4-methylbenzensulfonyl)propionamidino]} malonate (Table 1, entry 16): white solid (92 %); R_f 0.40 (EtOAc/hexane = 1/2); mp: 101-102 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.72 (m, 1H), 5.10 (m, 2H), 4.21 (m, 5H), 3.46 (m, 1H), 2.92 (m, 2H), 2.69 (d, J = 7.4 Hz, 2H), 2.36 (s, 3H), 2.17 (m, 2H), 1.26 (m, 12H), 1.18 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 164.9, 141.7, 141.3, 132.5, 128.9, 126.0, 119.2, 61.6, 57.2, 49.6, 47.9, 38.0, 29.9, 28.2, 21.4, 20.5, 20.0, 14.0; IR (KBr) ν 2976, 1731, 1543, 1374, 1274, 1140, 1086, 550 cm⁻¹; HRMS (FAB) m/z calcd. for C₂₆H₄₁N₂O₆S [$M+H$]⁺: 509.2685, found: 509.2683.

***N*¹,*N*¹-Diisopropyl-*N*²-(2-pyridinesulfonyl)-2-phenylacetamidine (Table 1, entry 17):** pale yellow solid (59 %); R_f 0.30 (EtOAc/hexane = 1/1); mp: 110-111 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.58 (td, J = 0.7, 4.7 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.77 (td, J = 1.8, 7.8 Hz, 1H), 7.31 (m, 1H), 7.25-7.10 (m, 5H), 4.44 (s, 2H), 3.99 (quintet, J = 6.6 Hz, 1H), 3.40 (m, 1H), 1.30 (d, J = 6.8 Hz, 6H), 0.83 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 160.1, 149.3, 137.4, 134.8, 128.7, 127.8, 126.6, 125.4, 120.9, 50.6, 48.2, 39.0, 19.6; IR (KBr) ν 2973, 1541, 1446, 1374, 1283, 1107, 803, 548 cm⁻¹; HRMS (FAB) m/z calcd. for C₁₉H₂₆N₃O₂S [$M+H$]⁺: 360.1746, found: 360.1746.

***N*¹,*N*¹-Diisopropyl-*N*²-(methanesulfonyl)-2-phenylacetamidine (Table 1, entry 18):** white solid (90 %); R_f 0.23 (EtOAc/hexane = 1/2); mp: 123-124 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.25 (m, 2H), 7.25-7.10 (m, 3H), 4.30 (s, 2H), 3.97 (quintet, J = 6.6 Hz, 1H), 3.46 (m, 1H), 3.03 (s, 3H), 1.47 (d, J = 6.8 Hz, 6H), 0.86 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 134.8, 128.9, 128.0, 126.8, 50.3, 47.9, 43.7, 39.4, 19.9, 19.8; IR (KBr) ν 2972, 1550, 1374, 1268, 1115, 806, 518 cm⁻¹; HRMS (FAB) m/z calcd. for C₁₅H₂₅N₂O₂S [$M+H$]⁺: 297.1636, found: 297.1644.

***N*¹-Benzyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (Table 1, entry 19):** white solid (68 %, a mixture of two isomers with a ratio 1:8, which is tentatively assigned as *Z/E* of the generated imino C=N double bond); R_f 0.52 (EtOAc/hexane = 1/1); mp: 110-111 °C (CH₂Cl₂/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.2 Hz, 2H), 7.35-7.15 (m, 10H), 7.03 (m, 2H), 5.68 (br. s, 1H), 4.38 (d, J = 5.6 Hz, 2H), 4.30 (s, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 142.1, 140.5, 136.3, 132.9, 130.0,

129.3, 129.1, 128.6, 128.1, 127.6, 127.5, 126.3, 45.8, 39.6, 21.4; IR (KBr) ν 3307, 3032, 2926, 1556, 1273, 1144, 1093, 733, 694 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 379.1480, found: 379.1478.

***N*¹-Isopropyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (Table 1, entry 20):** white solid (75 %, a mixture of two isomers with a ratio 1:6, which is tentatively assigned as *Z/E* of the generated imino C=N double bond); R_f 0.47 (EtOAc/hexane = 1/1); mp: 110-111 °C (CH_2Cl_2 /hexane); ¹H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 7.8 Hz, 2H), 7.40-7.30 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 5.14 (br. s, 1H), 4.20 (s, 2H), 4.06 (septet, J = 6.6 Hz, 1H), 2.37 (s, 3H), 0.98 (d, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl_3) δ 165.3, 141.9, 140.8, 133.1, 129.9, 129.3, 129.1, 127.9, 126.2, 43.8, 39.6, 21.5, 21.4; IR (KBr) ν 3307, 2979, 1556, 1271, 1143, 1090, 732, 699, 557, 532 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$., found:.

***N*¹-Methyl-*N*¹-phenyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (Table 1, entry 21):** white solid (97 %); R_f 0.60 (EtOAc/hexane = 1/1); mp: 131.5-133.5 °C (CH_2Cl_2 /hexane); ¹H NMR (400 MHz, CDCl_3) δ 7.85 (d, J = 7.7 Hz, 2H), 7.30-7.15 (m, 5H), 7.15-6.95 (m, 3H), 6.85-6.70 (m, 4H), 4.22 (s, 2H), 3.31 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 166.4, 142.6, 142.0, 141.0, 134.7, 129.5, 129.1, 128.4, 128.2, 127.2, 126.4, 126.4, 41.1, 37.7, 21.4; IR (KBr) ν 3063, 1539, 1496, 1278, 1146, 1090, 764, 700, 686, 552 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$ $[M+H]^+$: 379.1480, found: 379.1484.

***N*¹-[2-(Methoxycarbonyl)pyrrolidinyl]-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (Table 1, entry 22):** white foam (70 %, a mixture of two isomers with a ratio 1:15, which is tentatively assigned as *Z/E* of the generated imino C=N double bond); R_f 0.28 (EtOAc/hexane = 1/2); ¹H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.2 Hz, 2H), 7.30-7.10 (m, 7H), 4.57 (d, J = 15.7 Hz, 1H), 4.53 (dd, J = 3.8, 8.8 Hz, 1H), 4.16 (d, J = 15.7 Hz, 1H), 3.48 (s, 3H), 3.36 (m, 2H), 2.33 (s, 3H), 2.11 (m, 1H), 1.95-1.75 (m, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 171.6, 163.9, 141.8, 140.7, 133.2, 128.8, 128.7, 128.2, 126.7, 126.2, 61.0, 51.9, 47.9, 37.7, 28.9, 24.4, 21.3; IR (KBr) ν 2953, 1744, 1542, 1278, 1144, 1089, 556 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_4\text{S}$ $[M+H]^+$: 401.1535, found: 401.1539.

***N*¹-[(1-Methoxycarbonyl)-3-methylbutyl]-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (Table 1, entry 23):** white foam (95 %, a mixture of two isomers with a ratio >1:20, which is tentatively assigned as *Z/E* of the generated imino C=N double bond); R_f 0.33 (EtOAc/hexane = 1/2); ¹H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.3 Hz, 2H), 7.40-7.25 (m, 3H), 7.25-7.15 (m, 4H), 5.67 (d, J = 7.2 Hz, 1H), 4.50 (m, 1H), 4.31 (d, J = 17.4 Hz, 1H), 4.24 (d, J = 17.4 Hz, 1H), 3.56 (s, 3H), 2.37 (s, 3H), 1.48 (m, 1H), 1.35 (m, 2H), 0.73 (dd, J = 2.4, 6.3 Hz, 6H); ¹³C NMR (100 MHz, CDCl_3) δ 172.0, 165.8, 142.2, 140.3, 132.7, 129.9, 129.3, 129.0, 128.1, 126.3, 52.8, 52.2, 40.5, 39.5, 24.7, 22.4, 22.0, 21.4; IR (KBr) ν 3302,

2957, 1747, 1549, 1278, 1146, 1089, 732, 697 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 417.1848, found: 417.1844.

***N*¹-2-[(*R*)-Methyl-3-phenylpropionyl]-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (eq. 3):** white solid (95 %); R_f 0.30 (EtOAc/hexane = 1/2); $[\alpha]_{\text{D}}^{23} = +44.5$ ($c = 2.2$ in CHCl_3); mp: 125-126 °C ($\text{CH}_2\text{Cl}_2/\text{hexane}$); ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H) 7.35-7.20 (m, 5H), 7.20-6.95 (m, 5H), 6.73 (d, $J = 7.0$ Hz, 2H), 5.63 (d, $J = 6.2$ Hz, 1H), 4.71 (q, $J = 6.4$ Hz, 1H), 4.30 (d, $J = 17.5$ Hz, 1H), 4.15 (d, $J = 17.5$ Hz, 1H), 3.59 (s, 2H), 3.05 (dd, $J = 5.6, 13.9$ Hz, 1H), 2.88 (dd, $J = 5.6, 13.9$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 165.7, 142.6, 140.4, 134.8, 132.4, 130.0, 129.4, 129.2, 128.9, 128.7, 128.2, 127.2, 126.4, 54.9, 52.4, 39.5, 36.5, 21.5; IR (KBr) ν 3312, 2926, 1746, 1549, 1280, 1146, 1092, 698 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 451.1692, found: 451.1698; Chiralcel OD-H, hexane/*i*-PrOH (80/20), 0.7 mL/min, 20 °C, major 20.8 min (*R*-form), minor 18.0 min (*S*-form).

Appendix I

Spectral Copies of ^1H and ^{13}C NMR of New Compounds Obtained in this Study

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamide (Table 1, entry 1)**

N,N'-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(4-trifluoromethylphenyl)acetamidine (Table 1, entry 2)

N,N'-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(4-methylphenyl)acetamidine (Table 1, entry 3)

N,N'-Diisopropyl-*N*²-(4-methylbenzenesulfonyl)-2-(4-phenyloxyphenyl)acetamidine (Table 1, entry 4)

*N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(pyridin-2-yl)acetamidine (Table 1, entry 5)

*N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(pyridin-3-yl)acetamidine (Table 1, entry 6)

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(thien-3-yl)acetamidine (Table 1, entry 7)**

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-hexanamidine (Table 1, entry 8)**

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-(3,3-dimethyl)butanamidine (Table 1, entry 9)**

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-(5-hydroxy)pentanamidine (Table 1, entry 10)**

***N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-(5-chloro)pentanamidine (Table 1, entry 11)**

*N*¹,*N*¹,*N*³,*N*³-Tetraisopropyl-*N*²,*N*⁴-di(4-methylbenzensulfonyl)-octan-1,8-diamidine (Table 1, entry 12)

*N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(trimethylsilyl)acetamidine (Table 1, entry 13)

Ethyl 3-{[*N*¹,*N*¹-diisopropyl-*N*²-(4-methylbenzensulfonyl)amidino]} propionate (Table 1, entry 14)

*N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-2-(cyclohexen-1-yl)acetamidine (Table 1, entry 15)

Diethyl (3-propenyl) {3-[*N*¹,*N*¹-diisopropyl-*N*²-(4-methylbenzensulfonyl)propionamidino]} malonate
(Table 1, entry 16)

*N*¹,*N*¹-Diisopropyl-*N*²-(2-pyridinesulfonyl)-2-phenylacetamide (Table 1, entry 17)

*N*¹,*N*¹-Diisopropyl-*N*²-(methanesulfonyl)-2-phenylacetamidine (Table 1, entry 18)

*N*¹-Benzyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamide (Table 1, entry 19)

***N*¹-Isopropyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamide (Table 1, entry 20)**

*N*¹-Methyl-*N*¹-phenyl-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamidine (Table 1, entry 21)

*N*¹-[2-(Methoxycarbonyl)pyrrolidinyl]-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamide (Table 1, entry 22)

*N*¹-[(1-Methoxycarbonyl)-3-methylbutyl]-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamide (Table 1, entry 23)

Isotope experiment (eq. 1)

Cross scrambling experiment (eq. 2).

*N*¹-2-[(*R*)-Methyl-3-phenylpropionyl]-*N*²-(4-methylbenzensulfonyl)-2-phenylacetamide (eq. 3)

Appendix II

X-Ray Crystallographic Data for

*N*¹,*N*¹-Diisopropyl-*N*²-(4-methylbenzensulfonyl)-

2-(4-phenyloxyphenyl)acetamidine

(Table 1, entry 4)

Table 1. Crystal data and structure refinement for pho.

Identification code	pho
Empirical formula	C ₂₇ H ₃₂ N ₂ O ₃ S
Formula weight	464.61
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	?, ?
Unit cell dimensions	a = 14.971(5) Å alpha = 90 deg. b = 8.349(3) Å beta = 98.835(7) deg. c = 21.008(7) Å gamma = 90 deg.
Volume	2594.7(15) Å ³
Z, Calculated density	4, 1.189 Mg/m ³
Absorption coefficient	0.154 mm ⁻¹
F(000)	992
Crystal size	? x ? x ? mm
Theta range for data collection	2.63 to 28.03 deg.
Limiting indices	-18 ≤ h ≤ 19, -10 ≤ k ≤ 10, -27 ≤ l ≤ 15
Reflections collected / unique	16108 / 6077 [R(int) = 0.2345]
Completeness to theta = 28.03	96.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6077 / 0 / 367
Goodness-of-fit on F ²	0.695
Final R indices [I > 2sigma(I)]	R1 = 0.0596, wR2 = 0.1261
R indices (all data)	R1 = 0.1844, wR2 = 0.1657
Extinction coefficient	0.00115(18)
Largest diff. peak and hole	0.190 and -0.273 e.Å ⁻³

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

	x	y	z	$U(\text{eq})$
S(1)	0.94854(7)	0.35816(10)	0.32527(5)	0.0631(3)
O(1)	0.89928(19)	0.4155(3)	0.26499(13)	0.0939(9)
O(2)	1.02660(16)	0.4523(3)	0.35189(15)	0.0886(9)
N(2)	1.04334(16)	-0.0438(3)	0.28548(13)	0.0470(7)
O(3)	0.92310(17)	0.2729(3)	-0.02392(12)	0.0787(8)
N(1)	0.97206(18)	0.1718(3)	0.31985(13)	0.0529(8)
C(1)	0.6918(6)	0.3442(9)	0.5221(4)	0.113(2)
C(2)	0.7554(3)	0.3440(5)	0.4734(2)	0.0747(12)
C(3)	0.8407(4)	0.4099(7)	0.4859(3)	0.0843(17)
C(4)	0.8991(3)	0.4140(5)	0.4435(2)	0.0741(12)
C(5)	0.8748(2)	0.3481(4)	0.38195(17)	0.0543(9)
C(6)	0.7887(3)	0.2794(5)	0.3682(2)	0.0687(11)
C(7)	0.7329(4)	0.2802(6)	0.4117(3)	0.0794(14)
C(8)	1.0294(2)	0.1160(4)	0.28404(16)	0.0454(8)
C(9)	1.0042(2)	-0.1481(4)	0.33117(19)	0.0535(9)
C(10)	0.9024(2)	-0.1633(4)	0.3166(2)	0.0778(12)
C(11)	1.0360(3)	-0.1053(5)	0.40202(18)	0.0836(12)
C(12)	1.0983(2)	-0.1247(4)	0.24308(18)	0.0601(10)
C(13)	1.0454(3)	-0.2538(4)	0.2026(2)	0.0864(13)
C(14)	1.1865(2)	-0.1884(5)	0.2788(2)	0.1035(16)
C(15)	1.0764(2)	0.2195(4)	0.24141(16)	0.0530(9)
C(16)	1.0321(2)	0.2288(4)	0.17007(17)	0.0487(9)
C(17)	0.9503(2)	0.1559(4)	0.14723(19)	0.0551(9)
C(18)	0.9119(3)	0.1666(4)	0.08204(18)	0.0592(10)
C(19)	0.9533(2)	0.2547(4)	0.04196(18)	0.0532(9)
C(20)	1.0349(3)	0.3314(4)	0.0633(2)	0.0600(10)
C(21)	1.0714(3)	0.3186(4)	0.1279(2)	0.0558(10)
C(22)	0.8373(3)	0.2078(5)	-0.04928(18)	0.0622(10)
C(23)	0.7608(4)	0.2876(6)	-0.0453(3)	0.0872(16)
C(24)	0.6781(3)	0.2279(6)	-0.0752(2)	0.0941(15)
C(25)	0.6766(4)	0.0851(6)	-0.1089(2)	0.0843(15)
C(26)	0.7540(4)	0.0066(6)	-0.1119(2)	0.0807(14)
C(27)	0.8363(3)	0.0636(5)	-0.0813(2)	0.0753(13)

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

S(1)-O(1)	1.446(3)	O(1)-S(1)-O(2)	115.57(17)
S(1)-O(2)	1.447(2)	O(1)-S(1)-N(1)	110.31(17)
S(1)-N(1)	1.603(3)	O(2)-S(1)-N(1)	112.40(15)
S(1)-C(5)	1.746(4)	O(1)-S(1)-C(5)	108.81(16)
N(2)-C(8)	1.350(4)	O(2)-S(1)-C(5)	108.68(18)
N(2)-C(12)	1.467(4)	N(1)-S(1)-C(5)	99.83(16)
N(2)-C(9)	1.482(4)	C(8)-N(2)-C(12)	122.8(3)
O(3)-C(19)	1.397(4)	C(8)-N(2)-C(9)	121.3(3)
O(3)-C(22)	1.420(4)	C(12)-N(2)-C(9)	115.9(2)
N(1)-C(8)	1.310(4)	C(19)-O(3)-C(22)	117.8(3)
C(1)-C(2)	1.500(6)	C(8)-N(1)-S(1)	123.8(2)
C(2)-C(3)	1.380(6)	C(3)-C(2)-C(7)	114.4(5)
C(2)-C(7)	1.393(6)	C(3)-C(2)-C(1)	122.4(6)
C(3)-C(4)	1.340(6)	C(7)-C(2)-C(1)	123.1(5)
C(4)-C(5)	1.401(5)	C(4)-C(3)-C(2)	124.3(5)
C(5)-C(6)	1.400(5)	C(3)-C(4)-C(5)	119.9(5)
C(6)-C(7)	1.331(6)	C(6)-C(5)-C(4)	116.9(4)
C(8)-C(15)	1.496(4)	C(6)-C(5)-S(1)	122.5(3)
C(9)-C(10)	1.513(4)	C(4)-C(5)-S(1)	120.6(3)
C(9)-C(11)	1.534(5)	C(7)-C(6)-C(5)	120.8(5)
C(12)-C(14)	1.511(4)	C(6)-C(7)-C(2)	123.6(5)
C(12)-C(13)	1.518(5)	N(1)-C(8)-N(2)	116.8(3)
C(15)-C(16)	1.545(4)	N(1)-C(8)-C(15)	123.3(3)
C(16)-C(21)	1.362(5)	N(2)-C(8)-C(15)	119.9(3)
C(16)-C(17)	1.386(4)	N(2)-C(9)-C(10)	113.8(3)
C(17)-C(18)	1.404(5)	N(2)-C(9)-C(11)	113.4(3)
C(18)-C(19)	1.340(4)	C(10)-C(9)-C(11)	111.6(3)
C(19)-C(20)	1.390(4)	N(2)-C(12)-C(14)	112.9(3)
C(20)-C(21)	1.387(5)	N(2)-C(12)-C(13)	111.9(3)
C(22)-C(23)	1.339(6)	C(14)-C(12)-C(13)	111.7(3)
C(22)-C(27)	1.379(5)	C(8)-C(15)-C(16)	116.0(2)
C(23)-C(24)	1.392(6)	C(21)-C(16)-C(17)	117.7(3)
C(24)-C(25)	1.385(6)	C(21)-C(16)-C(15)	119.6(3)
C(25)-C(26)	1.341(6)	C(17)-C(16)-C(15)	122.6(3)
C(26)-C(27)	1.383(6)	C(16)-C(17)-C(18)	121.1(4)

C(19)-C(18)-C(17)	119.2(4)
C(18)-C(19)-C(20)	121.2(4)
C(18)-C(19)-O(3)	124.9(3)
C(20)-C(19)-O(3)	113.8(3)
C(21)-C(20)-C(19)	118.3(4)
C(16)-C(21)-C(20)	122.3(4)
C(23)-C(22)-C(27)	121.3(4)
C(23)-C(22)-O(3)	121.3(4)
C(27)-C(22)-O(3)	117.3(4)
C(22)-C(23)-C(24)	120.3(5)
C(25)-C(24)-C(23)	118.8(5)
C(26)-C(25)-C(24)	120.0(5)
C(25)-C(26)-C(27)	121.6(5)
C(22)-C(27)-C(26)	118.0(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2$) for pho. 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(1)	0.0777(7)	0.0382(5)	0.0710(7)	0.0049(5)	0.0040(6)	0.0093(5)
O(1)	0.136(2)	0.0745(18)	0.0668(18)	0.0181(17)	0.0028(17)	0.0468(17)
O(2)	0.0862(19)	0.0446(14)	0.134(3)	-0.0118(17)	0.0126(17)	-0.0172(14)
N(2)	0.0419(15)	0.0407(15)	0.0554(19)	-0.0006(15)	-0.0022(14)	0.0020(13)
O(3)	0.0863(19)	0.0866(19)	0.0573(17)	0.0156(16)	-0.0078(14)	-0.0191(15)
N(1)	0.0592(17)	0.0326(14)	0.063(2)	-0.0020(15)	-0.0010(15)	0.0061(13)
C(1)	0.133(6)	0.103(4)	0.115(5)	0.009(4)	0.060(5)	0.016(4)
C(2)	0.085(3)	0.058(2)	0.081(3)	0.013(3)	0.015(3)	0.019(2)
C(3)	0.104(5)	0.083(3)	0.062(4)	-0.018(3)	0.002(3)	0.007(3)
C(4)	0.070(3)	0.082(3)	0.068(3)	-0.013(3)	0.005(3)	0.004(2)
C(5)	0.057(2)	0.0424(19)	0.058(2)	0.0005(19)	-0.0080(19)	0.0133(17)
C(6)	0.067(3)	0.073(3)	0.062(3)	-0.009(3)	-0.001(3)	0.004(2)
C(7)	0.057(3)	0.086(3)	0.094(4)	-0.008(3)	0.005(3)	-0.002(3)
C(8)	0.0424(19)	0.0378(18)	0.049(2)	0.0036(17)	-0.0144(17)	-0.0019(15)
C(9)	0.057(2)	0.0379(19)	0.066(3)	0.004(2)	0.0110(19)	-0.0007(18)
C(10)	0.066(2)	0.057(2)	0.113(3)	0.004(2)	0.019(2)	-0.0110(19)
C(11)	0.101(3)	0.069(3)	0.077(3)	0.027(3)	0.000(2)	0.004(2)
C(12)	0.054(2)	0.047(2)	0.078(3)	-0.003(2)	0.006(2)	0.0006(17)
C(13)	0.094(3)	0.062(3)	0.103(3)	-0.017(3)	0.013(2)	-0.002(2)
C(14)	0.057(2)	0.088(3)	0.159(5)	-0.002(3)	-0.003(3)	0.025(2)
C(15)	0.052(2)	0.0408(18)	0.059(2)	0.0022(19)	-0.0117(17)	-0.0074(16)
C(16)	0.052(2)	0.0350(17)	0.058(2)	0.0048(18)	0.0046(18)	0.0019(16)
C(17)	0.058(2)	0.046(2)	0.059(3)	0.011(2)	0.004(2)	-0.0130(18)
C(18)	0.060(2)	0.055(2)	0.058(3)	0.010(2)	-0.004(2)	-0.0133(19)
C(19)	0.058(2)	0.0448(19)	0.054(2)	0.007(2)	0.0023(19)	0.0015(17)
C(20)	0.067(3)	0.055(2)	0.059(3)	0.011(2)	0.012(2)	-0.007(2)
C(21)	0.053(2)	0.045(2)	0.067(3)	0.006(2)	0.001(2)	-0.0079(18)
C(22)	0.068(3)	0.063(3)	0.053(2)	0.011(2)	0.000(2)	-0.001(2)
C(23)	0.100(4)	0.063(3)	0.092(4)	-0.014(3)	-0.009(3)	0.022(3)
C(24)	0.079(4)	0.090(4)	0.104(4)	0.000(3)	-0.015(3)	0.025(3)
C(25)	0.070(3)	0.085(4)	0.086(4)	0.003(3)	-0.022(3)	-0.003(3)
C(26)	0.095(4)	0.064(3)	0.079(3)	-0.009(3)	-0.001(3)	-0.015(3)
C(27)	0.082(3)	0.059(3)	0.086(3)	-0.004(3)	0.015(3)	0.012(3)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($\text{\AA}^2$) for pho.

	x	y	z	U(eq)
H(10A)	0.8849	-0.1908	0.2721	0.093
H(10B)	0.8752	-0.0632	0.3253	0.093
H(10C)	0.8827	-0.2455	0.3432	0.093
H(11A)	1.1007	-0.0977	0.4097	0.100
H(11B)	1.0169	-0.1871	0.4291	0.100
H(11C)	1.0103	-0.0045	0.4116	0.100
H(12)	1.1140	-0.0436	0.2130	0.072
H(13A)	0.9911	-0.2084	0.1794	0.104
H(13B)	1.0301	-0.3378	0.2302	0.104
H(13C)	1.0816	-0.2968	0.1727	0.104
H(14A)	1.2189	-0.1032	0.3029	0.124
H(14B)	1.2222	-0.2308	0.2485	0.124
H(14C)	1.1743	-0.2717	0.3078	0.124
H(15A)	1.1377	0.1802	0.2430	0.064
H(15B)	1.0803	0.3271	0.2590	0.064
H(9)	1.0299(16)	-0.254(3)	0.3166(12)	0.037(7)
H(17)	0.9203(15)	0.100(3)	0.1761(12)	0.024(7)
H(18)	0.850(2)	0.122(4)	0.0699(15)	0.069(10)
H(1A)	0.712(3)	0.288(6)	0.569(3)	0.15(2)
H(6)	0.784(2)	0.235(5)	0.326(2)	0.098(14)
H(20)	1.0641(18)	0.386(4)	0.0316(15)	0.052(9)
H(27)	0.888(2)	0.010(4)	-0.0834(17)	0.071(12)
H(4)	0.961(3)	0.458(5)	0.4429(19)	0.105(15)
H(21)	1.119(2)	0.359(5)	0.134(2)	0.095(16)
H(24)	0.618(2)	0.289(4)	-0.0716(16)	0.090(12)
H(7)	0.685(2)	0.236(4)	0.4027(16)	0.060(13)
H(26)	0.751(2)	-0.087(5)	-0.137(2)	0.099(15)
H(25)	0.626(2)	0.056(5)	-0.1283(19)	0.085(15)
H(1B)	0.677(3)	0.453(6)	0.540(2)	0.129(19)
H(23)	0.766(3)	0.370(5)	-0.028(2)	0.081(16)
H(3)	0.851(3)	0.441(5)	0.5174(18)	0.068(16)
H(1C)	0.636(3)	0.290(6)	0.510(3)	0.14(3)

Table 6. Torsion angles [deg] for pho.

O(1)-S(1)-N(1)-C(8)	68.4(3)	C(9)-N(2)-C(12)-C(14)	-69.0(4)
O(2)-S(1)-N(1)-C(8)	-62.2(3)	C(8)-N(2)-C(12)-C(13)	-122.7(3)
C(5)-S(1)-N(1)-C(8)	-177.2(3)	C(9)-N(2)-C(12)-C(13)	58.0(4)
C(7)-C(2)-C(3)-C(4)	-0.2(7)	N(1)-C(8)-C(15)-C(16)	-95.9(4)
C(1)-C(2)-C(3)-C(4)	-179.1(5)	N(2)-C(8)-C(15)-C(16)	82.3(4)
C(2)-C(3)-C(4)-C(5)	-0.1(7)	C(8)-C(15)-C(16)-C(21)	-179.1(3)
C(3)-C(4)-C(5)-C(6)	-0.3(6)	C(8)-C(15)-C(16)-C(17)	4.5(5)
C(3)-C(4)-C(5)-S(1)	177.9(3)	C(21)-C(16)-C(17)-C(18)	3.6(5)
O(1)-S(1)-C(5)-C(6)	46.6(3)	C(15)-C(16)-C(17)-C(18)	-179.9(3)
O(2)-S(1)-C(5)-C(6)	173.2(3)	C(16)-C(17)-C(18)-C(19)	-2.9(5)
N(1)-S(1)-C(5)-C(6)	-68.9(3)	C(17)-C(18)-C(19)-C(20)	2.0(5)
O(1)-S(1)-C(5)-C(4)	-131.5(3)	C(17)-C(18)-C(19)-O(3)	178.9(3)
O(2)-S(1)-C(5)-C(4)	-4.9(3)	C(22)-O(3)-C(19)-C(18)	7.1(5)
N(1)-S(1)-C(5)-C(4)	112.9(3)	C(22)-O(3)-C(19)-C(20)	-175.8(3)
C(4)-C(5)-C(6)-C(7)	1.1(6)	C(18)-C(19)-C(20)-C(21)	-1.9(5)
S(1)-C(5)-C(6)-C(7)	-177.0(3)	O(3)-C(19)-C(20)-C(21)	-179.1(3)
C(5)-C(6)-C(7)-C(2)	-1.6(7)	C(17)-C(16)-C(21)-C(20)	-3.5(5)
C(3)-C(2)-C(7)-C(6)	1.1(6)	C(15)-C(16)-C(21)-C(20)	179.9(3)
C(1)-C(2)-C(7)-C(6)	180.0(5)	C(19)-C(20)-C(21)-C(16)	2.7(6)
S(1)-N(1)-C(8)-N(2)	178.8(2)	C(19)-O(3)-C(22)-C(23)	82.4(5)
S(1)-N(1)-C(8)-C(15)	-3.0(4)	C(19)-O(3)-C(22)-C(27)	-101.2(4)
C(12)-N(2)-C(8)-N(1)	173.6(3)	C(27)-C(22)-C(23)-C(24)	-1.7(7)
C(9)-N(2)-C(8)-N(1)	-7.1(4)	O(3)-C(22)-C(23)-C(24)	174.6(4)
C(12)-N(2)-C(8)-C(15)	-4.6(5)	C(22)-C(23)-C(24)-C(25)	0.1(7)
C(9)-N(2)-C(8)-C(15)	174.6(3)	C(23)-C(24)-C(25)-C(26)	0.4(7)
C(8)-N(2)-C(9)-C(10)	69.0(4)	C(24)-C(25)-C(26)-C(27)	0.8(7)
C(12)-N(2)-C(9)-C(10)	-111.7(3)	C(23)-C(22)-C(27)-C(26)	2.9(6)
C(8)-N(2)-C(9)-C(11)	-60.1(4)	O(3)-C(22)-C(27)-C(26)	-173.6(3)
C(12)-N(2)-C(9)-C(11)	119.3(3)	C(25)-C(26)-C(27)-C(22)	-2.4(7)
C(8)-N(2)-C(12)-C(14)	110.3(4)		

Symmetry transformations used to generate equivalent atoms: