Electronic Supplementary Information

cis-Stereoselective Nickel-Catalyzed Cyclization/Alkylation and Arylation Reactions of Allenyl-Aldehydes and -Ketones with Organozinc Reagents

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General. All reagents were obtained from commercial sources and used without further purification unless stated otherwise. THF was distilled from sodium-benzophenone under N_2. ^{1}H NMR were conducted at 500 MHz in $CDCl_3$, and chemical shifts are reported δ units relative to the tetramethylsilane (TMS) signal at 0.00 ppm. Coupling constants (*J*) are reported in Hz. For thin-layer chromatography (TLC), Merck precoated plates (silica gel 60 F_{254}, 0.25 mm) were used. Silica gel 60 (TA792685, 230-400 mesh) from Merck was used for column chromatography. The reported yields are for chromatographically pure isolated products.

***N*-Buta-2,3-dienyl-4-methyl-*N*-(2-oxo-butyl)-benzenesulfonamide (1c)**

(i) To a solution of *N*-Buta-2,3-dienyl-*N*-(2-oxo-ethyl)-4-methyl-benzenesulfonamide (**1a**) (300 mg, 1.13 mmol) in THF (10 mL) at 0 ℃ was added EtMgBr (0.60 mL, 3.0 M in diethyl ether, 1.80 mmol). After 1 h the reaction mixture was quenched by aq. NH_4Cl (5 mL) and extracted with ethyl acetate (20 mL x 3). The organic extracts are washed with saturated $NaHCO_3$ (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue is subjected to SiO_2 column chromatography (1:2 EtOAc/hexane, R_f = 0.30) to give *N*-Buta-2,3-dienyl-*N*-(2-hydroxy-butyl)-4-methyl-benzene-sulfonamide (220 mg, 66%). (ii) *N*-Buta-2,3-dienyl-*N*-(2-hydroxy-butyl)-4-methyl-benzene-sulfonamide was followed by PCC-oxidation to give *N*-Buta-2,3-dienyl-4-methyl-*N*-(2-oxo-butyl)-benzenesulfonamide (**1c**) (270 mg, 82%). A oil; TLC, SiO_2, 1 : 2 EtOAc/hexane, R_f = 0.52; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (t, 3H, *J* = 7.3 Hz), 2.43 (s, 3H), 2.54 (q, 2H, *J* = 7.3 Hz), 3.38 (dt, 2H, *J* =

2.2, 7.3 Hz), 3.97 (s, 2H), 4.70 (dt, 2H, *J* = 2.2, 6.6), 4.96 (tt, 1H, *J* = 7.0, 7.0), 7.31 (d, 2H, *J* = 8.1 Hz), 7.71 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.8, 21.9, 30.1, 33.2, 48.4, 55.3, 76.8, 85.8, 108.2, 127.8, 130.1, 136.7, 144.1, 207.1, 210.3; HRMS calcd for $C_{15}H_{19}NO_3S$ 293.1086. found**:** 293.1087.

Octa-6,7-dien-2-one (1g)

A oil; TLC, SiO_2, EtOAc / hexanes 1 : 5, R_f = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (q, 2H, *J* = 7.3 Hz), 1.87 (m, 2H), 2.00 (s, 3H), 2.34 (d, 2H, *J* = 7.3 Hz), 4.53 (m, 2H), 4.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.1, 27.6, 42.8, 75.1, 89.4, 208.7; HRMS calcd for $C_8H_{12}O$ 124.0888. found**:** 124.0887.

4-Isopropenyl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (3a). Typical Procedure:

To a stirred solution of $Ni(COD)_2$ (10 mg, 0.038 mmol) in dry THF under N_2 is sequentially added 1a (100 mg, 0.38 mmol) and Me_2Zn (0.57 mL, 2.0 M in toluene, 1.14 mmol). The mixture is stirred at 0 ^{o}C for 10 min, quenched by the addition of 2 N HCl (5 mL), and extracted with ethyl acetate. The organic extracts are washed with saturated $NaHCO_3$ (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue is subjected to SiO_2 column chromatography (1:1 EtOAc/hexane, R_f = 0.29) to give 4-isopropenyl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (3a) (82 mg, 77%). A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79 (t, 3H, *J* = 0.7 Hz), 2.42 (s, 3H), 2.62 (m, 1H), 3.31 (dd, 1H, *J* = 9.3, 11.1 Hz), 3.45 (dd, 1H, *J* = 1.3, 11.5 Hz), 3.54 (dd, 1H, *J* = 3.7, 11.5 Hz), 4.27 (m, 1H), 5.03 (dd, 1H, *J* = 1.2, 2.9 Hz), 7.32 (d, 2H, *J* = 8.3 Hz), 7.78 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.9, 23.3, 48.1, 50.9, 56.4, 70.6, 114.3, 127.9, 130.1, 134.5, 139.9, 143.8; HRMS calcd for $C_{14}H_{19}NO_5S$ 281.1086. found: 281.1071.

4-(1-Ethyl-vinyl)-1-(toluene-4sulfonyl)-pyrrolidin-3-ol (3b)

A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 1, R_f = 0.43; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, 3H, *J* = 7.3 Hz), 1.98-2.09 (m, 2H), 2.43 (s, 3H), 2.69 (m, 1H), 3.30 (dd, 1H, *J* = 9.2, 11.4 Hz), 3.44 (d, 1H, *J* = 11.4 Hz), 3.55 (m, 2H), 4.23 (dd, 1H, *J* = 3.4, 4.0 Hz). 4.78 (s, 1H), 5.05 (s, 1H), 7.32 (d, 2H, *J* = 8.1 Hz), 7.75 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.1, 21.6, 29.1, 48.0, 49.6, 55.9, 70.1, 111.9, 127.5, 129.7, 134.1, 143.5, 145.1; HRMS calcd for $C_{15}H_{21}NO_3S$: 295.1242. found: 295.1234.

4-(1-Butyl-vinyl)-1-(toluene-4sulfonyl)-pyrrolidin-3-ol (3c)

A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 2, R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 7.3 Hz), 1.25-1.43 (m, 4H), 2.00 (m, 2H), 2.43 (s, 3H), 2.67 (m, 1H), 3.28 (dd, 1H, *J* = 9.5, 11.7 Hz), 3.44 (d, 1H, *J* = 11.7 Hz), 3.55 (m, 2H), 4.22 (dd, 1H, *J* = 3.4, 4.0 Hz). 4.77 (s, 1H), 5.04 (s, 1H), 7.32 (d, 2H, *J* = 8.1 Hz), 7.74 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.0, 22.7, 30.3, 36.6, 48.5, 49.8, 56.3, 70.5, 113.3, 127.8, 130.1, 134.5, 143.8, 144.1; HRMS calcd for $C_{17}H_{25}NO_3S$: 323.1555. found: 323.1562.

4-(1-Phenyl-vinyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (**3d**). **Typical Procedure:**

To a stirred solution of $ZnCl_2$ (1.14 mL, 1.0 M in diethyl ether, 1.14 mmol) in THF at 0 ^{o}C under N_2, phenyllithium (0.95 mL, 1.8 M in cyclohexane-ether 70 to 30, 1.17 mmol) is added. After stirring for 30 min at 0 ^{o}C, a solution of $Ni(COD)_2$ (10.4 mg, 0.038 mmol) in dry THF is added and the resulting mixture is immediately transferred by cannula to a solution of **1a** (100 mg, 0.38 mmol) in THF. The mixture is stirred at 0 ^{o}C for 30 min under N_2, quenched with 2 N HCl (5 mL), and extracted with ethyl acetate. The organic extracts are washed with saturated $NaHCO_3$ (10 mL), dried over $MgSO_4$, and concentrated *in vacuo* giving a residue, which is subjected to SiO_2 column chromatography (1:2 EtOAc/hexane, R_f = 0.23) to give 4-(1-phenyl-vinyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (**3d**) (108 mg, 83%). A white solid: mp 120 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.27 (m, 1H), 3.38 (dd, 1H, *J* = 11.5, 0.6 Hz), 3.40 (dd, 1H, *J* = 11.4, 9.0 Hz), 3.60 (dd, 1H, *J* = 11.5, 4.2 Hz), 3.74 (dd, 1H, *J* = 9.0, 7.0 Hz), 4.16 (dd, 1H, *J* = 7.0, 4.6 Hz), 5.05 (t, 1H, *J* = 1.5 Hz), 5.45 (dd,1H, *J* = 1.5, 0.7), 7.29 (m, 2H), 7.31 (m, 2H), 7.33 (m, 1H), 7.35 (d, 2H, *J* = 8.3), 7.76 (d, 2H, *J* = 8.3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.9, 48.9, 49.1, 56.2, 70.8, 116.5, 126.5, 127.9, 128.6, 129.1, 130.1, 134.5, 140.9, 143.7, 143.9; HRMS calcd for $C_{19}H_{21}NO_3S$ 343.1242 found 343.1229.

4-Isopropenyl-3-methyl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (3e)

A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 2, R_f = 0.28; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (s, 3H), 1.78 (s, 3H), 2.43 (s, 3H), 2.51 (dd, 1H, *J* = 7.7, 10.6 Hz), 3.341 (m, 3H), 3.55 (dd, 1H, *J* = 7.7, 9.9 Hz), 4.78 (s, 1H), 5.06 (dd, 1H, *J* = 1.5, 1.8 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 7.74 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 24.4, 24.6, 50.6, 54.2, 60.5, 76.7, 114.9, 127.5, 129.7, 134.1, 140.1, 143.5; HRMS calcd for $C_{15}H_{21}NO_5S$ 295.1242. found: 295.1242.

4-(1-Ethyl-vinyl)-1-(toluene-4sulfonyl)-pyrrolidin-3-ol (3f)

A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.20; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (t, 3H, *J* = 7.3 Hz), 1.23 (s, 3H), 2.02-2.09 (m, 2H), 2.44 (s, 3H), 2.53 (dd, 1H, *J* = 7.3, 11.4 Hz)), 3.32 (m, 2H), 3.42 (d, 1H, *J* = 11.4 Hz), 3.56 (dd, 1H, *J* = 7.3, 9.5 Hz), 4.84 (s, 1H), 5.06 (d, 1H, *J* = 1.1 Hz), 7.32 (d, 2H, *J* = 8.1 Hz), 7.74 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.3, 21.6, 24.8, 30.9, 51.2, 53.1, 60.4, 76.6, 112.2, 127.5, 129.6, 134.1, 143.4, 145.9; HRMS calcd for $C_{16}H_{23}NO_3S$: 309.1399. found: 309.1398.

3-Methyl-4-(1-phenyl-vinyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (3g)

A white solid: mp 102 ℃; TLC, SiO_2, EtOAc / hexanes 1 : 2, R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 3H), 2.45 (s, 3H), 3.18 (dd, 1H, *J* = 11.4, 7.3 Hz), 3.36 (d, 1H, *J* = 11 Hz), 3.45 (m, 1H), 3.75 (dd, 1H, *J* = 9.5, 7.3 Hz), 5.15 (s, 1H), 5.47 (s, 1H), 7.31 (m, 7H), 7.77 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8, 25.1, 51.5, 52.1, 60.8, 77.5, 116.9, 126.7, 127.8, 128.2, 128.8, 129.9, 134.4, 142.6, 143.7, 144.1; HRMS calcd for $C_{20}H_{23}NO_3S$ 357.1399 found 357.1392.

3-Ethyl-4-(1-ethyl-vinyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (3h)

A colorless oil: TLC, SiO_2, EtOAc / hexanes 1 : 1, R_f = 0.38; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, 3H, *J* = 7.3 Hz), 1.01 (t, 3H, *J* = 7.3 Hz), 1.40-1.55 (m, 2H), 1.90-2.10 (m, 2H), 2.44 (s, 3H), 2.54 (dd, 1H, *J* = 7.3, 11.4 Hz), 3.30 (dd, 1H, *J* = 9.5, 11 Hz), 3.35 (s, 2H), 3.56 (dd, 1H, *J* = 7.3, 9.5 Hz), 4.84 (s, 1H), 5.04 (d, 1H, *J* = 0.7 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 7.74 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.1, 12.7, 22.0, 31.4, 31.8, 51.7, 52.4, 58.6, 80.0, 112.7, 127.9, 130.0, 134.6, 143.8, 146.5; HRMS calcd for $C_{17}H_{25}NO_3S$ 323.1555 found 323.1566.

3-Hydroxy-4-isopropenyl-cyclopentane-1,1-dicarboxylic acid diethyl ester (3i)

A colorless oil: TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.46; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (dd, 6H, *J* = 7.3, 12.1 Hz), 1.82 (s, 3H), 2.33 (m, 3H), 2.51 (m, 2H), 2.56 (m, 2H), 4.21 (q, 4H, *J* = 7.3 Hz), 4.28 (m, 1H), 4.89 (s, 1H), 5.04 (d, 1H, *J* = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 23.6, 34.8, 42.6, 52.5, 58.6, 62.1, 72.8, 113.2, 142.8, 173.1; HRMS calcd for $C_{14}H_{22}O_5$ 270.1467 found 270.1471.

3-Hydroxy-4-(1-phenyl-vinyl)cyclopentane-1,1-dicarboxylic acid diethyl ester (3j)

A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.38; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (t, 6H, *J* = 7.3 Hz), 2.52 (m, 3H), 2.67 (t, 1H, *J* = 13.2 Hz), 3.23 (m, 1H), 4.14 (m, 1H), 4.22 (q, 4H, *J* = 7.3 Hz), 5.24 (s, 1H), 5.47 (s, 1H), 7.33 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 35.3, 42.2, 50.1, 58.2, 61.9, 72.6, 115.4, 126.5, 128.0, 128.7, 141.8, 146.1, 172.6, 172.9; HRMS calcd for $C_{19}H_{24}O_5$ 332.1624 found 332.1627.

6-Isopropenyl-1-methyl-3-oxo-2-oxa-bicyclo [2, 2, 1] heptane-4-carboxylic acid ethyl ester (3k)

A colorless oil: TLC, SiO_2, EtOAc / hexanes 1 : 2, R_f = 0.34; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, 3H, *J* = 7.3 Hz), 1.52 (s, 3H), 1.75 (s, 3H), 2.06 (m, 1H), 2.10 (d, 1H, *J* = 10.3 Hz), 2.39 (dd, 1H, *J* = 10.3, 2.2 Hz), 2.51 (dd, 1H, *J* = 13.9, 11.0 Hz), 2.80 (m, 1H), 4.27 (q, 2H, *J* = 7.3 Hz), 4.85 (d, 1H, *J* = 0.4 Hz), 4.99 (dd, 1H, 1.8, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 17.6, 21.1, 33.5, 49.1, 52.6, 58.6, 62.1, 91.1, 116.4, 141.7, 168.5, 173.8; HRMS calcd for $C_{13}H_{18}O_4$ 238.1205 found 238.1204.

1-Mehtyl-3-oxo-6-(1-phenyl-vinyl)-2-oxa-bicyclo [2, 2, 1] heptane-4-carboxylic acid ethyl ester (3l)

A bright yellow oil: TLC, SiO_2, EtOAc / hexanes 1 : 2, R_f = 0.37; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, 3H, *J* = 7.3 Hz), 1.37 (s, 3H), 2.15 (ddd, 1H, *J* = 2.6, 5.5, 13.6 Hz), 2.21 (d, 1H, *J* = 10.6 Hz), 2.44 (dd, 1H, *J* = 2.6, 10.6 Hz), 2.72 (dd, 1H, *J* = 11.4, 13.6 Hz), 3.37 (dd, 1H, *J* = 5.5, 11.4 Hz), 4.28 (qd, 2H, *J* = 7.3, 2.6 Hz), 5.28 (d, 1H, *J* = 1.1 Hz), 5.45 (s, 1H), 7.29-7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 18.0, 35.3, 48.7, 49.7, 50.9, 58.2, 61.8, 90.0, 115.9, 126.5, 127.7, 128.5, 143.0, 145.0, 168.0, 173.4; HRMS calcd for $C_{18}H_{20}O_4$ 300.1362 found 300.1360.

2-(1-Phenyl-vinyl)-cyclopentanol (3m)

A colorless oil: TLC, SiO_2, EtOAc / hexanes 1 : 5, R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66 (m, 1H), 1.78 (m, 1H), 1.86 (m, 1H), 1.93 (m, 3H), 2.99 (m, 1H), 4.08 (dd, 1H, *J* = 4.0, 4.8 Hz), 5.22 (dd, 1H, *J* = 1.5, 1.8 Hz), 5.47 (dd, 1H, *J* = 1.1, 1.8), 7.30 (m, 1H), 7.34 (m, 2H), 7.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 27.4, 34.1, 51.7, 73.2, 115.2, 126.7, 128.1, 128.9, 142.7, 147.8; HRMS calcd for $C_{13}H_{16}O$ 188.1201 found 188.1205.

1-Methyl-2-(1-Phenyl-vinyl)-cyclopentanol (3n)

A colorless oil: TLC, SiO_2, EtOAc / hexanes 1 : 5, R_f = 0.53; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (s, 3H), 1.62-1.76 (m, 2H), 1.89-2.16 (m, 4H), 2.96 (dd, 1H, *J* = 7.3, 11.7 Hz)), 5.27 (dd, 1H, *J* = 1.1 1.5 Hz), 5.46 (d, 1H, *J* = 1.1 Hz), 7.28 (m, 1H), 7.33 (m, 2H), 7.38 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 28.0, 30.6, 40.8, 54.5, 79.0, 115.3, 126.9, 127.6, 128.6, 144.2, 148.8; HRMS calcd for $C_{14}H_{18}O$ 202.1358 found 202.1358.

4-Methyl-6-(toluene-4sulfonyl)-2,4a,5,6,7,7a-hexahydro-pyrano [2,3-c] pyrrole (5a)

A brown oil: TLC, SiO_2, EtOAc / hexanes 1 : 1, R_f = 0.50; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (d, 3H, J = 1.8 Hz), 2.28 (m, 1H), 2.42 (s, 3H), 2.87 (dd, 1H, *J* = 9.2, 11.0 Hz), 3.28 (d, 1H, *J* = 11.4 Hz), 3.70 (dd, 1H, *J* = 5.1, 11.4 Hz), 3.78 (dd, 1H, *J* = 8.4, 9.2 Hz), 3.98 (m, 3H), 5.44 (d. 1H, *J* = 1.5 Hz), 7.32 (d, 2H, *J* = 7.7 Hz), 7.72 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 21.0, 41.9, 50.1, 53.4, 63.8, 74.0, 120.2, 126.5, 128.6, 129.2, 132.9, 142.3; HRMS calcd for $C_{15}H_{19}NO_3S$ 293.1088 found 293.1086.

4-Ethyl-6-(toluene-4sulfonyl)-2,4a,5,6,7,7a-hexahydro-pyrano [2,3-c] pyrrole (5b)

A bright yellow oil; TLC, SiO_2, EtOAc / hexanes 1 : 1, R_f = 0.58; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, 3H, J = 7.3 Hz), 1.96 (m, 2H), 2.33 (m, 1H), 2.88 (dd, 1H, *J* = 9.2, 11.0 Hz), 3.28 (d, 1H, *J* = 11.7 Hz), 3.70 (dd, 1H, *J* = 5.1, 11.7 Hz), 3.78 (dd, 1H, *J* = 8.4, 9.2 Hz), 4.00 (m, 3H), 5.42 (s. 1H), 7.31 (d, 2H, *J* = 8.1 Hz), 7.72 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0, 21.9, 28.9, 42.2, 51.8, 54.8, 65.4, 75.7, 119.9, 127.9, 130.0, 134.4, 136.2, 143.8; HRMS calcd for $C_{16}H_{21}NO_3S$ 307.1242 found 307.1239.

Supplementary materials for 3a

NMR spectra and calculations

All NMR measurements were performed on a Bruker Avance 400 spectrometer system (9.4 T) at a temperature of 298 K. The NMR spectra of ^{1}H NMR, ^{13}C NMR, DEPT, *J*-Resolved, COSY, HMQC, HMBC, and NOESY were collected in $CHCl_3$-d with TMS as an internal reference. The concentration of the samples was 50 mM. For ^{1}H-NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32 K data points. The 90 ^{o} pulse was 10 μsec with a spectral width of 3378 Hz. ^{13}C NMR and DEPT spectra were obtained for a spectral width of 20964 Hz, collecting 64 K data points. The 90 ^{o} pulse was 10.4 μsec. Two-dimensional spectra were acquired with 2048 data points for t2 and 256 for t1 increments. All calculations were performed using MSI software (San Diego, U.S.A.) on a Silicon Graphics O2 workstation. The potentials were arranged using a consistent-valence force field and the calculation was performed for 500 ps. Among 500 calculated structures, ten structures with the lowest total energy were superimposed and used for analysis.

Result

The structures and nomenclatures of SKY-103 are shown in Fig. 1. The configuration of ring juncture protons can be determined based on the different distances between H3 and vinyl protons H6a/H6b. As shown in Fig. 2, while in the case of *cis* configuration, the distances of H3-H6a and H3-H6b calculated by molecular modeling are 3.31and/or 4.28 Å, respectively, in the case of *trans*, they are 4.79 and/or 5.07 Å, respectively. The 1D NOESY slices at H6a and H6b shown in Fig. 3 give 0.3% and 0.2% nOe for H3, respectively. When the distance between H6a and H6b is considered a reference, the distances between H6a and H3, and H6b and H3 are 3.42 and 3.67 Å, respectively. These values are fit to the *cis* configuration. In order to confirm the result, the relationship between coupling constants and the Karplus equation was used. The coupling constant between H3 and H4 obtained from the *J*-resolved spectrum is 6.0 Hz. The dihedral angle determined based on the Karplus equation is 32.4 °. While the angle of the *cis* isomer calculated by molecular modeling is 34.2 °, the angle of the *trans* isomer is 167.7 °. Therefore, the configuration of ring juncture protons is *cis*. Total assignments of the ^{1}H and ^{13}C NMR data of **3a** are listed in Table 1.

Fig. 1. The structures and nomenclatures of **3a**

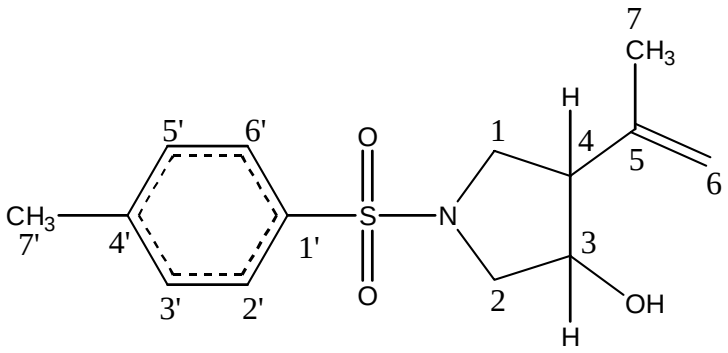


Fig. 2. The structures calculated by molecular modeling. (top: *cis*, bottom: *trans*)

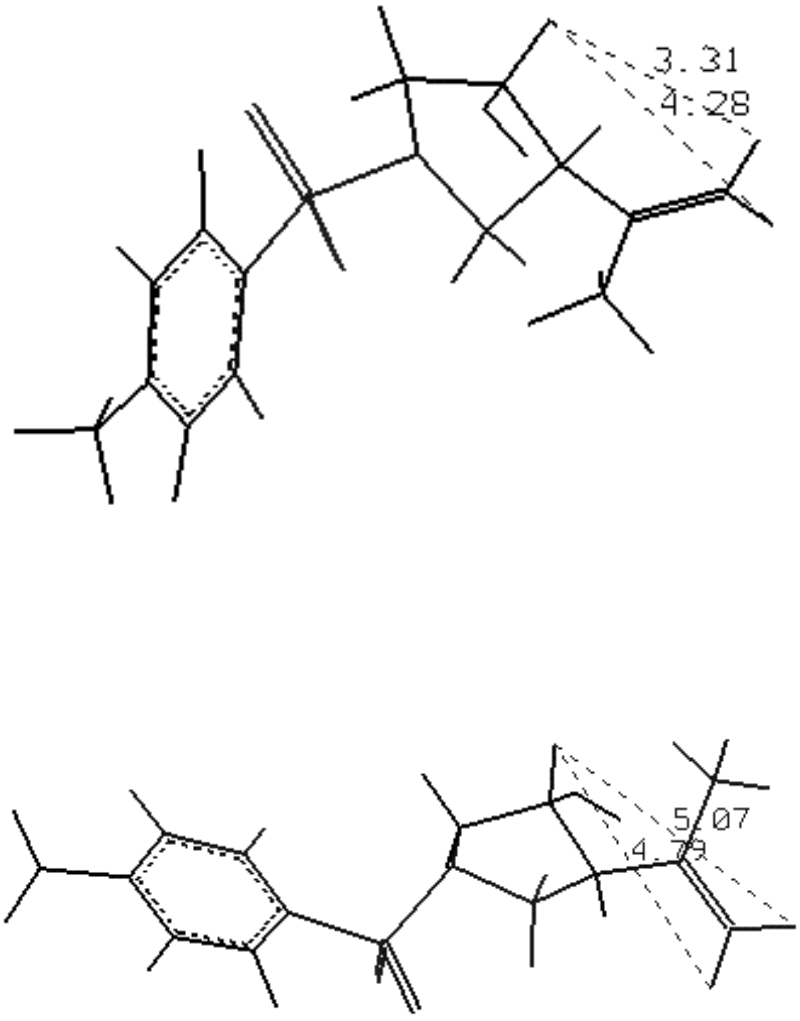
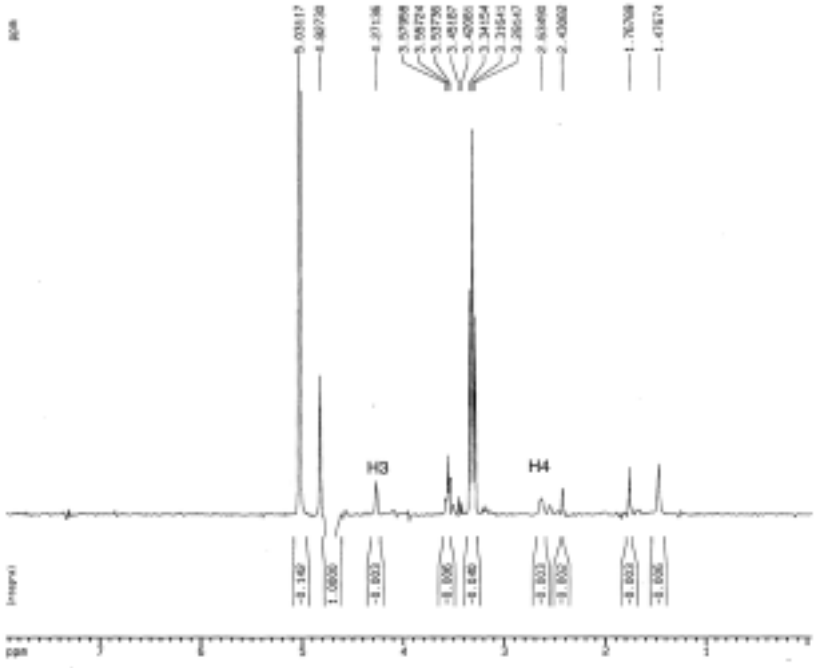


Fig. 3. The 1D slices of NOESY at H6a and H6b. (top : H6a, bottom : H6b)



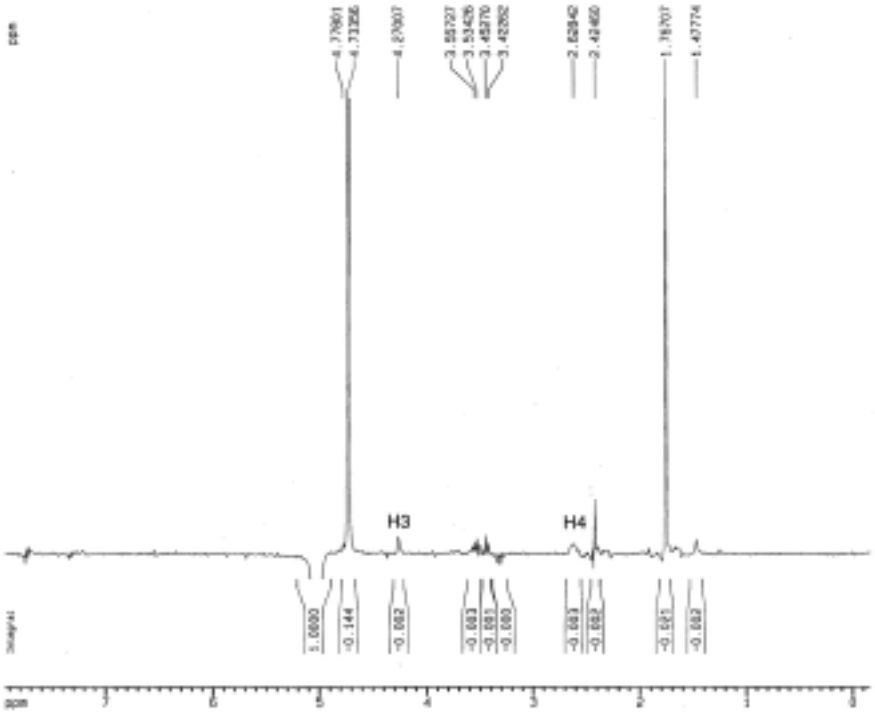

ppm
4.77601
4.73256
4.67607
3.55727
3.53426
3.45270
3.42352
2.62842
2.49460
1.78707
1.43774
H3
H4
Integral
1.0000
0.144
0.662
0.693
0.681
0.000
0.683
0.682
0.671
0.662
ppm

Table 1. Total assignments of the ^{1}H and ^{13}C NMR data of **3a**

δ of ^{13}C	CHn	δ of ^{1}H	Assignment
21.9	q	2.42(s)	7’
23.3	q	1.79(t 0.7)	7
48.1	t	3.31(dd 9.3, 11.1) 3.56(dd 7.4, 9.3)	1
50.9	d	2.62(m)	4
56.4	t	3.45(dd 1.3, 11.5) 3.54(dd 3.7, 11.5)	2
70.6	d	4.27(m)	3
114.3	t	4.73(ddd 1.2, 2.1,3.0) 5.03(dd 1.2, 2.9)	6
127.9	d	7.78(d 8.3)	2’, 6’
130.1	d	7.32(d 8.3)	3’, 5’
134.5	s	-	1’
139.9	s	-	5
143.8	s	-	4’

Supplementary materials for 3d

NMR spectra and calculations

All NMR measurements were performed on a Bruker Avance 400 spectrometer system (9.4 T) at a temperature of 298 K. The NMR spectra of ^{1}H NMR, ^{13}C NMR, DEPT, *J*-Resolved, COSY, HMQC, HMBC, and NOESY were collected in $CHCl_3$-d with TMS as an internal reference. The concentration of the samples was 50 mM. For ^{1}H-NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32 K data points. The 90 ^{o} pulse was 10.0 μsec with a spectral width of 3378 Hz. ^{13}C NMR and DEPT spectra were obtained for a spectral width of 20964 Hz, collecting 64 K data points. The 90 ^{o} pulse was 10.4 μsec. Two-dimensional spectra were acquired with 2048 data points for t2 and 256 for t1 increments. All calculations were performed using MSI software (San Diego, U.S.A.) on a Silicon Graphics O2 workstation. The potentials were arranged using a consistent-valence force field and the calculation was performed for 500 ps. Among 500 calculated structures, ten structures with the lowest total energy were superimposed and used for analysis.

Result

The structures and nomenclatures of **3d** are shown in Fig. 4. The configuration of ring juncture protons can be determined based on the different distances between H3 and vinyl protons H6a/H6b. As shown in Fig. 5, while in the case of *cis* configuration, the distances of H3-H6a and H3-H6b calculated by molecular modeling are 3.82 and/or 4.53 Å, respectively, in the case of *trans*, they are 4.39 and/or 4.25 Å, respectively. The 1D NOESY slices at H6a and H6b shown in Fig. 6 give 0.3% and 0.1% nOe for H3, respectively. When the distance between H6a and H6b is considered a reference, the distances between H6a and H3, and H6b and H3 are 3.85 and 4.53 Å, respectively. These values are fit to the *cis* configuration. In order to confirm the result, the relationship between coupling constants and the Karplus equation was used. The coupling constant between H3 and H4 obtained from the *J*-resolved spectrum is 4.6 Hz. The dihedral angle determined based on the Karplus equation is 40.5°. While the angle of the *cis* isomer calculated by molecular modeling is 43.4 °, the angle of the *trans* isomer is 175.7 °. Therefore, the configuration of ring juncture protons is *cis*. Total assignments of the ^{1}H and ^{13}C NMR data of **3d** are listed in Table 2.

Fig. 4. The structures and nomenclatures of **3d**

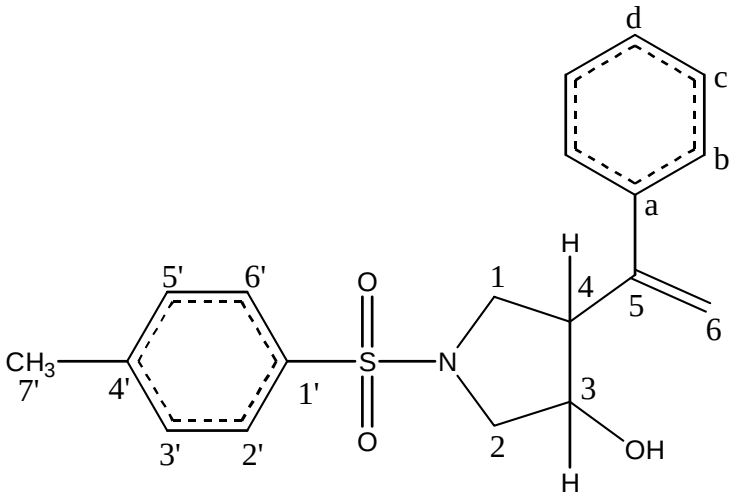


Fig. 5. The structures calculated by molecular modeling. (top: *cis*, bottom: *trans*)

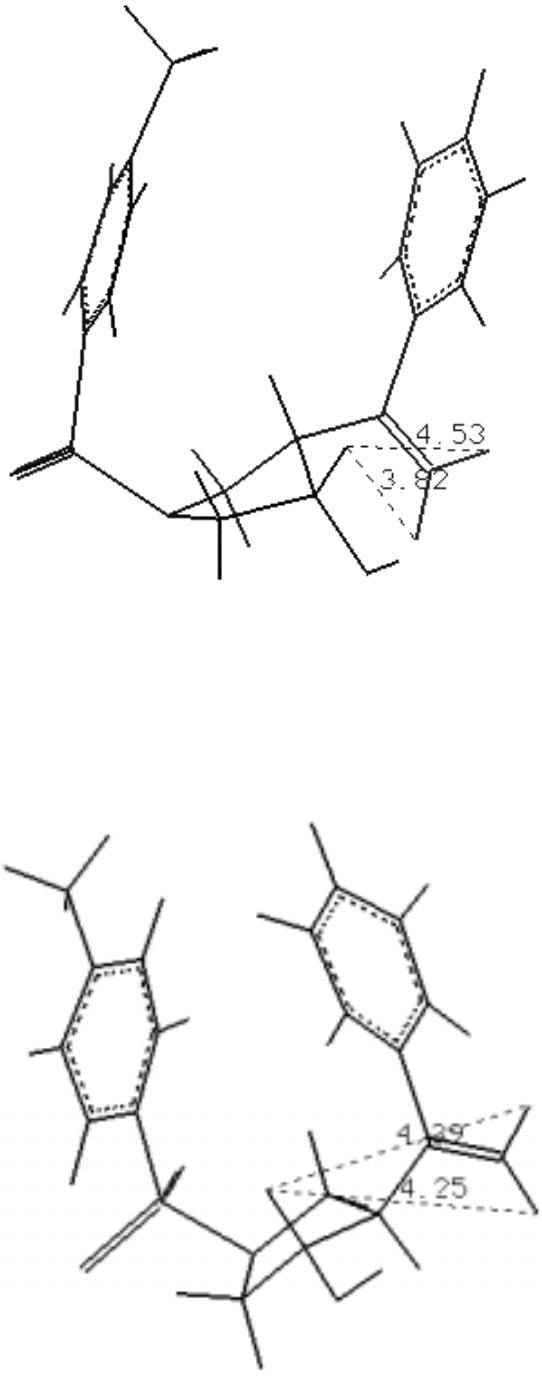
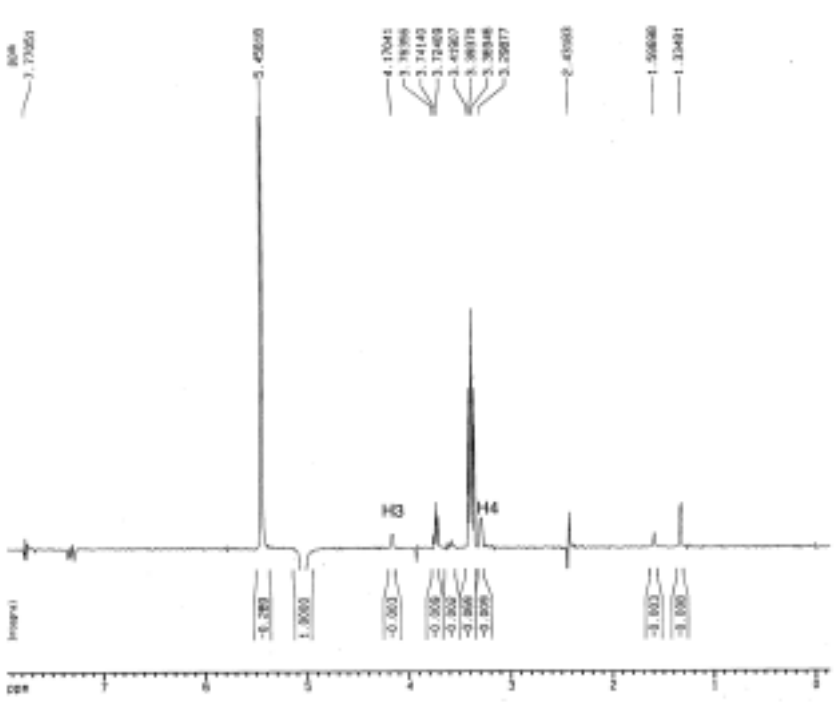


Fig. 6. The 1D slices of NOESY at H6a and H6b. (top : H6a, bottom : H6b)



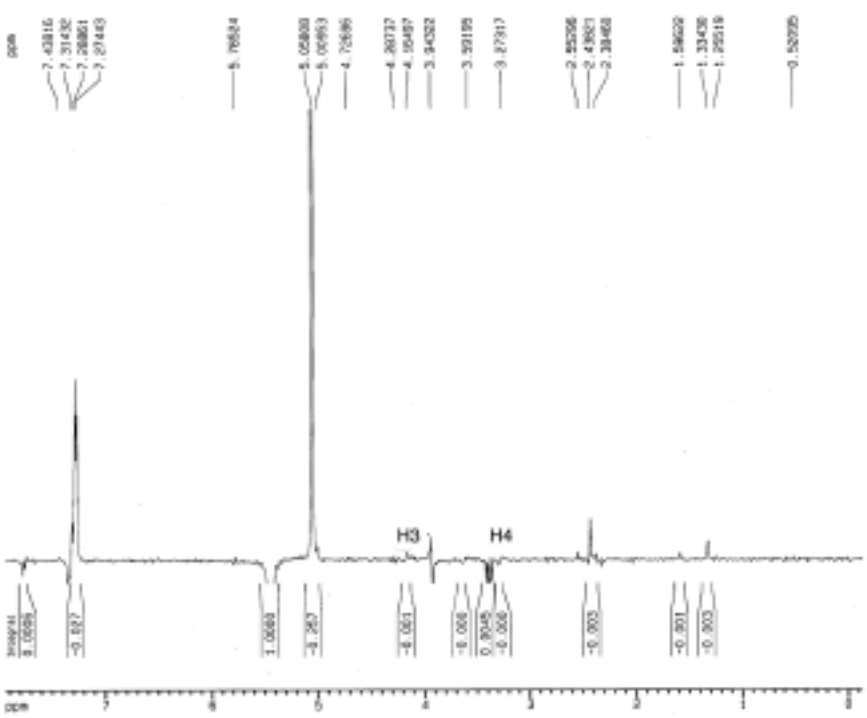


Table 2. Total assignments of the ^{1}H and ^{13}C NMR data of **3d**

δ of ^{13}C	CHn	δ of ^{1}H	Assignment
21.9	q	2.43(s)	7’
48.9	t	3.40(dd 9.0, 11.4) 3.74(dd 9.0, 7.0)	2
49.1	d	3.27(m)	4
56.2	t	3.38(dd 0.6, 11.5) 3.60(dd 4.2, 11.5)	1
70.8	d	4.16(dd 4.6, 7.0)	3
116.5	t	5.05(t, 1.5) 5.45(dd 0.7, 1.5)	6
126.5	d	7.29(m)	c
127.9	d	7.76(d 8.3)	2’, 6’

128.6	d	7.33(m)	d
129.1	d	7.31(m)	b
130.1	d	7.35(d 8.3)	3', 5'
134.5	s	-	1'
140.9	s	-	5
143.7	s	-	a
143.9	s	-	4'

X-ray crystallographic data

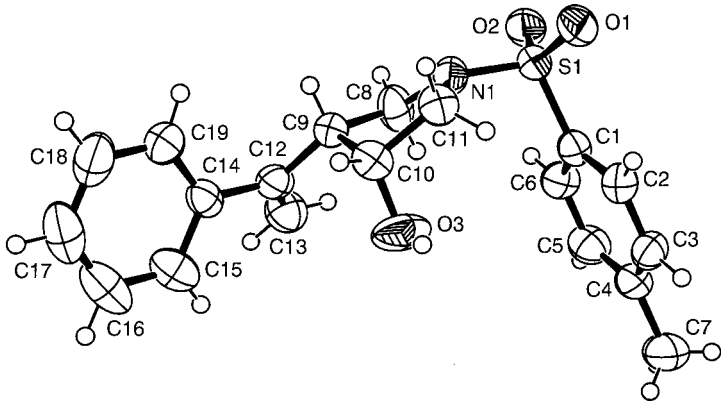


Figure 7. ORTEP drawing of **3d**

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

Identification code	**3d**	
Empirical formula	C38 H42 N2 O6 S2	
Formula weight	686.86	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.136(2) Å	a= 65.951(12)°.
	b = 12.7389(17) Å	b= 81.600(14)°.

	c = 13.752(2) Å g = 65.106(9)°.
Volume	1760.2(5) $Å^3$
Z	2
Density (calculated)	1.296 Mg/m^3
Absorption coefficient	0.200 mm^{-1}
F(000)	728
Crystal size	0.44 x 0.24 x 0.22 mm^3
Theta range for data collection	1.91 to 25.00°.
Index ranges	-14<=h<=0, -13<=k<=12, -16<=l<=16
Reflections collected	6251
Independent reflections	5946 [R(int) = 0.0213]
Completeness to theta = 25.00°	96.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5946 / 0 / 560
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1135
R indices (all data)	R1 = 0.0636, wR2 = 0.1253
Extinction coefficient	0.0031(7)
Largest diff. peak and hole	0.251 and -0.247 $e.Å^{-3}$

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **3d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5990(1)	6706(1)	4644(1)	46(1)
O(1)	5892(2)	7952(2)	4385(1)	61(1)
O(2)	4906(2)	6484(2)	4782(1)	59(1)
O(3)	9462(3)	4153(2)	5761(2)	86(1)
N(1)	6764(2)	5840(2)	5758(2)	48(1)
C(1)	6840(2)	6188(2)	3657(2)	43(1)
C(2)	7610(2)	6737(2)	3039(2)	50(1)
C(3)	8287(2)	6306(3)	2285(2)	54(1)
C(4)	8222(2)	5324(2)	2129(2)	55(1)
C(5)	7451(3)	4789(3)	2758(2)	60(1)
C(6)	6753(2)	5206(2)	3516(2)	53(1)
C(7)	8960(4)	4872(4)	1296(3)	80(1)
C(8)	6964(3)	4503(3)	6259(2)	59(1)
C(9)	7965(2)	3969(2)	7086(2)	46(1)
C(10)	8763(2)	4678(2)	6493(2)	50(1)
C(11)	7867(2)	5994(2)	5913(2)	50(1)
C(12)	8637(2)	2561(2)	7557(2)	48(1)
C(13)	8474(3)	1813(3)	7201(3)	65(1)
C(14)	9517(2)	2037(2)	8449(2)	48(1)
C(15)	10634(3)	1050(3)	8515(3)	68(1)
C(16)	11449(3)	535(3)	9351(4)	85(1)
C(17)	11177(3)	1000(4)	10128(3)	84(1)
C(18)	10091(3)	1985(4)	10080(2)	75(1)
C(19)	9266(3)	2501(3)	9249(2)	61(1)
S(2)	6519(1)	6284(1)	8762(1)	51(1)

O(4)	7666(2)	6359(2)	8432(2)	64(1)
O(5)	6445(2)	5085(2)	9194(2)	66(1)
O(6)	3654(2)	9880(2)	7169(2)	88(1)
N(2)	5615(2)	7135(2)	7724(2)	51(1)
C(20)	5941(2)	6975(2)	9704(2)	47(1)
C(21)	4998(3)	6755(3)	10346(2)	59(1)
C(22)	4507(3)	7356(3)	11037(2)	61(1)
C(23)	4941(2)	8158(2)	11127(2)	54(1)
C(24)	5890(3)	8347(3)	10495(2)	57(1)
C(25)	6391(2)	7769(2)	9784(2)	53(1)
C(26)	4397(3)	8802(3)	11894(3)	72(1)
C(27)	5617(3)	8374(3)	7005(2)	57(1)
C(28)	4331(2)	9163(2)	6567(2)	55(1)
C(29)	3812(2)	8209(2)	6719(2)	49(1)
C(30)	4365(3)	7190(3)	7785(2)	60(1)
C(31)	2445(2)	8770(2)	6583(2)	53(1)
C(32)	1729(3)	8434(3)	7367(3)	71(1)
C(33)	1943(2)	9749(3)	5515(2)	56(1)
C(34)	984(3)	10880(3)	5408(3)	87(1)
C(35)	533(4)	11801(4)	4423(4)	107(1)
C(36)	1021(4)	11620(4)	3531(4)	92(1)
C(37)	1970(3)	10518(4)	3605(3)	82(1)
C(38)	2431(3)	9593(3)	4583(3)	68(1)

Table 5. Bond lengths [Å] and angles [°] for **3d**.

S(1)-O(2)	1.4300(18)
S(1)-O(1)	1.4334(18)
S(1)-N(1)	1.618(2)
S(1)-C(1)	1.758(2)
O(3)-C(10)	1.415(4)
N(1)-C(8)	1.475(3)
N(1)-C(11)	1.488(3)
C(1)-C(2)	1.385(3)
C(1)-C(6)	1.389(3)
C(2)-C(3)	1.373(4)
C(3)-C(4)	1.386(4)
C(4)-C(5)	1.382(4)
C(4)-C(7)	1.499(4)
C(5)-C(6)	1.379(4)
C(8)-C(9)	1.520(4)
C(9)-C(12)	1.509(3)
C(9)-C(10)	1.525(3)
C(10)-C(11)	1.503(4)
C(12)-C(13)	1.324(4)
C(12)-C(14)	1.485(3)
C(14)-C(19)	1.390(4)
C(14)-C(15)	1.392(4)
C(15)-C(16)	1.379(5)
C(16)-C(17)	1.360(5)
C(17)-C(18)	1.371(5)
C(18)-C(19)	1.382(4)
S(2)-O(4)	1.4301(19)
S(2)-O(5)	1.4319(19)
S(2)-N(2)	1.616(2)
S(2)-C(20)	1.758(2)
O(6)-C(28)	1.408(3)

N(2)-C(30)	1.480(3)
N(2)-C(27)	1.483(3)
C(20)-C(25)	1.381(4)
C(20)-C(21)	1.392(4)
C(21)-C(22)	1.374(4)
C(22)-C(23)	1.382(4)
C(23)-C(24)	1.381(4)
C(23)-C(26)	1.506(4)
C(24)-C(25)	1.381(4)
C(27)-C(28)	1.507(4)
C(28)-C(29)	1.522(4)
C(29)-C(31)	1.510(3)
C(29)-C(30)	1.513(4)
C(31)-C(32)	1.327(4)
C(31)-C(33)	1.488(4)
C(33)-C(34)	1.384(4)
C(33)-C(38)	1.385(4)
C(34)-C(35)	1.376(6)
C(35)-C(36)	1.345(6)
C(36)-C(37)	1.365(5)
C(37)-C(38)	1.373(5)

O(2)-S(1)-O(1)	119.07(11)
O(2)-S(1)-N(1)	106.72(11)
O(1)-S(1)-N(1)	106.28(11)
O(2)-S(1)-C(1)	108.33(11)
O(1)-S(1)-C(1)	107.98(11)
N(1)-S(1)-C(1)	108.02(11)
C(8)-N(1)-C(11)	110.04(19)
C(8)-N(1)-S(1)	118.85(17)
C(11)-N(1)-S(1)	119.36(16)
C(2)-C(1)-C(6)	120.2(2)
C(2)-C(1)-S(1)	120.30(19)

C(6)-C(1)-S(1)	119.48(19)
C(3)-C(2)-C(1)	119.7(2)
C(2)-C(3)-C(4)	121.4(3)
C(5)-C(4)-C(3)	117.8(2)
C(5)-C(4)-C(7)	121.4(3)
C(3)-C(4)-C(7)	120.7(3)
C(6)-C(5)-C(4)	122.1(3)
C(5)-C(6)-C(1)	118.7(3)
N(1)-C(8)-C(9)	102.4(2)
C(12)-C(9)-C(8)	116.8(2)
C(12)-C(9)-C(10)	114.4(2)
C(8)-C(9)-C(10)	101.9(2)
O(3)-C(10)-C(11)	110.5(2)
O(3)-C(10)-C(9)	108.8(2)
C(11)-C(10)-C(9)	103.8(2)
N(1)-C(11)-C(10)	104.3(2)
C(13)-C(12)-C(14)	120.7(2)
C(13)-C(12)-C(9)	122.8(3)
C(14)-C(12)-C(9)	116.5(2)
C(19)-C(14)-C(15)	117.3(3)
C(19)-C(14)-C(12)	122.0(2)
C(15)-C(14)-C(12)	120.7(3)
C(16)-C(15)-C(14)	121.4(3)
C(17)-C(16)-C(15)	120.1(3)
C(16)-C(17)-C(18)	120.0(3)
C(17)-C(18)-C(19)	120.2(3)
C(18)-C(19)-C(14)	120.9(3)
O(4)-S(2)-O(5)	119.45(12)
O(4)-S(2)-N(2)	106.55(11)
O(5)-S(2)-N(2)	106.76(11)
O(4)-S(2)-C(20)	108.41(12)
O(5)-S(2)-C(20)	107.67(12)
N(2)-S(2)-C(20)	107.46(11)

C(30)-N(2)-C(27)	109.7(2)
C(30)-N(2)-S(2)	119.95(18)
C(27)-N(2)-S(2)	119.88(17)
C(25)-C(20)-C(21)	119.9(2)
C(25)-C(20)-S(2)	120.1(2)
C(21)-C(20)-S(2)	119.9(2)
C(22)-C(21)-C(20)	119.4(3)
C(21)-C(22)-C(23)	121.6(3)
C(24)-C(23)-C(22)	118.1(3)
C(24)-C(23)-C(26)	121.1(3)
C(22)-C(23)-C(26)	120.8(3)
C(25)-C(24)-C(23)	121.6(3)
C(24)-C(25)-C(20)	119.3(3)
N(2)-C(27)-C(28)	104.9(2)
O(6)-C(28)-C(27)	110.8(3)
O(6)-C(28)-C(29)	108.3(2)
C(27)-C(28)-C(29)	104.1(2)
C(31)-C(29)-C(30)	117.5(2)
C(31)-C(29)-C(28)	113.6(2)
C(30)-C(29)-C(28)	102.9(2)
N(2)-C(30)-C(29)	101.7(2)
C(32)-C(31)-C(33)	121.8(3)
C(32)-C(31)-C(29)	122.6(3)
C(33)-C(31)-C(29)	115.6(2)
C(34)-C(33)-C(38)	116.8(3)
C(34)-C(33)-C(31)	121.2(3)
C(38)-C(33)-C(31)	121.9(2)
C(35)-C(34)-C(33)	121.5(4)
C(36)-C(35)-C(34)	120.3(4)
C(35)-C(36)-C(37)	119.8(4)
C(36)-C(37)-C(38)	120.4(4)
C(37)-C(38)-C(33)	121.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3d**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	44(1)	41(1)	43(1)	-12(1)	2(1)	-12(1)
O(1)	73(1)	41(1)	58(1)	-17(1)	1(1)	-15(1)
O(2)	38(1)	63(1)	62(1)	-16(1)	4(1)	-17(1)
O(3)	78(2)	66(2)	108(2)	-38(1)	57(1)	-37(1)
N(1)	45(1)	49(1)	41(1)	-10(1)	1(1)	-19(1)
C(1)	41(1)	41(1)	41(1)	-11(1)	-3(1)	-15(1)
C(2)	53(2)	49(1)	45(1)	-13(1)	0(1)	-23(1)
C(3)	48(1)	61(2)	45(1)	-14(1)	6(1)	-22(1)
C(4)	47(1)	57(2)	48(1)	-19(1)	-4(1)	-7(1)
C(5)	64(2)	52(2)	69(2)	-30(1)	-2(1)	-19(1)
C(6)	52(2)	51(2)	58(2)	-21(1)	3(1)	-24(1)
C(7)	69(2)	86(3)	67(2)	-39(2)	4(2)	-6(2)
C(8)	52(2)	57(2)	57(2)	0(1)	-4(1)	-29(1)
C(9)	42(1)	45(1)	40(1)	-12(1)	4(1)	-12(1)
C(10)	47(1)	46(1)	58(2)	-19(1)	0(1)	-19(1)
C(11)	54(2)	48(1)	51(2)	-18(1)	-2(1)	-22(1)
C(12)	44(1)	46(1)	50(1)	-15(1)	10(1)	-18(1)
C(13)	70(2)	56(2)	69(2)	-23(2)	-2(2)	-25(2)
C(14)	44(1)	38(1)	52(1)	-7(1)	2(1)	-18(1)
C(15)	58(2)	49(2)	90(2)	-26(2)	-5(2)	-15(1)
C(16)	60(2)	51(2)	119(3)	-10(2)	-26(2)	-10(2)
C(17)	77(2)	80(2)	71(2)	10(2)	-23(2)	-41(2)
C(18)	81(2)	93(2)	47(2)	-14(2)	0(2)	-42(2)
C(19)	58(2)	62(2)	50(2)	-14(1)	7(1)	-21(1)

S(2)	46(1)	49(1)	55(1)	-22(1)	1(1)	-15(1)
O(4)	45(1)	79(1)	67(1)	-32(1)	6(1)	-21(1)
O(5)	69(1)	44(1)	76(1)	-21(1)	0(1)	-17(1)
O(6)	81(2)	69(2)	140(2)	-66(2)	29(2)	-39(1)
N(2)	51(1)	51(1)	51(1)	-19(1)	-1(1)	-22(1)
C(20)	46(1)	46(1)	45(1)	-15(1)	-1(1)	-16(1)
C(21)	65(2)	62(2)	57(2)	-20(1)	6(1)	-35(1)
C(22)	58(2)	70(2)	50(2)	-20(1)	11(1)	-29(2)
C(23)	53(2)	50(1)	44(1)	-14(1)	-8(1)	-9(1)
C(24)	58(2)	55(2)	60(2)	-24(1)	-6(1)	-21(1)
C(25)	47(1)	53(2)	58(2)	-20(1)	1(1)	-20(1)
C(26)	74(2)	71(2)	55(2)	-29(2)	-8(2)	-6(2)
C(27)	54(2)	54(2)	62(2)	-18(1)	3(1)	-26(1)
C(28)	51(2)	47(2)	63(2)	-17(1)	7(1)	-20(1)
C(29)	48(1)	49(1)	53(2)	-27(1)	4(1)	-16(1)
C(30)	58(2)	52(2)	72(2)	-15(1)	-10(1)	-29(1)
C(31)	47(1)	53(2)	66(2)	-30(1)	3(1)	-19(1)
C(32)	54(2)	79(2)	83(2)	-33(2)	11(2)	-30(2)
C(33)	43(1)	61(2)	68(2)	-30(1)	-1(1)	-19(1)
C(34)	65(2)	81(2)	89(3)	-40(2)	-4(2)	3(2)
C(35)	82(3)	73(3)	119(4)	-27(2)	-25(3)	9(2)
C(36)	82(3)	92(3)	84(3)	-6(2)	-26(2)	-38(2)
C(37)	72(2)	107(3)	68(2)	-28(2)	-1(2)	-42(2)
C(38)	55(2)	76(2)	70(2)	-30(2)	-1(2)	-20(2)

Table 7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3d**.

	x	y	z	U(eq)
H(2)	7670(30)	7400(30)	3100(20)	80
H(3)	8800(30)	6650(30)	1880(20)	80
H(5)	7360(30)	4160(30)	2670(20)	80
H(6)	6200(30)	4820(30)	3970(20)	80
H(7A)	8770(30)	4250(30)	1190(30)	80
H(7B)	8810(30)	5420(30)	670(30)	80
H(7C)	9780(30)	4510(30)	1430(20)	80
H(8A)	6270(30)	4400(30)	6580(20)	80
H(8B)	7280(30)	4140(30)	5740(30)	80
H(9)	7560(30)	4300(30)	7590(20)	80
H(10)	9270(30)	4680(30)	6970(20)	80
H(11A)	8170(30)	6390(30)	5220(30)	80
H(11B)	7690(30)	6490(30)	6320(20)	80
H(13A)	7940(30)	2110(30)	6610(30)	80
H(13B)	8860(30)	930(30)	7520(20)	80
H(15)	10800(30)	780(30)	7970(20)	80
H(16)	12170(30)	-110(30)	9370(30)	80
H(17)	11710(30)	650(30)	10720(30)	80
H(19)	8540(30)	3140(30)	9280(20)	80
H(18)	9920(30)	2270(30)	10630(30)	80
HO3	9630(40)	4440(40)	5430(30)	80
H(21)	4720(30)	6270(30)	10300(20)	80
H(22)	3910(30)	7200(30)	11460(20)	80
H(24)	6220(30)	8840(30)	10570(20)	80
H(25)	7020(30)	7940(30)	9340(20)	80
H(26A)	3720(30)	9550(30)	11620(20)	80

H(26B)	4230(30)	8200(30)	12540(30)	80
H(26C)	4900(30)	9040(30)	12120(30)	80
H(27A)	5840(30)	8760(30)	7390(20)	80
H(27B)	6170(30)	8260(30)	6430(30)	80
H(28)	4320(30)	9770(30)	5760(20)	80
H(29)	4140(30)	7870(30)	6200(20)	80
H(30A)	4420(30)	6340(30)	7920(20)	80
H(30B)	3850(30)	7460(30)	8440(20)	80
H(32A)	940(30)	8770(30)	7260(30)	80
H(32B)	2090(30)	7780(30)	8130(30)	80
H(34)	680(30)	10980(30)	6060(30)	80
H(35)	-30(30)	12490(30)	4470(30)	80
H(36)	730(30)	12250(30)	2900(30)	80
H(37)	2280(30)	10480(30)	2970(30)	80
H(38)	3090(30)	8820(30)	4610(20)	80
HO6	3810(30)	10460(30)	6920(30)	80

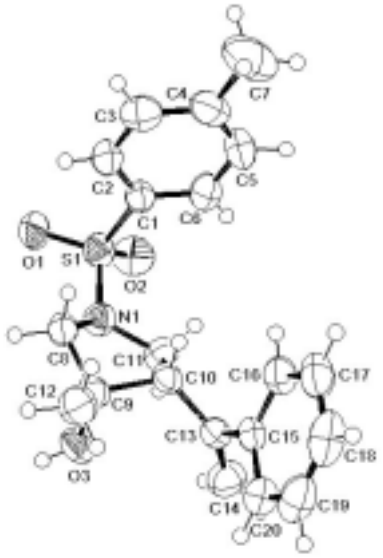


Figure 8. ORTEP drawing of **3g**

Table 8. Crystal data and structure refinement for **3g**.

Identification code	**3g**	
Empirical formula	C20 H23 N O3 S	
Formula weight	357.45	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.324(2) Å	a= 81.54(2)°.
	b = 9.548(3) Å	b= 66.499(12)°.
	c = 11.620(3) Å	g = 85.044(18)°.
Volume	938.0(4) $Å^3$	
Z	2	
Density (calculated)	1.266 Mg/m^3	
Absorption coefficient	0.191 mm^{-1}	
F(000)	380	

Crystal size	0.24 x 0.10 x 0.08 mm^3
Theta range for data collection	1.93 to 25.00°.
Index ranges	0<=h<=11, -11<=k<=11, -12<=l<=13
Reflections collected	3502
Independent reflections	3281 [R(int) = 0.0357]
Completeness to theta = 25.00°	99.4 %
Absorption correction	Empirical
Max. and min. transmission	0.7373 and 0.6937
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3281 / 0 / 307
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1046
R indices (all data)	R1 = 0.1198, wR2 = 0.1277
Extinction coefficient	0.013(2)
Largest diff. peak and hole	0.168 and -0.201 e.$Å^{-3}$

Table 9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **3g**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2920(1)	2787(1)	7664(1)	52(1)
O(1)	3409(3)	4049(3)	7930(2)	63(1)
O(2)	3509(3)	1424(3)	8009(2)	69(1)
O(3)	4628(3)	3627(3)	3468(3)	61(1)
C(1)	871(4)	2779(4)	8393(3)	46(1)
C(2)	10(5)	4023(4)	8719(4)	54(1)
C(3)	-1608(5)	4011(5)	9266(4)	61(1)
C(4)	-2397(5)	2781(5)	9490(3)	65(1)
C(5)	-1518(5)	1543(5)	9177(4)	74(1)

C(6)	102(5)	1528(4)	8629(4)	65(1)
C(7)	-4159(5)	2771(6)	10082(4)	109(2)
N(1)	3401(3)	2960(3)	6147(3)	49(1)
C(8)	2981(4)	4318(4)	5520(3)	47(1)
C(9)	3040(4)	3899(3)	4286(3)	45(1)
C(10)	2297(4)	2436(3)	4744(3)	43(1)
C(11)	3147(5)	1751(4)	5577(4)	53(1)
C(12)	2248(6)	4974(5)	3622(5)	62(1)
C(13)	2276(4)	1605(3)	3742(3)	45(1)
C(14)	3456(5)	766(5)	3132(4)	65(1)
C(15)	857(4)	1797(3)	3440(3)	44(1)
C(16)	-639(4)	1788(4)	4376(4)	52(1)
C(17)	-1949(5)	1959(4)	4081(5)	65(1)
C(18)	-1786(6)	2129(4)	2839(6)	73(1)
C(19)	-325(6)	2137(4)	1911(5)	68(1)
C(20)	996(5)	1971(4)	2184(4)	56(1)

Table 10. Bond lengths [Å] and angles [°] for **3g**.

S(1)-O(2)	1.433(2)
S(1)-O(1)	1.440(2)
S(1)-N(1)	1.622(3)
S(1)-C(1)	1.755(4)
O(3)-C(9)	1.430(4)
O(3)-HO3	0.78(4)
C(1)-C(6)	1.382(5)
C(1)-C(2)	1.387(5)
C(2)-C(3)	1.384(5)
C(2)-H(2)	0.86(3)
C(3)-C(4)	1.377(5)
C(3)-H(3)	0.95(3)
C(4)-C(5)	1.387(6)
C(4)-C(7)	1.507(5)
C(5)-C(6)	1.386(6)
C(5)-H(5)	0.95(4)
C(6)-H(6)	0.93(4)
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
N(1)-C(11)	1.493(4)
N(1)-C(8)	1.493(4)
C(8)-C(9)	1.523(5)
C(8)-H(8A)	1.01(3)
C(8)-H(8B)	0.98(3)
C(9)-C(12)	1.512(5)
C(9)-C(10)	1.539(4)
C(10)-C(13)	1.510(4)
C(10)-C(11)	1.525(5)
C(10)-H(10)	0.94(3)
C(11)-H(11A)	0.99(3)

C(11)-H(11B)	1.00(4)
C(12)-H(12A)	0.97(4)
C(12)-H(12B)	0.98(4)
C(12)-H(12C)	0.92(4)
C(13)-C(14)	1.322(5)
C(13)-C(15)	1.489(5)
C(14)-H(14A)	0.96(4)
C(14)-H(14B)	0.97(3)
C(15)-C(16)	1.385(5)
C(15)-C(20)	1.398(5)
C(16)-C(17)	1.386(5)
C(16)-H(16)	0.97(3)
C(17)-C(18)	1.376(6)
C(17)-H(17)	0.93(3)
C(18)-C(19)	1.359(6)
C(18)-H(18)	1.01(4)
C(19)-C(20)	1.381(5)
C(19)-H(19)	0.94(4)
C(20)-H(20)	0.96(3)

O(2)-S(1)-O(1)	120.10(16)
O(2)-S(1)-N(1)	107.18(15)
O(1)-S(1)-N(1)	106.35(15)
O(2)-S(1)-C(1)	107.77(17)
O(1)-S(1)-C(1)	107.24(16)
N(1)-S(1)-C(1)	107.65(15)
C(9)-O(3)-HO3	114(3)
C(6)-C(1)-C(2)	119.5(4)
C(6)-C(1)-S(1)	119.9(3)
C(2)-C(1)-S(1)	120.6(3)
C(3)-C(2)-C(1)	120.1(4)
C(3)-C(2)-H(2)	123(2)
C(1)-C(2)-H(2)	117(2)

C(4)-C(3)-C(2)	121.3(4)
C(4)-C(3)-H(3)	119(2)
C(2)-C(3)-H(3)	120(2)
C(3)-C(4)-C(5)	117.8(4)
C(3)-C(4)-C(7)	121.3(4)
C(5)-C(4)-C(7)	120.9(4)
C(6)-C(5)-C(4)	121.9(4)
C(6)-C(5)-H(5)	116(3)
C(4)-C(5)-H(5)	121(2)
C(1)-C(6)-C(5)	119.3(4)
C(1)-C(6)-H(6)	120(2)
C(5)-C(6)-H(6)	121(2)
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(11)-N(1)-C(8)	109.3(3)
C(11)-N(1)-S(1)	118.5(2)
C(8)-N(1)-S(1)	118.6(2)
N(1)-C(8)-C(9)	102.7(3)
N(1)-C(8)-H(8A)	109.6(18)
C(9)-C(8)-H(8A)	113.5(18)
N(1)-C(8)-H(8B)	112.3(16)
C(9)-C(8)-H(8B)	109.4(16)
H(8A)-C(8)-H(8B)	109(2)
O(3)-C(9)-C(12)	110.8(3)
O(3)-C(9)-C(8)	109.8(3)
C(12)-C(9)-C(8)	113.5(3)
O(3)-C(9)-C(10)	105.3(3)
C(12)-C(9)-C(10)	115.7(3)
C(8)-C(9)-C(10)	101.0(3)

C(13)-C(10)-C(11)	117.2(3)
C(13)-C(10)-C(9)	116.8(3)
C(11)-C(10)-C(9)	101.7(3)
C(13)-C(10)-H(10)	107.9(17)
C(11)-C(10)-H(10)	108.9(17)
C(9)-C(10)-H(10)	103.4(17)
N(1)-C(11)-C(10)	103.7(3)
N(1)-C(11)-H(11A)	108.2(18)
C(10)-C(11)-H(11A)	116.1(18)
N(1)-C(11)-H(11B)	109(2)
C(10)-C(11)-H(11B)	111(2)
H(11A)-C(11)-H(11B)	109(3)
C(9)-C(12)-H(12A)	111(2)
C(9)-C(12)-H(12B)	110(2)
H(12A)-C(12)-H(12B)	105(3)
C(9)-C(12)-H(12C)	111(2)
H(12A)-C(12)-H(12C)	113(3)
H(12B)-C(12)-H(12C)	107(3)
C(14)-C(13)-C(15)	120.6(3)
C(14)-C(13)-C(10)	122.8(3)
C(15)-C(13)-C(10)	116.6(3)
C(13)-C(14)-H(14A)	124(2)
C(13)-C(14)-H(14B)	120(2)
H(14A)-C(14)-H(14B)	116(3)
C(16)-C(15)-C(20)	117.5(3)
C(16)-C(15)-C(13)	122.0(3)
C(20)-C(15)-C(13)	120.6(3)
C(15)-C(16)-C(17)	121.4(4)
C(15)-C(16)-H(16)	119.0(18)
C(17)-C(16)-H(16)	119.6(18)
C(18)-C(17)-C(16)	120.2(4)
C(18)-C(17)-H(17)	122(2)
C(16)-C(17)-H(17)	118(2)

C(19)-C(18)-C(17)	119.1(4)
C(19)-C(18)-H(18)	125(2)
C(17)-C(18)-H(18)	116(2)
C(18)-C(19)-C(20)	121.6(5)
C(18)-C(19)-H(19)	120(2)
C(20)-C(19)-H(19)	118(2)
C(19)-C(20)-C(15)	120.3(4)
C(19)-C(20)-H(20)	123(2)
C(15)-C(20)-H(20)	117(2)

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3g**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	50(1)	56(1)	53(1)	-4(1)	-24(1)	-6(1)
O(1)	66(2)	70(2)	62(2)	-10(1)	-28(1)	-25(1)
O(2)	70(2)	68(2)	71(2)	0(1)	-36(2)	15(1)
O(3)	43(2)	62(2)	63(2)	-6(2)	-1(1)	-15(1)
C(1)	52(2)	41(2)	44(2)	-4(2)	-18(2)	-8(2)
C(2)	62(3)	43(2)	54(2)	-3(2)	-20(2)	-10(2)
C(3)	65(3)	63(3)	51(2)	-5(2)	-22(2)	9(2)
C(4)	53(2)	89(3)	47(2)	-3(2)	-15(2)	-11(2)
C(5)	70(3)	72(3)	76(3)	-7(2)	-19(2)	-32(3)
C(6)	68(3)	46(3)	73(3)	-13(2)	-18(2)	-8(2)
C(7)	60(3)	159(5)	92(4)	-8(3)	-13(3)	-14(3)
N(1)	52(2)	48(2)	49(2)	-5(1)	-23(1)	-2(1)
C(8)	46(2)	40(2)	54(2)	-5(2)	-18(2)	-8(2)
C(9)	34(2)	49(2)	45(2)	-4(2)	-9(2)	-4(2)
C(10)	33(2)	44(2)	45(2)	-6(2)	-8(2)	-3(2)

C(11)	60(3)	47(2)	52(2)	-7(2)	-25(2)	2(2)
C(12)	76(3)	52(3)	56(3)	0(2)	-25(3)	-1(2)
C(13)	41(2)	45(2)	44(2)	-7(2)	-9(2)	-6(2)
C(14)	54(3)	78(3)	65(3)	-24(2)	-20(2)	2(2)
C(15)	48(2)	35(2)	49(2)	-2(2)	-18(2)	-11(2)
C(16)	50(2)	52(2)	57(3)	-5(2)	-22(2)	-9(2)
C(17)	51(3)	56(3)	87(4)	-12(2)	-24(3)	-11(2)
C(18)	81(4)	47(2)	113(4)	-10(2)	-62(3)	-2(2)
C(19)	98(4)	48(2)	78(3)	-3(2)	-56(3)	-7(2)
C(20)	59(3)	50(2)	57(3)	-10(2)	-21(2)	-7(2)