

SUPPORTING INFORMATION

Novel Rearrangements of Enynes Catalyzed by PtCl₂

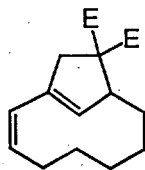
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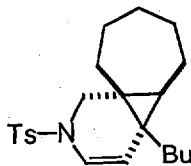
General. All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. Toluene was dried by distillation over Na/K alloy and transferred under Ar. Flash chromatography: Merck silica gel (230-400 mesh) using hexane/ethyl acetate in various proportions as eluent. NMR: Spectra were recorded on a Bruker DPX 300, AMX 400 or DMX 600 spectrometer in the solvents indicated. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The multiplicity in the ¹³C NMR spectra refers to the geminal protons (DEPT). IR: Nicolet FT-7199, wavenumbers in cm⁻¹. MS: Varian CH-5 (70 eV); HR-MS: Finnigan MAT SSQ 7000 (70 eV). Elemental analyses: Dornis & Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka) were used as received.

Representative Procedures and Analytical Data of New Compounds

Synthesis of Diethyl bicyclo[7.2.1]dodeca-1(12),2-dien-10,10-dicarboxylate (Table 1, entry 2):



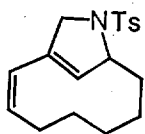
PtCl₂ (9 mg, 0.03 mmol) is added to a solution of diethyl (2-cyclooct-2-enyl-2-prop-2-ynyl)malonate (200 mg, 0.65 mmol) in toluene (30 mL) and the resulting mixture is stirred for 23 h at 80°C. Evaporation of the solvent followed by flash chromatography (hexane/ethyl acetate, 20:1) of the residue affords the title compound as a colorless syrup (166 mg, 83%). ¹H NMR (300 MHz, CDCl₃) δ 6.02 (d, 1H, J = 11.1 Hz), 5.75 (m, 1H), 5.62 (t, 1H, J = 1.8 Hz), 4.20 (m, 4H, J = 7.1 Hz), 3.61 (m, 1H), 3.53 (dd, 1H, J = 17.7, 1.5 Hz), 2.77 (d, 1H, J = 17.7 Hz), 2.13 (m, 1H), 1.52 (m, 3H), 1.30 (m, 6H), 1.25 (t, 6H, J = 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 172.3, 170.0, 136.5, 134.1, 132.5, 127.4, 63.4, 61.4, 61.2, 49.3, 43.0, 28.2, 28.0, 27.2, 24.3, 20.4, 14.1, 14.0; IR: 2977, 2934, 2867, 1733, 1598, 1466, 1366, 1298, 1247, 1153, 1074, 871, 709 cm⁻¹; MS (EI) m/z (rel. intensity) 306 ([M⁺] 33), 260 (38), 232 (44), 214 (39), 187 (26), 173 (19), 159 (100), 151 (22), 146 (49), 131 (18), 123 (12), 117 (38), 105 (21), 91 (42), 79 (32), 67 (12), 55 (10), 41 (14), 29 (64).

Synthesis of 6-Butyl-3(toluene-4-sulfonyl)-3-aza-tricyclo[5.5.0.0^{1,6}]dodec-4-ene (Table 2, entry 7):

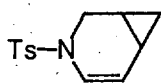
PtCl₂ (9 mg, 0.03 mmol) is added to a solution of *N*-cyclohept-1-enylmethyl-*N*-hept-2-ynyl-4-methylbenzenesulfonamide (240 mg, 0.64 mmol) in toluene (50 mL) and the resulting mixture is stirred for 8 h at 60°C. Evaporation of the solvent followed by flash chromatography (hexane/ethyl acetate, 4:1) of the residue affords the title compound as colorless crystals (208 mg, 87%). Mp = 93-94°C; ¹H NMR (300 MHz, CDCl₃) δ 7.67 (AA'XX', 2H), 7.31 (AA'XX', 2H), 6.29 (dd, 1H, J = 8.0, 0.8 Hz), 5.26 (d, 1H, J = 8.0 Hz), 3.99 (d, 1H, J = 11.7 Hz), 2.60 (d, 1H, J = 11.7 Hz), 2.42 (s, 3H), 1.90-1.60 (m, 5H), 1.50-0.98 (m, 12H), 0.87 (t, 3H, J = 6.7 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 143.5, 135.3, 129.7, 127.0, 120.3,

119.0, 46.4, 37.6, 33.9, 32.5, 29.9, 28.7, 28.5, 27.9, 27.8, 26.8, 25.8, 23.1, 21.5, 14.2; IR: 3051, 2951, 2922, 2857, 1641, 1595, 1465, 1453, 1349, 1167, 1099, 992, 819, 684, 546 cm^{-1} ; MS (EI) m/z (rel. intensity) 373 ($[\text{M}^+]$ 37), 316 (13), 218 (100), 189 (20), 148 (25), 136 (22), 91 (41), 79 (10), 67 (11), 55 (15), 41 (18); $\text{C}_{22}\text{H}_{31}\text{NO}_2\text{S}$ (373.21) *calcd.*: C, 71.12; H, 7.87; N, 3.77; *found.*: C, 70.46; H, 8.29; N, 3.57.

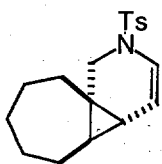
10-(Toluene-4-sulfonyl)-10-aza-bicyclo[7.2.1]dodeca-1(12),2-diene (4). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.63 (AA'XX', 2H), 7.24 (AA'XX', 2H), 5.79 (m, 1H), 5.65 (m, 1H), 5.24 (s, 1H), 4.62 (bs, 1H), 4.14 (m, 1H), 4.03 (m, 1H), 2.34 (s, 3H), 2.25-1.00 (m, 10H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.5, 136.0, 135.1, 129.7, 128.8, 128.2, 127.2, 123.6, 67.5, 58.4, 36.0, 28.4, 28.4, 25.6, 21.3, 20.3; IR: 3011, 2927, 2865, 1657, 1598, 1494, 1473, 1458, 1441, 1342, 1164, 1096, 814, 666, 581 cm^{-1} ; MS (EI) m/z (rel. intensity) 317 ($[\text{M}^+]$ 49), 274 (6), 260 (11), 235 (42), 162 (44), 155 (33), 135 (24), 118 (17), 106 (43), 91 (100), 80 (54), 79 (52), 77 (28), 67 (19), 65 (33), 55 (11), 53 (12), 41 (24), 39 (16) HR-MS *calcd.*: 317.14495; *found.*: 317.14487.



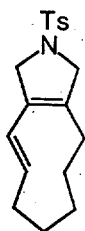
3-(Toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (6). Mp = 79-80°C; ^1H NMR (300 MHz, CDCl_3) δ 7.65 (AA'XX', 2H), 7.31 (AA'XX', 2H), 6.33 (d, 1H, $J = 8.1$ Hz), 5.40 (dd, 1H, $J = 8.0, 5.4$ Hz), 3.87 (d, 1H, $J = 11.6$ Hz), 3.04 (dd, 1H, $J = 11.6, 2.9$ Hz), 2.42 (s, 3H), 1.52 (m, 1H), 1.12 (vsept, 1H), 0.79 (dtd, 1H, $J = 8.3, 4.5, 0.7$ Hz), 0.34 (dt, 1H, $J = 5.3, 4.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 143.6, 134.8, 129.7, 127.0, 121.0, 112.1, 40.8, 21.5, 18.4, 13.3, 7.0; IR (KBr) 3100, 3077, 3006, 2977, 2923, 2861, 1939, 1646, 1597, 1446, 1343, 1177, 1108, 955, 711, 682 cm^{-1} ; MS (EI) m/z (rel. intensity) 249 ($[\text{M}^+]$ 28), 184 (10), 155 (9), 94 (100), 67 (54), 41 (20); $\text{C}_{13}\text{H}_{15}\text{NO}_2\text{S}$ (249.33) *calcd.*: C, 62.62; H, 6.06; N, 5.62; *found.*: C, 62.49; H, 6.08; N, 5.54.



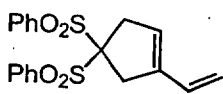
3-(Toluene-4-sulfonyl)-3-aza-tricyclo[5.5.0.0^{1,6}]dodec-4-ene (9). Mp = 93-94°C; ^1H NMR (600 MHz, CDCl_3) δ 7.65 (AA'XX', 2H), 7.31 (AA'XX', 2H), 6.24 (d, 1H, $J = 7.9$ Hz), 5.44 (dd, 1H, $J = 7.9, 5.7$ Hz), 3.97 (d, 1H, $J = 11.5$ Hz), 2.67 (d, 1H, $J = 11.5$ Hz), 2.42 (s, 3H), 2.00 (dt, 1H, $J = 14.2, 6.7$ Hz), 1.96 (dd, 1H, $J = 4.6, 6.9$ Hz), 1.79 (m, 1H), 1.64 (m, 1H), 1.61 (m, 1H), 1.42 (vq, 1H, $J = 12$ Hz), 1.19 (dd, 1H, $J = 14.3, 12.2$ Hz), 1.14 (m, 1H), 1.10 (m, 1H), 0.92 (dt, 1H, $J = 14.0, 10.5$ Hz), 0.85 (dd, 1H, $J = 5.4, 4.0$ Hz), 0.79 (ddd, 1H, $J = 10.1, 6.1, 3.9$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 143.5, 135.2, 129.7, 127.0, 120.3, 113.5, 46.5, 35.0, 33.9, 32.1, 30.9, 30.4, 28.8, 26.9, 25.7, 21.5; IR (KBr) 3098, 3029, 2915, 2853, 2842, 1647, 1596, 1496, 1459, 1347, 1168, 1099, 959, 823, 723, 682, 570 cm^{-1} ; MS (EI) m/z (rel. intensity) 317 ($[\text{M}^+]$ 58), 162 (100), 133 (35), 121 (10), 106 (12), 91 (49), 80 (24), 67 (17), 55 (16), 41 (15); HR-MS *calcd.*: 317.14495; *found.*: 317.14494.

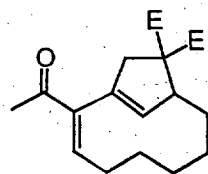


2-(Toluene-4-sulfonyl)-1,2,3,4,5,6,7,8-octahydro-2-aza-cyclopentacyclononene (10). ^1H NMR (300 MHz, CDCl_3) δ 7.73 (AA'XX', 2H), 7.33 (AA'XX', 2H), 5.63 (m, 1H, $J = 15.9, 4.5$ Hz), 5.45 (d, 1H, $J = 16.0$ Hz), 4.10 (m, 2H), 3.99 (m, 2H), 2.43 (s, 3H), 2.33 (m, 1H), 2.01 (m, 3H), 1.42 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.2, 137.4, 136.8, 134.3, 131.5, 129.7, 127.4, 121.3, 58.9, 56.8, 32.0, 28.5, 28.0, 27.8, 26.4, 21.5; IR (KBr) 3021, 2932, 2862, 2820, 1598, 1494, 1454, 1348, 1163, 1103, 977, 814, 668, 547 cm^{-1} ; MS (EI) m/z (rel. intensity) 317 ($[\text{M}^+]$ 83), 162 (100), 155 (10), 133 (34), 121 (11), 106 (17), 91 (74), 80 (31), 65 (22), 55 (25), 41 (30); $\text{C}_{18}\text{H}_{23}\text{NO}_2\text{S}$ (317.45) *calcd.*: C, 68.10; H, 7.30; N, 4.41; *found.*: C, 68.18; H, 7.24; N, 4.34.



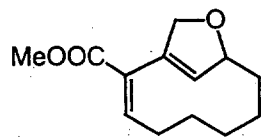
4,4-Bis-phenylsulfonyl-1-vinyl-cyclopentene (Table 1, entry 1): Mp = 114-115°C; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.89 (m, 4H), 7.63 (m, 2H), 7.49 (m, 4H), 6.08 (dd, 1H, $J = 17.3, 11.0$ Hz), 5.14 (m, 1H), 4.97 (m, 2H), 3.34 (s, 2H), 3.28 (s, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 140.0, 137.2, 135.0, 131.4, 131.0, 129.2, 126.1, 116.6, 91.3, 39.2, 37.7; IR: 3090, 3071, 2920, 2856, 1645, 1595, 1583, 1478, 1447, 1327, 1312, 1158, 1144, 1079, 999, 917, 758, 689 cm^{-1} ; MS (EI) m/z (rel. intensity) 374 ($[\text{M}^+]$ 1), 232 (30), 215 (27), 125 (31), 107 (48), 91 (100), 77 (32), 65 (20), 51 (11); $\text{C}_{19}\text{H}_{18}\text{O}_4\text{S}_2$ (374.48) *calcd.*: C, 60.94; H, 4.84; *found.*: C, 60.84; H, 4.92.



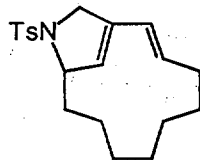
2-Acetyl-bicyclo[7.2.1]dodeca-1(12),2-dien-10,10-dicarboxylic acid diethyl ester (Table 1, entry 3):

E = COOEt

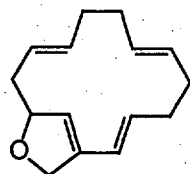
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.86 (dd, 1H, $J = 8.5, 7.1$ Hz), 5.53 (m, 1H), 4.16 (q, 4H, $J = 7.1$ Hz), 3.61 (m, 1H), 3.48 (m, 1H), 2.91 (dd, 1H, $J = 17.7, 1.8$ Hz), 2.15 (s, 3H), 1.70-1.30 (m, 10H), 1.21 (q, 6H, $J = 7.1$ Hz); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 198.4, 172.4, 170.3, 144.8, 141.6, 136.1, 134.3, 63.7, 61.9, 61.8, 50.2, 43.4, 28.7, 28.5, 26.9, 26.6, 25.5, 20.4, 14.4, 14.3; IR (KBr) 2978, 2934, 2867, 1732, 1690, 1670, 1592, 1466, 1246, 1154, 1096, 1074, 860 cm^{-1} ; MS (EI) m/z (rel. intensity) 348 ($[\text{M}^+]$ 25), 302 (21), 275 (50), 256 (31), 229 (48), 214 (14), 201 (51), 185 (23), 173 (68), 159 (28), 145 (10), 129 (14), 117 (19), 115 (15), 103 (11), 91 (22), 77 (11), 43 (100), 29 (43).

10-Oxa-bicyclo[7.2.1]dodeca-1(12),2-dien-2-carboxylic acid methyl ester (Table 1, entry 4):

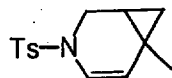
$^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 6.99 (dd, 1H, $J = 8.3, 6.2$ Hz), 5.67 (dd, 1H, $J = 4.0, 1.9$ Hz), 4.75 (dt, 1H, $J = 12.1, 2.9$ Hz), 4.66 (ddd, 1H, $J = 12.1, 5.4, 1.9$ Hz), 3.62 (s, 3H), 2.28 (m, 1H), 2.08 (m, 1H), 1.84 (m, 1H), 1.63-1.11 (m, 7H); $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 166.9, 147.6, 133.5, 132.4, 129.5, 86.1, 78.4, 52.1, 36.6, 29.4, 28.2, 26.4, 20.6; IR: 3073, 2927, 2867, 2848, 1718, 1661, 1613, 1460, 1435, 1264, 1030, 879, 752 cm^{-1} ; MS (EI) m/z (rel. intensity) 222 ($[\text{M}^+]$ 35), 190 (100), 179 (12), 163 (42), 152 (52), 147 (100), 140 (26), 119 (38), 107 (19), 91 (53), 77 (37), 55 (22), 41 (31); $\text{C}_{13}\text{H}_{18}\text{O}_3$ (222.13): *calcd.*: C, 70.24; H, 8.16; *found*: C, 70.38; H, 8.12.

12-(Toluene-4-sulfonyl)-10-aza-bicyclo[9.2.1]tetradeca-1(14),2-diene (Table 1, entry 5):

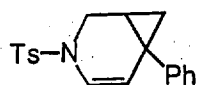
$^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.62 (AA'XX', 2H), 7.27 (AA'XX', 2H), 5.66 (m, 1H), 5.48 (m, 2H), 4.61 (bs, 1H), 4.06 (td, 1H, $J = 14.5, 1.5$ Hz), 3.94 (ddd, 1H, $J = 14.2, 5.2, 2.0$ Hz), 2.48 (m, 1H), 2.33 (s, 3H), 2.19 (m, 1H), 1.81 (m, 1H), 1.4-1.0 (m, 11H); $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 143.8, 136.9, 135.6, 134.7, 130.0, 127.5, 125.9, 121.4, 68.3, 59.6, 33.5, 28.8, 28.1, 25.2, 25.0, 24.0, 21.6, 19.6; IR: 3008, 2928, 2856, 1724, 1598, 1494, 1457, 1343, 1162, 1096, 815, 708, 668, 585 cm^{-1} ; MS (EI) m/z (rel. intensity) 345 ($[\text{M}^+]$), HR-MS *calcd.*: 345.17625; *found*: 345.17503.

14-Oxa-bicyclo[11.2.1]hexadeca-1(16),2,6,10-tetraene (Table 1, entry 6):

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 5.96 (d, 1H, $J = 16.1$ Hz), 5.41 (d, 1H, $J = 1.4$ Hz), 5.31 (m, 1H), 5.15-4.90 (m, 5H), 4.60 (d, 1H, $J = 11.5$ Hz), 4.44 (ddd, 1H, $J = 11.6, 4.5, 1.8$ Hz), 2.46 (m, 1H), 2.36-2.16 (m, 4H), 2.03-1.73 (m, 5H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 138.8, 135.2, 133.9, 131.4, 128.7, 125.4, 124.7, 123.4, 85.1, 75.2, 38.8, 33.5, 32.3, 32.2, 31.7; IR 3024, 2984, 2917, 2840, 1689, 1662, 1614, 1467, 1433, 1349, 1300, 1272, 1193, 1059, 1037, 1018, 960, 890, 840, 828, 776, 680 cm^{-1} ; MS (EI) m/z (rel. intensity) 216 ($[\text{M}^+]$ 2), 201 (2), 188 (2), 187 (3), 173 (2), 160 (3), 148 (3), 147 (2), 135 (3), 134 (3), 109 (4), 108 (45), 107 (100), 91 (5), 81 (5), 80 (10), 79 (41), 77 (12), 67 (7), 66 (4), 65 (4), 55 (4), 54 (7), 53 (5), 51 (3), 41 (9), 39 (9), 27 (4); HR-MS (CI) ($\text{C}_{15}\text{H}_{20}\text{O} + \text{H}$) *calcd.* 217.1592, *found* 217.1586; $\text{C}_{15}\text{H}_{20}\text{O}$ (216.32): *calcd.* C, 83.29; H, 9.32; *found* C, 83.38; H, 9.40.

6-Methyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (Table 2, entry 1):

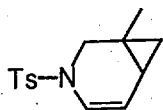
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.65 (AA'XX', 2H), 7.31 (AA'XX', 2H), 6.30 (d, 1H, $J = 8.1$ Hz), 5.23 (d, 1H, $J = 8.1$ Hz), 3.84 (d, 1H, $J = 11.5$ Hz), 3.03 (dd, 1H, $J = 11.5, 2.8$ Hz), 2.42 (s, 3H), 1.26 (m, 1H), 1.09 (s, 3H), 0.57 (dd, 1H, $J = 8.1, 4.4$ Hz), 0.45 (t, 1H, $J = 5.1$ Hz); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 143.6, 134.9, 129.7, 127.0, 120.2, 116.5, 40.9, 25.7, 23.2, 21.5, 20.8, 12.7; IR: 3065, 2955, 2925, 2871, 1645, 1597, 1494, 1449, 1348, 1166, 1116, 1091, 815, 667, 546 cm^{-1} ; MS (EI) m/z (rel. intensity) 263 ($[\text{M}^+]$ 18), 198 (7), 155 (20), 108 (100), 91 (53), 81 (29), 65 (19), 53 (15), 41 (20); HR-MS *calcd.*: 263.098001; *found*: 263.096516.



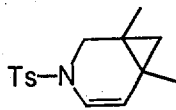
6-Phenyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (Table 2, entry 2): mp 103-105 $^\circ\text{C}$; $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.68 (AA'XX', 2H), 7.37 (AA'XX', 2H), 7.30-7.23 (m, 2H), 7.19-7.14 (m, 3H), 6.45 (dd,

1H, $J = 8.2, 0.7$ Hz), 5.52 (dd, 1H, $J = 8.3, 0.8$ Hz), 3.97 (m, 1H), 3.15 (dd, 1H, $J = 11.7, 2.7$ Hz), 2.44 (s, 3H), 1.74 (m, 1H), 1.36 (ddd, 1H, $J = 9.1, 5.0, 0.5$ Hz), 0.86 (dd, 1H, $J = 5.8, 5.2$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 144.5, 144.1, 135.1, 130.2, 128.7, 127.4, 127.1, 126.5, 121.3, 115.1, 41.0, 29.0, 22.0, 21.6, 21.2; IR 2923, 2876, 1635, 1595, 1492, 1444, 1397, 1377, 1338, 1308, 1280, 1245, 1162, 1119, 1098, 1036, 985, 951, 920, 902, 869, 817, 764, 722, 710, 697, 674, 642, 609, 566, 542 cm^{-1} ; MS (EI) m/z (rel. intensity) 327 (7), 326 (23), 325 ($[\text{M}^+]$ 100), 324 (58), 171 (13), 170 (100), 169 (27), 168 (46), 156 (13), 155 (12), 144 (10), 143 (76), 142 (29), 141 (34), 129 (10), 128 (45), 127 (11), 115 (30), 92 (10), 91 (57), 77 (8), 65 (23), 41 (14), 39 (11); HR-MS (EI) ($\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$) *calcd.* 325.1137, *found* 325.1134; $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$ (325.43): *calcd.* C, 70.12; H, 5.89; N, 4.30; *found* C, 69.89; H, 5.80; N, 3.94.

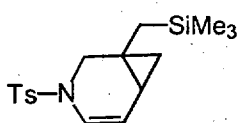
1-Methyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (Table 2, entry 3): Mp = 110–111°C; ^1H NMR (300 MHz, CDCl_3) δ 7.65 (AA'XX', 2H), 7.32 (AA'XX', 2H), 6.28 (d, 1H, $J = 7.9$ Hz), 5.40 (dd, 1H, $J = 7.9, 5.6$ Hz), 3.84 (d, 1H, $J = 11.3$ Hz), 2.72 (dd, 1H, $J = 11.3, 0.7$ Hz), 2.42 (s, 3H), 1.11 (s, 3H), 0.92 (m, 1H), 0.63 (ddd, 1H, $J = 8.1, 4.4, 1.2$ Hz), 0.56 (t, 1H, $J = 4.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 143.6, 134.9, 129.7, 127.0, 120.2, 112.7, 45.9, 25.7, 21.9, 21.5, 20.1, 15.8; IR (KBr) 3097, 3029, 2947, 2922, 2850, 1635, 1596, 1493, 1346, 1278, 1169, 1134, 1091, 816, 689, 544 cm^{-1} ; MS (EI) m/z (rel. intensity) 263 ($[\text{M}^+]$ 35), 155 (8), 108 (100), 91 (47), 81 (36), 65 (21), 53 (13), 41 (19); $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$ (263.10): *calcd.*: C, 63.85; H, 6.51; N, 5.32; *found*: C, 63.67; H, 6.55; N, 5.28.



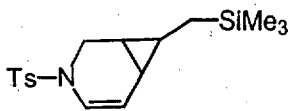
1,6-Dimethyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (Table 2, entry 4): mp 55–56°C; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.63 (AA'XX', 2H), 7.34 (AA'XX', 2H), 6.22 (dd, 1H, $J = 7.9, 1.0$ Hz), 5.19 (d, 1H, $J = 8.0$ Hz), 3.75 (d, 1H, $J = 11.3$ Hz), 2.65 (dd, 1H, $J = 11.3, 0.6$ Hz), 2.42 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H), 0.69 (d, 1H, $J = 4.3$ Hz), 0.33 (dd, 1H, $J = 4.3, 1.0$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 144.3, 135.2, 130.1, 127.3, 120.3, 118.5, 47.0, 29.7, 26.3, 21.6, 18.8, 18.0, 17.5; IR 3061, 2987, 2947, 2925, 2873, 1645, 1598, 1494, 1448, 1398, 1350, 1306, 1274, 1244, 1176, 1163, 1133, 1114, 1090, 1041, 990, 938, 901, 815, 844, 815, 739, 709, 697, 668, 636, 574, 556, 545 cm^{-1} ; MS (EI) m/z (rel. intensity) 277 ($[\text{M}^+]$ 25), 122 (100), 121 (14), 108 (50), 107 (35), 106 (36), 105 (11), 95 (27), 94 (29), 93 (16), 91 (37), 81 (13), 79 (16), 77 (11), 67 (10), 65 (16), 55 (12), 41 (17), 39 (13); $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$ (277.39): *calcd.* C, 64.95; H, 6.90; N, 5.05; *found* C, 65.08; H, 6.84; N, 4.96.



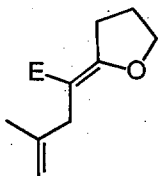
3-(Toluene-4-sulfonyl)-1-trimethylsilanylmethyl-3-aza-bicyclo[4.1.0]-hept-4-ene (Table 2, entry 5): Mp = 106–107°C; ^1H NMR (300 MHz, CDCl_3) δ 7.61 (AA'XX', 2H), 7.33 (AA'XX', 2H), 6.22 (d, 1H, $J = 7.9$ Hz), 5.42 (dd, 1H, $J = 7.9, 5.7$ Hz), 3.82 (d, 1H, $J = 11.5$ Hz), 2.68 (d, 1H, $J = 11.5$ Hz), 2.41 (s, 3H), 0.85 (m, 2H), 0.57 (m, 2H), 0.45 (t, 1H, $J = 4.3$ Hz), 0.00 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.3, 135.3, 130.1, 127.3, 120.3, 113.7, 46.3, 28.5, 25.3, 21.6, 20.9, 17.4, -0.2; IR (KBr) 3068, 2996, 2953, 2894, 2869, 1654, 1595, 1491, 1350, 1246, 1164, 1105, 859, 818, 689, 549 cm^{-1} ; MS (EI) m/z (rel. intensity) 335 ($[\text{M}^+]$ 21), 228 (13), 180 (83), 149 (32), 139 (10), 107 (17), 91 (34), 73 (34), 73 (100), 45 (9); HR-MS *calcd.*: 335.13753; *found*: 335.13746.



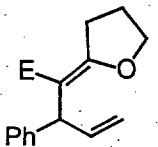
3-(Toluene-4-sulfonyl)-7-trimethylsilanylmethyl-3-aza-bicyclo[4.1.0]-hept-4-ene (Table 2, entry 6): ^1H NMR (300 MHz, CDCl_3) δ 7.62 (AA'XX', 2H), 7.27 (AA'XX', 2H), 6.30 (dd, 1H, $J = 8.2, 0.9$ Hz), 5.16 (dd, 1H, $J = 8.2, 0.8$ Hz), 3.78 (d, 1H, $J = 11.5$ Hz), 3.02 (dd, 1H, $J = 11.5, 2.9$ Hz), 2.39 (s, 3H), 1.03 (s, 3H), 0.77 (m, 1H), 0.67 (dd, 1H, $J = 14.4, 4.7$ Hz), 0.55 (m, 1H), 0.19 (dd, 1H, $J = 14.4, 9.7$ Hz), -0.13 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 143.5, 135.0, 129.7, 127.0, 119.3, 117.3, 40.1, 32.7, 27.6, 21.5, 17.4, 16.7, 15.7, -1.7; IR 3098, 3057, 3030, 2952, 2925, 2874, 1644, 1598, 1495, 1465, 1402, 1359, 1347, 1306, 1278, 1248, 1168, 1006, 930, 846, 815, 757, 710, 678, 636, 560, 548 cm^{-1} ; MS (EI) m/z (rel. intensity) 351 (2), 350 (6), 349 ($[\text{M}^+]$ 19), 348 (10), 276 (10), 249 (11), 248 (10), 194 (31), 180 (32), 155 (10), 149 (26), 121 (13), 120 (23), 106 (20), 94 (14), 91 (33), 73 (100); HR-MS (EI) ($\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SSi}$) *calcd.* 349.1532, *found* 349.1524; $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SSi}$ (349.57): *calcd.* C, 61.85; H, 7.79; N, 4.01; *found* C, 61.72; H, 7.71; N, 3.97.



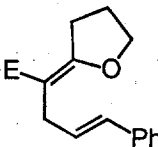
Compound 12. ^1H NMR (300 MHz, CD_2Cl_2) δ 4.60 (m, 2H), 4.20 (t, 2H, $J = 7.0$ Hz), 3.63 (s, 3H), 3.08 (t, 2H, $J = 7.8$ Hz), 2.99 (br. s, 2H), 2.06 (q, 2H, $J = 7.4$ Hz), 1.71 (d, 3H, $J = 0.6$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 172.1, 169.4, 145.1, 109.0, 100.4, 72.0, 51.0, 34.1, 31.4, 24.7, 22.8; IR 3077, 2983, 2948, 2904, 2843, 1704, 1634, 1436, 1373, 1319, 1308, 1277, 1214, 1179, 1109, 1068, 1036, 983, 937, 885, 855, 797, 773 cm^{-1} ; MS (EI) m/z (rel. intensity) 197 (12), 196 ($[\text{M}^+]$, 100), 165 (36), 164 (37), 137 (14), 136 (16), 123 (44), 122 (15), 121 (12), 119 (13), 113 (11), 109 (12), 108 (15), 101 (45), 95 (31), 94 (10), 93 (12), 91 (11), 79 (11), 69 (13), 67 (22), 65 (10), 59 (21), 55 (21), 42 (14), 41 (32), 39 (25), 29 (10), 27 (10); HR-MS (EI) ($\text{C}_{11}\text{H}_{16}\text{O}_3$) *calcd.* 196.1099, *found* 196.1099; $\text{C}_{11}\text{H}_{16}\text{O}_3$ (196.25): *calcd.* C, 67.32; H, 8.22; *found* C, 67.36; H, 8.26.



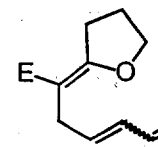
Compound 14. ^1H NMR (300 MHz, CD_2Cl_2) δ 7.28-7.11 (m, 5H), 6.44 (ddd, 1H, $J = 17.0, 10.1, 8.4$ Hz), 5.13 (ddd, 1H, $J = 17.0, 2.0, 1.1$ Hz), 5.11 (ddd, 1H, $J = 10.1, 2.1, 0.8$ Hz), 4.88 (d, 1H, $J = 8.4$ Hz), 4.23 (m, 2H), 3.58 (s, 3H), 3.12 (m, 2H), 2.08 (quint, 2H, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 172.1, 168.8, 144.2, 140.1, 128.1, 127.7, 125.8, 115.5, 104.7, 72.3, 50.8, 46.9, 32.1, 24.5; IR 3059, 3025, 2983, 2948, 2898, 2840, 1700, 1624, 1493, 1448, 1434, 1373, 1325, 1253, 1182, 1102, 1077, 1060, 1048, 1005, 980, 936, 916, 865, 777, 739, 701 cm^{-1} ; MS (EI) m/z (rel. intensity) 259 (18), 258 ($[\text{M}^+]$, 100), 229 (12), 227 (20), 226 (42), 215 (15), 214 (14), 199 (28), 198 (39), 197 (19), 185 (10), 181 (15), 142 (16), 141 (14), 129 (25), 128 (33), 127 (12), 121 (12), 117 (18), 115 (33), 101 (18), 91 (21), 77 (13), 59 (21), 42 (14), 41 (12); HR-MS (EI) ($\text{C}_{16}\text{H}_{18}\text{O}_3$) *calcd.* 258.1256, *found* 258.1255; $\text{C}_{16}\text{H}_{18}\text{O}_3$ (258.32): *calcd.* C, 74.40; H, 7.02; *found* C, 74.34; H, 7.10.



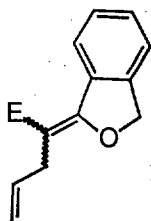
Compound 15 (as mixture with isomer 14; 14:15 = 7.1:1): ^1H NMR (300 MHz, CD_2Cl_2) δ 7.35-7.11 (m, 5H), 6.35 (m, 1H), 6.25 (dt, 1H, $J = 15.8, 6.2$ Hz), 4.23 (m, 2H), 3.68 (s, 3H), 3.20 (d, 2H, $J = 6.1$ Hz), 3.09 (m, 2H), 2.09 (quint, 2H, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ [resolved signals] 172.1, 169.2, 138.4, 129.5, 128.7, 127.0, 126.2, 100.3, 72.2, 51.1, 31.6, 29.9, 24.7; MS (EI) m/z (rel. intensity) 258 ($[\text{M}^+]$, 19), 227 (32), 226 (100), 199 (57), 198 (46), 197 (32), 181 (25), 170 (38), 169 (15), 167 (30), 165 (12), 157 (23), 155 (39), 154 (15), 142 (21), 141 (24), 130 (14), 129 (33), 128 (57), 127 (27), 117 (36), 116 (12), 115 (62), 92 (13), 91 (47), 77 (20), 71 (17), 69 (14), 65 (12), 59 (22), 53 (12), 51 (16), 42 (18), 41 (17), 39 (16).



Compound 17 (mixture of isomers, $E:Z = 7:1$): ^1H NMR (300 MHz, CD_2Cl_2) δ [E -isomer] 6.29 (dt, 1H, $J = 17.0, 10.3$ Hz), 6.03 (m, 1H), 5.72 (ddd, 1H, $J = 14.9, 6.8, 6.4$ Hz), 5.06 (m, 1H), 4.92 (m, 1H), 4.22 (t, 2H, $J = 7$ Hz), 3.66 (s, 3H), 3.06 (m, 4H), 2.07 (quint, 2H, $J = 7.4$ Hz); δ [Z -isomer] 6.84 (dddd, 1H, $J = 16.9, 11.2, 10.2, 1.1$ Hz), 5.94 (m, 1H), 5.45 (m, 1H), 5.12 (m, 2H), 4.22 (t, 2H, $J = 7$ Hz), 3.65 (s, 3H), 3.06 (m, 4H), 2.07 (quint, 2H, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ [E -isomer] 172.0, 169.2, 137.8, 134.0, 130.8, 114.7, 100.3, 72.1, 51.1, 31.5, 29.4, 24.7; δ [Z -isomer] 171.8, 169.2, 133.2, 131.6, 129.0, 116.5, 100.9, 72.1, 51.1, 31.5, 29.4, 25.2; IR 3084, 2988, 2949, 2899, 2841, 1704, 1632, 1602, 1455, 1436, 1373, 1319, 1308, 1204, 1183, 1150, 1107, 1078, 1065, 1005, 981, 935, 893, 777, 717 cm^{-1} ; MS (EI) m/z (rel. intensity) 209 (12), 208 ($[\text{M}^+]$, 90), 177 (27), 176 (25), 175 (11), 150 (12), 149 (100), 148 (49), 147 (30), 135 (20), 131 (12), 120 (16), 107 (28), 106 (14), 105 (33), 101 (16), 92 (13), 91 (32), 84 (15), 79 (40), 78 (22), 77 (45), 71 (13), 69 (16), 67 (30), 65 (16), 59 (22), 55 (14), 53 (18), 52 (10), 51 (16), 43 (12), 42 (28), 41 (51), 39 (35), 27 (19); HR-MS (EI) ($\text{C}_{12}\text{H}_{16}\text{O}_3$) *calcd.* 208.1099, *found* 208.1097; $\text{C}_{12}\text{H}_{16}\text{O}_3$ (208.26): *calcd.* C, 69.21; H, 7.74; *found* C, 69.18; H, 7.68.

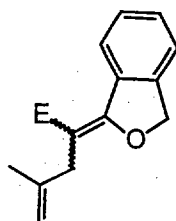


Compound 19a. (E -Isomer): ^1H NMR (300 MHz, CD_2Cl_2) δ 8.75 (d, 1H, $J = 7.6$ Hz), 7.49-7.36 (m, 3H), 5.92 (ddt, 1H, $J = 17.0, 10.0, 6.2$ Hz), 5.36 (br. s, 2H), 5.08 (ddd, 1H, $J = 17.1, 3.7, 1.7$ Hz), 4.95 (ddd, 1H, $J = 10.1, 3.4, 1.5$ Hz), 3.77 (s, 3H), 3.29 (dt, 2H, $J = 6.1, 1.5$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 168.9, 166.2, 144.0, 137.1, 131.6, 130.7, 128.3, 127.6, 121.0, 114.4, 103.2, 73.8, 51.4, 32.6; MS (EI) m/z (rel. intensity) 231 (16), 230 ($[\text{M}^+]$, 100), 212 (12), 199 (22), 198 (13), 171



(60), 170 (26), 169 (25), 153 (14), 149 (25), 143 (25), 142 (14), 141 (19), 135 (18), 129 (17), 128 (35), 115 (30), 91 (15), 90 (19), 89 (16); HR-MS (EI) ($C_{14}H_{14}O_3$) *calcd.* 230.0943, *found* 230.0942; $C_{14}H_{14}O_3$ (230.26): *calcd.* C, 73.03; H, 6.13; *found* C, 73.11; H, 6.05. (**Z**)-isomer: 1H NMR (300 MHz, CD_2Cl_2) δ 7.61 (dd, 1H, $J = 7.9, 0.9$ Hz), 7.28 (td, 1H, $J = 7.7, 1.5$ Hz), 7.20 (td, 1H, $J = 7.5, 1.3$ Hz), 7.06 (m, 1H), 5.93 (ddt, 1H, $J = 16.9, 10.2, 6.5$ Hz), 5.18 (ddd, 1H, $J = 17.1, 3.3, 1.6$ Hz), 5.10 (ddd, 1H, $J = 10.1, 3.1, 1.5$ Hz), 5.02 (s, 2H), 3.83 (s, 3H), 3.36 (dt, 2H, $J = 6.5, 1.5$ Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 167.6, 165.2, 134.0, 129.6, 128.5, 127.4, 126.9, 124.2, 123.5, 117.2, 108.7, 69.6, 51.7, 37.8; IR 3078, 2980, 2950, 2851, 1712, 1639, 1603, 1567, 1489, 1454, 1435, 1384, 1333, 1263, 1250, 1220, 1179, 1118, 1057, 1042, 1010, 995, 919, 869, 835, 786, 751, 721, 636 cm^{-1} ; MS (EI) *m/z* (rel. intensity) 231 (15), 230 ($[M^+]$ 100), 215 (25), 199 (34), 198 (11), 197 (10), 189 (14), 171 (14), 162 (10), 161 (22), 143 (12), 142 (11), 141 (17), 133 (17), 129 (12), 128 (16), 115 (16), 102 (12); HR-MS (EI) ($C_{14}H_{14}O_3$) *calcd.* 230.0943, *found* 230.0943; $C_{14}H_{14}O_3$ (230.26): *calcd.* C, 73.03; H, 6.13; *found* C, 72.86; H, 6.07.

Compound 19b. (E)-isomer: 1H NMR (300 MHz, CD_2Cl_2) δ 8.70 (m, 1H), 7.48-7.35 (m, 3H), 5.34 (br. s, 2H), 4.70 (m, 2H), 3.75 (s, 3H), 3.27 (m, 2H), 1.78 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 169.1, 166.0, 144.9, 144.0, 131.6, 130.6, 128.3, 127.5, 121.1, 109.4, 103.4, 73.7, 51.4, 36.1, 22.9; IR 3123, 3076, 2947, 2874, 1769, 1702, 1650, 1616, 1601, 1465, 1436, 1368, 1317, 1297, 1284, 1218, 1185, 1160, 1080, 1007, 888, 768, 722, 651 cm^{-1} ; MS (EI) *m/z* (rel. intensity) 245 (17), 244 ($[M^+]$ 100), 226 (10), 213 (26), 212 (19), 203 (26), 185 (22), 184 (14), 183 (18), 169 (17), 168 (10), 167 (34), 166 (15), 157 (15), 149 (50), 144 (13), 143 (12), 141 (16), 129 (18), 128 (10), 116 (10), 115 (33), 91 (21), 90 (17), 89 (15); HR-MS (EI) ($C_{15}H_{16}O_3$) *calcd.* 244.1099, *found* 244.1101; $C_{15}H_{16}O_3$ (244.29): *calcd.* C, 73.75; H, 6.60; *found* C, 73.68; H, 6.54. (**Z**)-isomer (resolved signals): 1H NMR (300 MHz, CD_2Cl_2) δ 7.57 (m, 1H), 7.29 (m, 1H), 7.21 (td, 1H, $J = 7.4, 1.3$ Hz), 7.07 (m, 1H), 3.84 (s, 3H), 3.36 (m, 2H), 1.78 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 167.7, 164.5, 142.2, 133.8, 128.5, 127.6, 127.0, 124.2, 123.5, 112.5, 69.4, 51.7, 41.1, 22.7.



X-Ray Structure of Compound 9

Responsible Scientist for X-Ray Structure Analysis: Dr. C. W. Lehmann
 lehmann@mpi-muelheim.mpg.de

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{18}H_{23}NO_2S$	
Color	white	
Formula weight	317.43 $g \cdot mol^{-1}$	
Temperature	293 K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	Pbca, (no. 61)	
Unit cell dimensions	a = 14.0709(4) Å	$\alpha = 90^\circ$
	b = 15.1637(5) Å	$\beta = 90^\circ$
	c = 15.7994(9) Å	$\gamma = 90^\circ$
Volume	3371.1(2) Å ³	
Z	8	
Density (calculated)	1.251 $Mg \cdot m^{-3}$	
Absorption coefficient	1.752 mm^{-1}	
F(000)	1360 e	
Crystal size	0.53 x 0.49 x 0.28 mm^3	
θ range for data collection	5.12 to 74.79°	

Index ranges	-16 ≤ h ≤ 17, 0 ≤ k ≤ 18, 0 ≤ l ≤ 19	
Reflections collected	6553	
Independent reflections	3467 [R _{int} = 0.0293]	
Reflections with I > 2σ(I)	2523	
Completeness to θ = 74.79°	89.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3467 / 0 / 292	
Goodness-of-fit on F ²	1.025	
Final R indices [I > 2σ(I)]	R ₁ = 0.0371	wR ² = 0.0999
R indices (all data)	R ₁ = 0.0566	wR ² = 0.1124
Extinction coefficient	0.00064(11)	
Largest diff. peak and hole	0.208 and -0.296 e · Å ⁻³	

Figure 1. ORTEP diagram of the molecular structure of compound 9. Anisotropic displacement parameter ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity.

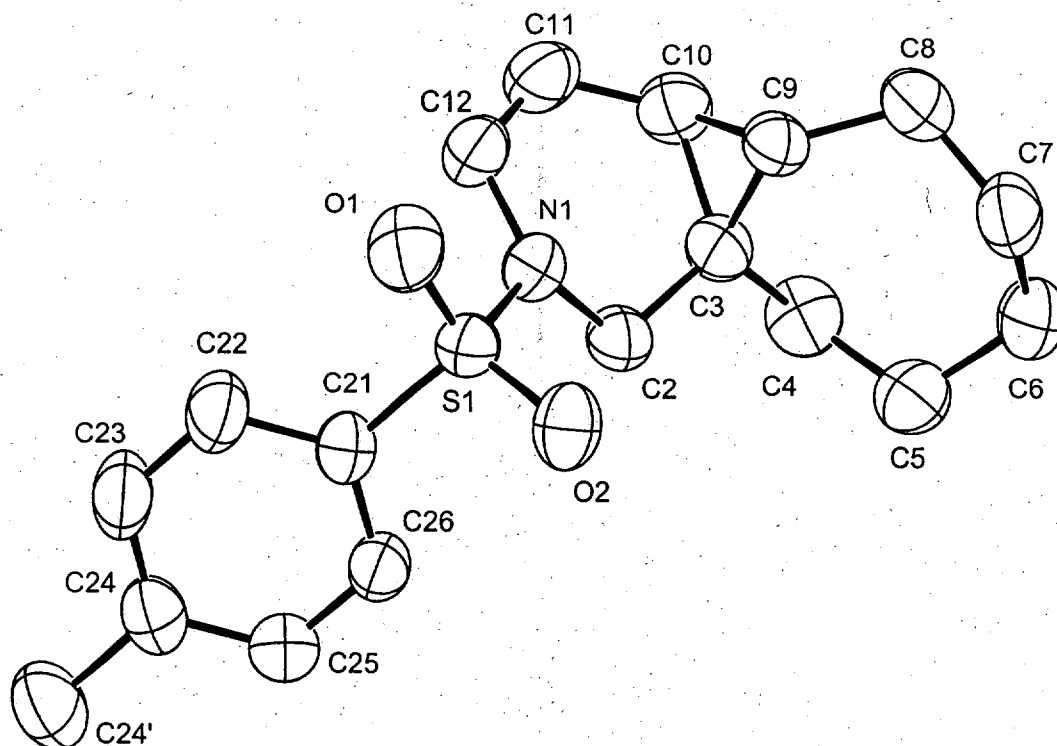


Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2).
 U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S(1)	0.7004(1)	0.0301(1)	0.4500(1)	0.052(1)
O(1)	0.8013(1)	0.0365(1)	0.4581(1)	0.070(1)
N(1)	0.6789(1)	0.0119(1)	0.3505(1)	0.052(1)
O(2)	0.6498(1)	-0.0355(1)	0.4967(1)	0.064(1)
C(2)	0.5815(1)	-0.0091(1)	0.3226(1)	0.051(1)
C(3)	0.5811(1)	-0.0659(1)	0.2440(1)	0.047(1)
C(4)	0.4822(1)	-0.0848(1)	0.2109(1)	0.061(1)
C(5)	0.4319(1)	-0.1581(1)	0.2593(1)	0.063(1)
C(6)	0.4601(1)	-0.2517(2)	0.2335(2)	0.068(1)
C(7)	0.5632(1)	-0.2767(1)	0.2458(2)	0.071(1)
C(8)	0.6342(1)	-0.2226(1)	0.1946(2)	0.067(1)
C(9)	0.6563(1)	-0.1347(1)	0.2356(1)	0.050(1)
C(10)	0.6635(1)	-0.0497(1)	0.1844(1)	0.058(1)
C(11)	0.7326(2)	0.0182(1)	0.2089(1)	0.064(1)
C(12)	0.7407(1)	0.0461(1)	0.2874(1)	0.060(1)
C(21)	0.6516(1)	0.1332(1)	0.4760(1)	0.048(1)
C(22)	0.7092(2)	0.2068(1)	0.4827(2)	0.067(1)
C(23)	0.6698(2)	0.2872(1)	0.5043(2)	0.071(1)
C(24)	0.5736(2)	0.2960(1)	0.5195(1)	0.058(1)
C(24')	0.5324(2)	0.3833(2)	0.5447(2)	0.077(1)
C(25)	0.5170(2)	0.2217(1)	0.5112(1)	0.055(1)
C(26)	0.5547(1)	0.1409(1)	0.4899(1)	0.050(1)

Table 3. Hydrogen coordinates and isotropic displacement parameters (\AA^2).

	x	y	z	U_{eq}
H(2B)	0.5502(15)	0.0483(14)	0.3069(13)	0.063(6)
H(2A)	0.5493(14)	-0.0409(13)	0.3712(12)	0.057(5)
H(4B)	0.4862(15)	-0.0998(15)	0.1497(14)	0.071(6)
H(4A)	0.4451(18)	-0.0272(16)	0.2122(15)	0.084(7)
H(5B)	0.4419(15)	-0.1480(14)	0.3215(15)	0.070(6)
H(5A)	0.359(2)	-0.1484(15)	0.2510(17)	0.095(8)
H(6B)	0.4448(16)	-0.2572(15)	0.1733(15)	0.073(6)
H(6A)	0.4162(17)	-0.2922(15)	0.2689(15)	0.081(7)
H(7B)	0.5780(17)	-0.2700(15)	0.3094(17)	0.082(7)
H(7A)	0.5718(17)	-0.3368(17)	0.2315(16)	0.086(7)
H(8B)	0.6082(17)	-0.2105(15)	0.1361(16)	0.083(7)
H(8A)	0.694(2)	-0.2558(17)	0.1878(17)	0.093(8)
H(9)	0.6979(15)	-0.1386(12)	0.2840(13)	0.059(5)
H(10)	0.6498(15)	-0.0543(13)	0.1286(14)	0.064(6)
H(11)	0.772(2)	0.0385(18)	0.1671(17)	0.093(9)
H(12)	0.7849(16)	0.0913(15)	0.3085(14)	0.071(6)
H(22)	0.779(2)	0.1990(17)	0.4707(16)	0.092(8)
H(23)	0.7092(19)	0.3391(18)	0.5110(18)	0.102(9)
H(24C)	0.561(2)	0.428(2)	0.514(2)	0.120(10)
H(24B)	0.546(2)	0.396(2)	0.601(2)	0.105(9)
H(24A)	0.466(3)	0.389(2)	0.531(2)	0.126(12)
H(25)	0.4500(17)	0.2267(15)	0.5207(14)	0.076(7)
H(26)	0.5137(13)	0.0892(12)	0.4810(11)	0.054(5)

Table 4. Bond lengths [Å] and angles [°].

S(1)-O(2)	1.4280(14)	S(1)-O(1)	1.4291(14)
S(1)-N(1)	1.6249(15)	S(1)-C(21)	1.7562(17)
N(1)-C(12)	1.421(2)	N(1)-C(2)	1.475(2)
C(2)-C(3)	1.512(2)	C(2)-H(2B)	1.01(2)
C(2)-H(2A)	1.01(2)	C(3)-C(9)	1.491(2)
C(3)-C(10)	1.514(3)	C(3)-C(4)	1.515(2)
C(4)-C(5)	1.523(3)	C(4)-H(4B)	1.00(2)
C(4)-H(4A)	1.02(3)	C(5)-C(6)	1.530(3)
C(5)-H(5B)	1.00(2)	C(5)-H(5A)	1.05(3)
C(6)-C(7)	1.512(3)	C(6)-H(6B)	0.98(2)
C(6)-H(6A)	1.03(2)	C(7)-C(8)	1.525(3)
C(7)-H(7B)	1.03(3)	C(7)-H(7A)	0.95(3)
C(8)-C(9)	1.513(3)	C(8)-H(8B)	1.01(3)
C(8)-H(8A)	0.98(3)	C(9)-C(10)	1.525(3)
C(9)-H(9)	0.96(2)	C(10)-C(11)	1.469(3)
C(10)-H(10)	0.90(2)	C(11)-C(12)	1.316(3)
C(11)-H(11)	0.92(3)	C(12)-H(12)	0.98(2)
C(21)-C(22)	1.383(2)	C(21)-C(26)	1.386(2)
C(22)-C(23)	1.382(3)	C(22)-H(22)	1.00(3)
C(23)-C(24)	1.382(3)	C(23)-H(23)	0.97(3)
C(24)-C(25)	1.387(3)	C(24)-C(24')	1.498(3)
C(24')-H(24C)	0.93(3)	C(24')-H(24B)	0.93(3)
C(24')-H(24A)	0.96(4)	C(25)-C(26)	1.378(2)
C(25)-H(25)	0.96(2)	C(26)-H(26)	0.983(19)
O(2)-S(1)-O(1)	119.83(9)	O(2)-S(1)-N(1)	106.79(8)
O(1)-S(1)-N(1)	106.36(9)	O(2)-S(1)-C(21)	107.77(9)
O(1)-S(1)-C(21)	107.84(8)	N(1)-S(1)-C(21)	107.72(8)
C(12)-N(1)-C(2)	115.97(16)	C(12)-N(1)-S(1)	120.23(13)
C(2)-N(1)-S(1)	119.88(12)	N(1)-C(2)-C(3)	111.81(14)
N(1)-C(2)-H(2B)	107.1(12)	C(3)-C(2)-H(2B)	106.8(12)
N(1)-C(2)-H(2A)	106.9(11)	C(3)-C(2)-H(2A)	110.4(11)
H(2B)-C(2)-H(2A)	113.8(17)	C(9)-C(3)-C(2)	118.00(14)
C(9)-C(3)-C(10)	60.99(12)	C(2)-C(3)-C(10)	114.58(15)
C(9)-C(3)-C(4)	119.28(15)	C(2)-C(3)-C(4)	113.25(15)
C(10)-C(3)-C(4)	121.29(16)	C(3)-C(4)-C(5)	113.03(16)
C(3)-C(4)-H(4B)	109.1(13)	C(5)-C(4)-H(4B)	110.3(13)
C(3)-C(4)-H(4A)	107.6(14)	C(5)-C(4)-H(4A)	112.2(14)
H(4B)-C(4)-H(4A)	104.2(19)	C(4)-C(5)-C(6)	115.00(19)
C(4)-C(5)-H(5B)	108.4(12)	C(6)-C(5)-H(5B)	111.4(12)
C(4)-C(5)-H(5A)	107.0(14)	C(6)-C(5)-H(5A)	110.5(13)
H(5B)-C(5)-H(5A)	103.8(19)	C(7)-C(6)-C(5)	116.52(17)
C(7)-C(6)-H(6B)	108.4(13)	C(5)-C(6)-H(6B)	106.4(14)
C(7)-C(6)-H(6A)	110.7(13)	C(5)-C(6)-H(6A)	104.6(13)
H(6B)-C(6)-H(6A)	110.1(19)	C(6)-C(7)-C(8)	115.2(2)
C(6)-C(7)-H(7B)	107.2(14)	C(8)-C(7)-H(7B)	109.4(13)
C(6)-C(7)-H(7A)	109.5(15)	C(8)-C(7)-H(7A)	107.9(16)
H(7B)-C(7)-H(7A)	107(2)	C(9)-C(8)-C(7)	112.38(18)
C(9)-C(8)-H(8B)	107.8(14)	C(7)-C(8)-H(8B)	110.2(13)
C(9)-C(8)-H(8A)	108.8(15)	C(7)-C(8)-H(8A)	109.9(15)
H(8B)-C(8)-H(8A)	108(2)	C(3)-C(9)-C(8)	120.52(17)
C(3)-C(9)-C(10)	60.24(12)	C(8)-C(9)-C(10)	122.01(17)
C(3)-C(9)-H(9)	113.7(12)	C(8)-C(9)-H(9)	114.2(11)
C(10)-C(9)-H(9)	115.6(12)	C(11)-C(10)-C(3)	117.16(17)
C(11)-C(10)-C(9)	119.79(18)	C(3)-C(10)-C(9)	58.77(11)

C(11)-C(10)-H(10)	116.9(13)	C(3)-C(10)-H(10)	115.5(14)
C(9)-C(10)-H(10)	116.0(13)	C(12)-C(11)-C(10)	122.14(18)
C(12)-C(11)-H(11)	121.3(17)	C(10)-C(11)-H(11)	116.5(17)
C(11)-C(12)-N(1)	119.38(18)	C(11)-C(12)-H(12)	126.8(13)
N(1)-C(12)-H(12)	113.8(13)	C(22)-C(21)-C(26)	119.75(16)
C(22)-C(21)-S(1)	120.52(15)	C(26)-C(21)-S(1)	119.73(12)
C(23)-C(22)-C(21)	119.75(19)	C(23)-C(22)-H(22)	122.9(15)
C(21)-C(22)-H(22)	117.4(15)	C(24)-C(23)-C(22)	121.42(19)
C(24)-C(23)-H(23)	117.6(16)	C(22)-C(23)-H(23)	121.0(16)
C(23)-C(24)-C(25)	117.89(18)	C(23)-C(24)-C(24')	120.7(2)
C(25)-C(24)-C(24')	121.4(2)	C(24)-C(24')-H(24C)	110(2)
C(24)-C(24')-H(24B)	111.1(19)	H(24C)-C(24')-H(24B)	105(3)
C(24)-C(24')-H(24A)	113(2)	H(24C)-C(24')-H(24A)	104(3)
H(24B)-C(24')-H(24A)	113(3)	C(26)-C(25)-C(24)	121.66(19)
C(26)-C(25)-H(25)	119.3(14)	C(24)-C(25)-H(25)	119.1(14)
C(25)-C(26)-C(21)	119.52(16)	C(25)-C(26)-H(26)	121.1(11)
C(21)-C(26)-H(26)	119.3(11)		

Table 5. Anisotropic displacement parameters (\AA^2).

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	0.050(1)	0.044(1)	0.062(1)	0.001(1)	-0.009(1)	-0.001(1)
O(1)	0.048(1)	0.067(1)	0.097(1)	-0.005(1)	-0.018(1)	0.004(1)
N(1)	0.045(1)	0.052(1)	0.059(1)	-0.007(1)	0.002(1)	-0.007(1)
O(2)	0.076(1)	0.048(1)	0.069(1)	0.011(1)	-0.007(1)	-0.005(1)
C(2)	0.043(1)	0.049(1)	0.060(1)	-0.006(1)	0.000(1)	0.003(1)
C(3)	0.045(1)	0.047(1)	0.048(1)	0.000(1)	-0.002(1)	0.006(1)
C(4)	0.053(1)	0.066(1)	0.064(1)	0.000(1)	-0.016(1)	0.007(1)
C(5)	0.045(1)	0.074(1)	0.070(1)	-0.009(1)	-0.009(1)	-0.001(1)
C(6)	0.062(1)	0.067(1)	0.075(1)	-0.012(1)	-0.006(1)	-0.012(1)
C(7)	0.070(1)	0.047(1)	0.094(2)	-0.009(1)	-0.002(1)	-0.002(1)
C(8)	0.064(1)	0.059(1)	0.079(1)	-0.018(1)	0.008(1)	0.004(1)
C(9)	0.046(1)	0.048(1)	0.056(1)	-0.004(1)	0.001(1)	0.005(1)
C(10)	0.066(1)	0.063(1)	0.047(1)	0.004(1)	0.005(1)	-0.001(1)
C(11)	0.064(1)	0.061(1)	0.069(1)	0.011(1)	0.015(1)	-0.005(1)
C(12)	0.054(1)	0.052(1)	0.076(1)	0.002(1)	0.009(1)	-0.009(1)
C(21)	0.050(1)	0.044(1)	0.049(1)	-0.001(1)	-0.006(1)	-0.005(1)
C(22)	0.052(1)	0.052(1)	0.096(2)	-0.008(1)	-0.005(1)	-0.010(1)
C(23)	0.068(1)	0.046(1)	0.098(2)	-0.008(1)	-0.005(1)	-0.013(1)
C(24)	0.074(1)	0.045(1)	0.054(1)	-0.002(1)	-0.002(1)	0.000(1)
C(24')	0.099(2)	0.052(1)	0.079(2)	-0.004(1)	0.005(1)	0.008(1)
C(25)	0.054(1)	0.056(1)	0.054(1)	-0.001(1)	0.004(1)	0.000(1)
C(26)	0.054(1)	0.047(1)	0.048(1)	-0.001(1)	0.003(1)	-0.009(1)