SUPPORTING INFORMATION

Platinum-Catalyzed Cycloisomerization Reactions of Enynes

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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 hexanes/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 ^{13}C 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: Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka) were used as received.

Synthesis of Diethyl bicyclo[7.2.1]dodeca-1(12),2-diene-10,10-dicarboxylate (14): $PtCl_2$ (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 (hexanes/ethyl acetate, 20:1) of the residue affords the title compound as a colorless syrup (166 mg, 83%). ^1H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 (50): $PtCl_2$ (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 (hexanes/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, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 ([M^+] 37), 316 (13), 218 (100), 189 (20), 148 (25), 136 (22), 91 (41), 79 (10), 67 (11), 55 (15), 41 (18); $C_{22}H_{31}NO_2S$ (373.21) *calcd.*: C, 71.12; H, 7.87; N, 3.77; *found.*: C, 70.46; H, 8.29; N, 3.57.

Compound **52**[16] was identified by comparison with an authentic sample prepared according to the literature. The analytical and spectroscopic data of all other products are in full agreement with the proposed structures and are compiled below.

3-Vinyl-cyclopent-3-ene-1,1-dicarboxylic acid diethylester (4): Colorless syrup; ^1H NMR (300 MHz, CD_2Cl_2) δ 6.41 (dd, 1H, *J* = 17.3, 10.7 Hz), 5.50 (m, 1H), 5.04 (d, 1H, *J* = 7.0 Hz), 5.00 (s, 1H), 4.09 (q, 4H, *J* = 7.1 Hz), 3.01 (m, 2H), 2.98 (m, 2H), 1.15 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 172.2, 140.4, 132.8, 127.5, 115.1, 62.0, 59.0, 41.0, 39.3, 14.2; IR (film) 3090, 3051, 2982, 2938, 2907, 2872, 1733, 1645, 1596, 1465, 1446, 1367, 1250, 1182, 1160, 1071 cm^{-1}; MS (EI) *m/z* (rel. intensity) 238 ([M^+] 27), 193 (10), 164 (100), 136 (17), 119 (18), 105 (41), 91

(94), 77 (17), 65 (18), 29 (61); $C_{13}H_{18}O_4$ (238.28) *calcd.*: C, 65.53; H, 7.61; *found*: C, 65.62; H, 7.70.

10-(Toluene-4-sulfonyl)-10-aza-bicyclo[7.2.1]dodeca-1(12),2-diene (8): Colorless syrup; ^{1}H 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 ([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 (26): mp 79-80°C; ^{1}H 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 (v.sept, 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 ([M$^+$] 28), 184 (10), 155 (9), 94 (100), 67 (54), 41 (20); $C_{13}H_{15}NO_2S$ (249.33) *calcd.*: C, 62.62; H, 6.06; N, 5.62; *found.*: C, 62.49; H, 6.08; N, 5.54.

Compound 27. mp 94-95°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (AA'XX', 2H), 7.33 (AA'XX', 2H), 6.36 (dd, 1H, J = 17.5, 10.6 Hz), 5.59 (s, 1H), 5.16 (d, 1H, J = 10.8 Hz), 5.02 (d, 1H, J = 17.6 Hz), 4.20 (m, 2H), 4.19 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 137.5, 134.1, 129.9, 129.8, 127.4, 123.3, 116.7, 55.0, 53.4, 21.5; IR (film) 3080, 2905, 2851, 1664, 1597, 1493, 1338, 1163, 1109, 892, 809, 733, 665, 589, 547 cm^{-1}; $C_{13}H_{15}NO_2S$ (249.33) *calcd.*: C, 62.62; H, 6.06; N, 5.62; *found*: C, 62.56; H, 5.97; N, 5.53.

3-(Toluene-4-sulfonyl)-3-aza-tricyclo[5.5.0.0^{1,6}]dodec-4-ene (29): mp 93-94°C; ^{1}H 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 ([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 (30): Colorless syrup; ^{1}H 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 ([M$^+$] 83), 162 (100), 155 (10), 133 (34), 121 (11), 106 (17), 91 (74), 80 (31), 65 (22), 55 (25), 41 (30); $C_{18}H_{23}NO_2S$ (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 (6): mp 114-115°C; ^{1}H 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 ([M$^+$] 1), 232 (30), 215 (27), 125 (31), 107 (48), 91 (100), 77 (32), 65 (20), 51 (11); $C_{19}H_{18}O_4S_2$ (374.48) *calcd.*: C, 60.94; H, 4.84; *found*: C, 60.84; H, 4.92.

10-(Toluene-4-sulfonyl)-10-aza-bicyclo[7.2.1]dodeca-1(12),2-diene-2-carboxylic acid methyl ester (10): mp 108-109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (AA'XX', 2H), 7.32 (AA'XX', 2H), 7.07 (dd, 1H, J = 8.1, 6.1 Hz), 5.45 (dt, 1H, J = 1.9, 1.8 Hz), 4.73 (m, 1H), 4.48 (dt, 1H, J = 14.3, 2.2 Hz), 4.23 (ddd, J = 14.2, 4.9, 1.7), 3.66 (s, 3H), 2.43 (s, 3H), 2.34-2.20 (m, 2H), 2.15-2.11 (m, 1H), 1.80-1.30 (m, 7H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 148.3, 143.3, 135.4, 131.9, 131.6, 129.8, 129.7, 128.8, 127.3, 67.2, 51.9, 35.7, 28.9, 27.4, 26.6, 21.5, 20.4. IR: 3023, 2999, 2948, 2926, 2873, 1715, 1616, 1597, 1493, 1459, 1471, 1435, 1341, 1261, 1242, 1157, 1090, 1058, 813, 670, 544 cm^{-1}; MS (EI) *m/z* (rel. intensity) 375 ([M$^+$] 91), 343 (51), 316 (10), 300 (15), 220

(100), 188 (61), 160 (89), 118 (17), 91 (99), 80 (18), 65 (20), 41 (13); $C_{20}H_{25}NO_4S$ (375.48) *calcd.*: C, 64.0; H, 6.7; N, 3.7; *found*: C, 64.08; H, 6.68; N, 3.64.

1-[10-(Toluene-4-sulfonyl)-10-aza-bicyclo[7.2.1]dodeca-1(12),2-dien-2-yl]-butan-1-one (12): mp 72-73 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (AA'XX', 2H), 7.29 (AA'XX', 2H), 6.88 (dd, 1H, J = 8.4, 6.9 Hz), 5.31 (dt, 1H, J = 2.2, 1.7 Hz), 4.73 (m, 1H), 4.35 (dt, 1H, J = 14.4, 2.2 Hz), 4.24 (ddd, 1H, J = 14.4, 4.8, 1.6 Hz), 2.42 (1H, dt, J = 16.5, 7.4 Hz), 2.39 (s, 3H), 2.30 (m, 1H), 2.32 (dt, 1H, J = 16.5, 7.4 Hz), 2.23 (m, 1H), 2.07 (dtd, 1H, J = 14.7, 7.0, 4.1 Hz), 1.64-1.40 (m, 6H), 1.51 (sext., 2H, J = 7.4 Hz), 1.14 (m, 1H), 0.83 (t, 3H, J = 7.4 Hz), ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.5, 145.6, 143.4, 138.6, 135.2, 132.6, 131.6, 129.8, 127.2, 67.3, 58.5, 40.4, 35.3, 28.5, 27.5, 25.5, 21.5, 19.1, 17.7, 13.7; IR: 3064, 2961, 2932, 2871, 1689, 1669, 1597, 1494, 1460, 1442, 1401, 1342, 1162, 1096, 1061, 1041, 1017, 815, 671, 594 cm^{-1}; Anal. *calcd.* for $C_{22}H_{29}NSO_3$ (387.54): C, 68.18; H, 7.54; N, 3.61; S, 8.27; *found*: C, 68.13; H, 7.56; N, 3.63; S, 8.31.

2-Acetyl-bicyclo[7.2.1]dodeca-1(12),2-dien-10,10-dicarboxylic acid diethyl ester (16): Colorless syrup; ^{1}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}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 ([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 (18): Colorless syrup; ^{1}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}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 ([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); $C_{13}H_{18}O_3$ (222.13): *calcd.*: C, 70.24; H, 8.16; *found*: C, 70.38; H, 8.12.

10,10-Bis-methansulfonyl-bicyclo[7.2.1]dodeca-1(12),2-diene (20): mp 168-171°C (decomp.); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.95 (m, 2H), 7.82 (m, 2H), 5.91 (m, 1H, *J* = 11.0 Hz), 5.83 (m, 1H, *J* = 7.9, 6.0 Hz), 5.78 (m, 1H), 3.90 (m, 1H), 3.45 (d, 1H, *J* = 17.8 Hz), 2.94 (d, 1H, *J* = 17.9 Hz), 2.24 (m, 2H), 1.95 (m, 2H), 1.42 (m, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 137.9, 137.6, 136.8, 136.6, 135.5, 130.9, 126.0, 123.9, 122.7, 46.9, 42.6, 28.4, 27.5, 26.8, 24.6, 21.0; IR (Film) 3091, 3013, 2959, 2929, 2868, 1637, 1575, 1464, 1443, 1334, 1317, 1153, 1132, 768 cm^{-1}; MS (EI) *m/z* (rel. intensity) 364 ([M$^+$] 15), 265 (13), 193 (55), 179 (53), 176 (72), 158 (100), 154 (68), 143 (18), 129 (42), 117 (51), 115 (66), 105 (22), 103 (33), 95 (15), 91 (86), 81 (19), 77 (52), 67 (25), 65 (26), 53 (17), 51 (16); HR-MS *calcd.*: 364.080304; *found*: 364.081470.

12-(Toluene-4-sulfonyl)-10-aza-bicyclo[9.2.1]tetradeca-1(14),2-diene (22): Colorless syrup; ^{1}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}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 ([M$^+$]), HR-MS *calcd.*: 345.17625; *found*: 345.17503.

14-Oxa-bicyclo[11.2.1]hexadeca-1(16),2,6,10-tetraene (24): Colorless syrup; R_f 0.39 (hexanes/ ethyl acetate, 10:1); ^{1}H NMR (300.1 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}C NMR (75.5 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 ([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, i-Butan) ($C_{15}H_{20}O$ + H) *calcd.* 217.1592, *found* 217.1586; Anal. *calcd.* for $C_{15}H_{20}O$ (216.32): 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 (32): Colorless syrup; ^{1}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}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 ([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-Methyl-7-phenyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (34): mp 117-123 °C (decomp.); R_f 0.40 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 7.65 (AA'XX', 2H), 7.32 (AA'XX', 2H), 7.27-7.12 (m, 3H), 6.98 (m, 2H), 6.38 (d, 1H, J = 8.2 Hz), 5.32 (d, 1H, J = 8.2 Hz), 4.00 (d, 1H, J = 11.6 Hz), 3.10 (dd, 1H, J = 11.6, 2.6 Hz), 2.39 (s, 3H), 1.86 (d, 1H, J = 6.0 Hz), 1.81 (dm, 1H, J = 6.0 Hz), 0.83 (s, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 144.4, 137.7, 135.0, 130.2, 128.9, 128.3, 127.3, 126.4, 120.9, 117.8, 40.7, 36.1, 29.7, 21.6, 20.7, 17.6; IR 3102, 3057, 3017, 2968, 2924, 2866, 1647, 1600, 1499, 1471, 1453, 1407, 1383, 1348, 1302, 1275, 1253, 1224, 1165, 1103, 1089, 1075, 1005, 982, 958, 936, 913, 882, 843, 814, 803, 789, 752, 715, 672, 634, 594, 549, 516 cm^{-1}; MS (EI) *m/z* (rel. intensity) 340 (11), 339 ([M$^+$] 47), 338 (18), 324 (8), 185 (14), 184 (100), 169 (11), 168 (11), 141 (8), 115 (10), 106 (9), 93 (11), 91 (64), 65 (7); HR-MS (EI) ($C_{20}H_{21}NO_2S$) *calcd.* 339.1293, *found* 339.1293; Anal. *calcd.* for $C_{20}H_{21}NO_2S$ (339.46): C, 70.77; H, 6.24; N, 4.13; *found*: C, 70.63; H, 6.18; N, 4.06.

6-Phenyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (36): mp 103-105 °C; R_f 0.37 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 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 (75.5 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 ([M$^+$] 100), 324 (58), 171 (13), 170 (100), 169 (27), 168 (46), 156 (13), 155 (12), 154 (8), 153 (9), 144 (10), 143 (76), 142 (29), 141 (34), 129 (10), 128 (45), 127 (11), 115 (30), 103 (8), 92 (10), 91 (57), 77 (8), 65 (23), 41 (14), 39 (11); HR-MS (EI) ($C_{19}H_{19}NO_2S$) *calcd.*

325.1137, *found* 325.1134; Anal. *calcd.* for $C_{19}H_{19}NO_2S$ (325.43): 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 (38): mp 110-111°C; ^{1}H 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 ([M^+] 35), 155 (8), 108 (100), 91 (47), 81 (36), 65 (21), 53 (13), 41 (19); $C_{14}H_{17}NO_2S$ (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 (40): mp 55-56 °C; R_f 0.41 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 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 (75.5 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) 278 (5), 277 ([M^+] 25), 262 (6), 212 (3), 155 (8), 123 (9), 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); HR-MS (EI) ($C_{15}H_{19}NO_2S$) *calcd.* 277.1137, *found* 277.1138; Anal. *calcd.* for $C_{15}H_{19}NO_2S$ (277.39): C, 64.95; H, 6.90; N, 5.05; *found*: C, 65.08; H, 6.84; N, 4.96.

6,7,7-Trimethyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (42): mp 76-78 °C; R_f 0.45 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 7.66 (AA'XX', 2H), 7.33 (AA'XX', 2H), 6.52 (d, 1H, *J* = 8.4 Hz), 4.88 (dd, 1H, *J* = 8.4, 0.8 Hz), 3.45 (dd, 1H, *J* = 12.2, 1.8 Hz), 3.37 (dd, 1H, *J* = 12.1, 5.9 Hz), 2.42 (s, 3H), 1.11 (s, 3H), 1.07 (s, 3H), 0.74 (m, 1H), 0.72 (s, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 144.3, 135.1, 130.0, 127.4, 121.8, 111.0, 38.9, 28.4, 28.2, 22.9, 21.6, 19.8, 19.1, 16.2; IR 3100, 3048, 2985, 2922, 2870, 1644, 1599, 1494,1466, 1402, 1379, 1357, 1341, 1312, 1261, 1253, 1206, 1170, 1154, 1101, 1045, 1026, 1016, 975, 962, 899, 811, 771,

731, 710, 694, 655, 634, 625, 564, 550, 535 cm^{-1}; MS (EI) *m/z* (rel. intensity) 292 (3), 292 (8), 291 ([M^+] 41), 290 (10), 276 (9), 248 (4), 155 (9), 137 (10), 136 (100), 121 (28), 120 (19), 119 (42), 107 (17), 94 (40), 93 (41), 91 (36), 80 (11), 65 (11), 43 (7), 41 (17); HR-MS (EI) ($C_{16}H_{21}NO_2S$) *calcd.* 291.1293, *found* 291.1290; Anal. *calcd.* for $C_{16}H_{21}NO_2S$ (291.42): C, 65.95; H, 7.26; N, 4.81; *found*: C, 65.82; H, 7.34; N, 4.74.

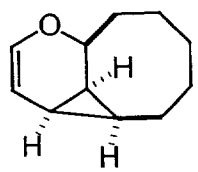
3-(Toluene-4-sulfonyl)-7-trimethylsilanyl-3-aza-bicyclo[4.1.0]hept-4-ene (44): Colorless syrup; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (AA'XX', 2H), 7.47 (AA'XX', 2H), 6.42 (d, 1H, *J* = 7.9 Hz), 5.59 (dd, 1H, *J* = 7.9, 5.4 Hz), 4.05 (d, 1H, *J* = 12.0 Hz), 3.26 (dd, 1H, *J* = 12.0, 2.5 Hz), 2.58 (s, 3H), 1.57 (m, 1H, *J* = 7.5, 1.9 Hz), 1.13 (dt, 1H, *J* = 7.8, 5.3 Hz), 0.00 (s, 9H), –0.31 (dd, 1H, *J* = 7.0, 5.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 134.9, 129.7, 126.9, 120.3, 113.9, 41.8, 23.4, 21.5, 14.7, 11.1, –2.6. IR (film) 3065, 3021, 2953, 2895, 1636, 1597, 1493, 1400, 1353, 1249, 1168, 1104, 946, 839, 688, 556 cm^{-1}; MS (EI) *m/z* (rel. intensity) 321 ([M^+] 7), 228 (16), 180 (72), 166 (34), 149 (55), 93 (52), 73 (100), 59 (15), 45 (12); HR-MS *calcd.*: 321.12188; *found*: 321.12152.

3-(Toluene-4-sulfonyl)-1-trimethylsilanylmethyl-3-aza-bicyclo[4.1.0]-hept-4-ene (46): 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 ([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.

6-Methyl-3-(toluene-4-sulfonyl)-7-trimethylsilanylmethyl-3-aza-bicyclo[4.1.0]hept-4-ene (48): Colorless syrup; R_f 0.26 (hexanes/ethyl acetate, 10:1); ^1H NMR (300.1 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 (75.5 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, 1383, 1359, 1347, 1306, 1278, 1248, 1168, 1108, 1068, 1006, 930, 846, 815, 757, 710, 693, 678, 636, 605, 560,

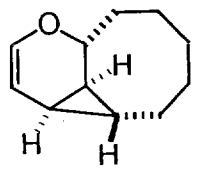
548, 531 cm^{-1}; MS (EI) *m/z* (rel. intensity) 351 (2), 350 (6), 349 ([M^+] 19), 348 (10), 276 (10), 249 (11), 248 (10), 228 (7), 195 (6), 194 (31), 180 (32), 155 (10), 149 (26), 139 (6), 121 (13), 120 (23), 106 (20), 94 (14), 93 (8), 91 (33), 74 (8), 73 (100), 65 (7), 59 (6), 45 (13); MS (APCIpos) 350 [349 [M] + H]$^+$; HR-MS (EI) ($C_{18}H_{27}NO_2SSi$) *calcd.* 349.1532, *found* 349.1524; Anal. *calcd.* for $C_{18}H_{27}NO_2SSi$ (349.57): C, 61.85; H, 7.79; N, 4.01; *found*: C, 61.72; H, 7.71; N, 3.97.

9-Oxa-tricyclo[6.4.0.0^{2,12}]dodec-10-ene (54): Colorless syrup; This product was obtained in form of two diastereoisomers (**54a** : **54b** = 2.2 : 1): Spectroscopic properties of **54a**: ^{1}H NMR (600 MHz, CD_2Cl_2) δ 6.22 (d, 1H, *J* = 6.0 Hz), 5.01 (ddd, 1H, *J* = 6.0, 4.0, 2.0 Hz), 4.12 (dt, 1H, *J* = 4.0, 1.5 Hz), 2.05 (m, 1H), 1.79 (m, 1H), 1.65-1.51 (m, 6H), 1.38 (m, 1H), 1.34 (m, 1H), 1.32 (m, 1H), 1.31 (m, 1H), 0.95 (dtd, 1H, *J* = 12.0, 8.0, 3.0 Hz); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 141.9, 101.0, 70.9, 36.1, 28.4, 26.1, 24.8, 24.8, 20.9, 20.4, 10.1; IR (film) 3063, 3019, 2983, 2923, 2862, 1644, 1460, 1238, 1090, 1037, 739 cm^{-1}; MS (EI) *m/z* (rel. intensity) 164 ([M^+] 48), 149 (6), 135 (11), 121 (29), 107 (69), 95 (17), 91 (28), 81 (100), 79 (49), 77 (26), 67 (43), 53 (20), 41 (45), 39 (31), 27 (22); HR-MS *calcd.*: 164.12012; *found*: 164.12062.



54a (major)

Spectroscopic properties of **54b**: ^{1}H NMR (600 MHz, CD_2Cl_2) δ 6.76 (dd, 1H, *J* = 5.9, 1.8 Hz), 5.05 (dd, 1H, *J* = 5.9, 3.7 Hz), 3.35 (dd, 1H, *J* = 9.0, 9.0 Hz), 1.97 (m, 1H), 1.89-1.79 (m, 3H), 1.68 (m, 1H), 1.54 (m, 1H), 1.43 (m, 1H), 1.29 (m, 1H), 1.23 (tdd, 1H, *J* = 8.1, 3.5, 1.8 Hz), 1.05 (m, 1H), 1.04 (dt, 1H, *J* = 9.0, 8.0 Hz), 0.96 (m, 1H, *J* = 10.8, 8.0, 5.7 Hz); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 151.7, 103.9, 79.5, 32.2, 31.2, 27.0, 25.8, 23.7, 21.5, 14.9, 13.8; IR (film) 3051, 2926, 2861, 1726, 1611, 1453, 1224, 1037, 743 cm^{-1}; MS (EI) *m/z* (rel. intensity) 164 ([M^+] 3), 121 (11), 107 (45), 96 (26), 91 (17), 81 (100), 79 (30), 77 (18), 67 (41), 55 (16), 41 (29), 39 (22), 27 (12); HR-MS (CI, *i*-Butan) *calcd.*: 165.12794; *found*: 165.12843.



54b (minor)

6-Oxa-tricyclo[5.4.1.0^{3,12}]dodec-2-ene-2-carboxylic acid methyl ester (61a): Colorless syrup; R_f 0.32 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 4.17 (m, 1H), 3.82-3.69 (m, 2H), 3.68 (s, 3H), 3.26 (m, 1H), 2.90 (m, 1H), 2.73 (m, 1H), 2.41 (m, 1H), 2.01-1.87 (m, 2H), 1.76-1.12 (m, 6H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 163.3, 159.3, 130.2, 78.9, 59.3, 50.9, 45.2, 45.0, 28.8, 28.6, 27.9, 26.2, 25.4; IR 2920, 2858, 1714, 1673, 1449, 1435, 1362, 1349, 1326, 1292, 1273,

1246, 1204, 1183, 1136, 1106, 1063, 1038, 1000, 952, 937, 844, 782, 766, 730, 575 cm^{-1}; MS (EI) *m/z* (rel. intensity) 223 (2), 222 ([M^+] 9), 204 (16), 192 (24), 191 (14), 190 (11), 177 (24), 164 (24), 163 (45), 162 (19), 160 (15), 151 (10), 145 (15), 134 (15), 133 (100), 132 (33), 131 (15), 119 (15), 117 (27), 105 (57), 104 (14), 103 (13), 93 (16), 92 (13), 91 (85), 83 (21), 79 (38), 78 (16), 77 (42), 67 (18), 65 (23), 59 (21), 55 (17), 53 (20), 51 (17), 43 (13), 41 (38), 39 (31), 29 (22), 27 (20); HR-MS (EI) ($C_{13}H_{18}O_3$) *calcd.* 222.1256, *found* 222.1259.

9-Oxa-bicyclo[6.3.1]dodeca-1(12),2-diene-2-carboxylic acid methyl ester (61b): Colorless syrup; R_f 0.36 (hexanes/ethyl acetate, 4:1); ^1H NMR (300.1 MHz, CD_2Cl_2) δ 7.10 (dd, 1H, J = 7.7, 5.4 Hz), 5.61 (s, 1H), 4.52 (m, 1H), 3.98 (dd, J = 4.6, 1.5 Hz), 3.94 (t, J = 3.2 Hz) [1H], 3.70 (m, 3H), 3.64 (m, 1H), 2.46 (m, 1H), 2.25 (m, 2H), 2.13-1.85 (m, 3H), 1.70 (m, 1H), 1.55-1.40 (m, 2H), 1.27 (m, 1H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 167.1, 148.6, 137.7, 132.8, 132.4, 73.9, 63.4, 51.8, 35.7, 31.1, 29.8, 28.6, 25.1; IR 3022, 2930, 2852, 1716, 1618, 1458, 1435, 1376, 1265, 1241, 1202, 1155, 1117, 1064, 1050, 995, 909, 890, 789, 766, 755, 719, 666 cm^{-1}; MS (EI) *m/z* (rel. intensity) 223 (5), 222 ([M^+] 34), 192 (5), 191 (10), 190 (11), 164 (12), 163 (100), 162 (30), 133 (15), 119 (14), 105 (25), 93 (14), 91 (42), 83 (56), 79 (25), 77 (25), 67 (13), 65 (12), 59 (14), 55 (13), 53 (11), 43 (10), 41 (19), 39 (16); HR-MS (EI) ($C_{13}H_{18}O_3$) *calcd.* 222.1256, *found* 222.1257.

***N*-Allyl-*N*-(1,1-dideutero-but-2-ynyl)-4-methyl-benzenesulfonamide (62):** Colorless syrup; R_f 0.38 (hexanes/ethyl acetate, 4:1); ^1H NMR (300.1 MHz, CD_2Cl_2) δ 7.72 (AA'XX', 2H), 7.33 (AA'XX', 2H), 5.74 (ddt, 1H, J = 17.1, 10.0, 6.3 Hz), 5.27 (dd(t), 1H, J = 17.1, 1.5, 1.4 Hz), 5.21 (dd(t), 1H, J = 10.0, 1.3, 1.2 Hz), 3.79 (dt, 2H, J = 6.3, 1.2 Hz), 2.42 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 143.9, 136.6, 132.8, 129.6, 128.1, 119.4, 82.0, 71.8, 49.3, 36.3 (quint), 21.5, 3.2; IR 3083, 3027, 2982, 2920, 2857, 2252, 2200, 2138, 2092, 1644, 1598, 1495, 1443, 1418, 1404, 1341, 1306, 1289, 1166, 1094, 1070, 1049, 1013, 992, 934, 876, 816, 801, 701, 662, 627, 569, 544 cm^{-1}; MS (EI) *m/z* (rel. intensity) 266 (1), 265 ([M^+] 6), 264 (2), 250 (6), 186 (16), 156 (5), 155 (56), 139 (13), 111 (8), 110 (100), 109 (14), 108 (11), 107 (7), 92 (14), 91 (98), 83 (15), 82 (13), 81 (10), 80 (24), 79 (10), 70 (10), 69 (10), 65 (28), 56 (6), 55 (31), 54 (7), 53 (7), 44 (25), 43 (6), 42 (8), 41 (22), 39 (16); HR-MS (EI) ($C_{14}H_{15}D_2NO_2S$) *calcd.* 265.1106, *found* 265.1104.

Deuterium Shift: 4,5-Dideutero-6-methyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (63) and **4-Deutero-6-methyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (64):** $PtCl_2$

(10 mg, 0.038 mmol) is added to a solution of **62** (200 mg, 0.754 mmol) in toluene (15 ml), and the resulting mixture is stirred at 80 °C for 48 h. After evaporation of the solvent the residue is purified by flash chromatography on silica (hexanes/ethyl acetate, 20:1) affording a mixture of the title compounds as a colorless oil (121 mg, 61 %). The product consists of a mixture of **63**:**64** ≈ 3:1. R_f 0.42 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (600.2 MHz, CD_2Cl_2) δ 7.63 (AA'XX', 2H), 7.34 (AA'XX', 2H), 5.24 (br. s, 0.24H) [**64**], 3.81 (dd, 1H, J = 11.5, 1.8 Hz), 3.02 (dd, 1H, J = 11.5, 2.9 Hz), 2.42 (s, 3H), 1.28 (dddd, 1H, J = 8.4, 4.7, 2.9, 1.7 Hz), 1.09 (s, 3H), 0.59 (dd(d), 1H, J = 8.4, 4.3, 0.6 Hz), 0.42 (dd, 1H, J = 4.7, 4.3 Hz); ^{2}H NMR (600.2 MHz, CD_2Cl_2) δ 6.31 (br. s), 5.24 (overlapped by solvent peak); ^{13}C NMR (150.9 MHz, CD_2Cl_2) δ 144.3, 135.2, 130.1, 127.3, 120.3 (t) [**64**], 120.2 (t) [**63**], 116.7 [**64**], 116.4 (t) [**63**], 41.4, 26.0 [**64**], 26.0 [**63**], 23.2 [**64**], 23.2 [**63**], 21.6, 21.1, 13.0 [**64**], 12.9 [**63**]; IR 3068, 3000, 2960, 2926, 2869, 2305, 2271, 1621, 1596, 1492, 1469, 1448, 1398, 1353, 1304, 1290, 1273, 1165, 1118, 1090, 1024, 1002, 971, 931, 869, 855, 816, 771, 730, 711, 693, 662, 623, 601, 570, 549, 536 cm^{-1}; HR-MS (EI) ([**63**], $C_{14}H_{15}D_2NO_2S$) *calcd.* 265.1106, *found* 265.1104.

Labeling Experiment in the Presence of D_2O. 5-Deutero-6-methyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (65) and **6-Methyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene (32):** To a solution of **31** (100 mg, 0.38 mmol) in toluene (10 ml) are added $PtCl_2$ (5 mg, 0.019 mmol) and D_2O (7.6 mg, 0.38 mmol). The resulting mixture is stirred at 80 °C for 48 h. The solvent is evaporated, and the residue is purified by flash chromatography on silica (hexanes/ethyl acetate, 20:1) affording a mixture of the title compounds as a colorless oil (35 mg, 35 %). The product consists of a mixture of **65**:**32** ≈ 1:3. R_f 0.42 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (600.2 MHz, CD_2Cl_2) δ 7.63 (AA'XX', 2H), 7.34 (AA'XX', 2H), 6.27 (dd, 0.75H, J = 8.2, 0.9 Hz) [**32**], 6.27 (br. s, 0.25H) [**65**], 5.24 (dd, 0.75H, J = 8.2, 0.8 Hz) [**32**], 3.81 (d, 1H, J = 11.5 Hz), 3.01 (dd, 1H, J = 11.5, 2.9 Hz), 2.42 (s, 3H), 1.28 (dddd, 1H, J = 8.4, 4.7, 2.9, 1.7 Hz), 1.09 (s, 3H), 0.59 (dd(d), 1H, J = 8.3, 4.3, 0.6 Hz), 0.43 (dd, 1H, J = 4.6, 4.3 Hz); ^{2}H NMR (600.2 MHz, CD_2Cl_2) δ 5.24 (overlapped by solvent peak); ^{13}C NMR (150.9 MHz, CD_2Cl_2) δ 144.3, 135.2, 130.1, 127.3, 120.5 [**32**], 120.5 [**65**], 116.9 [**32**], 116.6 (t) [**65**], 41.4, 26.0 [**32**], 26.0 [**65**], 23.2 [**32**], 23.2 [**65**], 21.6, 21.0, 13.0 [**32**], 12.9 [**65**].

2-(Dihydro-furan-2-(*E*)-ylidene)-4-methyl-pent-4-enoic acid methyl ester (70): Colorless syrup;

R_f 0.33 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 4.63 (m, 1H), 4.58 (m, 1H), 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 (quint, 2H, J = 7.4 Hz), 1.71 (d, 3H, J = 0.6 Hz); ^{13}C NMR (75.5 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, 1011, 983, 937, 885, 855, 825, 797, 773, 725 cm^{-1}; MS (EI) *m/z* (rel. intensity) 197 (12), 196 ([M$^+$] 100), 181 (5), 178 (2), 165 (36), 164 (37), 163 (9), 155 (9), 137 (14), 136 (16), 123 (44), 122 (15), 121 (12), 119 (13), 113 (11), 109 (12), 108 (15), 101 (45), 96 (9), 95 (31), 94 (10), 93 (12), 91 (11), 79 (11), 69 (13), 67 (22), 66 (9), 65 (10), 59 (21), 55 (21), 53 (9), 42 (14), 41 (32), 39 (25), 29 (10), 27 (10); HR-MS (EI) ($C_{11}H_{16}O_3$) *calcd.* 196.1099, *found* 196.1099; Anal. *calcd.* for $C_{11}H_{16}O_3$ (196.25): C, 67.32; H, 8.22; *found*: C, 67.36; H, 8.26.

2-(Dihydro-furan-2-(*E*)-ylidene)-3-phenyl-pent-4-enoic acid methyl ester (72): Colorless syrup; R_f 0.30 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 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 (tt, 2H, J = 7.5, 7.2 Hz); ^{13}C NMR (75.5 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 ([M$^+$] 100), 243 (4), 230 (8), 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) ($C_{16}H_{18}O_3$) *calcd.* 258.1256, *found* 258.1255; Anal. *calcd.* for $C_{16}H_{18}O_3$ (258.32): C, 74.40; H, 7.02; *found*: C, 74.34; H, 7.10.

2-(Dihydro-furan-2-(*E*)-ylidene)-5-phenyl-pent-4-(*E*)-enoic acid methyl ester (73): The compound is isolated as mixture with isomer **72** (**72**:**73** = 7.1:1); colorless syrup; R_f 0.28 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 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 (tt, 2H, J = 7.5, 7.2 Hz); ^{13}C NMR (75.5 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)

259 (3), 258 ([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).

2-(Dihydro-furan-2-(*E*)-ylidene)-hepta-4,6-dienoic acid methyl ester (75): Mixture of isomers rf. to the 4,6-diene-structure (*E*:*Z* = 7:1); colorless syrup; R_f 0.30 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ [(*E*)-isomer] 6.29 (dt, 1H, *J* = 17.0, 10.3 Hz), 6.03 (m, 1H), 5.72 (ddd(d), 1H, *J* = 14.9, 6.8, 6.4, 0.6 Hz), 5.06 (m, 1H), 4.92 (m, 1H), 4.22 (t, 2H, *J* = 7.0 Hz), 3.66 (s, 3H), 3.06 (m, 4H), 2.07 (tt, 2H, *J* = 7.6, 7.0 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* = 7.0 Hz), 3.65 (s, 3H), 3.18 (m, 2H), 3.04 (m, 2H), 2.07 (tt, 2H, *J* = 7.6, 7.0 Hz); ^{13}C NMR (75.5 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 ([M^+] 90), 193 (5), 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) ($C_{12}H_{16}O_3$) *calcd.* 208.1099, *found* 208.1097; Anal. *calcd.* for $C_{12}H_{16}O_3$ (208.26): C, 69.21; H, 7.74; *found*: C, 69.18; H, 7.68.

2-(3*H*-Isobenzofuran-1-ylidene)-pent-4-enoic acid methyl ester (77): (*E*)-isomer: Colorless syrup; R_f 0.31 (hexanes/ethyl acetate, 10:1); ^{1}H NMR (300.1 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 (dd(t), 1H, *J* = 17.1, 1.9, 1.7 Hz), 4.95 (dd(t), 1H, *J* = 10.1, 1.9, 1.5 Hz), 3.77 (s, 3H), 3.29 (dt, 2H, *J* = 6.1, 1.5 Hz); ^{13}C NMR (75.5 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 ([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), 77 (9), 63 (9), 41 (11), 39 (9); HR-MS (EI) ($C_{14}H_{14}O_3$) *calcd.* 230.0943, *found* 230.0942; Anal. *calcd.* for $C_{14}H_{14}O_3$ (230.26): C, 73.03; H,

6.13; *found*: C, 73.11; H, 6.05. **(Z)-isomer:** Colorless syrup; R_f 0.34 (hexanes/ethyl acetate, 10:1); ^{1}H NMR (300.1 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 (dd(t), 1H, J = 17.1, 1.8, 1.6 Hz), 5.10 (dd(t), 1H, J = 10.1, 1.6, 1.5 Hz), 5.02 (s, 2H), 3.83 (s, 3H), 3.36 (dt, 2H, J = 6.5, 1.5 Hz); ^{13}C NMR (75.5 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, 1202, 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), 90 (5), 76 (6), 41 (8); HR-MS (EI) ($C_{14}H_{14}O_3$) *calcd.* 230.0943, *found* 230.0943; Anal. *calcd.* for $C_{14}H_{14}O_3$ (230.26): C, 73.03; H, 6.13; *found*: C, 72.86; H, 6.07.

2-(3*H*-Isobenzofuran-1-ylidene)-4-methyl-pent-4-enoic acid methyl ester (79): (*E*)-isomer: Colorless syrup; R_f 0.34 (hexanes/ethyl acetate, 10:1); ^{1}H NMR (300.1 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 (75.5 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), 77 (7), 63 (7), 39 (9); HR-MS (EI) ($C_{15}H_{16}O_3$) *calcd.* 244.1099, *found* 244.1101; Anal. *calcd.* for $C_{15}H_{16}O_3$ (244.29): C, 73.75; H, 6.60; *found*: C, 73.68; H, 6.54. **(Z)-isomer:** The compound is isolated as mixture with the (*E*)-isomer (*E*:Z = 10.3:1): R_f 0.36 (hexanes/ethyl acetate, 10:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ [characteristic data, resolved signals] 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 (75.5 MHz, CD_2Cl_2) δ [characteristic data, resolved signals] 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; MS (EI) *m/z* (rel. intensity) 245 (15), 244 ([M$^+$] 100), 230 (9), 229 (52), 214 (13), 213 (60), 211 (14), 185 (17), 184 (14), 183 (18), 169 (15), 162 (45), 161 (24), 157

(13), 155 (14), 143 (24), 142 (23), 141 (26), 133 (37), 131 (11), 129 (23), 128 (15), 118 (17), 115 (40), 103 (12), 102 (20), 90 (13), 89 (12), 77 (16), 76 (13), 55 (16), 39 (14), 29 (15).

2-(Hexahydro-benzofuran-2-(*E*)-ylidene)-pent-4-enoic acid methyl ester (81): Colorless syrup; R_f 0.31 (hexanes/ethyl acetate, 10:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 5.83 (ddt, 1H, J = 17.1, 10.1, 6.1 Hz), 4.98 (dm, 1H, J = 17.1 Hz), 4.88 (dm, 1H, J = 9.9 Hz), 3.64 (s, 3H), 3.51 (td, 1H, J = 10.9, 3.8 Hz), 3.40 (dd, 1H, J = 17.1, 6.5 Hz), 3.03 (d, 2H, J = 6.0 Hz), 2.38 (dd, 1H, J = 17.1, 12.6 Hz), 2.22 (m, 1H), 2.04-1.87 (m, 2H), 1.76 (m, 1H), 1.63-1.17 (m, 5H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 170.9, 169.2, 137.4, 113.9, 101.6, 87.0, 51.0, 45.2, 37.7, 30.9, 30.4, 28.8, 25.8, 24.5; IR 3076, 2977, 2939, 2861, 1705, 1639, 1436, 1390, 1356, 1311, 1253, 1217, 1202, 1187, 1171, 1135, 1115, 1100, 1078, 1056, 1044, 1018, 995, 949, 909, 875, 835, 806, 778, 753, 693, 619, 576 cm^{-1}; MS (EI) *m/z* (rel. intensity) 237 (15), 236 ([M$^+$] 95), 205 (19), 204 (28), 177 (22), 176 (11), 175 (13), 167 (21), 154 (22), 141 (23), 140 (18), 135 (12), 123 (20), 122 (41), 119 (10), 113 (12), 109 (70), 108 (100), 98 (12), 95 (20), 91 (16), 82 (15), 81 (74), 80 (28), 79 (26), 77 (13), 67 (39), 59 (18), 55 (28), 54 (18), 53 (34), 43 (12), 41 (62), 39 (22), 29 (11), 27 (16); HR-MS (EI) ($C_{14}H_{20}O_3$) *calcd.* 236.1412, *found* 236.1413; Anal. *calcd.* for $C_{14}H_{20}O_3$ (236.31): C, 71.61; H, 8.53; *found*: C, 71.25; H, 8.41.

2-(Dihydro-furan-2-(Z)-ylidene)-pent-4-enenitrile (83): Colorless syrup; R_f 0.41 (hexanes/ethyl acetate, 1:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 5.80 (ddt, 1H, J = 17.0, 10.0, 6.2 Hz), 5.13 (d(q), 1H, J = 17.0, 1.7 Hz), 5.09 (d(q), 1H, J = 11.0, 1.7 Hz), 4.32 (t, 2H, J = 6.9 Hz), 2.80 (d(tt), 2H, J = 6.2, 1.5, 0.9 Hz), 2.66 (dd(t), 2H, J = 7.7, 7.2 Hz), 2.13 (dd(d), 1H, J = 7.3, 6.5 Hz), 2.09 (dd(d), 1H, J = 7.6, 6.9 Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 173.0, 134.6, 118.7, 116.3, 78.1, 73.6, 33.3, 28.9, 24.3; IR 3081, 2980, 2904, 2840, 2204, 1653, 1481, 1456, 1429, 1377, 1319, 1267, 1212, 1164, 1119, 1041, 988, 959, 930, 882, 850, 774, 724, 634 cm^{-1}; MS (EI) *m/z* (rel. intensity) 150 (9), 149 ([M$^+$] 77), 148 (15), 122 (21), 121 (88), 120 (13), 108 (27), 107 (100), 106 (25), 93 (13), 80 (61), 79 (79), 78 (15), 66 (8), 53 (17), 52 (70), 51 (16), 42 (42), 41 (33), 40 (11), 39 (33), 27 (19); HR-MS (EI) ($C_9H_{11}NO$) *calcd.* 149.0841, *found* 149.0843; Anal. *calcd.* for $C_9H_{11}NO$ (149.19): C, 72.46; H, 7.43; N, 9.39; *found*: C, 72.40; H, 7.48; N, 9.40.

2-(Dihydro-furan-2-(Z)-ylidene)-4-methyl-pent-4-enenitrile (85): Colorless syrup; R_f 0.42 (hexanes/ethyl acetate, 1:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 4.82 (m, 1H), 4.79 (m, 1H), 4.33 (t,

2H, J = 6.9 Hz), 2.75 (br. s, 2H), 2.66 (dd(t), 2H, J = 7.9, 7.3 Hz), 2.13 (dd(d), 1H, J = 7.9, 7.0 Hz), 2.08 (dd(d), 1H, J = 7.6, 6.9 Hz), 1.74 (m, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 173.4, 142.5, 118.8, 111.8, 78.2, 73.5, 37.5, 28.9, 24.3, 21.9; IR 3078, 2973, 2938, 2906, 2734, 2203, 1650, 1481, 1454, 1429, 1376, 1318, 1261, 1231, 1199, 1159, 1059, 1033, 973, 952, 929, 895, 855, 820, 778, 738, 667, 632, 596, 511 cm^{-1}; MS (EI) *m/z* (rel. intensity) 164 (12), 163 ([M$^+$] 100), 162 (19), 148 (75), 135 (42), 134 (14), 122 (53), 121 (22), 120 (23), 107 (10), 106 (68), 94 (14), 93 (22), 92 (11), 80 (95), 78 (9), 66 (23), 65 (13), 55 (18), 53 (10), 52 (28), 42 (26), 41 (26), 40 (10), 39 (35), 29 (9), 27 (14); HR-MS (EI) ($C_{10}H_{13}NO$) *calcd.* 163.0997, *found* 163.0999; Anal. *calcd.* for $C_{10}H_{13}NO$ (163.22): C, 73.58; H, 8.03; N, 8.58; *found*: C, 73.64; H, 7.96; N, 8.56.

Cyclohex-2-enyl-(dihydro-furan-2-(*Z*)-ylidene)-acetonitrile (87): mp 66-68 °C; R_f 0.17 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ 5.81 (dm, 1H, J = 10.0 Hz), 5.45 (dm, 1H, J = 10.0 Hz), 4.29 (t, 2H, J = 6.9 Hz), 2.81 (m, 1H), 2.67 (t, 2H, J = 7.9 Hz), 2.10 (quint, 2H, J = 7.4 Hz), 2.05-1.88 (m, 2H), 1.88-1.72 (m, 2H), 1.65-1.46 (m, 2H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 171.0, 129.8, 128.0, 117.8, 85.4, 72.5, 35.7, 28.9, 28.4, 24.4, 23.9, 21.4; IR 3020, 2987, 2931, 2859, 2837, 2202, 1653, 1643, 1447, 1431, 1375, 1318, 1284, 1253, 1223, 1169, 1138, 1052, 1036, 986, 948, 931, 872, 855, 821, 771, 746, 723, 650, 633 cm^{-1}; MS (EI) *m/z* (rel. intensity) 191 (1), 190 (14), 189 ([M$^+$] 100), 188 (19), 174 (27), 162 (11), 161 (88), 160 (11), 148 (11), 147 (10), 146 (13), 133 (38), 132 (22), 120 (10), 119 (30), 118 (9), 110 (9), 105 (32), 104 (13), 91 (32), 81 (11), 80 (16), 79 (17), 78 (10), 77 (13), 65 (11), 64 (10), 53 (9), 51 (9), 42 (27), 41 (20), 40 (20), 39 (18), 27 (10); HR-MS (EI) ($C_{12}H_{15}NO$) *calcd.* 189.1154, *found* 189.1153; Anal. *calcd.* for $C_{12}H_{15}NO$ (189.26): C, 76.16; H, 7.99; N, 7.40; *found*: C, 76.07; H, 8.06; N, 7.47.

2-(Dihydro-furan-2-(Z)-ylidene)-hepta-4,6-dienenitrile (89): Mixture of isomers rf. to the 4,6-diene-structure (*E*:*Z* = 12.5:1); colorless syrup; R_f 0.18 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ [(*E*)-isomer] 6.35 (dt, 1H, J = 17.0, 10.2 Hz), 6.14 (m, 1H), 5.68 (m, 1H), 5.17 (m, 1H), 5.04 (m, 1H), 4.33 (t, 2H, J = 6.9 Hz), 2.84 (br. d, 2H, J = 6.6 Hz), 2.66 (t(d), 2H, J = 7.8 Hz), 2.11 (tt, 2H, J = 7.7, 7.0 Hz); δ [(*Z*)-isomer] 6.66 (m, 1H), 5.88 (ddd, 1H, J = 16.9, 10.5, 6.5 Hz), 5.43 (m, 1H), 5.27 (m, 1H), 5.14 (m, 1H), 4.32 (t, 2H, J = 6.9 Hz), 2.95 (br. d, 2H, J = 7.1 Hz), 2.66 (t(d), 2H, J = 7.8 Hz), 2.11 (tt, 2H, J = 7.7, 7.0 Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ [(*E*)-isomer] 173.0, 136.8, 132.6, 130.4, 118.7, 116.6, 78.2, 73.6, 32.1, 28.9, 24.2; δ [(Z)-isomer, resolved

signals] 172.8, 131.7, 131.0, 127.8, 29.0, 27.4; IR 3085, 2990, 2969, 2904, 2741, 2203, 1689, 1650, 1602, 1480, 1455, 1428, 1377, 1318, 1258, 1164, 1040, 1008, 990, 973, 927, 858, 801, 768, 692, 635, 602 cm^{-1}; MS (EI) *m/z* (rel. intensity) 176 (13), 175 ([M^+] 100), 174 (21), 160 (12), 148 (9), 147 (15), 146 (15), 134 (11), 133 (20), 132 (24), 119 (16), 118 (18), 106 (23), 105 (44), 104 (43), 93 (9), 91 (11), 80 (28), 79 (14), 78 (34), 77 (25), 67 (18), 66 (11), 65 (19), 53 (10), 52 (24), 51 (17), 42 (38), 41 (38), 39 (37), 27 (21); HR-MS (EI) ($C_{11}H_{13}NO$) *calcd.* 175.0997, *found* 175.0997; Anal. *Calcd.* for $C_{11}H_{13}NO$ (175.23): C, 75.40; H, 7.48; N, 7.99; *found*: C, 75.31; H, 7.42; N, 8.09.

2-(3*H*-Isobenzofuran-1-ylidene)-pent-4-enenitrile (91): (Z)-isomer: mp 81 °C; R_f 0.18 (hexanes/ethyl acetate, 4:1); ^1H NMR (300.1 MHz, CD_2Cl_2) δ 7.69 (m, 1H), 7.55-7.42 (m, 3H), 5.97 (ddt, 1H, J = 17.0, 10.1, 5.7 Hz), 5.48 (s, 2H), 5.26 (dd(t), 1H, J = 17.0, 1.6, 1.6 Hz), 5.17 (dd(t), 1H, J = 10.1, 1.5, 1.5 Hz), 3.30 (m, 2H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 168.4, 143.7, 133.8, 131.5, 131.0, 129.0, 125.0, 122.1, 119.7, 116.9, 79.7, 75.3, 31.3; IR 3072, 3002, 2927, 2874, 2198, 1633, 1469, 1457, 1421, 1375, 1298, 1233, 1210, 1177, 1131, 1107, 1079, 999, 986, 936, 919, 847, 769, 752, 722, 656, 631, 591, 559 cm^{-1}; MS (EI) *m/z* (rel. intensity) 199 (1), 198 (15), 197 ([M^+] 100), 196 (54), 182 (12), 170 (28), 169 (13), 168 (22), 167 (8), 157 (8), 154 (12), 142 (10), 141 (13), 140 (10), 131 (8), 128 (8), 127 (7), 118 (34), 116 (11), 115 (35), 91 (8), 90 (39), 89 (25), 63 (12), 51 (8), 39 (13); HR-MS (EI) ($C_{13}H_{11}NO$) *calcd.* 197.0841, *found* 197.0841; Anal. *calcd.* for $C_{13}H_{11}NO$ (197.24): C, 79.17; H, 5.62; N, 7.10; *found*: C, 79.05; H, 5.59; N, 6.99. **(*E*)-isomer:** mp 66-68 °C; R_f 0.33 (hexanes/ethyl acetate, 4:1); ^1H NMR (400.1 MHz, CD_2Cl_2) δ 8.32 (m, 1H), 7.55-7.43 (m, 3H), 5.91 (ddt, 1H, J = 17.0, 10.0, 6.5 Hz), 5.44 (br. s, 2H), 5.22 (dd(t), 1H, J = 17.0, 1.7, 1.6 Hz), 5.13 (dd(t), 1H, J = 10.0, 1.6, 1.4 Hz), 3.14 (m, 2H); ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 167.4, 142.7, 134.5, 131.4, 131.0, 129.0, 124.3, 121.6, 120.3, 116.7, 79.7, 75.5, 32.1; IR 3085, 3004, 2932, 2874, 2855, 2197, 1641, 1632, 1514, 1469, 1455, 1434, 1406, 1373, 1300, 1270, 1204, 1159, 1004, 986, 950, 917, 869, 850, 772, 731, 722, 652, 614, 555, 543 cm^{-1}; MS (EI) *m/z* (rel. intensity) 199 (1), 198 (14), 197 ([M^+] 100), 196 (46), 182 (12), 170 (23), 169 (12), 168 (19), 167 (7), 157 (7), 154 (11), 142 (8), 141 (11), 131 (7), 128 (7), 127 (7), 118 (29), 116 (8), 115 (27), 90 (31), 89 (21), 63 (10), 39 (10); HR-MS (EI) ($C_{13}H_{11}NO$) *calcd.* 197.0841, *found* 197.0844; Anal. *calcd.* for $C_{13}H_{11}NO$ (197.24): C, 79.17; H, 5.62; N, 7.10; *found*: C, 79.06; H, 5.58; N, 6.98.

Cyclohept-2-enyl-(dihydro-furan-2-(*E*)-ylidene)-acetic acid methyl ester (93): Colorless syrup;

R_f 0.29 (hexanes/ethyl acetate, 4:1); ^{1}H NMR (400.1 MHz, CD_2Cl_2) δ 5.67(m, 1H), 5.64 (m, 1H), 4.20 (t(d), 2H, J = 7.0, 0.4 Hz), 3.64 (s, 3H), 3.63 (m, 1H), 3.01 (m, 2H), 2.18 (m, 1H), 2.12 (d(m), 1H, J = 11.5 Hz), 2.06 ((dd), 1H), 2.02 ([dd(d)], 1H), 1.97 (d(m), 1H, J = 13.6 Hz), 1.87 (dddd, 1H, J = 13.0, 12.3, 11.0, 3.0 Hz), 1.72 ([dt(ddd)], 1H, J = 13.2, 6.0, 3.2, 2.8, 1.0 Hz), 1.55 (d(m), 1H, J = 13.6 Hz), 1.47 (d(m), 1H, J = 13.2 Hz), 1.23 (d(tt), 1H, J = 13.6, 11.2, 2.8 Hz); ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 170.5, 169.4, 139.1, 129.5, 108.5, 72.0, 50.8, 39.2, 34.0, 32.5, 31.8, 29.3, 27.5, 24.7; IR 3019, 2984, 2917, 2850, 1700, 1624, 1434, 1373, 1326, 1277, 1258, 1180, 1122, 1105, 1065, 1044, 1009, 982, 936, 906, 880, 777, 715, 683 cm^{-1}; MS (EI) *m/z* (rel. intensity) 237 (12), 236 ([M$^+$] 71), 208 (13), 205 (17), 204 (28), 192 (29), 177 (31), 176 (24), 175 (12), 168 (15), 163 (17), 162 (26), 156 (10), 155 (100), 149 (15), 148 (16), 147 (17), 143 (22), 135 (15), 134 (12), 133 (18), 123 (35), 117 (11), 111 (20), 105 (14), 101 (22), 97 (14), 95 (14), 94 (13), 93 (12), 91 (27), 79 (31), 77 (23), 71 (13), 69 (13), 67 (15), 65 (17), 59 (29), 55 (20), 53 (13), 43 (13), 42 (15), 41 (38), 39 (18), 27 (10); HR-MS (EI) ($C_{14}H_{20}O_3$) *calcd.* 236.1412, *found* 236.1407; Anal. *calcd.* for $C_{14}H_{20}O_3$ (236.31): C, 71.16; H, 8.53; *found*: C, 71.17; H, 8.46.

X-Ray Structure of Compound **29**

Responsible Scientist for X-Ray Structure Analysis: Dr. C. W. Lehmann

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Figure 1. ORTEP diagram of the molecular structure of compound **29**. Anisotropic displacement parameter ellipsoids are drawn at 50% probability, hydrogen atoms are omitted for clarity.

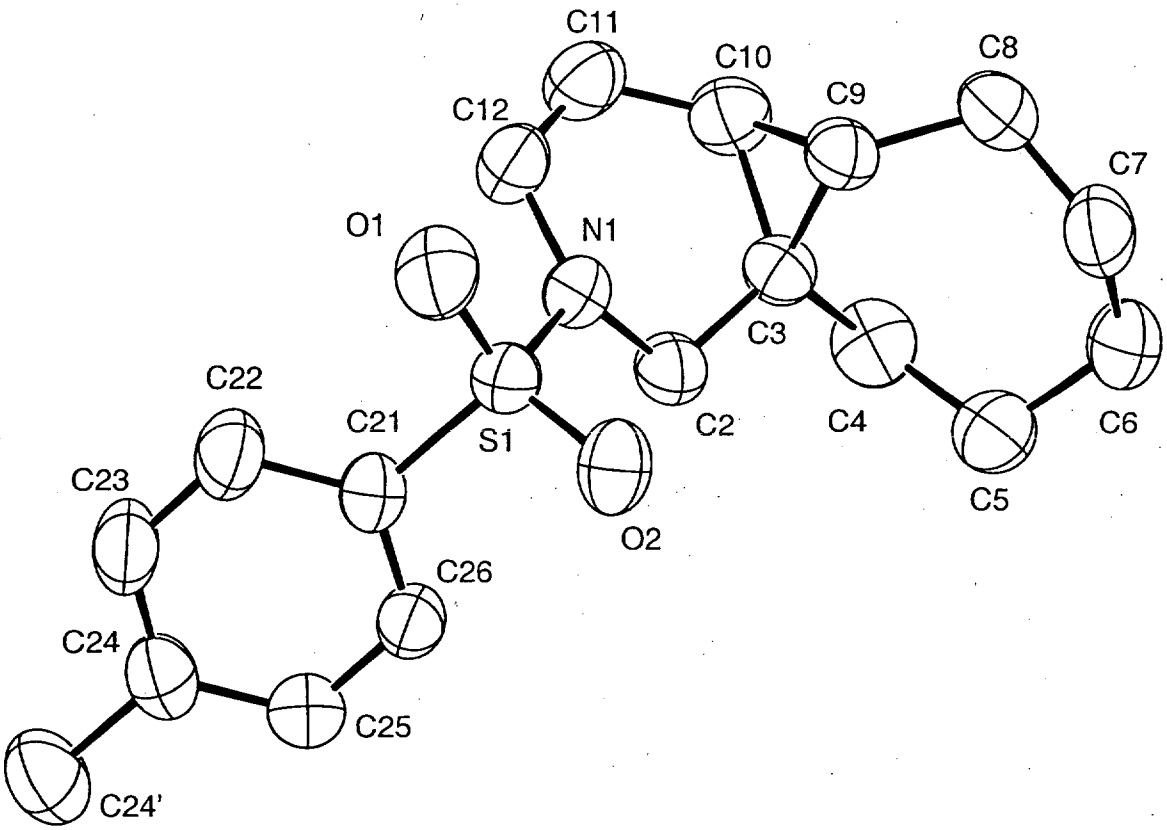

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{18} H_{23} N O_2 S$	
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	$\alpha = 90°$.
	b = 15.1637(5) Å	$\beta = 90°$.
	c = 15.7994(9) Å	$\gamma = 90°$.
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	$-16 \le h \le 17$, $0 \le k \le 18$, $0 \le l \le 19$	
Reflections collected	6553	
Independent reflections	3467 [$R_{int} = 0.0293$]	
Reflections with $I>2\sigma(I)$	2523	
Completeness to $\theta = 74.79°$	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 [$I>2\sigma(I)$]	$R_1 = 0.0371$	$wR^2 = 0.0999$
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 $e \cdot Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^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 ($Å^2$).

	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 ($Å^2$).
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	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)