

^1H and ^{13}C NMR data with assignment and full lists of IR and MS data for all new compounds.

1,5-Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]heptane (8)

^1H NMR (400 MHz) δ 1.13 (s, 18H, *t*-Bu), 1.42 (s, 12H, Me), 1.95 (s, 2H, CH_2); ^{13}C NMR (100.6 MHz) δ 28.7 (CH_3), 28.9 (CH_3), 40.6 (C), 45.4 (C), 66.7 (CH_2), 68.2 (C); MS m/z (rel intensity) 300 (M^+ , 29), 285 (3), 268 (1), 243 (1), 229 (96), 199 (100), 187 (13), 173 (10), 153 (11), 143 (65), 125 (14), 101 (25), 57 (46).

1,5-Di-*tert*-butyl-2,2,4,4-tetramethylcyclopentene (9)

^1H NMR (400 MHz) δ 1.25 (s, 12H, Me), 1.37 (s, 18H, *t*-Bu), 1.50 (s, 2H, CH_2); ^{13}C NMR (100.6 MHz) δ 32.4 (CH_3), 35.0 (CH_3), 35.6 (C), 46.7 (C), 64.5 (CH_2), 149.6 (C); MS (GC) m/z (rel intensity) 236 (M^+ , 44), 221 (18), 179 (61), 165 (44), 137 (26), 123 (100), 109 (49), 57 (84).

1,6-Di-*t*-butyl-2,2,5,5-tetramethylcyclohexene (10)

^1H NMR (400 MHz) δ 1.28 (s, 12H, Me), 1.37 (s, 18H, *t*-Bu), 1.44 (s, 4H, CH_2); ^{13}C NMR (100.6 MHz) δ 34.6 (CH_3), 35.4 (CH_3), 40.0 (CH_2), 43.1 (C), 43.4 (C), 153.7 (C); IR (KBr, cm^{-1}) 2922, 1456, 1397, 1384, 1362, 1188; MS m/z (rel intensity) 250 (M^+ , 24), 193 (6), 151 (6), 137 (100), 123 (18), 109 (18), 95 (15), 81 (12), 69 (13), 57 (65).

Diethyl 2,2,4,4-tetramethylglutarate (11)

^1H NMR (400 MHz) δ 1.12 (s, 12H, Me), 1.26 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.07 (s, 2H, CH_2), 4.11 (q, $J = 7.1$ Hz, 4H, CH_2CH_3); ^{13}C NMR (100.6 MHz) δ 14.1 (CH_3), 26.0 (CH_3), 41.6 (C), 49.2 (CH_2), 60.4 (CH_2), 178.3 ($\text{C}=\text{O}$); IR (neat, cm^{-1}) 2980, 1732 ($\text{C}=\text{O}$), 1480, 1456, 1394, 1368, 1336, 1282, 1198, 1150, 1030, 944, 860, 820, 766.

2,2,4,4,6,6,8,8-Octamethylnonane-3,7-dione (12)

^1H NMR (400 MHz) δ 1.21 (s, 12H, Me), 1.27 (s, 18H, *t*-Bu), 2.19 (s, 2H, CH₂); ^{13}C NMR (100.6 MHz) δ 28.3 (CH₃), 28.9 (CH₃), 46.3 (C), 49.2 (C), 51.0 (CH₂), 218.5 (C=O); IR (neat, cm⁻¹) 2968, 1684 (C=O), 1484, 1390, 1368, 1046, 976.

Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]heptane 6-*endo*, 7-*endo*-dioxide (13)

^1H NMR (400 MHz) δ 1.45 (s, 18H, *t*-Bu), 1.65 (s, 12H, Me), 2.52 (s, 2H, CH₂); ^{13}C NMR (100.6 MHz) δ 30.8 (CH₃), 32.4 (CH₃), 40.8 (C), 46.2 (C), 57.0 (CH₂), 97.8 (C); IR (KBr, cm⁻¹) 2964, 2932, 1482, 1390, 1374, 1208, 1064 (S=O); MS *m/z* (rel intensity) 332 (M⁺, 4), 316 (1), 268 (6), 211 (18), 183 (24), 155 (26), 112 (39), 97 (50), 57 (100).

Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]heptane 6-*endo*-oxide (14)

^1H NMR (400 MHz) δ 1.05 (d, *J* = 14.4 Hz, 1H, CH₂), 1.30 (s, 18H, *t*-Bu), 1.39 (s, 6H, Me), 1.54 (s, 6H, Me), 3.27 (d, *J* = 14.5 Hz, 1H, CH₂); ^{13}C NMR (100.6 MHz) δ 30.8 (CH₃), 31.9 (CH₃), 40.9 (C), 42.4 (C), 57.8 (CH₂), 89.5 (C); IR (KBr, cm⁻¹) 2968, 1478, 1460, 1402, 1386, 1370, 1218, 1080 (S=O); MS *m/z* (rel intensity) 316 (M⁺, 23), 300 (1), 268 (75), 253 (22), 211 (96), 197 (59), 183 (58), 155 (44), 153 (50), 141 (27), 127 (29), 109 (33), 97 (79), 57 (100).

1,5-Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]heptane 6-*endo*, 7-*exo*-dioxide (15)

^1H NMR (400 MHz) δ 1.35 (s, 6H, Me), 1.53 (s, 18H, *t*-Bu), 1.59 (d, *J* = 16 Hz, 1H, CH₂), 1.72 (s, 6H, Me), 1.85 (d, *J* = 16 Hz, 1H, CH₂); ^{13}C NMR (100.6 MHz) δ 28.6 (CH₃), 31.5 (CH₃), 32.0 (CH₃), 42.0 (C), 42.9 (C), 55.6 (CH₂), 92.6 (C); IR (KBr, cm⁻¹) 3004, 1964, 2928, 1478, 1404, 1394, 1374, 1364, 1212, 1086, 1072; MS *m/z*

(rel intensity) 332 (M^+ , 4), 316 (1), 268 (4), 211 (10), 183 (13), 155 (12), 155 (12), 112 (24), 97 (35), 57 (100).

2,2,4,4,6,6,8,8-Octamethylnonane-3,7-dithione S,S' -dioxide (16)

1H NMR (400 MHz) δ 1.47 (s, 12H, Me), 1.56 (s, 18H, *t*-Bu), 2.31 (s, 2H, CH_2); ^{13}C NMR (100.6 MHz) δ 29.9 (CH_3), 31.2 (CH_3), 43.8 (C), 45.3 (C), 47.9 (CH_2), 216.7 (C); IR (KBr, cm^{-1}) 2964, 2920, 1740, 1488, 1466, 1392, 1372, 1362, 1252, 1216, 1138, 1120, 1092, 1052, 976; MS m/z 332 (M^+ , trace).

2,2,4,4,6,6,8,8-Octamethyl-7-thioxononan-3-one (17)

1H NMR (400 MHz) δ 1.22 (s, 6H, Me), 1.26 (s, 9H, *t*-Bu), 1.39 (s, 6H, Me), 1.50 (s, 9H, *t*-Bu), 2.54 (s, 2H, CH_2); ^{13}C NMR (100.6 MHz) δ 29.03 (CH_3), 29.09 (CH_3), 32.6 (CH_3), 33.7 (CH_3), 46.4 (C), 50.1 (C), 53.4 (CH_2), 54.3 (C), 57.7 (C), 218.7 (C), 279.0 (C); IR (neat, cm^{-1}) 2968, 1684, 1484, 1390, 1368, 1222, 1122, 1084, 1044, 976, 958, 940; MS m/z (rel intensity) 284 (M^+ , 5), 227 (6), 199 (7), 183 (48), 171 (35), 157 (13), 143 (19), 127 (18), 109 (21), 97 (34), 57 (100).

1,5-Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]heptane S' -endo- S,S,S' -trioxide (18)

1H NMR (400 MHz) δ 1.517 (s, 6H, Me), 1.522 (s, 18H, *t*-Bu), 1.69 (d, $J = 15.0$ Hz, 1H, CH_2), 1.80 (s, 6H, Me), 2.90 (d, $J = 15.0$ Hz, 1H, CH_2); ^{13}C NMR (100.6 MHz) δ 26.8 (CH_3), 31.5 (CH_3), 34.4 (CH_3), 40.8 (C), 44.4 (C), 59.8 (CH_2), 106.9 (C); IR (KBr, cm^{-1}) 2960, 1470, 1392, 1376, 1304, 1204, 1144, 1096, 568; MS m/z (rel intensity) 348 (M^+ , 3), 300 (6), 285 (25), 279 (13), 267 (13), 227 (23), 211 (14), 183 (30), 171 (25), 160 (43), 149 (29), 143 (15), 125 (27), 111 (42), 97 (23), 83 (31), 69 (57), 57 (100).

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-dithiabicyclo[4.1.1]octane (21):

^1H NMR (400 MHz) δ 1.09 (br s, 6H, Me), 1.21 (s, 18H, *t*-Bu), 1.34 (br s, 6H, Me), 2.88 (br s, 4H, CH₂). The two singlets at 1.09 and 1.34 coalesced at 305 K to give $\Delta G^\ddagger = 15.1 \text{ kcal mol}^{-1}$ for the ring inversion;²⁹ ^{13}C NMR (100.6 MHz) δ 24.3 (br s, CH₃), 29.1 (br s, CH₃), 29.7 (CH₃), 43.1 (C), 45.0 (C), 45.4 (CH₂), 59.3 (C); MS m/z (rel intensity) 314 (M⁺, 30), 299 (6), 257 (12), 243 (26), 203 (100), 187 (18), 173 (23), 101 (48), 69 (30), 57 (35).

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dione diimine (23)

^1H NMR (300 MHz) δ 1.24 (s, 12H, Me), 1.25 (s, 18H, *t*-Bu), 1.42 (s, 4H, CH₂), 9.43 (br s, 2H, NH); ^{13}C NMR (50 MHz) δ 28.2 (CH₃), 29.9 (CH₃), 37.3 (CH₂), 41.3 (C), 44.6 (C), 192.2 (C).

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dione dihydrazone (24)

^1H NMR (CD₂Cl₂, 400 MHz) δ 1.13 (s, 12H, Me), 1.36 (s, 18H, *t*-Bu), 1.48 (s, 4H, CH₂), 5.26 (br s, 4H, NH₂); ^{13}C NMR (CD₂Cl₂, 100.6 MHz) δ 28.5, 29.2, 36.65, 36.68, 44.0, 173.5; IR (KBr, cm⁻¹) 3388, 3320, 3244, 2956, 1490, 1478, 1456, 1370, 1050, 752, 640; MS m/z (rel intensity) 310 (M⁺, 16), 294 (34), 279 (56), 253 (12), 223 (41), 211 (29), 169 (47), 155 (48), 142 (50), 127 (22), 111 (24), 99 (58), 69 (42), 57 (100).

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dithione (25)

^1H NMR (300 MHz) δ 1.410 (s, 18H, *t*-Bu), 1.413 (s, 12H, Me), 1.65 (s, 4H, CH₂); ^{13}C NMR (50 MHz) δ 31.2 (CH₃), 32.7 (CH₃), 40.3 (CH₂), 53.6 (C), 57.0 (C), 277.2 (C); MS m/z (rel intensity) 314 (M⁺, 71), 281 (17), 257 (8), 213 (14), 201 (24), 170 (46), 157 (38), 144 (41), 111 (61), 101 (54), 69 (100), 57 (72).

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dione (26)

^1H NMR (400 MHz) δ 1.23 (s, 18H, *t*-Bu), 1.24 (s, 12H, Me), 1.40 (s, 4H, CH₂); ^{13}C NMR (100.6 MHz) δ 26.4 (CH₃), 28.3 (CH₃), 36.8 (CH₂), 45.70 (C), 49.1 (C), 218.4 (C); IR (KBr, cm⁻¹) 2968, 1682 (C=O), 1482, 1388, 1368, 1046, 978, 734.

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-dithiabicyclo[4.1.1]octane 7-*endo*,8-*endo*-dioxide (27)

^1H NMR (300 MHz) δ 1.27 (pseudo d, J = 13 Hz, 2H, CH₂), 1.455 (s, 18H, *t*-Bu), 1.466 (s, 6H, Me), 3.82 (pseudo d, J = 13 Hz, 2H, CH₂); ^{13}C NMR (50 MHz) δ 28.3 (CH₃), 31.0 (CH₃), 35.2 (CH₃), 39.7 (CH₂), 43.1 (C), 47.1 (C), 96.5 (C); IR (KBr, cm⁻¹) 1928, 1464, 1408, 1394, 1372, 1194, 1170, 1148, 1104, 1058 (S=O).

7,8-Diaza-1,6-di-*tert*-butyl-2,2,5,5-tetramethyl-9-selenabicyclo[4.2.1]nonan-7-ene (34)

^1H NMR (400 MHz): at 298 K: δ 0.72 (br s, 1H, CH₂), 0.93 (br s, 1H, CH₂), 1.1–1.5 (m, 31H), 2.22 (br s, 1H, CH₂); at 273 K: δ 0.71 (dd, J = 15.2, 9.4 Hz, 1H, CH₂), 0.92 (dd, J = 14.8, 9.2 Hz, 1H, CH₂), 1.18 (s, 3H, Me), 1.25 (br s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu), 1.36 (s, 3H, Me), 1.38 (s, 3H, Me), 1.43 (s, 3H, Me), 2.20 (pseudo t, J = 13.7 Hz, 1H, CH₂); at 273 K one of the four CH₂ protons was not observed but, at 243 K, a part of an AB quartet due to the proton appeared at δ 1.21 owing to broadening of the singlet at δ 1.25; ^{13}C NMR (100.6 MHz, 263 K) δ 23.0 (Me), 30.3 (Me), 30.7 (Me), 31.1 (br s, *t*-Bu), 31.5 (Me), 32.5 (*t*-Bu), 40.9 (CH₂), 42.4 (C), 43.1 (C), 45.1 (CH₂), 46.8 (C), 124.9 (C), 127.2 (C): at this temperature the ring inversion is slow compared to the NMR time scale. One of the quaternary carbons was not observed; ^{77}Se NMR (76.3 MHz) δ 228; IR (KBr, cm⁻¹) 3000, 2924, 1472, 1368, 1034; MS m/z (rel intensity) 328 ($\text{M}^+ - \text{N}_2 - 2$, 10, ^{80}Se), 215 (52), 123 (22), 111 (32), 95 (15), 83 (22), 69 (48), 57 (100).

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-diselenabicyclo[4.1.1]octane**(35)**

^1H NMR (400 MHz) δ 1.11 (s, 6H, Me), 1.24 (s, 18H, *t*-Bu), 1.32 (br d, $J = 12.3$ Hz, 2H, CH₂), 1.40 (s, 6H, Me), 3.02 (br d, $J = 13.4$ Hz, 2H, CH₂); ^{13}C NMR (50 MHz) δ 24.6 (CH₃), 28.5 (CH₃), 30.2 (CH₃), 42.7 (C), 44.9 (C), 46.8 (C), 47.7 (CH₂); MS m/z (rel intensity) 410 (M^+ , 10, $^{80}\text{Se}_2$), 299 (25), 160 (24), 123 (36), 111 (56), 83 (35), 69 (94), 57 (100).

2,2,4,4,7,7,9,9-Octamethyl-8-selenoxodecan-3-one (36)

^1H NMR (400 MHz) δ 1.203 (s, 6H, Me), 1.208 (s, 9H, *t*-Bu), 1.44–1.49 (m, 2H, CH₂), 1.50 (s, 9H, *t*-Bu), 1.52 (s, 6H, Me), 1.76–1.80 (m, 2H, CH₂); ^{13}C NMR (100.6 MHz) δ 26.4 (CH₃), 28.3 (CH₃), 31.3 (CH₃), 32.5 (CH₃), 36.7 (CH₂), 39.7 (CH₂), 45.7 (C), 49.2 (C), 60.4 (C), 63.3 (C), 218.4 (C), 291.3 (C); IR (neat, cm^{-1}) 2962, 1684 (C=O), 1481, 1386, 1366, 1044, 973; MS m/z (rel intensity) 346 (M^+ , 26, ^{80}Se), 265 (38), 197 (79), 128 (78), 111 (75), 69 (96), 54 (100).

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-diselenabicyclo[4.1.1]octane 7-*endo*,8-*endo*-dioxide (39)

^1H NMR (400 MHz) δ 1.23–1.30 (m, 2H, CH₂), 1.47 (s, 6H, Me), 1.51 (s, 18H, *t*-Bu), 1.73 (s, 6H, Me), 4.30–4.37 (m, 2H); ^{13}C NMR (100.6 MHz) δ 28.4 (CH₃), 31.6 (CH₃), 35.4 (CH₃), 33.8 (CH₂), 43.9 (C), 49.0 (C), 97.3 (C); IR (KBr, cm^{-1}) 2952, 2912, 1480, 1391, 824 (Se=O).