Supporting Information - Experimental

(4-(triphenylmethyl)phenyl)acrylate (2a)

Acrylic acid chloride (0.5 mL, 5.5 mmol) was dissolved in 100 mL abs. dichloromethane and cooled down to -10°C. A solution of 4-(triphenylmethyl)phenol (1.9 g, 5.5 mmol) and triethylamine (0.6 g, 55 mmol) in 50 mL dichloromethane was added slowly. The reaction mixture was stirred for 1 h. The solvent was removed and the resulting solid was purified by column chromatography (dichloromethane) to yield a colourless solid **2a** (1.9 g, 4.8 mmol, 87%). M.p. 164°C; ^{1}H NMR (250 MHz, $CDCl_3$) 5.99 (dd, J = 1.3 Hz, J = 10.3 Hz, 1H; CH), 6.32 (dd, J = 10.3 Hz, J = 17.2 Hz, 1H; CH), 6.59 (dd, J = 1.3 Hz, J = 17.2 Hz, 1H; CH), 7.02 (d, J = 8.8 Hz, 2H; anil), 7.15-7.29 (m, 17H; anil, stop); ^{13}C-NMR (69.2 MHz, $CDCl_3$) 64.7 (Cq), 120.4, 126.1, 127.6, 128.1, 131.2, 132.2 (CH), 132.6 (CH_2), 144.5, 146.6, 148.6 (Cq), 164.6 (COOR); EI-MS (70 eV): *m/z* = 390.2 (M^+, 49%), 313.1 (M^+-C(Ph), 71%), 259.1 $(C(Ph)_3^+$, 100%), 165.0 $(C(Ph)_2^+$, 28%); Elemental analysis: calcd $C_{28}H_{22}O_2$: C 86.13; H 5.68; found C 86.15; H 5.74.

***N*-(4-(triphenylmethyl)phenyl)acrylamide (2b)**

Acrylic acid chloride (0.5 mL, 5.5 mmol) was dissolved in 100 mL abs. toluene and cooled down to -10°C. A solution of 4-(triphenylmethyl)aniline (1.9 g, 5.5 mmol) and triethylamine (0.6 g, 55 mmol) in 50 mL toluene was added slowly. The reaction mixture was stirred for 1 h. The colourless solid was filtered off and worked up by washing with dichloromethane which yielded the colourless product **2b** (1.6 g, 4.2 mmol, 76%). M.p. 264°C; ^{1}H NMR (400 MHz, [D_7]DMF) 5.73 (dd, J = 2.2 Hz, J = 10.1 Hz, 1H; CH), 6.32 (dd, J = 2.2 Hz, J = 16.9 Hz, 1H; CH), 6.59 (dd, J = 10.1 Hz, J = 16.9 Hz, 1H; CH), 7.18 (d, J = 8.9 Hz, 2H; anil), 7.21-7.36 (m, 15H; stop), 7.74 (d, J = 8.9 Hz, 2H; anil), 10.45 (s, 1H; amide); ^{13}C NMR (100.6 MHz, [D_7]DMF) 65.2 (Cq), 126.8 (CH_2), 119.2, 126.7, 128.6, 131.5, 131.8, 132.9 (CH), 138.2, 142.4, 147.6 (Cq), 164.2 (CON); EI-MS (70 eV): *m/z* = 389.2 (M^+, 41%), 312.2 (M^+-C(Ph), 100%), 258.1 $(C(Ph)_3^+$, 38%), 165.0 $(C(Ph)_2^+$, 20%); Elemental analysis: calcd $C_{28}H_{23}ONxH_2O$: C 82.53; H 6.18; N 3.43; found C 82.54; H 5.88; N 3.29.

4-(triphenylmethyl)phenyl)propiolate (3a)

A solution of propiolic acid (104 mg, 1.4 mmol), dimethylaminopyridine (DMAP) (10 mg, 0.08 mmol), and 4-(triphenylmethyl)phenol (1.5 g, 4.2 mmol) in 100 mL dichloromethane was cooled down to 0°C. After the addition of dicyclohexylcarbodiimide (DCC) (289 mg, 1.4 mmol) the mixture was stirred at 0°C for 5 min and another 3 h at RT. A colourless solid was filtered off and the solvent of the filtrate was removed. The resulting solid was purified by flash column chromatography (dichloromethane) to yield a colourless solid **3a** (205 mg, 0.53 mmol, 38%). M.p. 114°C; ^{1}H NMR (400 MHz, $CDCl_3$) 3.05 (s, 1H; CH), 7.03 (d, J = 8.8 Hz, 2H; phl), 7.18-7.28 (m, 17H; phl, stop); ^{13}C NMR (100.6 MHz, $CDCl_3$) 64.7 (Cq), 74.4 (CH), 76.5 (Cq), 120.1, 126.0, 127.5, 131.1, 132.1 (CH), 146.5, 148.7, 151.1 (Cq), 169.5 (COOR); EI-MS (70 eV): *m/z* = 388.1 (M^+, 37%), 311.1 (M^+-C(Ph), 100%), 259.1 (HO-C_6H_4-$C(Ph)_2^+$, 63%), 165.0 $(C(Ph)_2^+$, 42%); Elemental analysis: calcd $C_{28}H_{20}O_2$: C 86.35; H 5.43; found C 86.21; H 5.36.

***N*-(4-(triphenylmethyl)phenyl)propiolamide (3b)**
A solution of propiolic acid (210 mg, 3.0 mmol), dimethylaminopyridine (HOBT) (800 mg, 7.8 mmol), and 4-(triphenylmethyl)aniline (1.3 g, 3.9 mmol) in 100 mL dichloromethane was cooled down to 0°C. After the addition of dicyclohexylcarbodiimide (DCC) (800 mg, 3.9 mmol) the mixture was stirred at 0°C for 5 min and another 3 h at RT. A colourless solid was filtered off and the solvent of the filtrate was removed. The resulting solid was purified by flash column chromatography (dichloromethane) to yield a colourless solid **3b** (486 mg, 1.2 mmol, 42%). M.p. 242°C; ^{1}H NMR (400 MHz, [D$_7$]DMF) 4.30 (s, 1H; CH), 7.18-7.29 (m, 17H; anil, stop), 7.66 (d, J = 8.9 Hz, 2H; anil), 10.91 (s, 1H; amide); ^{13}C-NMR (100.6 MHz, [D$_7$]DMF) 65.3, 76.6 (Cq), 119.6, 126.7, 128.4, 131.5, 131.9 (CH), 143.3, 147.5 (Cq), 150.7 (CON), 177.9 (CH); EI-MS (70 eV): m/z = 387.2 (M^+, 40%), 310.1 (M^+-C(Ph), 100%), 258.1 (HN-C$_6$H$_4$-C(Ph)$_2^+$, 12%), 165.0 (C(Ph)$_2^+$, 38%).

General synthesis of the axles 7, 9a,b: A suspension of **1a,b** (0.05 mmol), **3a,b** (0.05 mmol), potassium carbonate (10 mg, 0.07 mmol), and [18]dibenzocrown-6 (2 mg, 0.005 mmol) in abs. chloroform was stirred for 7 d at RT. The solvent was removed and the solid purified by column chromatography.

(*E/Z*)-3-(4-(Triphenylmethyl)phenoxy)-(4-(triphenylmethyl)phenyl)acrylate (7): Purification (cyclohexane/ethyl acetate 5/1) yielded a colourless solid 7 (*E*-isomer 10 mg, 0.014 mmol, 66% of 41%; *Z*-isomer 6 mg, 0.008 mmol, 37% of 41%). *E*-isomer m.p. 253°C; ^{1}H NMR (400 MHz, CDCl$_3$) 5.72 (d, J = 12.2 Hz, 1H; CH), 6.99 (d, J = 8.7 Hz, 1H; phl), 7.00 (d, J = 7.9 Hz, 1H; phl), 7.20- 7.28 (m, 36H; phl, stop), 7.95 (d, J = 12.2 Hz, 1H; CH); ^{13}C NMR (100.6 MHz, CDCl$_3$) 64.5, 64.6 (Cq), 101.3 (CH), 116.9, 120.5, 126.0, 126.1, 127.4, 127.5, 127.6, 131.0, 131.1, 131.2, 132.1, 132.7, 160.6 (CH), 144.0, 144.1, 146.5, 146.6, 148.6, 153.3 (Cq), 165.6 (COOR); *Z*-isomer m.p. 203°C; ^{1}H NMR (400 MHz, CDCl$_3$) 5.23 (d, J = 8.5 Hz, 1H; CH), 6.77 (d, J = 8.7 Hz, 2H; phl), 6.80-7.29 (m, 37H; CH, phl, stop, tphl); MALDI-TOF-MS: m/z = 725.0 [M^+]; 747.0 [M+Na$^+$]; 759.0 [M+K$^+$]; Elemental analysis: calcd C$_{53}$H$_{40}$O$_3$: C 87.82; H 5.56; found C 86.99; H 5.52.

(*E/Z*)-3-(4-(Triphenylmethyl)phenyl)sulfanyl-(4-triphenylmethyl)phenyl)-acrylate (9a): Purification (dichloromethane/cyclohexane 1/1) yielded a colourless solid **9a** (*E*-isomer 6 mg, 0.008 mmol, 71% of 24%; *Z*-isomer 3 mg 0.004 mmol, 29% of 24%). *E*-isomer m.p. 213°C; ^{1}HNMR (400 MHz, CDCl$_3$) 5.61 (d, J = 15.1 Hz, 1H; CH), 6.54 (d, J = 8.8 Hz, 2H; phl), 6.89 (d, J = 8.8 Hz, 2H; phl), 6.95-7.23 (m, 35H; CH, phl, stop, tphl); *Z*-isomer m.p. 196°C; ^{1}H NMR(400 MHz, CDCl$_3$) 5.76 (d, J = 10.2 Hz, 1H; CH), 6.23 (d, J = 8.8 Hz, 2H; phl), 6.48 (d, J = 8.8 Hz, 2H; phl), 7.00-7.25 (m, 34H; phl, stop, tphl), 7.33 (d, J = 10.2 Hz, 1H; CH); FAB-MS: m/z = 742.0 [M+H$^+$].

(*Z*)-3-(4-(Triphenylmethyl)phenyl)sulfanyl-*N*-(4-(triphenylmethyl)phenyl)acrylamide (9b): Purification (dichloromethane/cyclohexane 3/1) yielded a colourless solid **9b** (*Z*-isomer 19.9 mg, 0.025 mmol, 53%). M.p. 186°C; ^{1}H NMR (400 MHz, CDCl$_3$) 4.91 (d, J = 9.8 Hz, 1H; CH), 6.55 (d, J = 8.1 Hz, 2H; tphl), 6.63 (d, J = 9.8 Hz, 1H; CH), 6.91-6.99 (m, 4H; phl, tphl), 7.18- 7.28 (m, 32H; phl, stop, tphl), 8.34 (s, 1H; amide); FAB-MS: m/z = 740.3 [M^+].

General synthesis of the [2]rotaxanes 6, 8a,b: A suspension of **1a,b** (0.10 mmol), **3a,b** (0.10 mmol), potassium carbonate (20 mg, 0.15 mmol), tetralactam **4** (100 mg, 0.10 mmol), and [18]dibenzocrown-6 (4 mg, 0.01 mmol) in abs. chloroform was stirred for 7 d at RT. The solvent was removed and the solid purified by column chromatography.

[2][(*E/Z*)-3-(4-(Triphenylmethyl)phenoxy)-(4-triphenylmethyl)phenyl)acrylate]-[11'-*tert*-butyl-5',17',23',35',38',40',43',45'-octamethyldispiro{cyclohexane-1,2'-[7,15,25,33]tertaazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24},1.^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20',1''-cyclohexane}-8',14',26',32'-tetrone]rotaxane (6): Purification (dichloromethane/ethyl acetate 25/1) yielded a colourless solid **6** (*E/Z*-isomers 22 mg, 0.013 mmol, 13%). M.p. 186°C; ^{1}H NMR (400 MHz, $CDCl_3$): *E*-isomer 1.35 (s, 9H; CCH_3), 1.63 (br, 8H; cyh), 1.82 (s, 12H; CH_3), 1.92 (s, 12H; CH_3), 2.19 (br, 4H; cyh), 2.28 (br, 8H; cyh), 5.38 (d, J = 12.1 Hz, 1H; CH), 6.29 (d, J = 8.8 Hz, 2H; phl), 6.45 (d, J = 8.8 Hz, 2H; phl), 6.70-7.29 (m, 43H; aryl, iso, phl, stop), 7.48 (t, J = 7.6 Hz, 1H; iso), 7.52 (d, J = 12.1 Hz, 1H; CH), 7.69 (s, 2H; *t*bi), 8.18 (d, J = 7.6 Hz, 2H; iso), 8.10 (s, 1H; *t*bi), 8.19 (s, 2H; amide), 8.22 (s, 2H; amide); *Z*-isomer: 1.42 (s, 9H; CCH_3), 1.50 (br, 8H; cyh), 1.88 (s, 12H; CH_3), 1.90 (s, 12H; CH_3), 2.21 (br, 8H; cyh), 2.33 (br, 4H; cyh), 5.00 (d, J = 8.5 Hz, 1H; CH), 5.10 (d, J = 8.7 Hz, 2H; phl), 6.51 (d, J = 8.7 Hz, 2H; phl), 6.73 (d, J = 8.8 Hz, 2H; phl), 6.80-7.29 (m, 42H; aryl, CH, iso, phl, stop), 7.65 (t, J = 7.6 Hz, 1H; iso), 7.99 (s, 1H; *t*bi), 8.18 (d, ^3J = 7.6 Hz, 2H; iso), 8.11 (s, 2H; *t*bi), 8.11 (s, 2H; amide), 8.12 (s, 2H; amide); ^{13}C NMR (100.6 MHz, $CDCl_3$) *E/Z*-isomeres 18.5, 18.6, 18.7 (CH_3), 23.0, 23.1, 35.3, 35.4, 35.5, 35.9, 36.1 (CH_2), 31.3 (CH_3), 45.2, 45.3 (Cq), 64.2, 64.4, 64.5 (Cq), 95.5, 95.6, 97.5, 99.7, 115.6, 116.8, 119.8, 120.2, 121.2, 121.6, 124.0, 124.5, 126.2, 126.3, 126.7, 127.7, 127.8, 129.1, 129.2, 130.0, 130.7, 130.8, 130.9, 131.4, 131.6, 131.7, 132.0, 132.6, 133.0 157.9, 161.9 (CH), 134.3, 134.4, 134.5, 134.6, 134.7, 134.8, 134.9, 135.0, 144.5, 144.8, 145.2, 146.1, 146.2, 146.3, 147.4, 146.8, 149.0, 153.1, 153.9, 154.2 (Cq), 164.6, 165.0, 165.1, 165.2, 165.4, 168.2 (CON); FAB-MS: *m/z*: 1686.0 [M^+].

[2][(*E/Z*)-3-(4-(Triphenylmethyl)phenyl)sulfanyl-(4-triphenylmethyl)phenyl)acylate]-[11'-*tert*-butyl-5',17',23',35',38',40',43',45'-octamethyldispiro{cyclohexane-1,2'-[7,15,25,33]tertaazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24},1.^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20',1''-cyclohexane}-8',14',26',32'-tetrone]rotaxane (8a): Purification (dichloromethane/ethyl acetate 25/1) yielded a colourless solid **8a** (*E/Z*-isomeres 33 mg, 0.019 mmol, 19%). M.p. 212°C; ^{1}H NMR (400 MHz, $CDCl_3$) *E*-isomer 1.43 (s, 9H; CCH_3), 1.52 (br, 8H; cyh), 1.66 (br, 8H; cyh), 1.85 (s, 12H; CH_3), 1.86 (s, 12H; CH_3), 2.23 (br, 4H; cyh), 5.10 (d, J = 8.8 Hz, 2H; phl), 5.56 (d, J = 15.1 Hz, 1H; CH), 6.25 (d, J = 9.2 Hz, 2H; phl), 6.54 (d, J = 8.8 Hz, 2H; phl), 6.76 (d, J = 9.2 Hz, 2H; phl), 6.94 (s, 4H; aryl), 6.98 (s, 4H; aryl), 7.00-7.25 (m, 32H; CH; iso, stop), 7.64 (t, J = 7.8 Hz, 1H; iso), 7.81 (s, 2H; amide), 8.02 (s, 2H; amide), 8.08 (d, ^3J = 7.8 Hz, 2H; iso), 8.22 (s, 2H; *t*bi), 8.24 (s, 1H; *t*bi); *Z*-isomer 1.36 (s, 9H; CCH_3), 1.53 (br, 8H; cyh), 1.62 (br, 8H; cyh), 1.87 (s, 12H; CH_3), 1.89 (s, 12H; CH_3), 2.25 (br, 4H; cyh), 5.15 (d, J = 8.8 Hz, 2H; phl), 5.67 (d, J = 10.2 Hz, 1H; CH), 6.48 (d, J = 8.8 Hz, 2H; phl), 6.84 (s, 8H; aryl), 7.00-7.25 (m, 34H; phl, stop), 7.33 (d, J = 10.2 Hz, 1H; CH), 7.64 (t, J = 7.8 Hz, 1H;

iso), 7.81 (s, 2H; amide), 7.99 (s, 2H; amide), 8.16 (s, 1H; *t*bi), 8.18 (d, J = 7.8 Hz, 2H; iso), 8.19 (s, 2H; *t*bi), 8.25 (s, 1H; iso); ^{13}C NMR (100.6 MHz, $CDCl_3$) *E/Z*-isomeres 18.5, 18.6, 18.7 (CH_3), 23.0, 23.1, 26.4, 35.6, 36.2 (CH_2), 31.3 (CH_3), 45.2, 45.3 (Cq), 64.3, 64.4, 64.8 (Cq), 111.1, 119.8, 122.3, 124.8, 126.3, 126.4, 126.5, 126.6, 126.7, 126.8, 127.7, 127.8, 127.9, 128.9, 129.0, 129.2, 130.3, 130.8, 130.9, 131.0, 131.6, 131.7, 131.8, 132.0, 132.5, 132.8, 153.2 (CH), 134.6, 134.7, 134.8, 134.8, 134.9, 135.0, 144.6, 145.9, 146.1, 146.2, 146.3, 147.5, 148.4, 148.8, 154.0 (Cq), 164.9, 165.2, 165.7, 166.5 (CON); FAB-MS: *m/z*: 1702.8 [M^+]; Elemental analysis: calcd $C_{117}H_{112}N_4O_6SxH_8O_4$: C 79.02; H 6.81; N 3.16; found C 79.09; H 7.02; N 2.70.

[2][(*Z*)-3-(4-(Triphenylmethyl)phenyl)sulfanyl-*N*-(4-(triphenylmethyl)phenyl)acrylamide]-[11'-*tert*-butyl-5',17',23',35',38',40',43',45'-octamethyldispiro{cyclohexane-1,2'[7,15,25,33]tertaazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24},1.^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20',1''-cyclohexane}-8',14',26',32'-tetrone]rotaxane (8b): Purification (dichloromethane/ethyl acetate 25/1) yielded a colourless solid **8b** (*Z*-isomer 65 mg, 0.039 mmol, 35%). M.p. 238°C; ^{1}H NMR (400 MHz, $CDCl_3$) 1.41 (s, 9H; CCH_3), 1.52 (br, 4H; cyh), 1.68 (br, 8H; cyh), 1.97 (s, 24H; CH_3), 2.29 (br, 4H; cyh), 5.91 (d, J = 9.8 Hz, 1H; CH), 6.48 (d, J = 8.1 Hz, 2H; phl), 6.63 (d, J = 9.8 Hz, 1H; CH), 6.75-6.92 (m, 14H; aryl, phl), 7.06-7.29 (m, 30H; stop), 7.57 (t, J = 7.6 Hz, 1H; iso), 7.69 (s, 1H; amide), 7.80 (s, 2H; amide), 7.84 (s, 2H; amide), 8.11 (d, J = 7.6 Hz, 2H; iso), 8.22 (s, 2H; *t*bi), 8.32 (s, 1H; *t*bi), 8.44 (s, 1H; iso); ^{13}C NMR (100.6 MHz, $CDCl_3$) 18.7, 18.8 (CH_3), 23.0, 26.4, 35.2, 35.5 (CH_2), 31.3 (CH_3), 45.2 (Cq), 64.3, 64.7 (Cq), 115.9, 118.9, 123.3, 126.1, 126.2, 126.3, 126.4, 126.6, 127.5, 127.6, 127.7, 127.9, 128.5, 129.3, 129.6, 130.9, 131.0, 131.1, 131.5, 132.2, 144.2 (CH), 134.2, 134.5, 135.1, 135.2, 143.1, 146.2, 146.5, 147.5, 148.4, 153.3 (Cq), 165.4, 165.6 (CON); FAB-MS: *m/z*: 1701.7 [M^+].

Syntheses of [2][Formaldehyddi-(4-(triphenylmethyl)phenyl)thioacetale]-[11'-*tert*-butyl-5',17',23',35',38',40',43',45'-octamethyldispiro{cyclohexane-1,2'[7,15,25,33]tertaazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24},1.^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20',1''-cyclohexane}-8',14',26',32'-tetrone]rotaxane 10b: A suspension of **1b** (35 mg, 0.10 mmol), potassium carbonate (20 mg, 0.15 mmol), tetralactam **4** (100 mg, 0.10 mmol), and [18]dibenzocrown-6 (4 mg, 0.01 mmol) in abs. Dichloromethane was stirred for 7 d at RT. The solvent was removed and purification by column chromatography (dichloromethane/ethyl acetate 25/1) yielded a colourless solid **10b** (19 mg, 0.01 mmol, 23%). M.p. 197°C; ^{1}H NMR (400 MHz, $CDCl_3$) 1.34 (s, 9H; *t*-Bu), 1.46 (br, 4H; CH_2), 1.55 (br, 8H; CH_2), 1.73 (s, 24H; Ar-CH_3), 2.21 (br, 4H; CH_2), 2.48 (s, 2H; CH_2), 5.83 (d, ^3J = 8.4 Hz, 4H; Ph-H), 6.78 (s, 4H; Ar-H), 6.81 (s, 4H; Ar-H), 6.90 (d, J = 8.4 Hz, 4H; Ph-H), 7.00-7.25 (m, 30H, Trityl-H), 7.59 (s, 1H; Iso-H) 7.62 (t, J = 7.9 Hz, 1H; Iso-H), 7.76 (s, 1H; *t*B-Iso-H), 8.13 (d, J = 7.9 Hz, 2H; Iso-H), 8.18 (s, 2H; *t*B-Iso-H); ^{13}CNMR (100.6 MHz, $CDCl_3$) 19.0 (CH_3), 22.9, 26.3, 35.5 (CH_2), 31.2 (CH_3), 45.1 (Cq), 47.4 (SCH_2S), 64.8 (Cq), 121.1, 123.6, 126.4, 126.5, 126.6, 127.8, 129.5, 130.5, 131.1, 132.4, 133.0 (CH), 134.6, 134.7, 134.9, 135.0, 145.8, 148.7, 148.9, 154.4 (Cq), 164.5, 165.1 (CON); FAB-MS: *m/z*: 1677.9 [M^+].