Synthesis and Properties of Bingel-type Methanofullerene- π - Extended-TTF Dyads and Triads

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Table of contents: Synthesis and experimental data for compounds 6, 8a-c, 9a-c, 10a-c, 11a, 15, 16, 17, 18, 19, 20a-c, 21, 22a-c. (12 pages).

Synthesis of 2-(tercbutyldiphenylsilyloxymethyl)anthraquinone (6): To a solution of 2-hydroxymethyl-9,10-antraquinone (**5**) (1.00 g, 4.20 mmol) in dry DMF (50 mL) at room temperature and under argon atmosphere, tercbutyldiphenylsilyl chloride (1.32 g, 1.25 mL, 5.03 mmol), and imidazol (1.43 g, 21 mmol), were added. The mixture was stirred for 16 h at room. Water (75 mL) was added and the residue extracted with ethylcetate (3 x 100 mL). The combined extracts were dried (MgSO₄), filtered out, and the solvent was removed under reduced pressure. Purification of the product was achieved by column chromatography on silica gel using hexane:dichloromethane mixture as eluent. Compound **6** was obtained in 89 % yield. m.p.: 118 -121 °C; Anal. for C₃₁H₂₈O₃Si: C, 78.04% (Calc.: 78.12), H, 6.01% (5.92); IR (KBr): 2940, 2869, 1680 (C=O), 1600 (C=O), 1475, 1435, 1395, 1375, 1365, 1330, 1300, 1270, 1160, 1145, 1120, 1115, 1080, 1000, 935, 850, 830 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz), δ : 8.33-8.25

(4H, m, ArH), 7.83-7.79 (3H, m, ArH), 7.73-7.70 (4H, m, ArH), 7.47-7.38 (6H, m, ArH), 4.92 (2H, s, CH₂), 1.16 (9H, s, CH₃); ¹³C-NMR (CDCl₃, 75 MHz), δ: 183.1 (C=O), 182.9 (C=O), 147.9, 135.4, 134.7, 134.0, 133.9, 133.4, 133.3, 132.8, 132.2, 131.2, 129.8, 129.5, 127.7, 127.6, 127.4, 127.0, 124.2, 64.8 (CH₂O), 26.7 (2CH₃), 26.4 (CH₃), 19.2 (C). MS m/z (%): 477 (M⁺, 5), 419 (M⁺-^tBu, 7), 341 (M⁺-^tBuPh, 100); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 330 (4.19), 278 (4.60), 254 (4.82), 232 (sh, 4.52) nm.

Synthesis of 9,10-bis(1,3-dithiol-2-ylidene)-2-(tercbutyldiphenylsilyloxymethyl)-9,10-dihydroanthracene derivatives (8a-c). To a solution of phosphonate esters (**7b-c**) (1 mmol) in dry THF (20 mL) at -78 °C and under argon atmosphere, n-BuLi (1.6 M) (1.1 mmol) was added with a syringe dropwise. After 30 min at -78 °C, a solution of 2-(tercbutyldiphenylsilyloxymethyl)anthraquinone (**6**) in dry THF (119 mg, 0.25 mmol) was added with a syringe into the solution of the phosphonate carbanion. The mixture was stirred for 1 h at -78 °C and then allowed to warm to 20 °C, and let to stand overnight. The THF was evaporated under reduced pressure, water (75 mL) added and the residue extracted with CH₂Cl₂ (3 x 75 mL). The combined extracts were dried (MgSO₄), filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane: dichloromethane mixtures as eluent.

9,10-bis(1,3-dithiol-2-ylidene)-2-(tercbutyldiphenylsilyloxymethyl)-9,10-dihydroanthracene (8a). 93 % yield; m.p.: 117-119 °C (dec). Anal. for C₃₇H₃₂S₄OSi: C, 68.39 % (Calc. 68.48), H, 5.10 % (4.97); IR (KBr): 3020, 3960, 3940, 2870, 1550, 1520, 1460, 1440, 1385, 1370, 1270, 1225, 1160, 1120, 945, 765 cm⁻¹; ¹H-NMR (CDCl₃, 200 MHz), δ: 7.72-7.64 (7H, m, ArH), 7.44-7.22 (10H, m, ArH), 6.30-6.27 (4H, m, CH=), 4.84 (1H, AB, *J* = 13.3 Hz, CH₂), 4.81 (1H, AB, *J* = 13.3 Hz, CH₂), 1.12 (9H, s, CH₃); ¹³C-NMR (CDCl₃, 50 MHz), δ: 138.9, 136.9, 135.6, 135.3, 135.0, 134.0, 133.4, 129.7, 125.9, 124.9, 124.8, 123.4, 122.4, 122.2, 117.3, 117.2, 117.1, 117.0, 65.4 (CH₂), 26.9 (3CH₃), 19.3 (C). MS m/z (%): 648 (M⁺,

100), 393 ($M^+ - t\text{BuPh}_2\text{SiO}$, 37); UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 430 (4.86), 410 (sh, 4.81), 364 (4.68), 270 (sh, 4.58), 242 (4.95) nm.

9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2-(tercbutyldiphenylsilyl-oxymethyl)-9,10-dihydroanthracene (8b). 80 % yield; m.p.: 112-115 °C (dec). Anal. for $\text{C}_{41}\text{H}_{40}\text{S}_8\text{OSi}$: C, 59.29 % (Calc.: 59.09), H, 5.23 % (4.84), S, 30.15 % (30.78); IR (KBr): 2960, 2930, 2860, 1540, 1500, 1470, 1450, 1430, 1380, 1315, 1280, 1215, 1190, 1155, 1115, 1090, 1000, 970, 900, 830, 800 cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz), δ : 7.66-7.26 (17H, m, ArH), 4.86 (1H, AB, $J = 15.3$ Hz, CH_2), 4.81 (1H, AB, $J = 15.3$ Hz, CH_2), 2.41 (3H, s, SCH_3), 2.40 (6H, s, SCH_3), 2.33 (3H, s, SCH_3), 1.15 (9H, s, CH_3) ; ^{13}C -NMR (CDCl_3 , 75 MHz), δ : 139.3, 135.6, 134.7, 134.6, 133.3, 133.2, 131.0, 130.4, 129.7, 127.8, 127.7, 126.3, 125.8, 125.7 (2), 125.6, 125.4, 125.3, 125.2, 123.7, 123.6, 122.7, 65.2 (CH_2), 26.9 (3CH_3), 19.3 (SCH_3), 19.0 (C) ; MS m/z (%): 832 (M^+ , 100), 786 ($M^+ - 3\text{CH}_3$, 7); UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 436 (4.56), 416 (hombro, 4.46), 368 (4.32), 274 (4.45), 242 (4.82) nm.

9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-2-

(tercbutyldiphenylsilyloxymethyl)-9,10-dihydroanthracene (8c). 90 % yield; m.p.: 136-139 °C (dec); Anal. for $\text{C}_{41}\text{H}_{36}\text{S}_8\text{OSi}$: C, 59.24 % (Calc.: 59.38), H, 4.51 % (4.38), S, 30.30 % (30.93) ; FTIR (KBr): 2926, 2854, 1508, 1458, 1425, 1284, 1111, 1086, 823, 756, 741 cm^{-1} ; ^1H -NMR (CDCl_3 , 300 MHz), δ : 7.75-7.23 (17H, m, ArH), 4.84 (1H, AB, $J = 15.3$ Hz, CH_2O), 4.80 (1H, AB, $J = 15.3$ Hz, CH_2O), 3.29 (8H, s, SCH_2), 1.14 (9H, s, CH_3); ^{13}C -NMR (CDCl_3 , 50 MHz), δ : 139.4, 135.6, 134.8, 134.7, 134.6, 133.4, 133.3, 129.8, 129.7, 129.1, 127.8, 127.7, 126.3, 125.6, 125.4, 124.2, 124.1, 123.8, 123.1, 111.0, 110.9, 110.8, 110.5, 65.3 (CH_2O), 29.6 (2SCH_2), 29.5 (2SCH_2), 26.9 (3CH_3), 19.3 (C) ; MS m/z (%): 828 (M^+ , 100); UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 446 (4.38), 424 (sh, 4.25), 386 (4.06), 276 (4.30), 244 (4.67) nm.

Synthesis of 9,10-bis(1,3-dithiol-2-ylidene)-2-hydroxymethyl-9,10-dihydroanthracenes (9a-c). To a solution of the **8a-c** (0.50 mmol) in dry DMF (50 mL) at room temperature and under argon atmosphere, tetrabutylammonium fluoride (0.23 g, 0.75 mmol) was added. The mixture was stirred at room temperature for 16 h. Water (75 mL)

was added and the residue extracted with CH₂Cl₂ (3 x 100 mL). The combined extracts were dried (MgSO₄), filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane: dichloromethane mixtures as eluent.

9,10-bis(1,3-dithiol-2-ylidene)-2-hydroxymethyl-9,10-dihydroanthracene (9a). 97% yield; m.p.: 269-270 °C (dec); Anal. for C₂₁H₁₄S₄O: C, 63.28% (Calc.: 64.43), H, 4.13% (3.44), S, 29.91 % (31.23); IR (KBr): 3400 (-OH, br), 3070, 2930, 2860, 1550, 1515, 1455, 1425, 1285, 1255, 1115, 1050, 1000, 845, 810 cm⁻¹; ¹H-NMR (DMSO, 200 MHz), δ: 7.66-7.57 (4H, m, ArH), 7.36-7.23 (3H, m, ArH), 6.74-6.73 (4H, m, CH=), 5.29 (1H, t, *J* = 5.6 Hz, -OH), 4.54 (2H, d, *J* = 5.6 Hz, CH₂); ¹³C-NMR (CDCl₃, 50 MHz), δ: 137.3, 134.8, 129.6, 127.7, 126.0, 125.2, 124.9, 124.5, 123.6, 117.2, 65.4 (CH₂); MS *m/z* (%): 410 (M⁺, 100), 393 (M⁺-OH, 1); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 434 (4.41), 412 (sh, 4.35), 268 (4.17), 272 (4.01), 244 (4.67) nm.

9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2-hydroxymethyl-9,10-dihydroanthracene (9b). 90 % yield; m.p.: 238-240 °C (dec). Anal. for C₂₅H₂₂S₈O: C, 50.29% (Calc.: 50.51), H, 3.80% (3.73); IR (KBr): 3400 (-OH, br), 2960, 2920, 2860, 1535, 1495, 1455, 1420, 1310, 1280, 1130, 970, 900, 835, 800 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz), δ: 7.59-7.55 (4H, m, ArH), 7.34-7.31 (3H, m, ArH), 4.77 (2H, d, *J* = 5.4 Hz, CH₂), 2.40-2.39 (12H, m, SCH₃); ¹³C-NMR (CDCl₃, 75 MHz), δ: 139.01, 134.87, 134.50, 133.99, 131.22, 130.97, 126.36, 126.33, 126.31, 125.64, 125.60, 125.36, 125.30, 124.84, 123.89, 123.44, 123.33, 65.14 (CH₂), 19.19 (SCH₃), 19.17 (SCH₃), 19.16 (SCH₃), 19.05 (SCH₃); MS *m/z* (%): 594 (M⁺, 100), 577 (M⁺-OH, 9); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 440 (4.92), 422 (sh, 4.84), 372 (4.68), 276 (4.81), 242 (5.15) nm.

9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-2-hydroxymethyl-9,10-dihydroanthracene (9c). 90 % yield; m.p.: 182-184 °C (dec). Anal. for C₂₅H₁₈S₈O: C,

51.13 % (Calc.: 50.86), H, 3.83 % (3.08); FTIR (KBr): 3400 (-OH, br), 2924, 2852, 2743, 1541, 1508, 1500, 754 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ : 7.53-7.50 (4H, m, ArH), 7.34-7.31 (3H, m, ArH), 4.77 (2H, d, $J = 5.7$ Hz, CH_2), 3.31-3.30 (8H, m, SCH_2); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz), δ : 139.1, 134.9, 134.6, 134.0, 130.0, 129.7, 126.4, 125.7, 125.5, 124.8, 124.0, 123.9, 123.8, 114.0, 110.9, 110.8, 65.1 (CH_2), 29.7 (SCH_2), 29.6 (2SCH_2), 29.3 (SCH_2); MS m/z (%): 590 (M^+ , 3); UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 442 (4.32), 424 (sh, 4.27), 378 (4.07), 276 (sh, 4.29), 236 (4.72) nm.

Synthesis of 9,10-bis(1,3-dithiol-2-ylidene)-2-(2,6-dioxa-3,5-dioxooctanyl)-9,10-dihydroanthracenes (10a-c). To a solution of **9a-c** (0.25 mmol) in dry CH_2Cl_2 (30 mL) at room temperature and under argon atmosphere, dry pyridine (20 μL , 0.25 mmol) was added. The mixture was cold in an ice bath. Ethoxycarbonilacetic acid chloride (37.6 mg, 0.25 mmol) in dry CH_2Cl_2 (1 mL) was added dropwise. The mixture was stirred at 0 $^\circ\text{C}$ for 2 h and then allowed to warm to 20 $^\circ\text{C}$, and let to stand overnight. Water (75 mL) was added and the residue extracted with CH_2Cl_2 (3 x 100 mL). The combined extracts were dried (Na_2SO_4), filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane: dichloromethane mixtures as eluent.

9,10-bis(1,3-dithiol-2-ylidene)-2-(2,6-dioxa-3,5-dioxooctanyl)-9,10-dihydroanthracene (10a). 97 % yield; m.p.: 171-173 $^\circ\text{C}$; Anal. for $\text{C}_{26}\text{H}_{20}\text{S}_4\text{O}_4$: C, 60.45 % (Calc.: 59.54), H, 4.64 % (3.85), S, 23.46 % (24.41); FTIR (KBr): 1979, 2949, 2924, 2861, 1730 (C=O), 1549, 1516, 1456, 1273, 1163, 1032, 754, 642 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz), δ : 7.68-7.67 (4H, m, ArH), 7.31-7.25 (3H, m, ArH), 6.29 (4H, s, CH=), 5.24 (2H, s, ArCH_2O), 4.25 (2H, q, $J = 7.1$ Hz, OCH_2), 3.45 (2H, s, CH_2), 1.25 (3H, t, $J = 7.1$ Hz, CH_3); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz), δ : 166.3 (C=O), 166.2 (C=O), 136.3, 136.1, 135.7, 134.5, 135.3, 135.2, 132.8, 126.0, 125.8, 125.1, 125.0, 124.9,

124.8, 121.7, 121.6, 117.2, 117.1, 66.9 (CH₂O), 61.5 (CH₂O), 41.5 (CH₂), 13.9 (CH₃);
 MS m/z (%): 524 (M⁺, 100), 480 (M⁺-OEt, 8), 452 (M⁺-CO₂Et, 6), 410 (59), 394 (56);
 UV-Vis (CH₂Cl₂) λ_{max} (log ε): 432 (4.40), 414 (sh, 4.33), 366 (4.18), 272 (4.08), 240
 (4.70) nm.

9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2-(2,6-dioxa-3,5-dioxooctanyl)-

9,10-dihydroanthracene (10b). 97 % yield; m.p.: 162-164 °C; Anal. for C₃₀H₂₈S₈O₄:
 C, 51.66 % (Calc.: 50.85), H, 4.23 % (3.99), S, 35.51 % (36.13); FTIR (KBr): 2910,
 2847, 1734 (C=O), 1587, 1499, 1408, 1284, 1063, 760 cm⁻¹; ¹H-NMR (CDCl₃, 200
 MHz), δ: 7.60-7.50 (4H, m, ArH), 7.33-7.28 (3H, m, ArH), 5.25 (2H, s, ArCH₂O), 4.21
 (2H, q, *J* = 7.2 Hz, OCH₂), 3.45 (2H, s, CH₂), 2.40 (12H, s, SCH₃), 1.25 (3H, t, *J* = 7.2
 Hz, CH₃); ¹³C-NMR (CDCl₃, 50 MHz), δ: 166.3 (2C=O), 134.9, 134.9, 134.8, 133.3,
 132.0, 126.4, 126.1, 125.6, 125.3, 125.1, 123.1, 66.9 (CH₂O), 61.6 (CH₂O), 41.6 (CH₂),
 19.0 (4SCH₃), 14.0 (CH₃); MS m/z (%): 708 (M⁺, 100), 663 (M⁺-OEt, 12), 577 (9), 530
 (30), 515 (11); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 438 (4.43), 420 (sh, 4.34), 370 (4.19),
 274 (4.34), 242 (4.68) nm.

9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-2-(2,6-dioxa-3,5-dioxooctanyl)-

9,10-dihydroanthracene (10c). 77 % yield; m.p.: 128-131 °C; Anal. for C₃₀H₂₄S₈O₄: C,
 52.01 % (Calc.: 51.14), H, 3.86 % (3.44), S, 35.88 % (36.33); FTIR (KBr): 2769, 1741
 (C=O), 1732 (C=O), 1506, 1506, 1145, 1412, 1406, 1368, 1330, 1287, 1265, 1141,
 1027, 759 cm⁻¹; ¹H-NMR (CDCl₃, 200 MHz), δ: 7.40-7.46 (4H, m, ArH), 7.33-7.28
 (3H, m, ArH), 5.25 (2H, s, ArCH₂O), 4.20 (2H, q, *J* = 7.1 Hz, OCH₂), 3.45 (2H, s,
 CH₂), 3.29 (8H, s, SCH₂), 1.25 (3H, t, *J* = 7.1 Hz, CH₃); ¹³C-NMR (CDCl₃, 50 MHz), δ:
 166.4 (C=O), 166.3 (C=O), 135.0, 134.7, 134.5, 133.4, 130.4, 130.3, 126.4, 126.1,
 125.7, 125.5, 125.3, 123.6, 111.0, 110.8, 66.9 (CH₂O), 61.6 (CH₂O), 41.6 (CH₂), 29.6

(SCH₂), 14.07 (CH₃); MS m/z (%): 704 (M⁺, 24), 573 (5); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 450 (4.40), 428 (sh, 4.28), 390 (4.07), 276 (4.32), 242 (4.68) nm.

Synthesis of 2,6-bis(2-hydroxyethyloxy)-9,10-anthraquinone (17). To a solution of anthraflavic acid (**15**) (240 mg, 1 mmol) in hot dry DMF (30 mL) at room temperature and under argon atmosphere, K₂CO₃ (4 mmol, 552 mg) was added, and the solution turned deep red. 2-Bromoethanol (6 mmol, 749.8 mg, 0.448 mL) and potassium iodide (catalic amount) were added. The mixture was stirred at 80-90 °C overnight. The reaction was monitored by tlc. 2-Bromoethanol, K₂CO₃ and KI were added every 24 h, in the same initial ammounts, until the anthraflavic acid was exhausted. The solution was poured on water and ice (75 mL) and the residue extracted with CHCl₃ (3 x 100 mL). The combined extracts were dried (MgSO₄), filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using ethyl acetate:methanol 10:1 mixture as eluent. Further purification was accomplished by crystallization from ethanol. Compound **17** was obtained in 83 % yield; m.p.: 214-216 °C. Anal. for C₁₈H₁₆O₆: C, 64.71 % (Calc.: 65.83), H, 5.10 % (4.91); FTIR (KBr): 3300 (OH), 3101 (OH), 3063, 2937, 2872, 1668 (C=O), 1583, 1522, 1508, 1489, 1458, 1431, 1329, 1311, 1232, 1171, 1155, 1080, 1041, 995, 970, 914, 872, 843, 746, 711, 656, 617 cm⁻¹; ¹H-NMR (DMSO, 200 MHz), δ: 8.09 (2H, d, J_{3,4} = 8.6 Hz, ArH₄), 7.54 (2H, d, J_{1,3} = 2.7 Hz, ArH₁), 7.63 (2H, dd, J_{3,4} = 8.6 Hz, J_{1,3} = 2.7 Hz, ArH₃), 4.97 (2H, t, J = 5.4 Hz, OH), 4.18 (4H, t, J = 4.6 Hz, ArOCH₂), 3.76 (4H, dt, J₁ = 5.4 Hz, J₂ = 4.6 Hz, CH₂OH); ¹³C-NMR (DMSO, 75 MHz), δ: 181.51 (2C=O), 163.98 (2ArC₂O), 135.56 (2ArCH), 129.87 (2ArC₄H), 126.71 (2ArCH), 120.97 (2ArC₃H), 111.16 (2ArC₁H), 70.81 (ArOCH₂), 59.72 (CH₂OH); MS m/z (%): 328 (M⁺, 95), 297 (M⁺-CH₂OH, 59); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 468 (3.61), 362 (3.30), 292 (sh, 3.48), 270 (3.62), 250 (3.98) nm.

Synthesis of 2,6-bis(2-tercbutyldiphenylsilyloxyethyloxy)-9,10-anthraquinone (18).

To a solution of **17** (328 mg, 1 mmol) in dry DMF (50 mL) at room temperature and under argon atmosphere, tercbutyldiphenylsilyl chloride (627 mg, 2.4 mmol, 0.593 mL), and imidazol (681 mg, 10 mmol), were added. The mixture was stirred at room temperature for 16 h. Water (100 mL) was added and the residue extracted with ethyl acetate (3 x 100 mL). The combined extracts were washed with a saturated solution of sodium chloride and dried (MgSO_4), filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane:dichloromethane mixture as eluent. Compound **18** was obtained in 65 % yield; m.p.: 118-121 °C. Anal. for $\text{C}_{50}\text{H}_{52}\text{Si}_2\text{O}_6$: C, 74.44 % (Calc.: 74.60), H, 6.71 % (6.32); FTIR (KBr): 2931, 2856, 1664 ($\text{C}=\text{O}$), 1583, 1489, 1473, 1427, 1359, 1331, 1309, 1269, 1236, 1151, 1128, 1113, 1080, 1049, 1007, 964, 910, 891, 843 cm^{-1} ; ^1H -NMR (CDCl_3 , 200 MHz), δ : 7.45 (2H, d, $J_{3,4} = 8.7$ Hz, ArH_4), 7.80-7.70 (9H, m, ArH), 7.46-7.36 (13H, m, ArH), 7.20 (2H, dd, $J_{3,4} = 8.7$ Hz, $J_{1,3} = 2.7$ Hz, ArH_3), 4.28 (4H, t, $J = 4.8$, ArOCH_2), 4.06 (4H, t, $J = 4.81$ OCH_2Si), 1.08 (18H, s, CH_3); ^{13}C -NMR (CDCl_3 , 50 MHz), δ : 182.14 ($2\text{C}=\text{O}$), 163.81 ($2\text{ArC}_2\text{O}$), 135.76, 135.61 (2ArCH), 134.78 (Ph), 133.32 (Ph), 129.75 ($2\text{ArC}_4\text{H}$), 127.71 (2ArCH), 127.13 (Ph), 120.89 ($2\text{ArC}_3\text{H}$), 110.74 ($2\text{ArC}_1\text{H}$), 69.74 (ArOCH_2), 62.39 (CH_2OSi), 26.76 (6CH_3), 19.20 (C); MS m/z (%): 806 ($\text{M}^+ + 1$, 27), UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 346 (4.32), 300 (4.72), 274 (4.79), 232 (4.35) nm.

Synthesis of 9,10-bis(1,3-dithiol-2-ylidene)-2,6-bis(2-tercbutyldiphenylsilyloxyethyloxy)-9,10-dihydroanthracene derivatives (20a-c). To a solution of phosphonate esters (**7b-c**) (1 mmol) in dry THF (20 mL) at -78 °C and under argon atmosphere, $n\text{-BuLi}$ 1.6 M (1.1 mmol) was added with a syringe dropwise. After 30 min at -78 °C, a solution **18**) in dry THF (134 mg, 0.16 mmol) was added with a syringe

into the solution of the phosphonate carbanion. The mixture was stirred at -78 °C for 1 h and then allowed to warm to 20 °C, and let to stand overnight. The THF was evaporated under reduced pressure, water (75 mL) added and the residue extracted with CH₂Cl₂ (3 x 75 mL). The combined extracts were dried (MgSO₄), filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane: dichloromethane mixtures as eluent.

9,10-bis(1,3-dithiol-2-ylidene)-2,6-bis(2-tercbutyldiphenylsilyloxyethyloxy)-9,10-dihydroanthracene (20a). 85 % yield; m.p.: 136-139 °C; Anal. for C₅₆H₅₆S₄O₄Si₂: C, 69.89 % (Calc.: 68.83), H, 5.78 % (5.78); FTIR (KBr): 2927, 2854, 2717, 1603, 1560, 1545, 1508, 1473, 1425, 1225, 1111, 823, 738, 700 cm⁻¹; ¹H-NMR (CDCl₃, 200 MHz), δ: 7.68-7.62 (8H, m, ArH), 7.58 (2H, d, J_{3,4} = 8.5 Hz, ArH₄), 7.42-7.34 (12H, m, 12 ArH), 7.23 (2H, d, J_{1,3} = 2.4 Hz, ArH₁), 6.99 (2H, dd, J_{3,4} = 8.5 Hz, J_{1,3} = 2.4 Hz, ArH₃), 6.28 (4H, m, CH=), 4.17 (4H, t, J = 4.6 Hz, ArOCH₂), 4.03 (4H, t, J = 4.6 Hz, OCH₂Si), 1.08 (18H, s, CH₃); ¹³C-NMR (CDCl₃, 50 MHz), δ: 156.93 (2C₂), 137.01, 135.67, 135.17, 134.79, 129.65, 127.72, 127.68, 117.06, 111.89, 110.86, 69.23 (ArOCH₂), 62.56 (CH₂OSi), 26.73 (3CH₃), 26.45 (3CH₃), 18.90 (C); MS m/z (%): 977 (M⁺, 87); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 424 (4.22), 408 (4.18), 362 (4.01), 264 (sh, 4.01), 242 (sh, 4.48), 232 (4.59) nm.

9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2,6-bis(2-tercbutyldiphenylsilyloxyethyloxy)-9,10-dihydroanthracene (20b). 95 % yield; m.p.: 87-90 °C (dec); Anal. for C₆₀H₆₄S₈O₄Si₂: C, 61.31 % (Calc.: 62.06), H, 5.46 % (5.51), S, 21.98 % (22.05); FTIR (KBr): 2926, 2854, 2738, 1605, 1560, 1541, 1498, 1471, 1450, 1427, 1313, 1286, 1221, 1111, 1061, 964, 821, 737 cm⁻¹; ¹H-NMR (CDCl₃, 200 MHz), δ: 7.74-7.72 (8H, m, ArH), 7.47-7.37 (14H, m, 12 ArH y 2ArH₄), 7.09 (2H, d, J_{1,3} = 2.4 Hz, ArH₁), 6.81 (2H, dd, J_{3,4} = 8.5 Hz, J_{1,3} = 2.4 Hz, ArH₃), 4.17 (2H, t, J = 4.6 Hz, ArOCH₂), 4.05 (4H, t, J

= 4.6 Hz, OCH₂Si), 2.41 (6H, s, SCH₃), 2.36 (6H, s, SCH₃), 1.09 (18H, s, CH₃); ¹³C-NMR (CDCl₃, 50 MHz), δ: 157.18 (2C₂), 135.63, 135.61, 133.50, 133.42, 129.66, 129.08, 127.67, 127.59, 126.53, 125.80, 125.60, 123.52, 111.95, 111.75, 69.28 (ArOCH₂), 62.62 (CH₂OSi), 26.80 (CH₃), 19.21 (SCH₃), 19.04 (C); MS m/z (%): 1160 (M⁺, 100), 1010 (20); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 430 (4.38), 414 (sh, 4.32), 366 (4.18), 280 (sh, 4.27), 250 (4.65), 232 (4.63) nm.

9,10-bis(1,3-dithiol-4,5-ethylendithio-2-ylidene)-2,6-bis(2-tercbutyldiphenylsilyloxyethyloxy)-9,10-dihydroanthracene (20c). 76 % yield; m.p.: 91-93 °C; Anal. for C₆₀H₆₀S₄O₈Si₂: C, 61.81 % (Calc.: 62.27), H, 5.45 % (5.23), S, 21.65 % (22.12); FTIR (KBr): 2926, 2854, 2742, 2345, 1605, 1560, 1508, 1466, 1456, 1425, 1286, 1221, 1111, 1061, 964, 821, 738 cm⁻¹; ¹H-NMR (CDCl₃, 200 MHz), δ: 7.78-7.75 (8H, m, ArH), 7.48-7.42 (14H, m, ArH), 7.08 (2H, d, J_{1,3} = 2.4 Hz, ArH₁), 6.84 (2H, dd, J_{3,4} = 8.5 Hz, J_{1,3} = 2.4 Hz, ArH₃), 4.21 (4H, t, J = 4.6 Hz, ArOCH₂), 4.08 (4H, t, J = 4.6 Hz, OCH₂Si), 3.25 (8H, s, SCH₂), 1.14 (18H, s, CH₃); ¹³C-NMR (CDCl₃, 50 MHz), δ: 157.22 (2C₂), 136.21, 135.59, 135.11, 134.72, 133.43, 129.63, 129.58, 127.90, 127.65, 127.60, 126.67, 123.95, 112.14, 111.72, 110.76, 110.68, 69.25 (2ArOCH₂), 62.59 (2CH₂OSi), 29.48 (4SCH₂), 26.51 (6CH₃), 19.20 (2C); MS m/z (%): 1156 (M⁺, 100), 1008 (19); UV-Vis (CH₂Cl₂) λ_{max} (log ε): 440 (4.37), 424 (sh, 4.28), 382 (4.09), 250 (4.65), 232 (4.71) nm.

Synthesis of 9,10-bis(1,3-dithiol-2-ylidene)-2,6-bis(2-hydroxyethyloxy)-9,10-dihydroanthracene (21). To a solution of **19** (0.50 mmol) in dry DMF (50 mL) at room temperature and under argon atmosphere, tetrabutylammonium fluoride (452 mg, 1.50 mmol) was added. The mixture was stirred for 16 h at room. Water (75 mL) was added and the residue extracted with CH₂Cl₂ (3 x 100 mL). The combined extracts were dried (MgSO₄), filtered out, and the solvent was removed under reduced pressure.

Purification of products was achieved by column chromatography on silica gel using hexane:dichloromethane mixture as eluent.

9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2,6-bis(2-hidroxyethyloxi)-9,10-dihydroanthracene (21). 85 % yield; m.p.: 222-224 °C (dec); FTIR (KBr): 3421 (br), 2958, 2939, 2873, 1655, 1597, 1525, 1498, 1458, 1429, 1373, 1309, 1298, 1257, 1159, 1107, 1064, 1022, 951 cm^{-1} ; MS m/z (%), 596 ($\text{M}^+ - \text{H}$, 3).

Synthesis of 9,10-bis(1,3-dithiol-2-ylidene)-2,6-bis(2-hydroxyethyloxy)-9,10-dihydroanthracenes (22a-c). To a solution of the 20a-c (0.50 mmol) in dry DMF (50 mL) at room temperature and under argon atmosphere, tetrabutylammonium fluoride (452 mg, 1.50 mmol) was added. The mixture was stirred for 16 h at room. Water (75 mL) was added and the residue extracted with CH_2Cl_2 (3 x 100 mL). The combined extracts were dried (MgSO_4), filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane:dichloromethane mixture as eluent.

9,10-bis(1,3-dithiol-2-ylidene)-2,6-bis(2-hydroxyethyloxy)-9,10-dihydroanthracene (22a). 84 % yield; m.p.: 199-201 °C (dec); Anal. for $\text{C}_{24}\text{H}_{20}\text{S}_4\text{O}_4$: C, 57.60 % (Calc.: 57.60), H, 4.20 % (4.03); FTIR (KBr): 3402 (OH, br), 3068 (OH), 2926, 2854, 1603, 1547, 1516, 1500, 1488, 1413, 1309, 1292, 1223, 1080, 1045, 933 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ : 7.60 (2H, d, $J_{3,4} = 8.5$ Hz, ArH_4), 7.25 (2H, d, $J_{1,3} = 2.3$ Hz, ArH_1), 6.84 (2H, dd, $J_{3,4} = 8.5$ Hz, $J_{1,3} = 2.3$ Hz, ArH_3), 6.39 (4H, s, CH=), 4.16 (4H, t, $J = 4.4$ Hz, CH_2O), 4.01 (4H, t, $J = 4.4$ Hz, CH_2O); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz), δ : 156.58 (2C_2), 137.44, 137.05, 135.14, 134.78, 134.25, 129.65, 128.85, 127.71, 126.15, 124.13, 121.71, 117.20, 117.08, 111.98, 111.02, 69.41 (2ArOCH_2), 61.50 ($2\text{CH}_2\text{OH}$); MS m/z (%): 500 (M^+ , 100); UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 424 (4.46), 408 (sh, 4.42), 362 (4.24), 242 (4.65) nm.

9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2,6-bis(2-hydroxyethyloxy)-9,10-dihydroanthracene (22b). 87 % yield; m.p.: 116-119 °C; Anal. for $C_{28}H_{28}S_8O_4$: C, 49.89 % (Calc. 49.12), H, 4.14 % (4.13); FTIR (KBr): 3421 (OH, br), 2924, 2854, 1603, 1508, 1498, 1219, 611 cm^{-1} ; 1H -NMR ($CDCl_3$, 300 MHz), δ : 7.45 (2H, d, $J_{3,4} = 8.6$ Hz, ArH₄), 7.08 (2H, d, $J_{1,3} = 2.7$ Hz, ArH₁), 6.85 (2H, dd, $J_{3,4} = 8.6$ Hz, $J_{1,3} = 2.7$ Hz, ArH₃), 4.15 (4H, t, $J = 4.2$ Hz, CH_2O), 4.01 (4H, t, $J = 4.2$ Hz, Ar CH_2O), 2.39 (12H, s, SCH_3); ^{13}C -NMR ($CDCl_3$, 50 MHz), δ : 156.87 ($2C_2$), 136.36, 134.78, 129.62, 127.99, 127.70, 126.66, 126.36, 125.37, 123.25, 112.04, 111.64, 69.44 (2 Ar CH_2O), 61.45 (2 CH_2OH), 19.21 (2 SCH_3), 19.06 (2 SCH_3); MS m/z (%): 685 ($M^+ - H$, 100), 534 (51); UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 430 (4.56), 414 (sh, 4.49), 366 (4.36), 278 (sh, 4.48), 248 (4.82) nm.

9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-2,6-bis(2-hydroxyethyloxy)-9,10-dihydroanthracene (22c). 75 % yield; m.p.: 171-173 °C (dec); Anal. for $C_{28}H_{24}S_8O_4$: C, 49.74 % (Calc.: 49.42), H, 3.72 % (3.56); FTIR (KBr): 3357 (OH), 2921, 2863, 1601, 1556, 1509, 1453, 1414, 1315, 1286, 1221, 1169, 1075, 1045, 944 cm^{-1} ; 1H -NMR ($CDCl_3$, 300 MHz), δ : 7.42 (2H, d, $J_{3,4} = 8.1$ Hz, ArH₄), 7.05 (2H, d, $J_{1,3} = 2.2$ Hz, ArH₁), 6.86 (2H, dd, $J_{3,4} = 8.1$ Hz, $J_{1,3} = 2.2$ Hz, ArH₃), 4.16 (4H, m, Ar CH_2O), 4.01 (4H, m, CH_2OH), 2.30 (8H, s, SCH_3); ^{13}C -NMR (DMSO, 75 MHz), δ : 156.25 ($2C_2$), 135.36, 127.11, 126.82, 126.43, 123.58, 112.31, 111.64, 110.25, 110.24, 69.93 (2Ar CH_2O), 61.45 (2 CH_2OH), 29.10 (4 SCH_2); MS m/z (%): 680 (M^+ , 100); UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 438 (3.75), 378 (3.48), 248 (4.02), 236 (4.02) nm.