Supplementary material of the communication:

Bromine catalyzed conversion of S-*tert.*butyl groups into versatile and for self-assembly processes accessible acetyl-protected thiols

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General: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultra Shield 300 MHz, the *J* values are given in Hz. MALDI-TOF spectra was perfomed on a PerSeptive Biosystems Voyager –DE PRO time-of-flight mass spectrometer and EI-MS on a LKB-9000S. Melting points were measured with a Büchi Melting Point B-540 apparatus. TLC was carried out on Merck silica gel 60 F_{254} plates and column chromatography using Merck silica gel 60 (0.040-0.063 mm). Elemental analyses were performed using the ThermoQuest FlashEA 1112 N/Protein Analyzer.

Preparation and characterization of substrates:

1,3-Di(*tert.*butylsulfanyl)-5-bromobenzene (b): To 1,3,5-Tribromobenzene (3.188 g, 10.13 mmol) dissolved in dry DMI (25 ml), sodium-2-methyl-2-propanethiolate (2.271 g, 20.25 mmol) was added portionwise. The reaction mixture was heated for 16 h to 120°C and subsequently poured into saturated NaCl-solution. The organic products were extracted with toluene, washed with water and dried over $MgSO_4$. Isolation by column chromatography

(silica gel, hexane/toluene 4/1) gave 1,3-di(*tert.*butylsulfanyl)-5-bromobenzene **(b)** (1.3169 g; 39%) as a white solid. Mp. 110.5-111.9°C; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.31 (18 H, s, CH_3), 7.65 (1 H, t, *J* 1.5, ArH), 7.68 (2 H, d, *J* 1.5, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 31.4 (CH_3), 47.2 ($C(CH_3)_3$), 121.8, 135.2, 140.3, 144.9; m/z (EI) 333.8 [M^+, 31%], 277.8 [21, M^+- C_4H_8], 221.8 [96, M^+- 2xC_4H_8]. Elemental analysis calcd (%) for $C_{14}H_{21}BrS_2$: C 50.44, H 6.35; found: C 50.66, H 6.05.

1-Phenoxy-3-*tert.*butylsulfanylpropane (e): To 3-phenoxypropyl bromide (1.1861 g, 5.51 mmol) dissolved in dry THF (25 ml) sodium 2-methyl-2-propanethiolate (0.1237 g, 11.0 mmol) was added portionwise. After refluxing for 16 h the reaction mixture was poured into saturated NaCl-solution. The organic products were extracted with CH_2Cl_2, washed with water and dried over $MgSO_4$. Column chromatography (silica gel, dichloromethane/hexane 1/2) provided 1-phenoxy-3-*tert.*butylsulfanylpropane **(e)** (0.654 g; 53%) as a colourless liquid. δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.33 (9 H, s, CH_3), 2.05 (2 H, q, *J* 6.6, CH_2), 2.72 (2 H, t, *J* 7.2, SCH_2), 4.06 (2 H, t, *J* 6.1, OCH_2), 6.88 (3 H, m, ArH), 7.26 (1 H, d, *J* 7.2, ArH), 7.29 (1 H, d, *J* 7.2, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 25.3 (SCH_2), 30.1 (CH_2), 31.4 (CH_3), 42.5 ($C(CH_3)_3$), 66.8 (OCH_2), 114.9, 121.1, 129.8, 159.3; m/z (EI) 224.1 [M^+, 96%], 168.1 [20, M^+-C_4H_8], 131.1 [87, M^+-C_6H_5O], 94.1 (100). Elemental analysis calcd (%) for $C_{13}H_{20}OS$: C 69.59, H 8.98; found: C 69.48, H 8.73.

4-*tert.*Butylsulfanyl-styrene (g): 4-Bromophenyl-*tert.*butyl sulfide (4.0633 g, 16.6 mmol), triphenylphosphine (2.1769 g, 8.3 mmol) and *trans*-bis(triphenylphosphane)platinum(II) chloride (0.5825 g, 0.83 mmol) were dissolved in dry DMF (20 ml). After addition of tributyl(vinyl)tin (6.3 ml, 21.5 mmol), the reaction mixture was heated to 120°C for 16 h. After evaporation of the solvents purification by column chromatography (silica gel, hexane/toluene 20/1) afforded 4-*tert.*butylsulfanyl-styrene **(g)** (0.82 g, 25% yield) as colour-

less liquid. δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.29 (9 H, s, CH_3), 5.30 (1 H, dd, *J* 11.0 and *J* 1.0, $=CH_2$), 5.78 (1 H, dd, *J* 17.6 and *J* 1.0, $=CH_2$) 6.72 (1 H, dd, *J* 18.0 and *J* 11.0, CH=), 7.36 (2 H, d, *J* 8.2, ArH), 7.49 (2 H, d, *J* 8.2, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 31.3 (CH_3), 46.5 ($C(CH_3)_3$), 115.2 ($=CH_2$), 126.6, 132.5, 136.6, 137.9; m/z (EI) 192.0 [M^+, 43%], 136.0 [100, M^+- C_4H_8]. Elemental analysis calcd (%) for $C_{12}H_{16}S$: C 74.94, H 8.39; found: C 74.69, H 8.39.

1-*tert.*-Butylsulfanyl-4-(2'-triisopropylsilylethynyl)-benzene (h): 1-*tert.*Butylsulfanyl-4-bromo-benzene (2.4782 g, 10.1 mmol), dry diisopropylamine (10 ml), trans-bis(triphenyl-phosphane)platinum(II) chloride (0.1772 g, 0.25 mmol) and copper(I) iodide (0.0962 g, 0.5 mmol) were dissolved in Ar-saturated, dry THF (70 ml). After addition of (triisopropyl-silyl)acetylene (4.5 ml, 20.2 mmol), the solution was stirred at 70°C for 3 h. After evaporation of the solvents, purification by column chromatography (silica gel, dichloromethane/hexane 2/1) provided 1-*tert.*-butylsulfanyl-4-(2'-triisopropylsilylethynyl)-benzene **(h)** (3.116 g, 89%) as a colourless liquid. δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.13 (18 H, s, CH_3), 1.28 (9 H, s, CH_3), 7.45 (4 H, d, *J* 3.6, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 11.7 (CH), 19.1 (CH_3), 31.3 (CH_3), 46.8 ($C(CH_3)_3$), 92.7, 106.8, 124.3, 132.3, 133.6, 137.5; m/z (EI) 346.1 [M^+, 53%], 247.0 [100, M^+- C_4H_8, - C_3H_7]. Elemental analysis calcd (%) for $C_{21}H_{34}SSi$: C 72.76, H 9.89; found: C 72.55, H 9.52.

9,10-Bis-(4-*tert.*-butylsulfanyl-phenylethynyl)-anthracene (i): 9,10-Dibromoanthracene (0.510 g, 1.52 mmol) was suspended in dry, Ar-saturated diethylamine (23 ml). Copper iodide (0.023 g, 0.12 mmol), *trans*-bis(triphenylphosphane)platinum(II) chloride (0.042 g, 0.60 mmol) and 1-*tert*.-butylsulfanyl-4-ethynyl-benzene (0.794 g, 4.17 mmol) were added subsequently. The reaction mixture was heated to reflux under an Ar-atmosphere for 6 h. Filtration and washing with CH_2Cl_2 followed by column chromatography (silica gel,

hexane/toluene 2/1) provided 9,10-bis-(4-*tert.*-butylsulfanyl-phenylethynyl)-anthracene **(i)** (0.595 g; 1.07 mmol; 70%) as a yellow-orange solid. Mp. 222.0–223.0°C (decomp.). δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.35 (18 H, s, CH_3), 7.61–7.68 (8 H, m, ArH), 7.74 (4 H, d, *J* 6.2, ArH), 8.67–8.70 (4 H, m, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 31.4 (CH_3), 47.1 ($C(CH_3)_3$), 88.4, 102.4 (C≡C), 118.8, 124.1, 127.4, 127.6, 132.0, 132.5, 134.2, 137.9; m/z (MALDI TOF) 553.95 [M^+], 497.88 [M^+ - *t*Bu], 330.91 [M^+ - *t*Bu, - PhS*t*Bu]. Elemental analysis calcd (%) for $C_{38}H_{34}S_2$: C 82.26, H 6.18; found: C 81.89, H 6.27.

1-*tert.*-Butylsulfanyl-4-ethynyl-benzene (j): 1-*tert*.-Butylsulfanyl-4-(triisopropylsilylethynyl)-benzene (0.7875 g, 2.27 mmol) was dissolved in THF (15 ml) and tetrabutylammonium fluoride trihydrate (1.420 g, 4.50 mmol) added in two portions at 0 °C. The ice bath was removed an the mixture stirred at RT for 2 h. Then the reaction mixture was filtered through a plug of silica gel, washed with CH_2Cl_2 several times and the solvents removed in vacuo afforded 1-*tert.*-butylsulfanyl-4-ethynyl-benzene **(j)** (0.4229 g, 98%) as a yellowish liquid without further purification. δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.28 (9 H, s, CH_3), 3.15 (1 H, s, ≡CH), 7.44 (2 H, d, *J* 8.2, ArH), 7.49 (2 H, d, *J* 8.2, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 31.0 (CH_3), 46.5 ($C(CH_3)_3$), 78.6, 83.1 (C≡C), 122.5, 132.1, 133.9, 137.2; m/z (EI) 190.1 [M^+], 134.0 [M^+ - C_4H_8]; Elemental analysis calcd (%) for $C_{12}H_{14}S$: C 75.74, H 7.42; found: C 75.44, H 7.04.

Characterization of reaction products:

Acetyl 4-bromo-thiophenolate (a): Column chromatography (silica gel, dichloromethane); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.43 (3 H, s, CH_3), 7.26 (2 H, d, *J* 8.6, ArH), 7.54 (2 H, d, *J* 8.6, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 30.6 (CH_3), 124.5, 127.3, 132.8, 136.3, 193.7 (C=O).

1,3-Acetylsulfanyl-5-bromobenzene (b): Column chromato-graphy (silica gel, hexane/ethyl acetate 9/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.44 (3 H, s, CH_3), 7.40 (1 H, t, *J* 1.5, ArH), 7.60 (2 H, d, *J* 1.5, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 30.7 (CH_3), 123.0, 130.9, 138.1, 138.7, 192.8 (C=O); m/z (EI) 305.7 [M^+, 30%], 263.7 [96, M^+-CH_2=C=O], 221.7 [30, M^+-*2x*CH_2=C=O]; Mp. 55.0-56.0°C. Elemental analysis calcd (%) for $C_{10}H_9BrO_2S_2$: C 39.35, H 2.97; found: C 39.58, H 2.88.

1-Acetoxy-4-acetylsulfanyl benzene (c): Column chromatography (silica gel, dichloromethane/hexane 2/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.31 (3 H, s, $OCOCH_3$), 2.42 (3 H, s, $SCOCH_3$), 7.15 (2 H, d, *J* 8.6, ArH), 7.42 (2 H, d, *J* 8.6, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 21.5 ($OCOCH_3$), 30.6 ($SCOCH_3$), 122.9, 125.5, 151.9, 169.5 (SC=O), 194.2 (OC=O); m/z (EI) 210.0 [M^+, 22%], 168.0 [76, M^+-CH_2=C=O], 126.0 [100, M^+- 2xCH_2=C=O]; Mp. 70.0-71.5°C.

1-Acetylsulfanyl-4-acetylsulfanylmethyl benzene (d): Column chromatography (silica gel, dichloromethane/hexane 2/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.35 (3 H, s, CH_3), 2.40 (3 H, s, CH_3), 4.11 (2 H, s, CH_2), 7.33 (4 H, s, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 30.5, 30.6, 33.3, 127.0, 130.0, 134.8, 139.6, 194.2 (C=O), 195.1 (C=O); m/z (EI) 239.9 [M^+, 21%], 198.0 [100,

M^+- CH_2=C=O], 123.1 [89, M^+- CH_2CO, - $SCOCH_3$]. Elemental analysis calcd (%) for $C_{11}H_{12}O_2S_2$: C 54.97, H 5.03; found: C 54.83, H 4.79.

1-Phenoxy-3-acetylsulfanylpropane (e): Column chromato-graphy (silica gel, dichloromethane/hexane 1/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.08 (2 H, q, *J* 6.6, CH_2), 2.35 (3 H, s, CH_3), 3.08 (2 H, t, *J* 7.0, SCH_2), 4.02 (2 H, t, *J* 6.0, OCH_2), 6.88-7.00 (3 H, m, ArH), 7.28 (1 H, d, *J* 7.2, ArH), 7.31 (1 H, d, *J* 7.2, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 26.3, 29.7, 31.1 (CH_2), 66.4 (OCH_2), 114.9, 121.2, 129.9, 159.2, 196.2 (C=O); m/z (EI) 210.0 [M^+, 17%], 117.1 [100, M^+-C_6H_5O].

4,4'-Diacetylsulfanyl-*trans*-stilbene (f): Column chromato-graphy (silica gel, dichloromethane/hexane 2/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.44 (3 H, s, CH_3), 7.14 (2 H, s, CH=CH), 7.41 (4 H, d, *J* 8.1, ArH), 7.55 (4 H, d, *J* 8.1, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 30.7 (CH_3), 127.6, 127.7, 129.5, 135.1, 138.5, 194.5 (C=O); Mp. 168.5-169.6°C.

4-Acetylsulfanyl-styrene (g): Column chromatography (silica gel, dichloromethane/hexane 2/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.42 (3 H, s, CH_3), 5.32 (1 H, d, *J* 10.7, =CH_2), 5.80 (1 H, d, *J* 17.4, =CH_2), 6.72 (1 H, dd, *J* 17.7 and *J* 10.8, ArCH=), 7.37 (2 H, d, *J* 8.2, ArH), 7.45 (2 H, d, *J* 8.2, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 30.6 (CH_3), 115.8 (=CH_2), 127.3, 127.8, 134.9, 136.4, 139.1, 194.6 (C=O); m/z (EI) 178.0 [M^+, 35%], 136.0 [100, M^+- CH_2=C=O].

1-Acetylsulfanyl-4-(2'-trisisopropylsilylethynyl)-benzene (h): Column chromatography (silica gel, dichloromethane/hexane 2/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.13 (9 H, s, CH_3), 2.42 (3 H, s, $SCOCH_3$), 7.35 (2 H, d, *J* 8.2, ArH), 7.50 (2 H, d, *J* 8.2, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 11.7 (CH), 19.0 (CH_3), 30.6 ($SCOCH_3$), 93.2 (C≡C), 106.6 (C≡C), 125.2,

128.2, 133.0, 134.5, 193.8 (C=O); m/z (EI) 332.0 [M^+, 35%], 289.0 [100, M^+ - CH_3CO^+]. Elemental analysis calcd (%) for $C_{19}H_{28}OSSi$: C 68.62, H 8.49; found: C 68.61, H 8.13.

9,10-Bis-(4'-acetylsulfanyl-phenylethynyl)-anthracene (i): Column chromatography (silica gel, dichloromethane/hexane 2/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.48 (6 H, s, CH_3), 7.51 (4 H, d, *J* 8.1, ArH), 7.65-7.68 (4 H, m, ArH), 7.81 (4 H, d, *J* 8.2, ArH), 8.65-8.69 (4 H, m, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 30.4 (CH_3), 88.1 (C≡C), 101.74 (C≡C), 118.4, 124.6, 127.1, 127.2, 128.6, 132.3, 134.5, 193.4 (C=O); m/z (MALDI TOF) 525.91 [M^+], 452.80 [M^+-SAc]; Mp. 248-249°C.

1-Acetylsulfanyl-4-ethynyl-benzene (j): Column chromato-graphy (silica gel, dichloromethane/hexane 2/1); δ_H(300 MHz; $CDCl_3$; Me_4Si) 2.41 (3 H, s, CH_3), 3.13 (1 H, s, C≡H), 7.35 (2 H, d, *J* 8.5, ArH), 7.50 (2 H, d, *J* 8.5, ArH); δ_C(75 MHz; $CDCl_3$; Me_4Si) 30.3 (CH_3), 78.8 (C≡C), 82.8 (C≡C), 123.3, 128.8, 132.7, 134.2, 193.3 (C=O); m/z (EI) 176.0 [M^+, 34%], 134.0 [100, M^+- CH_2=C=O].