10.1071/CH09308_AC

Australian Journal of Chemistry 2010, 63(2), 303–314

Accessory Publication

Preparation of Azobenzenealkanethiols for Self-Assembled Monolayers with Photoswitchable Properties

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Here the synthesis of the nitroso compounds **7**-**15** and **34** as well the coupling of these to form the azo compounds **16**-**24a,b** are described.

*Preparation of Nitrosobenzene compounds; 4-Methyl-1-nitrosobenzene **7**; Typical Procedure*

To a stirred solution of *p*-methylaniline (10.7 g, 100 mmol) in methanol (30 mL) was added a solution of ammonium molybdate tetrahydrate (2.7 g, 2.2 mmol) in water (40 mL) to yield a white suspension. After cooling the mixture to 0°C (ice bath), H_2O_2 (35 %, 40 mL) was added. The resulting solution was stirred for 2.5 h at 0°C, then carefully mixed with water (25 mL). The product was formed as an ochre precipitate, which was filtered, washed with water (15 mL) and cold methanol (15 mL) (11.8 g, 97 mmol, 98 % yield).

Yield: 11.8 g (97 mmol, 98 %), ochre solid.
^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 7.81 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, H_2), 7.39 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, H_3), 2.44 (s, 3H, H_5).
^{13}C NMR (100 MHz, $CDCl_3$), δ [ppm]: 165.59 (C_1), 147.22 (C_4), 129.72 (C_3), 121.28 (C_2), 21.95 (CH_3).

*1-Trifluoromethoxy-4-nitrosobenzene **8***

The resulting solution was stirred for 24 h at 2.5 °C (cooling with cryostat instead of an ice bath). At room temperature the product exists as green liquid. Therefore the product had to be separated by extraction with pentane. The solvent was removed *in vacuo* (pressure 900 mbar) (4.2 g, 22 mmol, 79 % yield).

Yield: 4.2 g (22 mmol, 79 %), green liquid.
^{1}H NMR (300 MHz, $CDCl_3$), δ [ppm]: 7.97 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H_3), 7.43 (dd, $^3J_{HH}$ = 9.0 Hz, $^5J_{HF}$ = 0.9 Hz, 2H, H_2).
^{13}C NMR (75 MHz, $CDCl_3$), δ [ppm]: 163.20 (C_4), 153.98 (d, $^3J_{CF}$ = 1.7 Hz, C_1-F), 122.81 (C_3), 120.64 (d, $^4J_{CF}$ = 0.8 Hz, C_2-F), 120.28 (q, $^1J_{CF}$ = 259.8 Hz, CF_3).
^{19}F NMR (200 MHz, $CDCl_3$), δ [ppm]: -57.54.

*4-Trifluoromethylnitrosobenzene **9***

Yield: 5.9 g (29 mmol, 97 %), beige solid.
^{1}H NMR (300 MHz, $CDCl_3$), δ [ppm]: 8.00 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H_2), 7.92 (d, 1H, $^3J_{HH}$ = 8.4 Hz, H_3).

^{13}C NMR (75 MHz, $CDCl_3$), δ [ppm]: 164.07 (C_1), 135.80 (q, $^3J_{CF}$ = 32.8 Hz, C_4-F), 126.87 (q, $^4J_{CF}$ = 3.8 Hz, C_3-F), 123.26 (q, $^1J_{CF}$ = 273.1 Hz, CF_3), 120.72 (C_2).
^{19}F NMR (200 MHz, $CDCl_3$), δ [ppm]: -63.09.

Nitrosobenzene ***10***

The mixture was stirred for 24 h at 2.5 °C (cooled by cryostat). The crude product was filtered and washed with water and methanol which was only pressed out. The product was used without further purification.

Yield: 6.5 g (61 mmol, 112 %, contaminated by water and methanol), light-brown solid.
^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 7.88 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H_2), 7.72-7.66 (m, 1H, H_4), 7.60 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H_3).
^{13}C NMR (100 MHz, $CDCl_3$), δ [ppm]: 165.80 (C_1), 135.52 (C_4), 129.22 (C_3), 120.84 (C_2).

1-Fluoro-4-nitrosobenzene ***11***

The mixture was stirred for 2 days at 2.5 °C (cooling with cryostat).

Yield: 6.0 g (50 mmol, 107 % contaminated by water and methanol), brown-yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 7.99-7.92 (m, 2H, H_3), 7.32-7.24 (m, 2H, H_2).
^{13}C NMR (100 MHz, $CDCl_3$), δ [ppm]: 166.84 (d, $^1J_{CF}$ = 260.8 Hz, 1F-C_1), 163.58 (d, $^4J_{CF}$ = 2.5 Hz, 1F-C_4), 123.91 (d, $^3J_{CF}$ = 10.2 Hz, 1F-C_3), 116.33 (d, $^2J_{CF}$ = 23.4 Hz, 1F-C_2).
^{19}F NMR (200 MHz, $CDCl_3$), δ [ppm]: -100.12.

1-Chloro-4-nitrosobenzene ***12***

The mixture was stirred for 5 days at room temperature.

Yield: 12.2 g (87 mmol, 202 % contaminated by water and methanol), beige solid.
^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 7.85 (d, $^3J_{HH}$ = 8.7 Hz, H, H_3), 7.59 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H_2).
^{13}C NMR (100 MHz, $CDCl_3$), δ [ppm]: 163.94 (C_4), 142.81 (C_1), 129.65 (C_2), 122.16 (C_3).

1-Bromo-4-nitrosobenzene ***13***

The mixture was stirred for 5 days at room temperature.

Yield: 8.1 g (44 mmol, 152 % contaminated by water and methanol), beige solid.
^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 7.77 (s, 4H, $H_{2,3}$).
^{13}C NMR (100 MHz, $CDCl_3$), δ [ppm]: 163.80 (C_4), 132.66 (C_2), 131.71 (C_1), 122.11 (C_3).

4-Methoxycarbonyl-1-nitrosobenzene ***14***

The mixture was stirred for 5 days at room temperature.

Yield: 9.4 g (57 mmol, 167 % contaminated by water and methanol), yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 8.27 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H_3), 7.91 (d, $^3J_{HH}$ = 8.6 Hz, 2H, H_2), 3.96 (s, 3H, $COOCH_3$).
^{13}C NMR (100 MHz, $CDCl_3$), δ [ppm]: 165.76 ($COOCH_3$), 164.32 (C_1), 135.12 (C_4), 130.99 (C_3), 120.34 (C_2), 52.74 ($COOCH_3$).

4-Cyano-1-nitrosobenzene ***15***

The mixture was stirred for 24 h at 2 °C. Recrystallization yielded 22.3 g of 4-Cyano-1-nitrosobenzene.

Yield: 22.3 g (169 mmol, 402 % contaminated by water and methanol), yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$), δ [ppm]: 7.98 (s, 4H, $H_{2,3}$).
^{13}C NMR (125 MHz, $CDCl_3$), δ [ppm]: 162.15 (C_1), 133.96 (C_3), 120.75 (C_2), 118.37 (C_4), 117.40 (CN).

1-Methoxy-4-nitrosobenzene ***34***

Yield: 1.77 g (13 mmol, 32 %), orange-yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 8.22-8.17 (m, 2H, H_3), 6.98-6.92 (m, 2H, H_2), 3.90 (s, 3H, CH_3O).
^{13}C NMR (100 MHz, $CDCl_3$), δ [ppm]: 164.55 ($C_{1,4}$), 125.86 (C_3), 113.96 (C_2), 55.92 (CH_3O).

Preparation of Azobenzenealkanethiolates; 4-[4-(p-Tolyldiazenyl)phenyl]butylethanethioate ***16a****; Typical procedure*

To a solution of 4-(4-aminophenyl)butylethane thioate **1a** (1.1 g, 4.8 mmol) in degassed acetic acid (30 mL) was added nitrosotoluene **7** (1.2 g, 10 mmol). The mixture was stirred at room temperature for three days. Thin layer chromatography was used to control if the turnover was complete. In the circumstance of an incomplete turnover more nitroso compound was added. This was continued until the reaction was finished. The solvent was removed *in vacuo* and the residue was dissolved in dichloromethane, washed with water and dried *in vacuo*. The residue was purified by chromatography on silica gel using dichloromethane/ petrol ether 3:7 > 7:3, only dichloromethane as eluent to yield 4-[4-(*p*-tolyldiazenyl)phenyl]butylethanethioate **16a** as an orange solid (1.3 g, 4.0 mmol, 83 % yield).

Yield: 1.3 g (4.0 mmol, 83 %), orange solid.
mp 65-68 °C. (Found: C 69.56, H 6.77, N 8.48, S 9.34. Calc. for $C_{19}H_{22}N_2OS$: C 69.90, H 6.79, N 8.58, S 9.82%).
ν_{max} (KBr)/cm^{-1} 3022 ($\nu_{(C\text{-}H\ ar)}$), 2931 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2856 ($\nu_{(-CH2)}$), 1693 ($\nu_{(C=O)}$), 1600 ($\nu_{(C\text{-}C\ ar)}$), 1579 ($\nu_{(C\text{-}C\ ar)}$), 1497, 1459 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1408, 1153, 1135, 826 ($\delta_{(C\text{-}H\ ar)}$).
^{1}H NMR (500 MHz, C_6D_6), δ [ppm]: 8.05 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H_2), 8.04 (d, $^3J_{HH}$ = 8.1 Hz, 2H, $H_{2'}$), 7.01 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_3), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 2H, $H_{3'}$), 2.73 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.30 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.03 (s, 3H, CH_3-ar), 1.88 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.45-1.33 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).
^{13}C NMR (125 MHz, C_6D_6), δ [ppm]: 194.25 ($CH_2CH_2CH_2CH_2SCOCH_3$), 151.83 (C_1), 151.60 ($C_{1'}$), 145.51 (C_4), 141.27 ($C_{4'}$), 130.00 ($C_{3'}$), 129.35 (C_3), 123.39 ($C_{2'}$), 123.33 (C_2), 35.34 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.37 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.15 ($CH_2CH_2CH_2CH_2SCOCH_3$),

29.59 ($CH_2CH_2CH_2CH_2SCOCH_3$),
28.96 ($CH_2CH_2CH_2CH_2SCOCH_3$),
21.23 (CH_3-ar).
m/z (EI) 326 (96%, M^+), 165 (11%, $C_{10}H_{14}S^+$), 149 (13%, $C_{10}H_{15}N$), 107 (41%, $C_7H_9N^+$), 91 (100%, $C_7H_7^+$), 65 (12%), 43 (39%, $C_2H_3O^+$ or $C_3H_7^+$).

3-[4-(p-Tolyldiazenyl)phenyl]propylethanethioate ***16b***

Yield: 1.6 g (5.1 mmol, 51 %), orange solid.
mp 82-84 °C. (Found: C 69.11, H 6.56, N 8.85, S 10.76. Calc. for $C_{18}H_{20}N_2OS$: C 69.20, H 6.45, N 8.97, S 10.26%).
ν_{max} (KBr)/cm^{-1} 3022 ($\nu_{(C\text{-}H\ ar)}$), 2930 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2860 ($\nu_{(-CH2)}$), 1695 ($\nu_{(C=O)}$), 1600 ($\nu_{(C\text{-}C\ ar)}$), 1496, 1403, 1153, 1135, 821 ($\delta_{(C\text{-}H\ ar)}$).
^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 8.04 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_2), 8.02 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $H_{2`}$), 7.00 (d, $^3J_{HH}$ = 9.3 Hz, 2H, $H_3$), 6.97 (d, $^3J_{HH}$ = 8.6 Hz, 2H, $H_{3`}$), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.37 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.03 (s, 3H, CH_3-ar), 1.88 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.72-1.57 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).
^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.11 ($CH_2CH_2CH_2SCOCH_3$), 151.86 (C_1), 151.55 ($C_{1`}$), 144.60 ($C_4$), 141.32 ($C_{4`}$), 130.00 (C_3), 129.37 ($C_{3`}$), 123.43 ($C_{2`}$), 123.34 (C_2) 34.85 ($CH_2CH_2CH_2SCOCH_3$),
31.33 ($CH_2CH_2CH_2SCOCH_3$),
30.16 ($CH_2CH_2CH_2SCOCH_3$),
28.67 ($CH_2CH_2CH_2SCOCH_3$),
21.25 (CH_3-ar).
m/z (EI) 312 (86%, M^+), 193 (39%, $C_{11}H_{13}OS^+$), 119 (18%, $C_7H_7N_2^+$), 107 (11%, $C_7H_9N^+$), 91 (100%, $C_7H_7^+$), 43 (24%, $C_2H_3O^+$ or $C_3H_7^+$).

4-{4-[(4-Trifluoromethoxyphenyl)diazenyl]phenyl} butylethanethioate ***17a***

Yield: 1.2 g (3.0 mmol, 67 %), orange solid.
mp 61-63 °C. (Found: C 57.72, H 4.93, N 6.98, S 8.27. Calc. for $C_{19}H_{19}F_3N_2O_2S$: C 57.57, H 4.83, N 7.07, S 8.09%).
ν_{max} (KBr)/cm^{-1} 3024 ($\nu_{(C\text{-}H\ ar)}$), 2930 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2855 ($\nu_{(-CH2)}$), 1690 ($\nu_{(C=O)}$), 1600 ($\nu_{(C\text{-}C\ ar)}$), 1495, 1459 ($\delta_{(-CH2)}$, $\delta_{(-CH3)}$), 1408, 1287, 1167, 1135, 858 ($\delta_{(C\text{-}H\ ar)}$).
^{1}H NMR (500 MHz, C_6D_6), δ [ppm]: 7.96 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_2), 7.77 (d, $^3J_{HH}$ = 8.9 Hz, 2H, $H_{2`}$), 7.02 (d, $^3J_{HH}$ = 8.2 Hz, 2H, $H_3$), 6.93 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $H_{3`}$), 2.72 (t, $^3J_{HH}$ = 6.8 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.31 (t, $^3J_{HH}$ = 7.0 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.45-1.34 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).
^{13}C NMR (125 MHz, C_6D_6), δ [ppm]: 194.25 ($CH_2CH_2CH_2CH_2SCOCH_3$), 151.44 (C_1), 151.32 ($C_{1`}$), 150.85 ($C_{4`}$), 146.42 (C_4), 129.44 (C_3), 124.59 ($C_{2`}$), 123.54 ($C_2$), 122.09 ($C_{3`}$), 121.06 (q, $^1J_{CF}$ = 257.6 Hz, CF_3), 35.36 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.33 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.15 ($CH_2CH_2CH_2CH_2SCOCH_3$),

29.60 ($CH_2CH_2CH_2CH_2SCOCH_3$),
28.91 ($CH_2CH_2CH_2CH_2SCOCH_3$).
^{19}F NMR (400 MHz, C_6D_6), δ [ppm]: -57.73.
m/z (EI) 396 (58%, M^+), 353 (37%, M^+-$C_3H_7^+$), 189 (17%, $C_6H_4F_3N_2O^+$), 165 (20%, $C_{10}H_{13}S^+$), 161 (100%, $C_7H_4F_3O^+$), 149 (17%, $C_{10}H_{15}N$), 123 (50%), 107 (67%, $C_7H_9N^+$), 95 (47%), 43 (40%, $C_2H_3O^+$ or $C_3H_7^+$).

3-{4-[(4-Trifluoromethoxyphenyl)diazenyl]phenyl} propylethanethioate ***17b***

Yield: 2.1 g (5.4 mmol, 61 %), orange solid.
mp 73-75 °C. (Found: C 56.24, H 4.65, N 7.31, S 8.56. Calc. for $C_{18}H_{17}F_3N_2O_2S$: C 56.54, H 4.48, N 7.33, S 8.39%).
ν_{max} (KBr)/cm^{-1} 3030 ($\nu_{(C\text{-}H\ ar)}$), 2934 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2863 ($\nu_{(-CH2)}$), 1689 ($\nu_{(C=O)}$), 1602 ($\nu_{(C\text{-}C\ ar)}$), 1496, 1459 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1406, 1262, 1167, 1104, 855 ($\delta_{(C\text{-}H\ ar)}$).
^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.93 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_2), 7.76 (d, $^3J_{HH}$ = 8.9 Hz, 2H, $H_{2`}$), 6.97 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_3$), 6.93 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{3`}$), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.38 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.03 (s, 3H, CH_3-ar), 1.90 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.73-1.59 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).
^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.10 ($CH_2CH_2CH_2SCOCH_3$), 151.48 (C_1), 151.28 ($C_{1`}$), 150.88 (d, $^3J_{CF}$ = 1.7 Hz, 1F-$C_{4`}$), 145.49 (C_4), 129.45 (C_3), 124.60 ($C_{2`}$), 123.57 ($C_2$), 121.05 (q, $^1J_{CF}$ = 257.7 Hz, $CF_3$), 121.47 ($C_{2`}$) 34.87 ($CH_2CH_2CH_2SCOCH_3$),
31.30 ($CH_2CH_2CH_2SCOCH_3$),
30.15 ($CH_2CH_2CH_2SCOCH_3$),
28.64 ($CH_2CH_2CH_2SCOCH_3$).
^{19}F NMR (300 MHz, C_6D_6), δ [ppm]: -57.51.
m/z (EI) 382 (100%, M^+), 279 (23%, $C_{14}H_{11}F_3N_2O^+$), 193 (56%, $C_{11}H_{13}OS^+$), 161 (89%, $C_7H_4F_3O^+$), 107 (14%, $C_7H_9N^+$), 95 (53%), 43 (55%, $C_2H_3O^+$ or $C_3H_7^+$).

4-{4-[(4-Trifluoromethylphenyl)diazenyl]phenyl} butylethanethioate ***18a***

Yield: 1.3 g (3.4 mmol, 76 %), orange solid.
mp 53-55 °C. (Found: C 59.90, H 5.14, N 7.31, S 8.50. Calc. for $C_{19}H_{19}F_3N_2OS$: C 59.99, H 5.03, N 7.36, S 8.43%).
ν_{max} (KBr)/cm^{-1} 3023 ($\nu_{(C\text{-}H\ ar)}$), 2930 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2854 ($\nu_{(-CH2)}$), 1689 ($\nu_{(C=O)}$), 1602 ($\nu_{(C\text{-}C\ ar)}$), 1500, 1459 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1407, 1322, 1170, 1136, 853 ($\delta_{(C\text{-}H\ ar)}$).
^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.95 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{2`}$), 7.77 (d, $^3J_{HH}$ = 8.1 Hz, 2H, $H_2$), 7.37 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{3`}$), 7.01 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 2.72 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.31 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.90 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.49-1.30 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).
^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.25 ($CH_2CH_2CH_2CH_2SCOCH_3$), 154.88 (d, $^5J_{CF}$ = 0.8 Hz, $C_{1`}$), 151.43 ($C_1$), 146.93 ($C_4$), 132.01 (q, $^2J_{CF}$ = 32.3 Hz, $C_{4`}$), 129.46 (C_3), 126.45 (q, $^3J_{CF}$ = 3.7 Hz, $C_{3`}$), 124.65 (q, $^1J_{CF}$ = 272.3 Hz, $CF_3$), 123.72 ($C_{2`}$), 123.25 (C_2), 35.37 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.28 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.15 ($CH_2CH_2CH_2CH_2SCOCH_3$),
29.59 ($CH_2CH_2CH_2CH_2SCOCH_3$),
28.90 ($CH_2CH_2CH_2CH_2SCOCH_3$).
^{19}F NMR (300 MHz, C_6D_6), δ [ppm]: -62.12.
m/z (EI) 380 (100%, M^+), 337 (34%, M^+-$C_3H_7^+$), 145 (81%, $C_7H_5F_3^+$), 123 (52%), 107 (94%, $C_7H_9N^+$), 43 (52%, $C_2H_3O^+$ or $C_3H_7^+$).

3-{4-[(4-Trifluoromethylphenyl)diazenyl]phenyl} propylethanethioate ***18b***

Yield: 2.2 g (6.0 mmol, 67 %), orange solid.
mp 63-65 °C. (Found: C 58.44, H 4.84, N 7.45, S 8.95. Calc. for $C_{18}H_{17}F_3N_2OS$: C 59.00, H 4.68, N 7.65, S 8.75%).
ν_{max} (KBr)/cm^{-1} 2933 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2863 ($\nu_{(-CH2)}$), 1687 ($\nu_{(C=O)}$), 1603 ($\nu_{(C-C\ ar)}$), 1500, 1458 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1406, 1323, 1171, 1105, 851 ($\delta_{(C-H\ ar)}$).
^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.93 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{2`}$), 7.76 (d, $^3J_{HH}$ = 8.2 Hz, 2H, $H_2$), 7.36 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{3`}$), 6.97 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.37 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 1.90 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.73-1.58 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).
^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.11 ($CH_2CH_2CH_2SCOCH_3$), 154.84 (d, $^5J_{CF}$ = 1.1 Hz, $C_{1`}$), 151.46 ($C_1$), 146.01 ($C_4$), 132.02 (q, $^2J_{CF}$ = 32.3 Hz, $C_{4`}$), 129.48 (C_3), 126.45 (q, $^3J_{CF}$ = 3.8 Hz, $C_{3`}$), 124.63 (q, $^1J_{CF}$ = 272.3 Hz, $CF_3$), 123.76 ($C_{2`}$), 123.26 (C_2), 34.88 ($CH_2CH_2CH_2SCOCH_3$),
31.27 ($CH_2CH_2CH_2SCOCH_3$),
30.16 ($CH_2CH_2CH_2SCOCH_3$),
28.62 ($CH_2CH_2CH_2SCOCH_3$).
^{19}F NMR (300 MHz, C_6D_6), δ [ppm]: -62.11.
m/z (EI) 366 (97%, M^+), 193 (89%, $C_{11}H_{13}OS^+$), 145 (100%, $C_7H_5F_3^+$), 107 (22%, $C_7H_9N^+$), 43 (62%, $C_2H_3O^+$ or $C_3H_7^+$).

4-[4-(Phenyldiazenyl)phenyl]butylethanethioate ***19a***

Yield: 3.1 g (10 mmol, 84 %), orange liquid.
(Found: C 68.77, H 6.64, N 8.78, S 11.47. Calc. for $C_{18}H_{20}N_2OS$: C 69.20, H 6.45, N 8.97, S 10.26%).
ν_{max} (KBr)/cm^{-1} 3043 ($\nu_{(C-H\ ar)}$), 2934 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2858 ($\nu_{(-CH2)}$), 1690 ($\nu_{(C=O)}$), 1602 ($\nu_{(C-C\ ar)}$), 1499, 1484, 1444 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1415, 1353, 1135, 848 ($\delta_{(C-H\ ar)}$).
^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 8.08-7.98 (m, 4H, $H_{2`,2}$), 7.24-7.14 (m, 2H, $H_{3`}$), 7.13-7.05 (m, 1H, $H_{4`}$), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 2.72 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.29 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.47-1.30 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).
^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.25 ($CH_2CH_2CH_2CH_2SCOCH_3$), 153.34 ($C_{1`}$), 151.68 ($C_1$), 145.84 ($C_4$), 130.89 ($C_{4`}$), 129.35 ($C_{3`}$), 129.27 ($C_3$), 123.48 ($C_{2`}$), 123.24 (C_2), 35.34 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.34 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.18 ($CH_2CH_2CH_2CH_2SCOCH_3$),
29.57 ($CH_2CH_2CH_2CH_2SCOCH_3$),

28.94 ($CH_2CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 312 (12%, M^+), 123 (16%), 107 (26%, $C_7H_9N^+$), 103 (41%), 77 (38%, $C_6H_5^+$), 43 (100%, $C_2H_3O^+$ or $C_3H_7^+$).

*3-[4-(Phenyldiazenyl)phenyl]propylethanethioate **19b***

Yield: 2.0 g (6.7 mmol, 70 %), orange solid.

mp 47-49 °C. (Found: C 68.21, H 6.20, N 9.23, S 11.00. Calc. for $C_{17}H_{18}N_2OS$: C 68.42, H 6.08, N 9.39, S 10.75%).

ν_{max} (KBr)/cm^{-1} 2935 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2894 ($\nu_{(-CH2)}$), 1688 ($\nu_{(C=O)}$), 1603 ($\nu_{(C-C\ ar)}$), 1502, 1482, 1441 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1413, 1355, 1139, 844 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 8.09-8.01 (m, 2H, $H_{2`}$), 7.98 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_2$), 7.23-7.14 (m, 2H, $H_{3`}$), 7.13-7.05 (m, 1H, $H_{4`}$), 6.96 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.36 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 1.88 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.72-1.58 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.11 ($CH_2CH_2CH_2SCOCH_3$), 153.32 ($C_{1`}$), 151.75 ($C_1$), 144.92 ($C_4$), 130.93 ($C_{4`}$), 129.37 (C_3), 129.28 ($C_{3`}$), 123.52 ($C_{2`}$), 123.25 (C_2), 34.84 ($CH_2CH_2CH_2SCOCH_3$),

31.31 ($CH_2CH_2CH_2SCOCH_3$),

30.17 ($CH_2CH_2CH_2SCOCH_3$),

28.66 ($CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 298 (100%, M^+), 293 (30%), 193 (67%, $C_{11}H_{13}OS^+$), 107 (24%, C_7H_9N), 77 (85%, $C_6H_5^+$), 43 (57%, $C_2H_3O^+$ or $C_3H_7^+$).

*4-{4-[(4-Fluorophenyl)diazenyl]phenyl}butyl ethanethioate **20a***

Yield: 2.3 g (7.0 mmol, 70 %), orange solid.

mp 57-59 °C. (Found: C 65.20, H 5.95, N 8.35, S 9.87. Calc. for $C_{18}H_{19}FN_2OS$: C 65.43, H 5.80, N 8.48, S 9.70%).

ν_{max} (KBr)/cm^{-1} 3058 ($\nu_{(C-H\ ar)}$), 2935 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2860 ($\nu_{(-CH2)}$), 1692 ($\nu_{(C=O)}$), 1592 ($\nu_{(C-C\ ar)}$), 1495, 1459 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1405, 1352, 1222, 1135, 1100, 847 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.96 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_2), 7.87-7.78 (m, 2H, $H_{2`}$), 7.01 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_3$), 6.85-6.74 (m, 2H, $H_{3`}$), 2.72 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.31 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.90 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.48-1.31 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.25 ($CH_2CH_2CH_2CH_2SCOCH_3$), 164.53 (d, $^1J_{CF}$ = 251.1 Hz, $C_{4`}$), 151.45 ($C_1$), 149.70 (d, $^4J_{CF}$ = 3.0 Hz, $C_{1`}$), 145.94 (C_4), 129.37 (C_3), 125.13 (d, $^3J_{CF}$ = 8.8 Hz, $C_{2`}$), 123.40 ($C_2$), 116.13 (d, $^2J_{CF}$ = 22.8 Hz, $C_{3`}$), 35.34 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.38 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.18 ($CH_2CH_2CH_2CH_2SCOCH_3$),

29.58 ($CH_2CH_2CH_2CH_2SCOCH_3$),

28.93 ($CH_2CH_2CH_2CH_2SCOCH_3$).

^{19}F NMR (300 MHz, C_6D_6), δ [ppm]: -109.56.

m/z (EI) 330 (28%, M^+), 165 (10%, $C_{10}H_{14}S^+$), 149 (12%, $C_{10}H_{15}N$), 123 (49%, $C_6H_4FN_2^+$), 107 (100%, $C_7H_9N^+$), 95 (11%, $C_6H_4F^+$), 59 (15%), 43 (89%, $C_2H_3O^+$ or $C_3H_7^+$).

3-{4-[(4-Fluorophenyl)diazenyl])phenyl}propyl ethanethioate ***20b***

Yield: 2.3 g (7.3 mmol, 76 %), orange solid.

mp 82-84 °C. (Found: C 64.38, H 5.56, N 8.73, S 10.51. Calc. for $C_{17}H_{17}FN_2OS$: C 64.53, H 5.42, N 8.85, 10.13%).

ν_{max} (KBr)/cm^{-1} 2934 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2862 ($\nu_{(-CH2)}$), 1690 ($\nu_{(C=O)}$), 1592 ($\nu_{(C-C\ ar)}$), 1495, 1456 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1404, 1350, 1225, 1135, 1102, 848 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.94 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_2), 7.87-7.78 (m, 2H, $H_{2'}$), 6.97 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_3), 6.83-6.73 (m, 2H, $H_{3'}$), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.38 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.73-1.59 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.11 ($CH_2CH_2CH_2SCOCH_3$), 164.57 (d, $^1J_{CF}$ = 251.3 Hz, $C_{4'}$), 151.53 (C_1), 149.69 (d, $^4J_{CF}$ = 3.1 Hz, $C_{1'}$), 145.03 (C_4), 129.41 (C_3), 125.14 (d, $^3J_{CF}$ = 8.9 Hz, $C_{2'}$), 123.44 (C_2), 116.14 (d, $^2J_{CF}$ = 22.8 Hz, $C_{3'}$), 34.85 ($CH_2CH_2CH_2SCOCH_3$),

31.31 ($CH_2CH_2CH_2SCOCH_3$),

30.17 ($CH_2CH_2CH_2SCOCH_3$),

28.65 ($CH_2CH_2CH_2SCOCH_3$).

^{19}F NMR (300 MHz, C_6D_6), δ [ppm]: -109.50.

m/z (EI) 316 (53%, M^+), 240 (20%, M^+-$C_6H_4^{+\bullet}$), 193 (39%, $C_{11}H_{13}OS^+$), 135 (20%), 123 (35%, $C_6H_4FN_2^+$), 107 (27%, $C_7H_9N^+$), 95 (100%, $C_6H_4F^+$), 43 (54%, $C_2H_3O^+$ or $C_3H_7^+$).

4-{4-[(4-Chlorophenyl)diazenyl]phenyl}butyl ethanethioate ***21a***

Yield: 2.2 g (6.3 mmol, 76 %), orange solid.

mp 79-81 °C. (Found: C 62.33, H 5.61, N 8.11, S 9.26. Calc. for $C_{18}H_{19}ClN_2OS$: C 62.33, H 5.52, N 8.08, S 9.24%).

ν_{max} (KBr)/cm^{-1} 2931 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2857 ($\nu_{(-CH2)}$), 1694 ($\nu_{(C=O)}$), 1574 ($\nu_{(C-C\ ar)}$), 1481, 1458 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1407, 1150, 1136, 1086, 842 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.95 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_2), 7.73 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{2'}$), 7.11 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{3'}$), 7.00 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_3), 2.72 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.30 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.45-1.31 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.23 ($CH_2CH_2CH_2CH_2SCOCH_3$), 151.51 ($C_{1'}$), 151.45 (C_1), 146.23 (C_4), 136.81 ($C_{4'}$), 129.52 ($C_{3'}$), 129.39 (C_3), 124.41 ($C_{2'}$), 123.51 (C_2) 35.36 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.31 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.18 ($CH_2CH_2CH_2CH_2SCOCH_3$),

29.58 ($CH_2CH_2CH_2CH_2SCOCH_3$),

28.96 ($CH_2CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 346 (79%, M^+), 303 (17%, M^+-$C_3H_7^+$), 165 (20%, $C_{10}H_{13}S^+$), 149 (31%, $C_{10}H_{15}N$), 107 (100%, $C_7H_9N^+$), 91 (12%, $C_6H_4Cl^+$), 43 (67%, $C_2H_3O^+$ or $C_3H_7^+$).

3-{4-[(4-Chlorophenyl)diazenyl]phenyl}propyl ethanethioate ***21b***

Yield: 2.5 g (7.5 mmol, 76 %), orange solid.

mp 97-99 °C. (Found: C 61.15, H 5.23, N 8.32, S 9.95. Calc. for $C_{17}H_{17}ClN_2OS$: C 61.34, H 5.15, N 8.42, S 9.63%).

ν_{max} (KBr)/cm^{-1} 2924 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2830 ($\nu_{(-CH2)}$), 1691 ($\nu_{(C=O)}$), 1570 ($\nu_{(C-C\ ar)}$), 1476, 1448 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1398, 1132, 1082, 838 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.94 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_2), 7.74 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{2`}$), 7.10 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{3`}$), 6.96 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.37 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.72-1.58 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.10 ($CH_2CH_2CH_2SCOCH_3$), 151.52 ($C_{1`}$), 151.50 ($C_1$), 145.32 ($C_4$), 136.86 ($C_{4`}$), 129.53 ($C_{3`}$), 129.42 ($C_3$), 124.42 ($C_{2`}$), 123.55 (C_2) 34.86 ($CH_2CH_2CH_2SCOCH_3$),

31.29 ($CH_2CH_2CH_2SCOCH_3$),

30.18 ($CH_2CH_2CH_2SCOCH_3$),

28.65 ($CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 332 (62%, M^+), 256 (18%), 221 (15%), 139 (26%, $C_6H_4ClN_2^+$), 111 (100%, $C_5H_3OS^+$), 107 (36%, $C_7H_9N^+$), 91 (12%, $C_7H_7^+$), 89 (18%, $C_4H_7S^+$), 75 (23%, $C_2H_3OS^+$), 51 (11%, $C_4H_3^+$).

4-{4-[(4-Bromophenyl)diazenyl]phenyl}butyl ethanethioate ***22a***

Yield: 2.7 g (7.0 mmol, 77 %), orange solid.

mp 80-82 °C. (Found: C 54.95, H 5.11, N 7.14, S 8.46. Calc. for $C_{18}H_{19}BrN_2OS$: C 55.25, H 4.89, N 7.16, S 8.19%).

ν_{max} (KBr)/cm^{-1} 3022 ($\nu_{(C-H\ ar)}$), 2932 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2856 ($\nu_{(-CH2)}$), 1693 ($\nu_{(C=O)}$), 1571 ($\nu_{(C-C\ ar)}$), 1478, 1459 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1408, 1136, 1066, 837 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.95 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_2), 7.66 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{2`}$), 7.27 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{3`}$), 7.00 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_3), 2.72 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.30 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.47-1.31 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.23 ($CH_2CH_2CH_2CH_2SCOCH_3$), 151.86 ($C_{1`}$), 151.46 ($C_1$), 146.27 ($C_4$), 132.53 ($C_{3`}$), 129.40 (C_3), 125.33 ($C_{4`}$), 124.62 ($C_{2`}$), 123.53 (C_2) 35.36 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.30 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.19 ($CH_2CH_2CH_2CH_2SCOCH_3$),

29.58 ($CH_2CH_2CH_2CH_2SCOCH_3$),

28.93 ($CH_2CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 392 (100%, M^+), 349 (20%, M^+-$C_3H_7^+$), 155 (65%, C_6H_5Br), 149 (27%, $C_{10}H_{15}N$), 107 (85%, $C_7H_9N^+$), 91 (11%, $C_7H_7^+$), 43 (60%, $C_2H_3O^+$ or $C_3H_7^+$).

3-{4-[(4-Bromophenyl)diazenyl]phenyl}propyl ethanethioate ***22b***

Yield: 2.6 g (6.9 mmol, 69 %), orange solid.

mp 101-103 °C. (Found: C 54.17, H 4.82, N 7.29, S 8.61. Calc. for $C_{17}H_{17}BrN_2OS$: C 54.12, H 4.54, N 7.42, S 8.50%).

ν_{max} (KBr)/cm^{-1} 2931 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2860 ($\nu_{(-CH2)}$), 1695 ($\nu_{(C=O)}$), 1570 ($\nu_{(C-C\ ar)}$), 1477, 1451 ($\delta_{(-CH2)}$, $\delta_{(-CH3)}$), 1394, 1135, 1065, 836 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.93 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_2), 7.65 (d, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{2'}$), 7.27 (d, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{3'}$), 6.96 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.37 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.72-1.58 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.10 ($CH_2CH_2CH_2SCOCH_3$), 151.83 ($C_{1'}$), 151.52 (C_1), 145.36 (C_4), 132.54 ($C_{3'}$), 129.43 (C_3), 125.38 ($C_{4'}$), 124.63 ($C_{2'}$), 123.57 (C_2) 34.87 ($CH_2CH_2CH_2SCOCH_3$),
31.28 ($CH_2CH_2CH_2SCOCH_3$),
30.18 ($CH_2CH_2CH_2SCOCH_3$),
28.65 ($CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 376 (73%, M^+), 193 (100%, $C_{11}H_{13}OS^+$), 183 (14%, $C_6H_5BrN_2^+$), 165 (11%, $C_{10}H_{13}S^+$), 155 (67%, C_6H_5Br), 107 (28%, $C_7H_9N^+$), 91 (9%, $C_7H_7^+$), 43 (92%, $C_2H_3O^+$ or $C_3H_7^+$).

Methyl 4-{[4-(4-(acetylthio)butyl)phenyl]diazenyl} benzoate ***23a***

Yield: 2.2 g (6.0 mmol, 64 %), orange solid.

mp 87-89 °C. (Found: C 64.75, H 6.19, N 7.51, S 8.90. Calc. for $C_{20}H_{22}N_2O_3S$: C 64.84, H 5.99, N 7.56, S 8.66%).

ν_{max} (KBr)/cm^{-1} 2944 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2858 ($\nu_{(-CH2)}$), 1711 ($\nu_{(C=O,\ COOCH3)}$), 1683 ($\nu_{(C=O)}$), 1601 ($\nu_{(C-C\ ar)}$), 1498, 1439, 1407, 1276, 1143, 1108, 864 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (500 MHz, C_6D_6), δ [ppm]: 8.16 (d, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{3'}$), 7.98 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $H_{2'}$), 7.92 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H_2), 7.00 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H_3), 3.48 (s, 3H, $COOCH_3$), 2.73 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.30 (t, $^3J_{HH}$ = 7.0 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.45-1.33 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (125 MHz, C_6D_6), δ [ppm]: 194.27 ($CH_2CH_2CH_2CH_2SCOCH_3$), 166.07 ($COOCH3$), 155.62 ($C_{1'}$), 151.60 (C_1), 146.67 (C_4), 132.30 ($C_{4'}$), 130.93 ($C_{3'}$), 129.44 (C_3), 123.72 ($C_{2'}$), 122.98 (C_2), 51.70 ($COOCH_3$), 35.37 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.29 ($CH_2CH_2CH_2CH_2SCOCH_3$),
30.17 ($CH_2CH_2CH_2CH_2SCOCH_3$),
29.60 ($CH_2CH_2CH_2CH_2SCOCH_3$),
28.64 ($CH_2CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 370 (73%, M^+), 327 (16%, $C_{18}H_{19}N_2O_2S^+$), 298 (18%, M^+-C_2H_3OS), 165 (20%, $C_{10}H_{13}S^+$), 149 (37%, $C_{10}H_{15}N$), 135 (100%, $C_8H_7O_2$), 123 (59%), 107 (63%, $C_7H_9N^+$), 57 (15%, $C_4H_9^+$), 43 (24%, $C_2H_3O^+$ or $C_3H_7^+$).

Methyl 4-{[4-(3-(acetylthio)propyl)phenyl] diazenyl} benzoate ***23b***

Yield: 2.9 g (8.0 mmol, 89 %), orange solid.

mp 115-117 °C. (Found: C 63.85, H 5.72, N 7.82, S 8.83. Calc. for $C_{19}H_{20}N_2O_3S$: C 64.02, H 5.66, N 7.86, S 9.00%).

ν_{max} (KBr)/cm^{-1} 2998 ($\nu_{(C\text{-}H\ ar)}$), 2935 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2860 ($\nu_{(-CH2)}$), 1720 ($\nu_{(C=O,\ COOCH3)}$), 1692 ($\nu_{(C=O)}$), 1601 ($\nu_{(C\text{-}C\ ar)}$), 1497, 1435, 1403, 1275, 1135, 1107, 867 ($\delta_{(C\text{-}H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 8.16 (d, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{3'}$), 7.95 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{2'}$), 7.92 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H_2), 6.96 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 3.48 (s, 3H, COOCH_3), 2.70 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 2.37 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CH_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2SCOCH_3$), 1.73-1.58 (m, 2H, $CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.11 ($CH_2CH_2CH_2SCOCH_3$), 166.07 (*C*OOCH3), 155.60 ($C_{1'}$), 151.61 (C_1), 145.77 (C_4), 132.33 ($C_{4'}$), 130.93 ($C_{3'}$), 129.46 (C_3), 123.75 ($C_{2'}$), 122.98 (C_2), 51.71 (COO*C*H$_3$), 34.89 ($CH_2CH_2CH_2SCOCH_3$),

31.27 ($CH_2CH_2CH_2SCOCH_3$),

30.17 ($CH_2CH_2CH_2SCOCH_3$),

28.64 ($CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 356 (79%, M^+), 193 (70%, $C_{11}H_{13}OS^+$), 135 (100%, $C_8H_7O_2^+$), 107 (16%, $C_7H_9N^+$), 43 (25%, $C_2H_3O^+$ or $C_3H_7^+$).

4-{4-[(4-Cyanophenyl)diazenyl]phenyl}butyl ethanethioate ***24a***

Yield: 1.36 g (4.0 mmol, 81 %), orange solid.

mp 91-93 °C. (Found: C 67.32, H 5.73, N 12.37, S 9.42. Calc. for $C_{19}H_{19}N_3OS$: C 67.63, H 5.68, N 12.45, S 9.50%).

ν_{max} (KBr)/cm^{-1} 2930 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2856 ($\nu_{(-CH2)}$), 2228 ($\nu_{(-CN)}$), 1688 ($\nu_{(C=O)}$), 1601 ($\nu_{(C\text{-}C\ ar)}$), 1498, 1453 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1410, 1358, 1137, 1103, 852 ($\delta_{(C\text{-}H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.90 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{2'}$), 7.56 (d, $^3J_{HH}$ = 8.7 Hz, 2H, H_2), 7.06 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{3'}$), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_3), 2.72 (t, $^3J_{HH}$ = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 2.31 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.91 (s, 3H, $CH_2CH_2CH_2CH_2SCOCH_3$), 1.47-1.31 (m, 4H, $CH_2CH_2CH_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.31 ($CH_2CH_2CH_2CH_2SCOCH_3$), 154.50 ($C_{1'}$), 151.31 (C_1), 147.33 (C_4), 133.11 ($C_{3'}$), 129.52 (C_3), 123.76 ($C_{2'}$), 123.22 (C_2), 118.45 (*C*N), 114.26 ($C_{4'}$), 35.37 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.24 ($CH_2CH_2CH_2CH_2SCOCH_3$),

30.20 ($CH_2CH_2CH_2CH_2SCOCH_3$),

29.58 ($CH_2CH_2CH_2CH_2SCOCH_3$),

28.89 ($CH_2CH_2CH_2CH_2SCOCH_3$).

m/z (EI) 337 (28%, M^+), 295 (65%, M^+-$C_3H_7^+$), 165 (20%, $C_{10}H_{13}S^+$), 149 (31%, $C_{10}H_{15}N$), 123 (74%), 107 (100%, $C_7H_9N^+$), 102 (89%, $C_7H_5N^+$), 91 (18%, $C_7H_7^+$), 43 (85%, $C_2H_3O^+$ or $C_3H_7^+$).

3-{4-[(4-Cyanophenyl)diazenyl]phenyl}propyl ethanethioate ***24b***

Yield: 2.12 g (6.6 mmol, 55 %), orange solid.

For the SAM preparation the purity was not good enough. Therefore small amounts of compound **24b** were purified by vapour crystallization. This was repeated until the defined purity was obtained.

mp 94-96 °C. (Found: C 66.72, H 5.36, N 12.99, S 9.54. Calc. for $C_{18}H_{17}N_3OS$: C 66.85, H 5.30, N 12.99, S 9.91%).

ν_{max} (KBr)/cm^{-1} 2929 ($\nu_{(-CH3)}$,$\nu_{(-CH2)}$), 2855 ($\nu_{(-CH2)}$), 2228 ($\nu_{(-CN)}$), 1687 ($\nu_{(C=O)}$), 1599 ($\nu_{(C-C\ ar)}$), 1495, 1452 ($\delta_{(-CH2),}$ $\delta_{(-CH3)}$), 1416, 1259, 1221, 1156, 1138, 1106, 853 ($\delta_{(C-H\ ar)}$).

^{1}H NMR (300 MHz, C_6D_6), δ [ppm]: 7.90 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, $H_{2`}$), 7.55 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, $H_2$), 7.00 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, $H_{3`}$), 6.95 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, H_3), 2.70 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2C\mathit{H}_2SCOCH_3$), 2.36 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, $C\mathit{H}_2CH_2CH_2SCOCH_3$), 1.89 (s, 3H, $CH_2CH_2CH_2SCOC\mathit{H}_3$), 1.72-1.58 (m, 2H, $CH_2C\mathit{H}_2CH_2SCOCH_3$).

^{13}C NMR (75 MHz, C_6D_6), δ [ppm]: 194.11 ($CH_2CH_2CH_2S\mathit{C}OCH_3$), 154.48 ($C_{1`}$), 151.43 ($C_1$), 146.36 ($C_4$), 133.09 ($C_{3`}$), 129.54 ($C_3$), 123.79 ($C_{2`}$), 123.21 ($C_2$), 118.42 ($\mathit{C}N$), 114.36 ($C_{4`}$), 34.88 ($\mathit{C}H_2CH_2CH_2SCOCH_3$),
31.25 ($CH_2\mathit{C}H_2CH_2SCOCH_3$),
30.16 ($CH_2CH_2CH_2SCO\mathit{C}H_3$),
28.61 ($CH_2CH_2\mathit{C}H_2SCOCH_3$).

m/z (EI) 323 (95%, M^+), 193 (89%, $C_{11}H_{13}OS^+$), 107 (22%, $C_7H_9N^+$), 102 (65%, $C_7H_5N^+$), 91 (14%, $C_7H_7^+$), 43 (100%, $C_2H_3O^+$ or $C_3H_7^+$).