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Aromatic Thioesters as Protecting Groups for Thiols Against 1,2-Didehydrobenzenes

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Divalent sulfur compounds usually react with 1,2-didehydrobenzenes to give a palette of unspecific products. To identify a suitable protecting group for thiols under the reaction conditions typically used for the synthesis of triptycenes, that is, 1,2-didehydrobenzene generated in situ from 2-diazoniobenzenecarboxylate at elevated temperatures, a wide-ranging optimization study was conducted. Of several acyl groups investigated, the benzoyl group turned out to be optimal. The efficiency of this protecting group was demonstrated by the successful transformation of an electron-poor (thus unreactive) anthracene derivative to the corresponding triptycenethiol derivative.

Aromatic moieties are frequently used frameworks in the construction of so-called molecular machines.[1,2] In particular, the rigid triptycene moiety is often used in molecular mechanics, for example, as a mechanical gear.[3–6] The aim is to mount these molecular machines onto surfaces, during which process the thiol–metal interaction can be successfully exploited.[7–10] Although triptycenes are usually prepared by the [4+2] cycloaddition of 1,2-didehydrobenzenes ("benzynes") to the central ring of anthracene derivatives,[11–14] the high reactivity of the 1,2-didehydrobenzene derivatives, in particular towards divalent sulfur atoms, makes the two chemistries hardly compatible. In this manuscript we identify a suitable protecting group for the thiol group under the harsh reaction conditions employed in triptycene formation.

1,2-Didehydrobenzene derivatives are frequently used reagents for the introduction of 1,2-substituted benzene rings into organic molecules.[15–19] Typical reactions include their insertion into E–H and E–C bonds (where E = O, S, N, …)[17] as well as [4+2] cycloaddition reactions.[18] Since these reagents are highly reactive and can only be isolated at low temperatures in inert matrices, they are usually generated in situ from suitable precursors. This high reactivity also poses problems with regard their selectivity: often, unwanted insertions into E–C bonds occur, particularly if E has a high electron density.

The formation of triptycenes through the [4+2] cycloaddition of 1,2-didehydrobenzenes to the central ring of anthracene derivatives proceeds well as long as the anthracene carries neither groups that react with the 1,2-didehydrobenzenes nor electron-withdrawing groups.[20] It has been known for some time that the presence of divalent sulfur efficiently suppresses the formation of triptycenes through the formation of a number of byproducts mostly deriving from the insertion of the phenylene unit into the S–H or S–C bonds.[21] The only effective protecting group for this purpose reported so far is the *tert*-butyl group: the *tert*-butyl ether derivative of 9-anthracenethiol was transformed into the corresponding triptycene derivative with a yield of 36%.[22] Our attempts to use this protecting group with other anthracenethiols, for example, with 1–3 methylene groups between the sulfur atom and the anthracene backbone, resulted in only trace amounts of triptycenes accompanied by a large variety of unidentified products. Evidently the sulfur atom can only be shielded from electrophilic attack of the 1,2-didehydrobenzene by a direct attachment of the *tert*-butylthio group onto the anthracene system. Another disadvantage of the *tert*-butyl group is the need for somewhat inconvenient conditions for its removal (usually mercury salts[23,24] or HF[25]).

We therefore decided to look for another protecting group which should be easily introduced as well as removed after the reaction. The basic idea was to diminish the electron density at the sulfur atom by using an electron-withdrawing group. One of the most frequently used electron-withdrawing groups is the carbonyl group which can be easily attached to sulfur atoms to form thioesters. These esters are known to be stable under a variety of conditions, but are easily cleaved by bases, thus making it an attractive protecting group in reactions carried out under (slightly) acidic and neutral conditions.[26] Since a variety of methods for generating 1,2-didehydrobenzenes are known,[27–32] it should be almost always possible to find a method compatible with the functional groups present.

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Results and Discussion

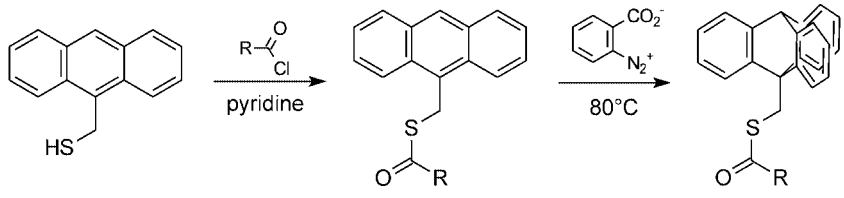
In our initial experiments we used the acetic thioester of 9-(mercaptomethyl)anthracene (**2b**) as a model substance and tried to generate the 1,2-didehydrobenzene by the well-established elimination reaction of 2-diazoniobenzenecarboxylate,[29,30] which in turn was generated in situ by the diazotization of anthranilic acid with isopentyl nitrite. This route was chosen because the reagents are cheap and therefore permit multigram syntheses if required. Unfortunately, this reaction yielded only small amounts of the corresponding triptycene derivative, accompanied by significant amounts of unidentified polar substances probably stemming from the oxidation of the thioester by the nitrite ester (or NO^+ generated by it). To avoid the presence of any nitroxide species in the cycloaddition reaction, we decided to isolate the diazonium salt beforehand and then generate the 1,2-didehydrobenzene by thermolysis of this compound with CO_2 and N_2 being the only side-products. By using this strategy, we were immediately able to obtain 9-(acetylthiomethyl)triptycene (**3b**) in 60% yield.

Since the electronic effect of a thioester is not only determined by the carbonyl group but also by the group attached to it, we decided to study a variety of thioesters more or less systematically, exploring the influence of the acyl group. The thioesters were synthesized by acylation of 9-mercaptomethylanthracene (**1**)[33] in THF with an excess of the corresponding acyl chlorides in the presence of pyridine (Table 1). This procedure turned out to be superior to a number of other methods, but nevertheless could not provide a number of sterically hindered derivatives, such as the 2,4,6-triisopropylbenzoic, 2,4,6-trichlorobenzoic, 2,4,6-trinitrobenzoic,[34] perfluorobenzoic, and 2,6-dimethylbenzoic thioesters. Even the 2-methylbenzoic thioester **2j** and the ferrocenyl ester **2k** were obtained in such low yields (36 and 46%, respectively) that their use as protecting groups would not be attractive.

To determine the efficiency of triptycene formation we decided not to isolate the products, but to determine the conversion by ^1H NMR spectroscopy of the raw products using dimethyl sulfone as the internal standard. The results of this relatively quick approach, which allowed several repetitions of the individual experiments for statistical purposes, are summarized in Table 1.

The first entry in Table 1 gives the results of the experiment performed with unprotected 9-mercaptomethylanthracene, used to verify that this compound has the same problems as reported previously for anthracene-9-thiol. As expected, no triptycene derivative could be obtained owing to the reaction of the thiol group with the 1,2-didehydrobenzene. In contrast, all the thioesters **2** gave the corresponding triptycene derivatives **3** in medium-to-good yields. Surprisingly the use of electron-withdrawing groups such as CF_3 (**2d**) or CCl_3 (**2e**) did not result in higher yields, but in comparable (CCl_3) or even lower (CF_3) yields of triptycenes than obtained with the acetic thioester. This is in line with the observation that the electron-rich *tert*-butyl group (pivaloyl thioester **2c**) promotes the formation of triptycenes. Anyway, the best yields were obtained by using aromatic thioesters: the 4-methylbenzoyl derivative **2h** turned out to be the best protecting group (81%), directly followed by the benzoyl group (**2f**, 79%). Also in this case, the introduction of electron-withdrawing groups, such as in the 3,5-dinitrobenzoyl derivative **2g**, resulted in lower yields. Surprisingly the electron-rich 4-methoxy derivative **2i** bucks the trend, giving somewhat lower yields than the benzoic thioester. As a result, we focused our attention on the benzoyl group as protecting group as it is easily and efficiently introduced and gives very satisfactory yields of triptycenes. Another advantage is that the benzoyl groups cannot only be

Table 1. Yields for the formation of 9-anthrylmethyl thioesters **2** and the corresponding triptycene derivatives **3**.



1 **2b-k** **3b-k**

Entry	R	Yield [%][a] of **2**	Yield [%][b] of **3**
a	H	n/a	0
b	CH_3CO	n/a	60 ± 5
c	$(H_3C)_3CCO$	84	71 ± 10
d	CF_3CO	50	51 ± 13
e	CCl_3CO	67	64 ± 11
f	C_6H_5CO	92	79 ± 6
g	3,5-$(O_2N)C_6H_3CO$	83	54 ± 1
h	4-$(H_3C)C_6H_4CO$	65	81 ± 2
i	4-$(H_3CO)C_6H_4CO$	65	73 ± 1
j	2-$(H_3C)C_6H_4CO$	36	74 ± 1
k	$(C_5H_5)Fe(C_5H_4)CO$	46	72 ± 4

[a] Isolated yield. [b] As determined by quantitative NMR spectroscopy.

used to protect existing thiol groups, but, since thiobenzoic acid is commercially available, it can also be used to introduce the sulfur atom into a molecule in the first place, either by nucleophilic substitution or by addition to double bonds.

As part of our optimization experiments, the optimal stoichiometric amount of the 1,2-didehydrobenzene precursor was determined. Generally, an excess of this reagent might result in unwanted side-reactions with the functional groups (in particular, the protected thio group) present in the already formed triptycene derivative. Even if this was not the case, oligomerization products, such as bi- and triphenylene, can complicate the isolation of the triptycenes. Therefore, the course of triptycene formation from the benzoyl derivative **2f** was followed by GLC. The transformation as a function of added equivalents of 2-diazoniobenzenecarboxylate is depicted in Figure 1.

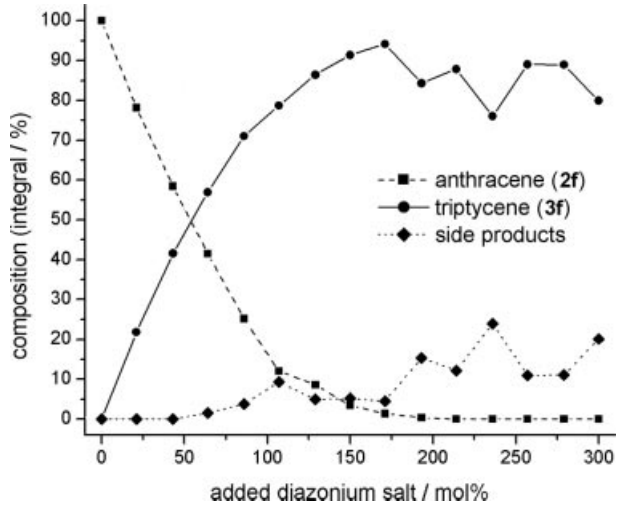


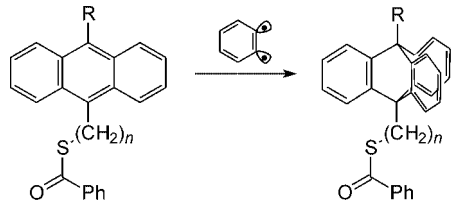
Figure 1. Progress of the triptycene formation as a function of added 1,2-didehydrobenzene precursor.

As is clearly visible, the yield of triptycene constantly increases until about 150 mol-% of the 1,2-didehydrobenzene precursor has been added. If more precursor is then added, the yield of triptycene levels off and the formation of byproducts (as the sum of several peaks in the GLC) becomes significant. Therefore it seems advisable to restrict the amount of 2-diazoniobenzenecarboxylate to 1.5 mol equivalents.

To explore the scope of the benzoyl group as a protecting group we synthesized benzoyl-protected anthracene thiols with longer chain lengths (**4** and **5**), as well as one derivative with a nitrile group in the 10 position (**6**).[35] The latter was of interest because it has been reported that as a result of reduced electron density, anthracenes with nitrile groups attached to the central ring would not form triptycenes,[20] or rather would react with one of the terminal rings instead of the central one.[36]

If compounds **4**–**6** are allowed to react under the usual conditions, the corresponding triptycenes **7**–**9** were obtained in good-to-very-good yield (Table 2). Even the nitrile-substituted derivative **9**, which was the only one to be isolated, could be obtained, although an increased amount of 2-diazoniobenzenecarboxylate had to be added (400 mol-%) to force complete consumption of the anthracene derivative. Evidently the electron-withdrawing capabilities of the nitrile group are almost compensated by the electron-donating properties of the CH_2-S-Bzl group.

Table 2. The yields for [4+2] cycloaddition to different benzoic thioesters.



n = 1, R = H: **2f**
n = 2, R = H: **4**
n = 3, R = H: **5**
n = 1, R = CN: **6**

n = 1, R = H: **3f**
n = 2, R = H: **7**
n = 3, R = H: **8**
n = 1, R = CN: **9**

Thiobenzoate	Product	Yield [%]
AnthCH_2SBzl (**2f**)	**3f**	79 ± 6
Anth$(CH_2)_2$SBzl (**4**)	**7**	88 ± 1
Anth$(CH_2)_3$SBzl (**5**)	**8**	80 ± 2
10-NC-AnthCH_2SBzl (**6**)	**9**	62[a]

[a] Isolated yield.

Triptycene **9** was deprotected to obtain the free thiol **10**. Although with other derivatives the use of lithium aluminium hydride would have been advantageous, the presence of the nitrile group forbade the use of this reagent with this molecule. We therefore cleaved the thioester hydrolytically using potassium hydroxide in a mixture of water, ethanol and THF (0.3:10:10).

The resulting thiol **10** (55% isolated yield) readily crystallized when hexane was allowed to diffuse into the chloroform solution, permitting the analysis of its structure by X-ray diffraction (Figure 2).[37]

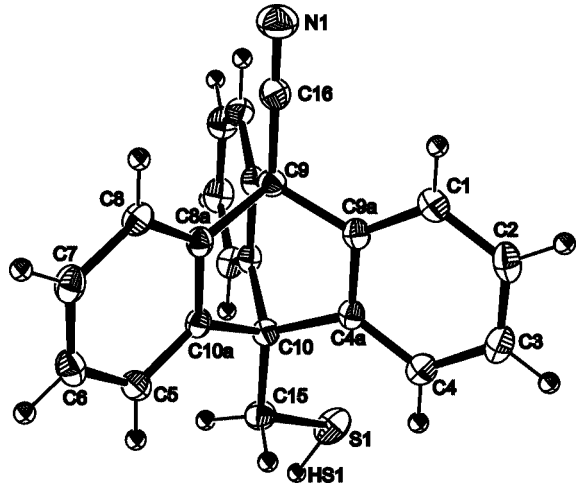


Figure 2. Structure of **10**, as determined by X-ray diffraction.

As can be seen in Figure 2, both the nitrile group and the sulfur functionality were not altered by the 1,2-didehydrobenzene, while the triptycene was formed as expected. This clearly shows that even with a deactivating group pres-

ent in the anthracene system, the protecting group withstands prolonged attack by an excess of the 1,2-didehydrobenzene.

In conclusion, the benzoyl group is suitable for protecting thiols against the action of the reactive species, 1,2-didehydrobenzene. Some other aromatic acyl groups work similarly well, but since the reagents used to introduce the thiobenzoyl group, such as benzoyl chloride and thiobenzoic acid (which can also be used to introduce the sulfur atom into the molecule in the first place, see the Supporting Information), are inexpensive reagents, they will be preferred in most cases.

Experimental Section

General Procedure for the Preparation of 2c–k: Using N_2 as an inert gas, a solution of 9-(mercaptomethyl)anthracene (**1**) (1.50 g, 6.69 mmol) in absolute THF (30 mL) was dropped into a solution of pyridine (1.06 g, 13.4 mmol) and the acyl chloride (13.4 mmol) in absolute THF (10 mL). After stirring at room temperature for 16 h the mixture was washed with sodium acetate buffer solution (twice) and water. The organic solvent was removed in vacuo and the residue was recrystallized from acetonitrile. NMR spectra were recorded with an Avance 400 (Bruker) and a Gemini 2000 BB (Varian). The melting points were determined with an apparatus according to Dr. Tottoli and are not corrected. GLC was carried out using a Perkin Elmer 8420 equipped with a 25 m methyl silicon column (0.25 mm, 0.33 microns, pre-pressure 350 kPa N_2). Elemental analyses were performed with a CHN-O-rapid (Heraeus).

***S*-(9-Anthryl)methyl Thiopivalate (2c):** Following the general procedure pivaloyl chloride (1.62 g, 13.4 mmol) was used to obtain a yellow solid. Yield: 1.73 g (5.61 mmol, 84%). R_f = 0.50 (silica gel, ethyl acetate/*n*-hexane, 1:9 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 [s, 9 H, $C(CH_3)_3$], 5.12 (s, 2 H, CH_2), 7.48 (ddd, J = 8.5, 6.5, 1.1 Hz, 2 H, 3-H, 6-H), 7.56 (ddd, J = 8.9, 6.5, 1.4 Hz, 2 H, 2-H, 7-H), 8.01 (d, J = 8.5 Hz, 2 H, 4-H, 5-H), 8.20 (d, J = 8.9 Hz, 2 H, 1-H, 8-H), 8.41 (s, 1 H, 10-H) ppm; ^3J(7-H,8-H) = 8.9 Hz, ^3J(5-H,6-H) = 8.5 Hz, ^3J(6-H,7-H) = 6.5 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.1 (CH_2), 27.3 [$C(CH_3)_3$], 47.8 [$C(CH_3)_3$], 124.0 (C-1, C-8), 125.1 (C-3, C-6), 126.4 (C-2, C-7), 127.7 (C-10), 127.9 (C-4a, C-10a), 129.2 (C-4, C-5), 130.1 (C-8a, C-9a), 131.5 (C-9) ppm. $C_{20}H_{20}OS$ (308.44): calcd. C 77.88, H 6.54, S 10.30; found C 77.65, H 6.71, S 10.30.

***S*-(9-Anthryl)methyl Trifluorothioacetate (2d):** Trifluoroacetyl chloride (2.49 g, 18.9 mmol) was condensed into a solution of pyridine in THF at –40 °C. The reaction was completed at room temperature according the general procedure. Yield: 1.07 g (3.34 mmol, 50%) of yellow crystals. M.p. 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.36 (s, 2 H, CH_2), 7.53 (m, J = 8.4, 6.6 Hz, 2 H, 3-H, 6-H), 7.63 (m, J = 8.9, 6.6 Hz, 2 H, 2-H, 7-H), 8.07 (m, J = 8.4 Hz, 2 H, 4-H, 5-H), 8.16 (m, J = 8.9 Hz, 2 H, 1-H, 8-H), 8.51 (s, 1 H, 10-H) ppm; ^3J(7-H,8-H) = 8.9 Hz, ^3J(5-H,6-H) = 8.4 Hz, ^3J(6-H,7-H) = 6.6 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.9 (CH_2), 123.2 (C-1, C-8), 125.3 (C-3, C-6), 127.2 (C-2, C-7), 129.0 (C-10), 129.5 (C-4, C-5), 130.3 (C-4a, C-10a), 131.4 (C-8a, C-9a), 185 (C=O) ppm. The signals of C-9 and CF_3 could not be detected.

***S*-(9-Anthryl)methyl Trichlorothioacetate (2e):** Following the general procedure trichloroacetyl chloride (2.44 g, 13.4 mmol) was used to obtain yellow crystals which where treated with hot *n*-hexane. Yield: 1.67 g (4.50 mmol, 67%). M.p. 68–71 °C. R_f = 0.55 (silica gel, ethyl acetate/*n*-hexane, 1:9 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (s, 2 H, CH_2), 7.53 (ddd, J = 8.5, 6.6, 0.9 Hz, 2 H, 3-H, 6-H), 7.63 (ddd, J = 8.9, 6.6, 1.3 Hz, 2 H, 2-H, 7-H), 8.07 (d, J = 8.5 Hz, 2 H, 4-H, 5-H), 8.20 (d, J = 8.9 Hz, 2 H, 1-H, 8-H), 8.51 (s, 1 H, 10-H) ppm; ^3J(7-H,8-H) = 8.9 Hz, ^3J(5-H,6-H) = 8.5 Hz, ^3J(6-H,7-H) = 6.6 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.7 (CH_2), 123.4 (C-1, C-8), 125.3 (C-3, C-6), 127.0 (C-2, C-7), 127.7 (C-4a, C-10a), 128.8 (C-10), 129.5 (C-4, C-5), 130.3 (C-8a, C-9a), 131.4 (C-9), 176.3 (C=O) ppm. The signal of CCl_3 could not be detected.

***S*-(9-Anthryl)methyl Thiobenzoate (2f):** Following the general procedure benzoyl chloride (1.88 g, 13.4 mmol) was used to obtain yellow crystals. Yield: 2.02 g (6.15 mmol, 92%). M.p. 119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.38 (s, 2 H, CH_2), 7.44 (m, 2 H, 3-H, 6-H), 7.50 (m, 2 H, 2-H, 7-H), 7.57 (m, 3 H, 3′-H, 4′-H, 5′-H), 8.00 (m, 2 H, 2′-H, 6′-H), 8.04 (m, 2 H, 4-H, 5-H), 8.30 (m, 2 H, 1-H, 8-H), 8.46 (s, 1 H, 10-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5 (CH_2), 124.0 (C-1,C-8), 125.2 (C-2,C-7), 126.5 (C-3′, C-5′), 127.3 (C-2′, C-6′), 127.9 (C-10), 128.7 (C-3, C-6), 129.3 (C-4, C-5), 130.2 (C-4a, C-10a), 131.5 (C-8a, C-9a), 133.5 (C-4′), 192 (C=O) ppm. The signals of C-1′ and C-9 could not be detected. $C_{22}H_{16}OS$ (328.43): calcd. C 80.45, H 4.91, S 9.76; found C 79.68, H 4.95, S 9.37.

***S*-(9-Anthryl)methyl 3,5-Dinitrothiobenzoate (2g):** Following the general procedure 3,5-dinitrobenzoyl chloride (3.09 g, 13.4 mmol) was used. Trituration with hot acetonitrile gave an orange powder. Yield: 2.32 g (5.54 mmol, 83%). M.p. 224 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.51 (s, 2 H, CH_2), 7.53 (ddd, J = 8.4, 6.6, 0.8 Hz, 2 H, 3-H, 6-H), 7.62 (ddd, J = 8.9, 6.6, 1.3 Hz, 2 H, 2-H, 7-H), 8.07 (d, J = 8.4 Hz, 2 H, 4-H, 5-H), 8.23 (d, J = 8.9 Hz, 2 H, 1-H, 8-H), 8.50 (s, 1 H, 10-H), 9.10 (d, J = 2.1 Hz, 2 H, 2′-H, 6′-H), 9.21 (t, J = 2.1 Hz, 1 H, 4′-H) ppm; ^4J(4′-H,2′-H) = 2.1 Hz, ^3J(7-H,8-H) = 8.9 Hz, ^3J(5-H,6-H) = 8.4 Hz, ^3J(6-H,7-H) = 6.6 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.4 (CH_2), 122.4 (C-4′), 123.4 (C-1, C-8), 125.4 (C-3, C-6), 127.0 (C-2, C-7), 127.1 (C-2′, C-6′), 128.7 (C-10), 129.5 (C-4, C-5), 130.2 (C-4a, C-10a), 131.5 (C-8a, C-9a), 139.3 (C-1′), 148.6 (C-3′, C-5′), 188.0 (C=O) ppm. The signal of C-9 could not be detected. $C_{22}H_{14}N_2O_5S$ (418.42): calcd. C 63.15, H 3.37, N 6.70, S 7.66; found C 62.87, H 3.29, N 6.66, S 7.50.

***S*-(9-Anthryl)methyl 4-Methylthiobenzoate (2h):** By using freshly distilled 4-methylbenzoyl chloride (1.95 g, 12.6 mmol), a yellow solid was obtained. Yield: 2.13 g (6.2 mmol, 65%). M.p. 113–115 °C. R_f = 0.23 (*n*-hexane/CH_2Cl_2, 2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 5.33 (s, 2 H, CH_2), 7.18 (d, J = 8.1 Hz, 2 H, 3′-H, 5′-H), 7.45 (dd, J = 7.6, 7.2 Hz, 2 H, 3-H, 6-H), 7.54 (dd, 2 H, 2-H, 7-H), 7.87 (d, J = 8.2 Hz, 2 H, 2′-H, 6′-H), 7.98 (d, J = 8.3 Hz, 2 H, 4-H, 5-H), 8.27 (d, J = 8.9 Hz, 2 H, 1-H, 8-H), 8.39 (s, 1 H, 10-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (CH_3), 26.3 (CH_2), 124.0 (C-1, C-8), 125.1 (C-3, C-6), 126.4 (C-2, C-7), 127.4 (C-2′, C-6′), 127.4 (C-9), 127.8 (C-10), 129.2 (C-3′, C-5′), 129.3 (C-4, C-5), 130.1 (C-4a, C-5a), 131.4 (C-8a, C-9a), 134.0 (C-1′), 144.4 (C-4′) 191.5 (C=O) ppm. $C_{23}H_{18}OS$ (342.45): calcd. C 80.67, H 5.30, S 9.36; found C 80.61, H 5.40, S 9.55.

***S*-(9-Anthryl)methyl 4-Methoxythiobenzoate (2i):** The thioester was obtained as a yellow solid starting from 4-methoxybenzoyl chloride (3.20 g, 20.7 mmol). Yield: 2.20 g (6.1 mmol, 65%). M.p. 127–130 °C. R_f = 0.37 (*n*-hexane/CH_2Cl_2, 1:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 5.34 (s, 2 H, CH_2), 6.89 (d, J = 9.0 Hz, 2 H, 3′-H, 5′-H), 7.48 (ddd, J = 8.4, 6.5, 1.1 Hz, 2 H, 3-H, 6-H), 7.56 (ddd, J = 8.8, 6.5, 1.4 Hz, 2 H, 2-H, 7-H), 7.96 (d, J = 9.0 Hz, 2 H, 2′-H, 6′-H), 8.01 (d, J = 8.4 Hz, 2 H, 4-H, 5-H), 8.30 (d, J = 8.9 Hz, 2 H, 1-H, 8-H), 8.43 (s, 1 H, 10-H) ppm; ^3J(1-H,2-

H) = 8.9 Hz, ^3J(3-H,4-H) = 8.4 Hz, ^3J(2-H,3-H) = 6.5 Hz, ^3J(2′-H,3′-H) = 9.0 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.4 (CH_2), 55.5 (CH_3), 113.8 (C-3′, C-5′), 124.1 (C-1, C-8), 125.2 (C-3, C-6), 126.5 (C-2, C-7), 127.6 (C-9), 127.8 (C-10), 129.3 (C-4, C-5), 129.5 (C-1′), 129.6 (C-2′, C-6′), 130.2 (C-4a, C-10a), 131.5 (C-8a, C-9a), 163.9 (C-4′), 190.4 (C=O) ppm. $C_{23}H_{18}O_2S$ (358.45): calcd. C 77.07, H 5.06, S 8.95; found C 77.05, H 5.17, S 9.06.

***S*-(9-Anthryl)methyl 2-Methylthiobenzoate (2j):** Following the general procedure using 2-methylbenzoyl chloride (3.70 g, 21.7 mmol), a yellow solid was obtained. Yield: 1.15 g (3.4 mmol, 36%). M.p. 65–67 °C. R_f = 0.62 (*n*-hexane/CH_2Cl_2, 1:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59 (s, 3 H, CH_3), 5.34 (s, 2 H, CH_2), 7.16 (m, 1 H, 5′-H), 7.25 (m, 1 H, 3′-H), 7.36 (m, 1 H, 4′-H), 7.48 (ddd, *J* = 8.4, 6.5, 1.0 Hz, 2 H, 3-H, 6-H), 7.57 (ddd, *J* = 8.9, 6.5, 1.4 Hz, 2 H, 2-H, 7-H), 7.72 (m, 1 H, 6′-H), 8.02 (td, *J* = 8.4, 0.7 Hz, 2 H, 4-H, 5-H), 8.30 (dd, *J* = 8.9, 0.8 Hz, 2 H, 1-H, 8-H), 8.43 (s, 1 H, 10-H) ppm; ^3J(1-H, 2-H) = 8.9 Hz, ^3J(3-H, 4-H) = 8.4 Hz, ^3J(2-H, 3-H) = 6.5 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7 (CH_3), 27.0 (CH_2), 124.0 (C-1, C-8), 125.1 (C-3, C-6), 125.7 (C-5′), 126.5 (C-2, C-7), 127.6 (C-9), 127.8 (C-10), 128.5 (C-6′), 129.3 (C-4, C-5), 130.2 (C-4a, C-10a), 131.5 (C-8a, C-9a), 131.6 (C-3′), 131.8 (C-4′), 136.9 (C-1′), 137.0 (C-2′), 194.2 (C=O) ppm. $C_{23}H_{18}OS$ (342.45): calcd. C 80.67, H 5.30, S 9.36; found C 80.46, H 5.36, S 9.43.

***S*-(9-Anthryl)methyl Ferrocenethiocarboxylate (2k):** Ferrocenecarbonyl chloride[38] (0.66 g, 2.7 mmol) was transformed according to the general procedure. The product was purified by column chromatography (alumina, 100 mL, CH_2Cl_2/*n*-hexane starting from 1:4 v/v) to yield a red solid. Yield: 0.46 g (1.1 mmol, 46%). R_f = 0.56 (alumina, CH_2Cl_2/*n*-hexane, 1:1 v/v). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.14 (s, 5 H, unsubst. ferrocenyl), 4.56 (t, *J* = 1.9 Hz, 2 H, 2,5-ferrocenyl), 4.84 (t, *J* = 1.9 Hz, 2 H, 3,4-ferrocenyl), 5.31 (s, 2 H, CH_2), 7.54 (m, 2 H, 3-H, 6-H), 7.63 (m, 2 H, 2-H, 7-H), 8.11 (m, 2 H, 4-H, 5-H), 8.30 (m, 2 H, 1-H, 8-H), 8.60 (s, 1 H, 10-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 23.7 (CH_2), 67.9 (3,4-ferrocenyl), 69.6 (unsubst. ferrocenyl), 71.4 (2,5-ferrocenyl), 77.6 (1-ferrocenyl), 123.2, 124.6, 125.7, 127.9, 128.3, 128.7, 130.3 (anthracene-C), 191.2 (C=O) ppm. The signals from the anthracene moiety are somewhat complex probably due to some anisotropy.

General Procedure for the Preparation of Triptycene Derivatives 3b–k: TFA (two drops) was added to a solution of 2-aminobenzoic acid (0.4 g, 3 mmol) in THF (25 mL). After cooling to 0 °C, isopentyl nitrite (0.53 g, 4.5 mmol) was added dropwise and then the solution was stirred at room temperature for 30 min. After cooling to 0 °C again, the precipitate formed was filtered off and washed with THF and suspended in 1,4-dioxane.

Caution: *Dry diazonium salts are extremely unstable. To avoid ignition by mechanical means (scratching or impact) soft fluoropolymer apparatuses were used throughout the preparation of this compound.*

A solution of the respective anthracene derivative (**2a**–**k**, 1.000 mmol, exactly determined) in 1,4-dioxane (10 mL) was heated to 80 °C. After adding the suspension of the diazonium salt slowly, the reaction mixture was refluxed for 1 h and stirred at room temperature for 16 h. The organic solvent was removed in vacuo. A defined amount of the internal standard (dimethyl sulfone in $CDCl_3$) was added and the precipitate was dissolved in $CDCl_3$. The yield of the reaction was determined using quantitative ^{1}H NMR spectroscopy.

Supporting Information (see also the footnote on the first page of this article): X-ray structure of **2g**, preparation of intermediates as well as the complete synthesis of **10** and full spectroscopic data for all new compounds.

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