Synthesis of 9-Anthryl Ethers from *trans*-9,10-Dihydro-9,10-dimethoxyanthracene by Acid-Catalyzed Transetherification

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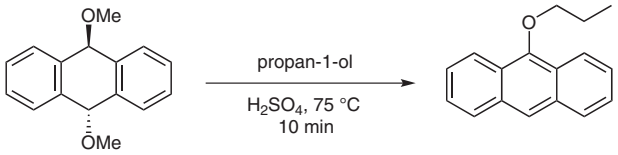
Abstract: During a study of electrophilic aromatic addition reactions (Ad_EAr) to anthracene, anthryl ethers at the C9-position of anthracene were obtained as the major products when *trans*-9,10-dihydro-9,10-dimethoxyanthracene was reacted (10 minutes at 75 °C) with various alcohols. 9-Anthryl ethers with primary, secondary, cyclic alcohols, and polyethylene glycol (PEG) were isolated in 47–73% yields under optimized conditions. It is hoped that the devised method offers a new synthetic route for the preparation of anthryl ethers via the acid-catalyzed transetherification of *trans*-9,10-dihydro-9,10-dimethoxyanthracene with various alcohols.

Key words: transetherification, anthryl ethers, *trans*-9,10-dihydro-9,10-dimethoxyanthracene

Anthracene and its derivatives have been utilized for a variety of optical electronic devices, such as light emitting diodes,[1] field effect transistors,[2] and fluorescent chemosensors.[3] In particular, anthryl ethers have attracted considerable interest due to their unique chemical reactivities and photochromic properties for the construction of photoresponsive supramolecular systems[4] and for the synthesis of triptycenes and triptycene quinones.[5] Several methods have been devised to synthesize 9-anthryl ethers, such as, the etherification of 9-anthrone with alcohols under acidic conditions,[6] alkylation via aromatization by phase transfer catalysis,[7] and direct alkoxylation using cerium(IV) tetrakistrifluoroacetate (CTFA).[8] However, these methods are limited, because the starting 9-anthrol is as the minor tautomeric form of the 9-anthrol and 9-anthrone tautomerization. Thus, under the William ether synthetic conditions, 10-alkylated 9-anthrone could be obtained as major product.

Even though the B-rings are much more reactive towards reagents, 9-alkoxyanthracenes are produced with difficulty. In addition, previously described methods require high reaction temperatures and long reaction times, and stoichiometric amounts or large excesses of reagents. Furthermore, it has been reported that the hydrolysis of 9-anthryl ethers produces 9-anthrone and alcohols in the presence of strong acid.[9] The above limitations encouraged us to develop a new methodology for the synthesis of 9-alkoxyanthracenes. Recently, various anthryl ethers were prepared with common functional groups, by reacting 2-methoxyanthracene with various alcohols and thiols in the presence of trifluoromethanesulfonic acid.[10,11]

Here, we describe an efficient method for the synthesis of 9-alkoxyanthracene from *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**1**) via acid-catalyzed transetherification using primary, secondary, or cyclic alcohols, polyethylene glycol (PEG), or natural alcohols like dihydrocholesterol or epiandrosterone.



1 **2c** (65%)

Scheme 1 Preparation of 9-propoxyanthracene from *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**1**) in the presence of H_2SO_4 in propan-1-ol

Recently, we described electrophilic aromatic addition (Ad_EAr) reactions of fused aromatic compounds, such as, naphthalenes and quinolines.[12] During our study of anthracene Ad_EAr reactions,[13] we found *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**1**) was converted into 9-alkoxylated anthracene by transetherification at the C9-position, and that the addition of a catalytic amount of sulfuric acid accelerated this reaction and improved the selectivity for 9-anthryl ethers synthesis. In addition, we also reported the selective re-aromatization to 9-methoxyanthracene (**2a**) from **1** by an elimination reaction in a basic methanolic solution at room temperature, and 9-propoxyanthracene (**2c**) (65% yield) from **1** in the presence of propan-1-ol and sulfuric acid when reacted for 10 minutes at 75 °C in addition to 9-methoxyanthracene (**2a**) and anthracene (**3**). We believe that this phenomenon offers a valuable means of producing anthryl ethers on the B-ring of anthracene.[13]

Table 1 summarizes the results of reactions between *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**1**) and a number of alcohols under various conditions. To determine optimal conditions, we carried out the reaction using different acids at different concentrations. When **1** was heated in propan-1-ol at 75 °C for 10 minutes without any additive, the undesired products 9-methoxyanthracene (**2a**) and anthracene (**3**) were obtained (entry 1, Table 1). However, by including a Lewis acid at only the 0.01 to 0.5

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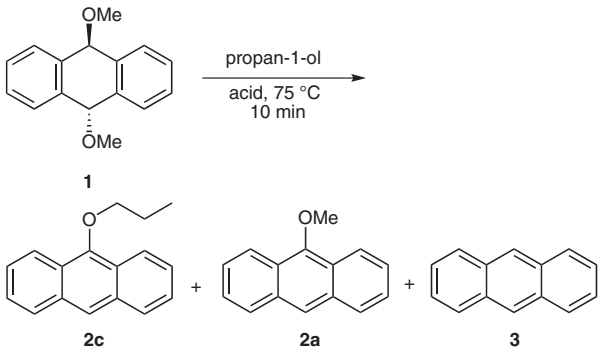
mol% level, transetherification occurred to produce different products (entries 2–4). The reaction was then carried out using different Lewis acids also at 75 °C for 10 minutes, and with the exception of lanthanum(III) trifluoromethanesulfonate [$La(OTf)_3$], transetherification yields were reduced as acid concentrations were increased. In addition, the side products **2a** and **3** were produced regardless of reaction conditions. The reaction was also carried out at a reaction temperature of 0 °C for 10 minutes (entry 13). The intriguing result of the above exercise was that 9-propoxyanthracene (**2c**) production was greatest in the presence of sulfuric acid, which also produced lowest levels of side products and only a trace amount of compound **3** (Scheme 1).

Under optimized conditions (Table 1, entry 12, at 75 °C for 10 minutes), the transetherifications of a variety of 9-alkoxyanthracene derivatives **2a–v** were attempted from **1** (Table 2). Primary, secondary, cyclic alcohols, PEG, and even allyl alcohol reacted well. In case of primary alcohols, transetherification yields were 65–68%, which are much higher than previously reported (entries 2–6).[8,9,14] When 2-methoxyethanol was used, transetherification gave the corresponding 9-(2-methoxyethoxy)anthracene (**2g**) in good yield (73%, entry 7). On the other hand, when

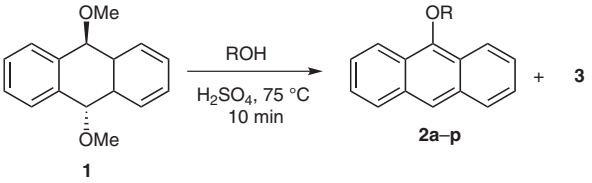
Table 1 Acids Screened for the Transetherification of *trans*-9,10-Dihydro-9,10-dimethoxyanthracene (**1**) in Propan-1-ol[a]



Entry	Lewis acids (equiv)	Yield (%)[b]		
		2c	**2a**	**3**
1	none	–	74	13
2	$FeCl_3$ (1.0)	29	15	13
3	$FeCl_3$ (0.5)	30	15	10
4	$FeCl_3$ (0.05)	42	25	2
5	$AlCl_3$ (1.0)	42	30	3
6	$La(OTf)_3$ (1.0)	47	26	5
7	$La(OTf)_3$ (0.5)	44	21	7
8	$La(OTf)_3$ (0.05)	34	23	5
9	$Sc(OTf)_3$ (1.0)	32	12	12
10	$Sc(OTf)_3$ (0.5)	34	13	5
11	$Sc(OTf)_3$ (0.05)	45	18	7
12	H_2SO_4 (0.05)	65	15	trace
13[c]	H_2SO_4 (0.05)	30	35	16

[a] All reactions were carried out on a 0.5 mmol scale of **1** in 2.0 mL of propan-1-ol at 75 °C for 10 min.
[b] Isolated yield.
[c] Reaction temperature was 0 °C.

Table 2 Transetherification from *trans*-9,10-Dihydro-9,10-dimethoxyanthracene (**1**) with Alcohols in the Presence of Sulfuric Acid[a]



Entry	Alcohol	Yield (%)[b]		
		2a–v	**2a**	**3**
1	methanol	– (**2a**)	74	13
2[c]	ethanol	68 (**2b**)	14	6
3	propan-1-ol	65 (**2c**)	15	trace
4	butan-1-ol	67 (**2d**)	19	5
5	pentan-1-ol	68 (**2e**)	12	7
6	hexan-1-ol	65 (**2f**)	19	8
7	2-methoxyethanol	73 (**2g**)	8	5
8	1-bromoethanol	25 (**2h**)	trace	5
9[c]	benzyl alcohol	55 (**2i**)	15	5
10	allyl alcohol	57 (**2j**)	13	6
11	ethylene glycol	40 (**2k**)	12	15
12	propane-1,3-diol	44 (**2l**)	21	12
13	butane-1,4-diol	46 (**2m**)	28	9
14	triethylene glycol	65 (**2n**)	23	4
15	isoamyl alcohol	53 (**2o**)	19	11
16	propan-2-ol	22[c] (**2p**)	10	1
17	*tert*-butanol	– (**2q**)	63	4
18	cyclopentanol	43 (**2r**)	30	7
19	cyclohexanol	37 (**2s**)	47	4
20	cycloheptanol	29 (**2t**)	29	10
21[d]	dihydrocholesterol	8 (**2u**)	62	11
22[d]	epiandrosterone	10 (**2v**)	68	trace

[a] All reactions were carried out using 0.5 mmol reaction scale of **1** in 2.0 mL of each alcohol in the presence of a catalytic amount of H_2SO_4 (2.0 L) at 75 °C for 10 min.
[b] Isolated yields.
[c] NMR-determined yield.
[d] The reaction was carried out using 1.0 mmol of **1** in toluene (2.0 mL).

1-bromoethanol was used, we obtained the desired product **2h** in only 25% yield (entry 8). Furthermore, when benzyl alcohol (entry 9) was used, the product **2i** was not obtained in a pure form because of its poor stability. However, reaction with allyl alcohol produced the desired product **2j**, and this was stable enough to be isolated in a pure form at a yield of 57% (entry 10). The reaction was also performed using four diols (entries 11–14), to see whether intramolecular-annulated crown ether of anthracene at C9 and C10-position formed or not. However, when triethylene glycol was used (entry 14), only 9-alkoxyanthracene (**2n**) was achieved as usual (65%). The transetherification of **1** with isoamyl alcohol, propan-2-ol, or *tert*-butanol (entries 15–17, Table 2) suggested that the course of the reaction is influenced by steric effects. In contrast to the primary alcohols, as mentioned above (entries 2–6, Table 2), transetherification with propan-2-ol produced 9-isopropoxyanthracene (**2p**) in 22% yield, and *tert*-butanol formed 9-methoxyanthracene (**3**) in high yield (63%) rather than 9-(*tert*-butoxy)anthracene (**2q**).

Acid-catalyzed transetherification using cyclic alcohols, such as cyclopentanol, cyclohexanol, and cycloheptanol provided **2r**, **2s**, and **2t** (entries 18–20), respectively. The preparation of 9-anthryl cyclopentyl ether **2r** was achieved by the Buchwald group via the palladium-catalyzed intermolecular coupling of 9-bromoanthracene and cyclopentanol in 48% yield.[15] This method is also useful for producing anthryl ethers via palladium-catalyzed intermolecular carbon–oxygen bond formation. The other two compounds **2s** and **2t** have not been previously synthesized. Finally, the application of this methodology to dihydrocholesterol and epiandrosterone afforded the desired transetherification products **2u**,**v** in low yields (8 and 10%, respectively), which was expected based on steric considerations, in addition to the undesired byproducts (**3** and **2a**).

In summary, we describe the synthesis of 9-anthryl ethers via the acid-catalyzed transetherification of *trans*-9,10-dihydro-9,10-dimethoxyanthracene with different alcohols. This devised transetherification method was found to be more efficient than any other reported procedure for the preparation of 9-alkoxyanthracene from *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**1**). It is hoped that this convenient and selective transetherification will be found to be a generally useful method for the preparation of a variety of 9-alkoxyanthracenes.

All chemicals were purchased from commercial sources (Sigma-Aldrich, TCI, Acros) and used without further purification. Analytical TLC was carried out on pre-coated plates (Merck, silica gel $60F_{254}$). Flash column chromatography was performed with silica gel (Merck, 230–400 mesh, ASTM). ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400-MR (400 MHz) and Varian Gemini 2000 (200 MHz) spectrometers at ambient temperature. Mass spectra were obtained on an HP590 GC/MS 5972 MSD spectrometer.

9-Anthryl Ethers; General Procedure

A catalytic amount of H_2SO_4 (2.0 L) was added to a solution of *trans*-9,10-dihydro-9,10-dimethoxyanthracene (**1**, 0.5 mmol) in an appropriate alcohol (2.0 mL). This mixture was then heated at 75 °C for 10 min, cooled to r.t., and extracted with EtOAc (3 × 10 mL) and H_2O (10 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by flash column chromatography (30% CH_2Cl_2–hexane).

9-Methoxyanthracene (2a)

Pale yellow solid; mp 93.2–93.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.16 (s, 3 H), 7.46–7.51 (m, 4 H), 7.99 (dd, *J* = 7.2, 2.0 Hz, 2 H), 8.23 (s, 1 H), 8.30 (d, *J* = 6.8 Hz, 1 H), 8.31 (d, *J* = 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.2, 122.2, 122.3, 124.4, 125.2, 125.5, 128.4, 132.4, 152.2.

MS (EI): *m/z* (%) = 208 [M$^+$], 193 (100), 176, 165, 163, 139, 115, 104.

HRMS (EI): *m/z* calcd for $C_{15}H_{12}O$ [M$^+$]: 208.0888; found: 208.0890.

Registry No. 2395-96-2.

9-*n*-Propoxyanthracene (2c)

Yield: 65%; white solid; mp 75.5–77.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.4 Hz, 3 H), 2.07–2.12 (m, 2 H), 4.18 (t, *J* = 6.8 Hz, 2 H), 7.45–7.50 (m, 4 H), 7.98–8.01 (m, 2 H), 8.22 (s, 1 H), 8.30–8.33 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.7, 23.9, 77.6, 121.9, 122.4, 124.7, 125.0, 125.4, 128.4, 132.4, 151.4.

MS (EI): *m/z* (%) = 236 [M$^+$], 194 (100), 165, 139.

HRMS (EI): *m/z* calcd for $C_{17}H_{16}O$ [M$^+$]: 236.1201; found: 236.1204.

Registry No. 92830-42-7.

9-*n*-Butoxyanthracene (2d)

Yield: 67%; white solid; mp 87.1–87.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.4 Hz, 3 H), 1.70–1.79 (m, 2 H), 2.04–2.11 (m, 2 H), 4.24 (t, *J* = 6.6 Hz, 2 H), 7.55–7.46 (m, 4 H), 8.02–8.00 (m, 2 H), 8.23 (s, 1 H), 8.36–8.32 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 19.5, 32.7, 75.9, 121.9, 122.4, 124.7, 125.0, 125.4, 128.4, 132.4, 151.5.

MS (EI): *m/z* (%) = 250 [M$^+$], 194 (100), 165, 139.

HRMS (EI): *m/z* calcd for $C_{18}H_{18}O$ [M$^+$]: 250.1358; found: 250.1359.

Registry No. 92830-43-8.

9-*n*-Pentoxyanthracene (2e)

Yield: 68%; pale yellow solid; mp 55.7–56.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 8.4 Hz, 3 H), 1.48–1.54 (m, 2 H), 1.66–1.70 (m, 2 H), 2.07–2.14 (m, 2 H), 4.22 (t, *J* = 7.4 Hz, 2 H), 7.45–7.52 (m, 4 H), 7.99–8.02 (m, 2 H), 8.22 (s, 1 H), 8.31–8.33 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.4, 30.4, 76.2, 121.9, 122.4, 124.7, 125.0, 125.4, 128.4, 132.4, 151.5.

MS (EI): *m/z* (%) = 264 [M$^+$], 194 (100), 165, 139.

HRMS (EI): *m/z* calcd for $C_{19}H_{20}O$ [M$^+$]: 264.1514; found: 264.1513.

Registry No. 112607-81-5.

9-*n*-Hexoxyanthracene (2f)

Yield: 65%; yellow solid; mp 42.4–43.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 5.2 Hz, 3 H), 1.42–1.66 (m, 4 H), 1.66–1.69 (m, 2 H), 2.04–2.08 (m, 2 H), 4.20 (t, *J* = 6.6 Hz, 2 H), 7.44–7.50 (m, 4 H), 7.98–8.01 (m, 2 H), 8.22 (s, 1 H), 8.29–8.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.9, 30.6, 31.8, 76.2, 121.9, 122.4, 124.7, 125.0, 125.4, 128.4, 132.4, 151.5.

MS (EI): *m/z* (%) = 278 [M$^+$], 194 (100), 165, 139.

HRMS (EI): *m/z* calcd for $C_{20}H_{22}O$ [M$^+$]: 278.1671; found: 278.1673.

Registry No. 1126-82-6.

9-(2-Methoxyethoxy)anthracene (2g)
Yield: 73%; white solid; mp 106.9–108.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.59 (s, 3 H), 3.91 (t, *J* = 4.6 Hz, 2 H), 4.37 (t, *J* = 4.6 Hz, 2 H), 7.45–7.52 (m, 4 H), 7.98–8.01 (m, 2 H), 8.24 (s, 1 H), 8.31–8.39 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.7, 72.3, 75.0, 122.7, 122.8, 125.0, 125.5, 125.8, 128.7, 132.7, 151.1.

MS (EI): *m/z* (%) = 252 [M$^+$], 194 (100), 165, 139, 115.

HRMS (EI): *m/z* calcd for $C_{17}H_{16}O_2$ [M$^+$]: 252.1150; found: 252.1152.

Registry No. 112607-85-9.

9-(2-Bromoethoxy)anthracene (2h)
Yield: 25%; white solid; mp 112.3–115.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (t, *J* = 6.0 Hz, 2 H), 4.53 (t, *J* = 6.2 Hz, 2 H), 7.47–7.53 (m, 4 H), 7.99–8.02 (m, 2 H), 8.26 (s, 1 H), 8.34–8.37 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.4, 74.7, 122.0, 122.7, 124.5, 125.45, 125.47, 128.4, 132.2, 149.8.

MS (EI): *m/z* (%) = 302 [M$^+$], 300 [M$^+$], 193 (100), 165, 139, 115.

HRMS (EI): *m/z* calcd for $C_{16}H_{13}BrO$ [M$^+$]: 300.0150; found: 300.0148.

Registry No. 86129-58-0.

9-Allyloxyanthracene (2j)
Yield: 57%; yellow solid; mp 95.9–97.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.75–4.77 (m, 2 H), 5.38–5.41 (m, 1 H), 5.59–5.64 (m, 1 H), 6.29–6.39 (m, 1 H), 7.46–7.52 (m, 4 H), 7.99–8.03 (m, 2 H), 8.24 (s, 1 H), 8.31–8.35 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.4, 117.6, 122.2, 122.3, 124.7, 125.1, 125.4, 128.3, 132.3, 133.8, 150.9.

MS (EI): *m/z* (%) = 234 [M$^+$], 193 (100), 165, 163, 139, 115.

HRMS (EI): *m/z* calcd for $C_{17}H_{14}O$ [M$^+$]: 234.1045; found: 234.1045.

Registry No. 125340-11-6.

9-(2-Hydroxyethoxy)anthracene (2k)
Yield: 40%; yellow solid; mp 106.2–108.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.80 (br s, 1 H), 4.17 (t, *J* = 4.4 Hz, 2 H), 4.31 (t, *J* = 4.4 Hz, 2 H), 7.45–7.48 (m, 4 H), 7.97–8.00 (m, 2 H), 8.22 (s, 1 H), 8.32–8.35 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 62.4, 76.5, 122.0, 122.5, 124.5, 125.3, 125.4, 128.4, 132.3, 150.3.

MS (EI): *m/z* (%) = 238 [M$^+$], 194 (100), 165, 151, 115.

HRMS (EI): *m/z* calcd for $C_{16}H_{14}O_2$ [M$^+$]: 238.0994; found: 238.0990.

Registry No. 86129-59-1.

9-(3-Hydroxy-*n*-propoxy)anthracene (2l)
Yield: 44%; pale yellow solid; mp 89.3–90.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (br s, 1 H), 2.29–2.32 (m, 2 H), 4.15 (t, *J* = 5.8 Hz, 2 H), 4.36 (t, *J* = 6.0, 2 H), 7.45–7.51 (m, 4 H), 7.98–8.01 (m, 2 H), 8.23 (s, 1 H), 8.28–8.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.1, 61.2, 74.1, 122.1, 122.4, 124.6, 125.3, 125.5, 128.5, 132.4, 150.8.

MS (EI): *m/z* (%) = 252 [M$^+$], 194 (100), 165, 152, 129.

HRMS (EI): *m/z* calcd for $C_{17}H_{16}O_2$ [M$^+$]: 252.1150; found: 252.1150.

9-(4-Hydroxy-*n*-butoxy)anthracene (2m)
Yield: 46%; white solid; mp 72.1–74.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94–2.01 (m, 3 H), 2.10–2.17 (m, 2 H), 3.83 (t, *J* = 6.4 Hz, 2 H), 4.22 (t, *J* = 6.4 Hz, 2 H), 7.44–7.51 (m, 4 H), 7.98–8.00 (m, 2 H), 8.21 (s, 1 H), 8.27–8.30 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2, 29.7, 62.8, 75.8, 122.1, 122.3, 124.6, 125.1, 125.4, 128.4, 132.4, 151.1.

MS (EI): *m/z* (%) = 266 [M$^+$], 208, 194 (100), 165, 152, 129.

HRMS (EI): *m/z* calcd for $C_{18}H_{18}O_2$ [M$^+$]: 266.1307; found: 266.1305.

9-(8-Hydroxy-3,6-dioxaoctoxy)anthracene (2n)
Yield: 65%; yellow solid; mp 44.6–46.2 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.03 (br s, 1 H), 3.64–3.68 (m, 2 H), 3.75–3.80 (m, 6 H), 3.93–3.97 (m, 2 H), 4.33–4.37 (m, 2 H), 7.40–7.53 (m, 4 H), 7.93–7.98 (m, 2 H), 8.19 (s, 1 H), 8.36–8.41 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 61.6, 70.3, 70.4, 70.7, 72.5, 74.5, 122.2, 122.3, 124.5, 125.1, 125.3, 128.2, 132.2, 150.6.

MS (EI): *m/z* (%) = 326 [M$^+$], 208 (100), 180, 152, 119.

HRMS (EI): *m/z* calcd for $C_{20}H_{22}O_4$ [M$^+$]: 326.1518; found: 326.1521.

9-Isoamyloxyanthracene (2o)
Yield: 53%; white solid; mp 63.9–65.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 6.4 Hz, 6 H), 1.92–1.98 (m, 2 H), 2.00–2.05 (m, 1 H), 4.20 (t, *J* = 6.6 Hz, 2 H), 7.41–7.47 (m, 4 H), 7.95–7.98 (m, 2 H), 8.19 (s, 1 H), 8.25–8.28 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.8, 25.2, 39.5, 74.7, 121.9, 122.5, 124.7, 125.0, 125.4, 128.4, 132.5, 151.6.

MS (EI): *m/z* (%) = 264 [M$^+$], 194 (100), 178, 165, 151.

HRMS (EI): *m/z* calcd for $C_{19}H_{20}O$ [M$^+$]: 264.1514; found: 264.1517.

9-Cyclopentoxyanthracene (2r)
Yield: 43%; yellow solid; mp 77.7–79.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69–1.85 (m, 4 H), 2.06–2.19 (m, 4 H), 4.92–4.95 (m, 1 H), 7.43–7.50 (m, 4 H), 7.97–8.00 (m, 2 H), 8.20 (s, 1 H), 8.29–8.32 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1, 33.4, 88.6, 122.1, 123.4, 125.1, 125.6, 125.7, 128.7, 132.8, 151.2.

MS (EI): *m/z* (%) = 262 [M$^+$], 194 (100), 165, 139, 115.

HRMS (EI): *m/z* calcd for $C_{19}H_{18}O$ [M$^+$]: 262.1357; found: 262.1358.

Registry No.188527-60-8.

9-Cyclohexoxyanthracene (2s)
Yield: 37%; yellow solid; mp 104.3–106.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19–1.28 (m, 3 H), 1.59–1.61 (m, 1 H), 1.72–1.84 (m, 4 H), 2.10–2.14 (m, 2 H), 4.21–4.26 (m, 1 H), 7.43–7.47 (m, 4 H), 7.96–7.99 (m, 2 H), 8.19 (s, 1 H), 8.31–8.33 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 25.6, 33.5, 84.3, 121.6, 123.1, 124.6, 125.2, 125.5, 128.2, 132.3, 150.1.

MS (EI): *m/z* (%) = 276, 194 (100), 165, 139, 115.

HRMS (EI): *m/z* calcd for $C_{20}H_{20}O$ [M$^+$]: 276.1514; found: 276.1516.

9-Cycloheptoxyanthracene (2t)
Yield: 29%; yellow solid; mp 90.6–93.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31–1.40 (m, 2 H), 1.56–1.65 (m, 4 H), 1.75–1.81 (m, 2 H), 1.95–2.04 (m, 2 H), 2.11–2.19 (m, 2 H), 4.45–4.52 (m, 1 H), 7.42–7.48 (m, 4 H), 7.95–7.99 (m, 2 H), 8.19 (s, 1 H), 8.27–8.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.8, 28.5, 34.6, 86.8, 121.6, 123.2, 124.6, 125.3, 125.6, 128.3, 132.4, 150.3.

MS (EI): *m/z* (%) = 290 [M$^+$], 194 (100), 178, 165, 152, 139.

HRMS (EI): *m/z* calcd for: $C_{21}H_{22}O$ [M$^+$]: 290.1671; found: 290.1666.

3-(*O*-Anthracen-9-yl)-3α,5α-dihydrocholestane (2u); Typical Procedure
A catalytic amount of H_2SO_4 (3.0 L) and solution of 3α,5α-dihydro-3-cholesterol (194 mg, 0.5 mmol) in toluene (1 mL) was added to a solution of *trans*-9,10-dihydro-9,10-dimethoxyanthracene (0.5 mmol) in toluene (1.0 mL). The mixture was then heated at 75 °C for 10 min, cooled to r.t., and extracted with EtOAc (3 × 10 mL) and H_2O (10 mL). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by flash column chromatography (30% CH_2Cl_2–hexane), to provide **2u** as a white solid (22 mg; 8%); mp 239.4–240.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (s, 2 H), 0.84–0.89 (m, 10 H), 0.91–0.97 (m, 5 H), 0.99–1.11 (m, 8H), 1.17–1.35 (m, 10 H), 1.42–1.63 (m, 4 H), 1.69–1.83 (m, 4 H), 1.92–2.17 (m, 3 H), 4.24–4.27 (m, 1 H), 7.43–7.46 (m, 4 H), 7.96–7.99 (m, 2 H), 8.19 (s, 1 H), 8.30–8.33 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 12.9, 19.0, 21.6, 22.9, 23.2, 24.1, 24.5, 28.3, 28.6, 29.1, 29.5, 32.4, 35.77, 35.84, 36.0, 36.1, 36.5, 37.4, 39.8, 40.3, 42.9, 45.3, 54.6, 56.5, 56.7, 85.3, 122.0, 123.6, 125.1, 125.7, 125.9, 128.6, 132.7, 150.6.

MS (EI): *m/z* (%) = 564 [M$^+$], 549, 508, 479, 449, 438, 402, 371, 355, 316, 275, 257, 231, 215, 194 (100), 165, 135.

HRMS (EI): *m/z* calcd for $C_{41}H_{56}O$ [M$^+$]: 564.4331; found: 564.4331.

3-(*O*-Anthracen-9-yl)-3β,5α-androstanone (2v)
Compound **2v** was prepared using a similar procedure as that described above for **2u** from 3β,5α-androstanon-3-ol (143 mg, 0.5 mmol). A white solid (23 mg; 10%) was obtained; mp 206.6–208.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50–0.63 (m, 1 H), 0.78–1.09 (m, 8 H), 1.11–1.33 (m, 4 H), 1.39–1.61 (m, 4 H), 1.69–1.85 (m, 6 H), 1.89–2.11 (m, 4 H), 2.35–2.48 (m, 1 H), 4.12–4.33 (m, 1 H), 7.40–7.49 (m, 4 H), 7.95–7.99 (m, 2 H), 8.19 (s, 1 H), 8.29–8.34 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 13.8, 20.4, 21.7, 28.3, 29.1, 30.8, 31.5, 34.9, 35.4, 35.8, 36.9, 44.9, 47.7, 51.3, 54.3, 84.6, 121.7, 123.1, 124.7, 125.3, 125.6, 128.3, 132.3, 150.2, 221.2.

MS (EI): *m/z* (%) = 466 [M$^+$], 429, 384, 355, 290, 223, 194 (100), 180, 152, 107.

HRMS (EI): *m/z* calcd for $C_{33}H_{38}O_2$ [M$^+$]: 466.2872; found: 466.2872.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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