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EPR studies on carboxylic esters. Part 16. Indirect generation of the elusive radical anions of alkyl anthracene-9-carboxylates†

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ABSTRACT: Electroreduction of dioxygen in aprotic media yields superoxide anions $O_2^{\cdot -}$. These highly reactive radical anions easily attack sensitive arenes. It is, therefore, not possible to generate the radical anions of anthracene-9-carboxylic esters (**1**) by direct *in situ* electroreduction. Because derivatives substituted in the 10-position are stable against these radicals, indirect generation of the radical anion $\mathbf{1}^{\cdot -}$ was realized in order to be able to measure its EPR spectrum. In a series of EPR experiments we were able to study the influence of various substituents on both the stability of the anthracene derivatives against superoxide and the spin density distribution. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: carboxylic esters; alkyl anthracene-9-carboxylate radical anions; electron paramagnetic resonance

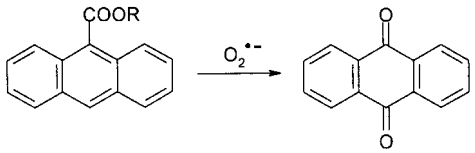
INTRODUCTION

We have been engaged for many years in the investigation of spin density distributions of aromatic ester[1,2] and thioester[3] radical anions. *In situ* electroreduction in dry DMF of aromatic compounds with electron-withdrawing groups in general most conveniently achieved the corresponding rather persistent radical anions. In contrast, the radical anions of *tert*-butyl anthracene-9-carboxylate (**1**) and similar 9-substituted anthracene derivatives have turned out to be very difficult to observe since these compounds are extremely sensitive to residual oxygen. Because traces of oxygen cannot be completely excluded, electroreduction even at −0.3 V (vs Ag/AgBr) inevitably produces superoxide anions $O_2^{\cdot -}$. These highly reactive radical anions, even in trace amounts, easily attack sensitive 9-substituted anthracenes and unavoidably lead to the formation of anthraquinone (**2**) and eventually to its exceptionally stable radical anion $\mathbf{2}^{\cdot -}$ (Scheme 1). Several other anthracene derivatives with an electron-withdrawing group in 9-position (COOMe, COOPh, CSOMe, COMe, NO_2) have been investigated but in all cases only the EPR spectrum of $\mathbf{2}^{\cdot -}$ was observed.

Even after nearly complete removal of oxygen, the narrow but intense EPR spectrum of anthraquinone radical anions still dominates the broad spectrum of the anthracene radical anions (Fig. 1) and prohibits proper recording and interpretation of the latter. This unusual oxidation of sensitive arenes in the presence of dissolved oxygen has been found useful for the degradation of polyhalogenated aromatic hydrocarbons by electrochemically generated superoxide ions[4] in aprotic solvents such as DMF. In order to avoid the contamination of $\mathbf{1}^{\cdot -}$ with $\mathbf{2}^{\cdot -}$, we generated the radical anions by an indirect route.

RESULTS AND DISCUSSION

Anthracene derivatives substituted in the 10-position are stable against superoxide anions owing to steric hindrance. This is demonstrated for the 10-methyl (**3**) and 10-phenyl (**4**) derivatives, which we have investigated. Figure 2 shows the broad spectrum of *tert*-butyl 10-methylanthracen-9-carboxylate (**3**), which is dominated by the large coupling constant (quadruplet) of the methyl group in 10-position.



1 **2**

Scheme 1. Oxidation of **1**, initiated by the electrochemical reduction of O_2 to $O_2^{\cdot -}$

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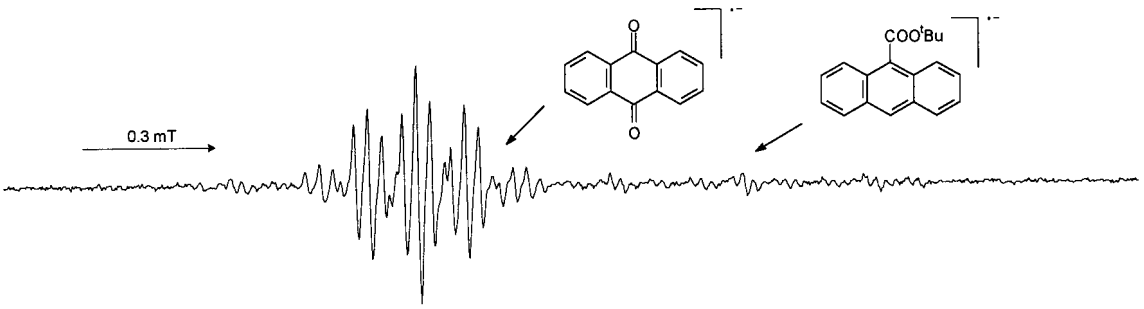


Figure 1. EPR spectrum obtained from a mostly oxygen-free solution of **1**

As a consequence of these observations, we envisaged an indirect generation of the radical anion $\mathbf{1}^{\cdot-}$. According to our experiences with the electroreductive dehalogenation of xenobiotic chloroarenes,[5] we decided to start with haloanthracene-9-carboxylic esters and produce the radical anion $\mathbf{1}^{\cdot-}$ by a three-step electroreductive procedure.

Cyclovoltammetric measurements of the *tert*-butyl 10-haloanthracene-9-carboxylic **5** (X = Br, Cl) show irreversible behaviour, i.e. their radical anions eliminate halide ions. Therefore, we first pre-electrolysed the halo derivatives **5** in dry DMF at −0.5 V (vs Ag/AgBr) until the complete consumption of traces of oxygen. Then electroreductive dehalogenation to form **1** was achieved at −0.8 V (Scheme 2). In this array of reactions, two electrons are transferred to the organic substrate. The halide ion is eliminated simultaneously with or after the first single electron transfer (SET) or immediately with the second SET.[3,6] Subsequently the anion is protonated. Finally, the radical anion $\mathbf{1}^{\cdot-}$ was generated at −1.1 V and proved to be persistent enough. Its EPR spectrum could be recorded (Fig. 3), the proton HFS coupling constants were determined, related to spin densities by McConnell's relation ($Q = -2.4$ mT) and theoretically by use of DFT calculations. The calculations lead to a satisfactory agreement between the experimental and theoretical data. Furthermore, a torsion angle of ca 20° between the anthracene moiety and the ester group of the radical anions $\mathbf{1}^{\cdot-}$, $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$ results from the DFT calculations (cf. Table 1).

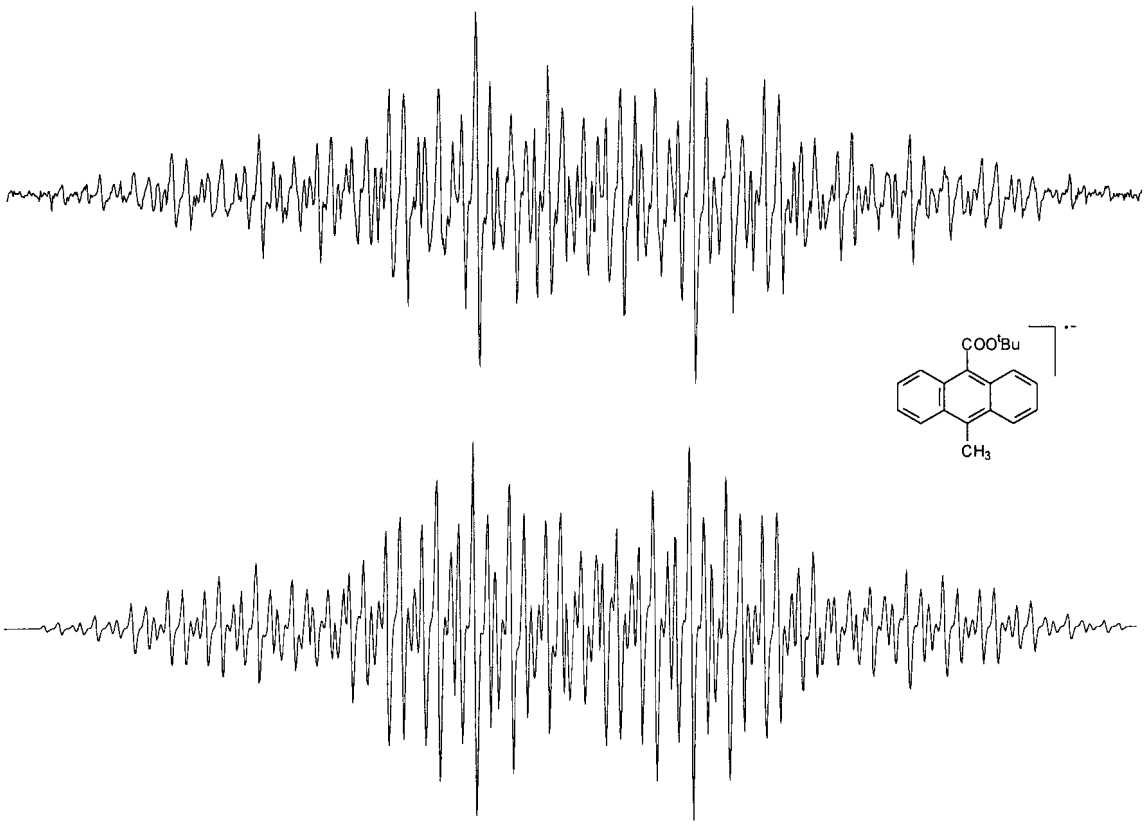
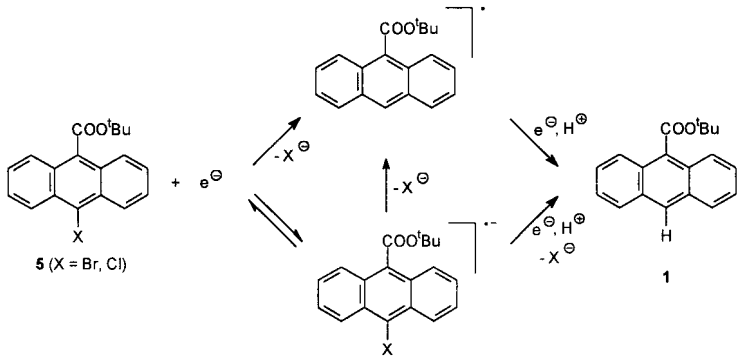


Figure 2. Experimental (above) and simulated (below) EPR spectra of $\mathbf{3}^{\cdot-}$



Scheme 2. Electrochemical generation of **1**

Further investigations were performed in order to study the influence of various substituents in the 4- and 5-positions on both the stability of the anthracene derivatives against superoxide and the spin density distribution. Oxidation to the corresponding anthraquinones did not occur during the measurements. Only the sensitive ester **9**, which is difficult to prepare in a pure state, was oxidized to 1,8-diphenylanthraquinone radical anions after *in situ* electroreduction in the same way as $\mathbf{1}^{\cdot-}$. The observed spectra of *tert*-butyl 4-chloro- (**6**) and *tert*-butyl 4-phenylanthracene-9-carboxylate (**7**) were difficult to simulate, because the spectra originate from up to eight different HFS coupling constants. The spin density and hence the proton HFS coupling constant in the 10-position are very large and decrease with the number of substituents (see Table 2).

As one would expect, the spectra of the 4,5-disubstituted derivatives **8** and **9** are easier to interpret because of their symmetry. In contrast to **5** with a halogen substituent in the 10-position, the halogen substituents in 4- and 5-positions are still persistent. This can be explained qualitatively by the spin densities, which in these positions are smaller $(\rho_\mu^\pi = 0.104)$ and so the radical anions are long-lived enough to be detected spectroscopically by EPR.[3]

COMPUTATIONAL

EPR spectra simulations were carried out using the Simfonia program (Bruker). Spin densities were computed using Gaussian 98 on a Hewlett-Packard 9000 V2250 (PA 8200). Geometry optimizations and spin density calculations were performed by the B3LYP/6–31G* method. The initial molecular modelling and Gaussian *Z*-matrices were generated with Spartan 5.0 (Wavefunction) on a Silicon Graphics Indigo (R 10000).

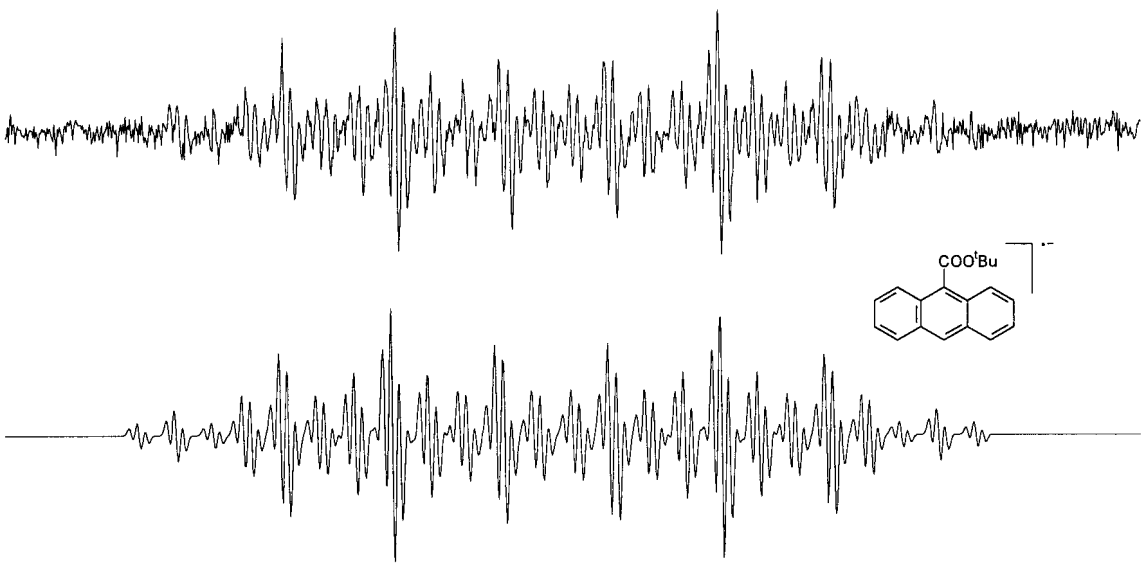


Figure 3. Experimental (above) and simulated (below) EPR spectrum of $\mathbf{1}^{\cdot-}$, generated indirectly from *tert*-butyl 10-bromoanthracene-9-carboxylate (**5**, X = Br)

Table 1. Experimental and theoretical spin densities in $\mathbf{1}^{\cdot-}$, $\mathbf{3}^{\cdot-}$ and $\mathbf{4}^{\cdot-}$ and torsion angle between arene ring and ester group

Species		1/8	2/7	3/6	4/5	10	Angle ArCOOR (°)
$\mathbf{1}^{\cdot-}$	Exp.	0.037	0.103	0.008	0.111	0.327	
	DFT	0.039	0.083	0.012	0.137	0.423	20
$\mathbf{3}^{\cdot-}$	Exp.	0.047	0.094	0.019	0.113	0.279	
	DFT	0.023	0.090	0.021	0.133	0.405	19
$\mathbf{4}^{\cdot-}$	Exp.	0.045	0.092	0.015	0.124		
	DFT	0.022	0.083	0.016	0.116		23

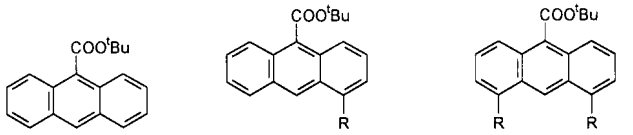
EXPERIMENTAL

General. Melting-points were determined on an Elektrothermal melting-moint apparatus and are uncorrected. Fourier transform (FT) IR spectra were recorded on an ATI Mattson Genesis as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX 400 and DRX 500 spectrometers. Chemical shifts are reported in ppm (δ) vs tetramethylsilane. The assignments are supported by ^{1}H–^{13}C correlations (HMQC, HMBC). High-resolution mass spectrometry (HRMS) was carried out on a VG Analytical 70-2050 S. EPR measurements were performed with a Bruker ESP 300 spectrometer operated in the X-band. The radical anions were generated under argon by *in situ* electroreduction at the appropriate reduction potentials. A solution containing 10^{-3} mol l^{-1} ester and 0.1 mol l^{-1} of tetrapropylammonium bromide in dry DMF was used as the electrolyte supporting solvent and a silver wire was used as the internal reference electrode.

Solvents and reagents. N,N-Dimethylformamide (DMF) was refluxed with calcium hydride for 6 h, fractionally distilled and stored under argon. Tetrapropylammonium bromide was recrystallized from 2-butanone. 9-Acetylanthracene (Aldrich) was recrystallized before use.

tert-Butyl (**1**), methyl and phenyl anthracene-9-carboxylate,[7] 9-nitroanthracene,[8] 10-chloroanthracene-9-carboxylic acid and 10-methylanthracene-9-carboxylic acid,[9] 10-bromoanthracene-9-carboxylic acid,[10] 10-phenylanthracene-9-carboxylic acid,[11] 4,5-dichloroanthracene-9-carboxylic acid[12] and 10-bromo-1,8-diphenylanthracene[13] were prepared according to the literature procedures. 4-Chloroanthracene-9-carboxylic acid and 4-phenylanthracene-9-carboxylic acid were prepared similarly to the 4,5-di substituted derivatives.[12]

Table 2. Spin density ρ_μ^π in the 10-position in the radical anions of **1, 6, 7, 8** and **9**



1	**6**	**7**	**8**	**9**
	R = Cl	R = Ph	R = Cl	R = Ph
0.327	0.313	0.302	0.289	0.273

O-Methyl anthracene-9-carbothioate. A solution of 2.6 g (11 mmol) of methyl anthracene-9-carboxylate and 2.9 g (7.3 mmol) of 2,4-bis(4-methoxyphenyl)-λ^5 1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson's reagent) in 11 ml of chlorobenzene was refluxed for 24 h. The solvent was removed and the residue was chromatographed over silica gel with light petroleum–ethyl acetate (10:1) as eluent to yield *O*-methyl anthracene-9-carbothioate (37 mg, 1%) as a pale yellow solid: m.p. 95–96 °C; IR (KBr), 3078, 3054, 3029, 2988, 2936, 1625, 1444, 1288, 1237, 1197, 1170, 1143, 1003, 889, 841, 785, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), δ 4.49 (s, CH_3), 7.45 (ddd, J = 8 Hz, J = 8 Hz, J = 1 Hz, 3-H, 6-H), 7.48 (ddd, J = 8 Hz, J = 8 Hz, J = 1 Hz, 2-H, 7-H), 7.97 (dd, J = 8 Hz, J = 1 Hz, 1-H, 4-H, 5-H, 8-H), 8.45 (s, 10-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 59.34 (q, CH_3), 124.78 (d, C-1, C-8), 125.29 (d, C-3, C-6), 126.58 (d, C-2, C-7), 127.23 (s, C-8a, C-9a), 128.18 (d, C-10), 128.40 (d, C-4, C-5), 130.98 (s, C-4a, C-10a), 136.41 (s, C-9), 216.97 (s, C=S) ppm.

1,8-Diphenylanthracene-9-carboxylic acid. A volume of 0.35 ml (0.56 mmol) of a 1.6 M solution of *n*-butyllithium in diethyl ether was added to a solution of 208 mg (0.51 mmol) of 10-bromo-1,8-diphenylanthracene in 10 ml of diethyl ether. The reaction mixture was stirred for 10 min and then poured on dry-ice. Diethyl ether and water were added and the aqueous layer was separated and acidified. Diethyl ether was added to extract the acid and the solvent was removed. The residue was chromatographed over silica gel with light petroleum–ethyl acetate (1:1) as eluent to yield 1,8-diphenylanthracene-9-carboxylic acid (70 mg, 37%) as a pale yellow solid: m.p. 195 °C; IR (KBr), 3002, 2955, 2922, 2854, 1707, 1461, 1378, 1246, 824, 762, 744, 701 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6), δ 7.35 (t, J = 7 Hz, 4′-H, 4″-H), 7.43–7.50 (m, 2′-H, 2″-H, 3-H, 3′-H, 3″-H, 5′-H, 5″-H, 6-H, 6′-H, 6″-H), 7.66 (dd, J = 9 Hz, J = 7 Hz, 2-H, 7-H), 8.09 (dd, J = 9 Hz, J = 1 Hz, 1-H, 8-H), 8.64 (s, 10-H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6), δ 124.48 (d,

C-1, C-8), 125.02 (d, C-10), 126.25 (d, C-3, C-6), 126.62 (d, C-2, C-7), 127.11 (s, C-8a, C-9a), 127.37 (d, C-4′, C-4″), 128.23 (d, C-3′, C-3″, C-5′, C-5″), 128.75 (s, C-4a, C-10a), 129.77 (d, C-2′, C-2″, C-6′, C-6″), 130.65 (s, C-9), 139.43 (s, C-1′, C-1″), 140.26 (s, C-4, C-5), 170.52 (s, C=O) ppm; HRMS, calculated for $C_{27}H_{18}O_2$, *m/z* 374.1307; found, *m/z* 374.1317.

Preparation of tert-butyl anthracene-9-carboxylates. Typical procedure. Trifluoroacetic anhydride (4 mmol) was added to a suspension of the respective anthracene-9-carboxylic acid (1 mmol) in 10 ml of toluene. The mixture was stirred for 10 min before the addition of *tert*-butanol (13 mmol). After 15 min the solution was diluted with diethyl ether and aqueous sodium hydroxide (10%) was added to extract the acid. The organic layer was washed with water and dried. The solvent was removed and the residue was chromatographed over silica gel with light petroleum–ethyl acetate (10:1) as eluent to yield the corresponding ester.

*tert-Butyl 10-methylanthracene-9-carboxylate (**3**).* Yield 55%, yellow solid: m.p. 165–166 °C; IR (KBr), 3088, 3067, 2967, 2927, 1715, 1445, 1390, 1367, 1287, 1234, 1147, 996, 836, 761, 738, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.77 [s, $C(CH_3)_3$], 3.11 (s, CH_3), 7.50–7.53 (m, 2-H, 3-H, 6-H, 7-H), 8.04–8.06 (m, 1-H, 8-H), 8.29–8.32 (m, 4-H, 5-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 14.35 (q, CH_3), 28.44 (q, $C(CH_3)_3$), 82.76 [s, $C(CH_3)_3$], 124.98 (d, C-4, C-5), 125.25 (d, C-2, C-7), 125.54 (d, C-1, C-8), 126.11 (d, C-3, C-6), 127.43 (s, C-8a, C-9a), 128.71 (s, C-9), 129.46 (s, C-4a, C-10a), 132.47 (s, C-10), 169.57 (s, C=O) ppm; calculated for $C_{20}H_{20}O_2$, C 82.16, H 6.89; found, C 81.20, H 7.00%.

*tert-Butyl 10-phenylanthracene-9-carboxylate (**4**).* Yield 32%, yellow solid: m.p. 177 °C; IR (KBr), 3060, 2973, 2931, 1715, 1443, 1368, 1299, 1237, 1160, 1140, 999, 777, 740, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.80 (s, CH_3), 7.33 (ddd, J = 9 Hz, J = 7 Hz, J = 1 Hz, 3-H, 6-H), 7.37 (dd, J = 8 Hz, J = 1.5 Hz, 2′-H, 6′-H), 7.48–7.58 (m, 2-H, 3′-H, 4′-H, 5′-H, 7-H), 7.64 (d, J = 7 Hz, 4-H, 5-H), 8.09 (d, J = 7 Hz, 1-H, 8-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 28.48 (q, CH_3), 82.96 [s, $C(CH_3)_3$], 124.85 (d, C-1, C-8), 125.26 (d, C-3, C-6), 126.36 (d, C-2, C-7), 127.28 (d, C-4, C-5), 127.43 (s, C-4a, C-10a), 127.65 (d, C-4′), 128.39 (d, C-3′, C-5′), 129.72 (s, C-8a, C-9a), 129.88 (s, C-9), 131.04 (d, C-2′, C-6′), 138.45 (s, C-1′), 139.08 (s, C-10), 169.29 (s, C=O) ppm.

tert-Butyl 10-chloroanthracene-9-carboxylate. Yield 75%, yellow solid: m.p. 187 °C; IR (KBr), 3081, 3070, 2971, 2926, 2857, 1713, 1655, 1647, 1637, 1627, 1510, 1292, 1265, 1241, 1149, 994, 932, 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.78 [s, $C(CH_3)_3$], 7.58 (ddd, J = 8 Hz, J = 8 Hz, J = 1 Hz, 2-H, 7-H), 7.62 (ddd, J = 9 Hz, J = 8 Hz, J = 1 Hz, 3-H, 6-H), 8.05 (ddd, J = 8 Hz, J = 1 Hz, J = 1 Hz, 1-H, 8-H), 8.55 (ddd, J = 9 Hz, J = 1 Hz, J = 1 Hz, 4-H, 5-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 28.44 (q, CH_3), 83.34 [s, $C(CH_3)_3$], 125.19 (d, C-4, C-5), 125.24 (d, C-1, C-8), 126.81 (d, C-3, C-6), 126.93 (d, C-2, C-7), 128.17 (s, C-8a, C-9a), 128.35 (s, C-4a, C-10a), 129.54 (s, C-9), 130.54 (s, C-10), 168.62 (s, C=O) ppm; HRMS, calculated for $C_{19}H_{17}ClO_2$, *m/z* 312.0917/314.0888; found, *m/z* 312.0925/314.0897.

tert-Butyl 10-bromoanthracene-9-carboxylate. Yield 74%, yellow solid: m.p. 185–188 °C; IR (KBr), 3075, 3056, 2971, 2927, 1714, 1442, 1364, 1290, 1262, 1242, 1148, 997, 903, 760, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.77 (s, CH_3), 7.52–7.56 (m, 2-H, 7-H), 7.56–7.61 (m, 3-H, 6-H), 8.03 (dd, J = 7 Hz, J = 1 Hz, 1-H, 8-H), 8.55 (dd, J = 8 Hz, J = 2 Hz, 4-H, 5-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 28.42 (q, CH_3), 83.37 [s, $C(CH_3)_3$], 124.58 (s, C-10), 125.25 (d, C-1, C-8), 126.89 (d, C-4, C-5), 127.17 (d, C-2, C-7), 128.18 (d, C-3, C-6), 128.29 (s, C-8a, C-9a), 130.07 (s, C-4a, C-10a), 130.55 (s, C-9), 168.64 (s, C=O) ppm.

*tert-Butyl 4-chloro anthracene-9-carboxylate (**6**).* Yield 55%, yellow solid: m.p. 134 °C; IR (KBr), 3062, 2977, 2929, 1717, 1452, 1390, 1365, 1351, 1263, 1236, 1174, 1155, 1144, 1010, 945, 885, 848, 808, 765, 739, 721, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.78 [s, $C(CH_3)_3$], 7.42 (dd, J = 9 Hz, J = 7 Hz, 2-H), 7.53 (ddd, J = 8 Hz, J = 7 Hz, J = 1 Hz, 6-H), 7.58 (ddd, J = 8 Hz, J = 7 Hz, J = 1 Hz, 7-H), 7.59 (dd, J = 7 Hz, J = 1 Hz, 3-H), 7.98 (d, J = 9 Hz, 1-H), 8.05 (dd, J = 8 Hz, J = 1 Hz, 8-H), 8.09 (dd, J = 8 Hz, J = 1 Hz, 5-H), 8.94 (s, 10-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 28.45 [q, $C(CH_3)_3$], 83.28 [s, $C(CH_3)_3$], 124.26 (d, C-1), 124.75 (d, C-8), 125.42 (d, C-3), 125.63 (d, C-10), 126.01 (d, C-2), 126.06 (d, C-6), 127.48 (d, C-7), 128.24 (s, C-8a), 128.40 (s, C-4a), 128.61 (s, C-9a), 129.12 (d, C-5), 130.44 (s, C-9), 131.57 (s, C-10a), 132.35 (s, C-4), 168.67 (s, C=O) ppm; HRMS, calculated for $C_{19}H_{17}ClO_2$, *m/z* 312.0917/314.0888; found, *m/z* 312.0914/314.0892.

*tert-Butyl 4-phenylanthracene-9-carboxylate (**7**).* Yield 70%, yellow solid: m.p. 90 °C; IR (KBr), 3056, 2976, 2929, 1717, 1689, 1457, 1369, 1258, 1231, 1172, 1153, 1143, 760, 733, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.80 [s, $C(CH_3)_3$], 7.41 (dd, J = 7 Hz, J = 1 Hz, 3-H), 7.42 (ddd, J = 8 Hz, J = 7 Hz, J = 1 Hz, 6-H), 7.48–7.57 (m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H, 7-H), 7.58 (dd, J = 9 Hz, J = 7 Hz, 2-H), 7.87 (dd, J = 8 Hz, J = 1 Hz, 5-H), 8.04 (dddd, J = 9 Hz, J = 1 Hz, J = 1 Hz, J = 1 Hz, 8-H), 8.07 (ddd, J = 9 Hz, J = 1 Hz, J = 1 Hz, 1-H), 8.50 (s, 10-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 28.50 [q, $C(CH_3)_3$], 82.97 [s, $C(CH_3)_3$], 124.48 (d, C-1), 124.67 (d, C-8), 125.31 (d, C-6), 126.20 (d, C-2, C-3), 126.91 (d, C-7), 127.20 (d, C-10), 127.54 (d, C-4′), 127.65 (s, C-9a),

128.13 (s, C-8a), 128.43 (d, C-3′, C-5′), 129.03 (d, C-5), 129.78 (s, C-4a), 129.96 (s, C-9), 130.16 (d, C-2′, C-6′), 131.06 (s, C-10a), 140.61 (s, C-1′), 140.64 (s, C-4), 169.23 (s, C═O) ppm; HRMS, calculated for $C_{25}H_{22}O_2$, *m/z* 354.1620; found, *m/z* 354.1614.

*tert-Butyl 4,5-dichloroanthracene-9-carboxylate (**8**).* Yield 11%, yellow solid: m.p. 148–149 °C; IR (KBr), 3004, 2979, 2932, 1717, 1619, 1551, 1476, 1414, 1395, 1369, 1352, 1253, 1211, 1153, 881, 847, 813, 761, 735, 672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.77 [s, $C(CH_3)_3$], 7.48 (dd, J = 9 Hz, J = 7 Hz, 2-H, 7-H), 7.65 (dd, J = 7 Hz, J = 1 Hz, 3-H, 6-H), 7.97 (ddd, J = 9 Hz, J = 1 Hz, J = 1 Hz, 1-H, 8-H), 9.39 (s, 10-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 28.41 [q, $C(CH_3)_3$], 83.67 [s, $C(CH_3)_3$], 122.87 (d, C-10), 124.08 (d, C-1, C-8), 126.12 (d, C-3, C-6), 126.86 (d, C-2, C-7), 128.93 (s, C-8a, C-9a), 128.97 (s, C-4a, C-10a), 131.28 (s, C-9), 132.96 (s, C-4, C-5), 168.31 (s, C═O) ppm; calculated for $C_{19}H_{16}Cl_2O_2$, C 65.72, H 4.64; found, C 65.19, H 4.57%.

*tert-Butyl 4,5-diphenylanthracene-9-carboxylate (**9**).* Yield 31%, yellow solid: m.p. 207 °C; IR (KBr), 3061, 3031, 3004, 2978, 2928, 1709, 1687, 1655, 1639, 1561, 1449, 1365, 1280, 1253, 1171, 1142, 1032, 847, 821, 764, 743, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), δ 1.82 [s, $C(CH_3)_3$], 7.29–7.43 (m, 2′-H, 2″-H, 3-H, 3′-H, 3″-H, 4′-H, 4″-H, 5′-H, 5″-H, 6-H, 6′-H, 6″-H), 7.58 (dd, J = 9 Hz, J = 7 Hz, 2-H, 7-H), 8.05 (ddd, J = 9 Hz, J = 1 Hz, J = 1 Hz, 1-H, 8-H), 8.64 (s, 10-H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$), δ 28.52 [q, $C(CH_3)_3$], 83.00 [s, $C(CH_3)_3$], 124.22 (d, C-1, C-8), 126.07 (d, C-3, C-6), 126.22 (d, C-10), 126.52 (d, C-2, C-7), 127.30 (d, C-4′, C-4″), 127.89 (s, C-8a, C-9a), 128.13 (d, C-3′, C-3″, C-5′, C-5″), 128.70 (s, C-9), 129.54 (s, C-4a, C-10a), 129.96 (d, C-2′, C-2″, C-6′, C-6″), 140.15 (s, C-1′, C-1″), 140.98 (s, C-4, C-5), 169.40 (s, C═O) ppm; HRMS, calculated for $C_{31}H_{26}O_2$, *m/z* 430.1933; found, *m/z* 430.1929.

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