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Synthesis of 2,5-dihydrobenzo[*b*]oxepins and 5,6-dihydro-2*H*-benzo[*b*]oxocines based on [3+3] cyclizations of 1,3-bis(silyl enol ethers)

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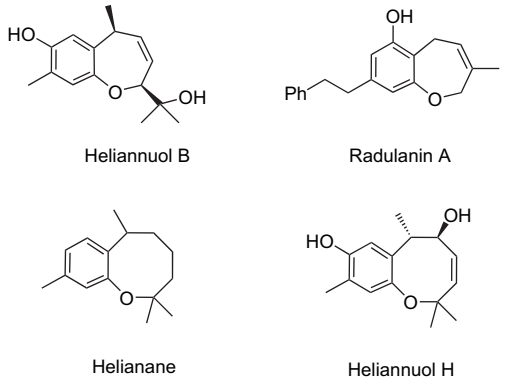
Abstract—Functionalized 2,5-dihydrobenzo[*b*]oxepins and 5,6-dihydro-2*H*-benzo[*b*]oxocines were prepared based on a '[3+3] cyclization–olefin-metathesis' strategy.

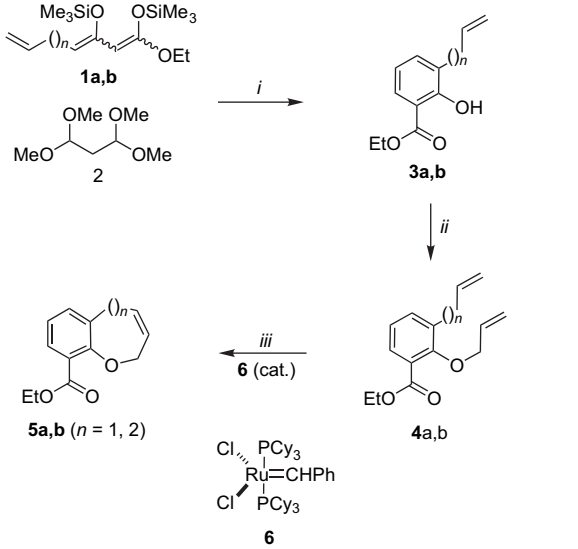
1. Introduction

2,3,4,5-Tetrahydrobenzo[*b*]oxepins are present in a number of natural products (e.g., heliannuols C and D[1] or plumbagic acid lactone).[2] 3,4,5,6-Tetrahydro-2*H*-benzo[*b*]oxocines occur in heliannuols A and K,[1,3] helianane[4] and protosappanine B.[5] 2,5-Dihydrobenzo[*b*]oxepins occur in heliannuol B[1] and in radulanins A, H and L.[6] 5,6-Dihydro-2*H*-benzo-[*b*]oxocines are present in heliannuols G and H,[4] specionine[7] and sophoroside A.[7] Benzene-fused oxygen heterocycles are available by combination of the directed-*ortho*-metallation (DoM) or arenes with ring-closing metathesis (RCM).[8] A number of benzo[*b*]oxepin and benzo[*b*]oxocine natural products were prepared by RCM.[9] Recently, we reported[10] the synthesis of 2,5-dihydrobenzo[*b*]oxepins and 5,6-dihydro-2*H*-benzo[*b*]oxocines based on the combination of formal [3+3] cyclizations[11] of 1,3-bis(silyl enol ethers)[12] with RCM. Herein, we report full details of these studies.



2. Results and discussion

The known 1,3-bis(silyl enol ethers) **1a**,**b** are prepared as reported (Scheme 1).[13,14] The $TiCl_4$ mediated [3+3]



Scheme 1. Synthesis of **5a**,**b**: (i) $TiCl_4$, CH_2Cl_2, −78→20 °C; (ii) $H_2C{=}CH{-}CH_2Br$ (1.5 equiv), NaH (2.0 equiv), TBAI (2.0 equiv), THF, 0 °C, 24 h, 0→20 °C, 8–12 h; (iii) **6** (5 mol %), CH_2Cl_2 (1.5 equiv), 20 °C, 6–8 h.

Keywords: Cyclizations; Heterocycles; Medium-sized rings; Ring-closing metathesis; Silyl enol ethers.
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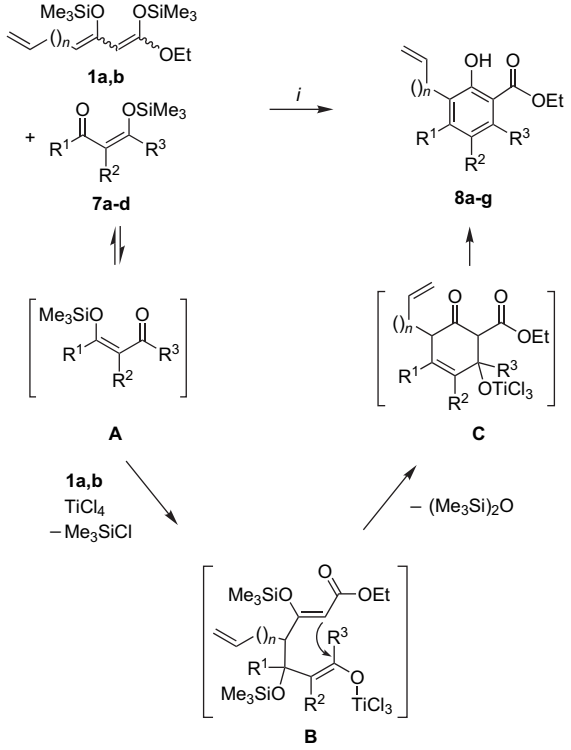
Table 1. Products and yields

1	3–5	*n*	3 (%)[a]	4 (%)[a]	5 (%)[a]
a	**h**	1	45	86	99
b	**i**	2	53	84	75

[a] Yields of isolated products.

cyclization of **1a** and **1b** with 1,1,3,3-tetramethoxypropane (**2**) affords salicylates **3a** and **3b**, respectively (Scheme 1, Table 1). Allylation of the hydroxy group affords the allylic ethers **4a** and **4b**. Application of the Mitsunobu reaction for O-allylation was not successful. Compounds **4a** and **4b** are transformed into the desired 2,5-dihydrobenzo[*b*]oxepin **5a** and 5,6-dihydro-2*H*-benzo[*b*]oxocine **5b** by RCM using Grubbs' I catalyst (**6**).[15,16] Migration of the olefin functionality during RCM (to form cyclic enol ethers) is *not* observed.[17]

The known silyl enol ethers **7a–d** are prepared from pentane-2,4-dione, 3-methylpentane-2,4-dione, heptane-3,5-dione and 2-acetyltetralone.[13,14] The $TiCl_4$ mediated [3+3] cyclization of 1,3-bis(silyl enol ethers) **1a**,**b** with **7a–d** affords the salicylates **8a–g** (Scheme 2, Table 2). Derivatives **8d** and **8g** are formed with very good regioselectivity. The cyclization proceeds by $TiCl_4$ mediated isomerization of **7** by shift of the silyl group (intermediate **A**), $TiCl_4$ mediated attack of carbon atom C-4 of **1a**,**b** onto the carbon located next to substituent R^1 to give intermediate **B** (conjugate addition), cyclization (intermediate **C**), and subsequent aromatization.[11,13] The yields of **8a–g** are similar to those reported for related [3+3] cyclizations[11] and are not decreased by the presence of the additional alkenyl moiety in the 1,3-bis-(silyl enol ether).



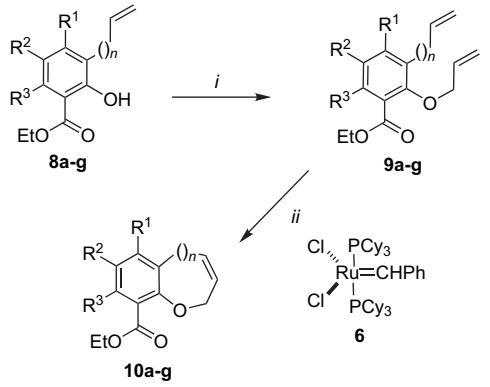
Scheme 2. Synthesis of **8a–g**: (i) $TiCl_4$ (1.0 equiv), CH_2Cl_2, −78→20 °C.

Table 2. Products and yields

1	7	8–10	*n*	R^1	R^2	R^3	8 (%)[a]	9 (%)[a]	10 (%)[a]
a	**a**	**a**	1	Me	H	Me	44	85	90
a	**b**	**b**	1	Me	Me	Me	52	95	93
a	**c**	**c**	1	Et	H	Et	31	78	91
a	**d**	**d**	1	Me	$(CH_2)_2C_6H_4$		43	77	80
b	**b**	**e**	2	Me	Me	Me	47	76	76
b	**c**	**f**	2	Et	H	Et	50	82	91
b	**d**	**g**	2	Me	$(CH_2)_2C_6H_4$		33	96	70

[a] Yields of isolated products.

The sodium hydride mediated reaction of **8a–g** with allyl bromide and homoallyl bromide affords the arylethers **9a–g**, which are transformed into the desired 2,5-dihydrobenzo-[*b*]oxepins **10a–d** and 5,6-dihydro-2*H*-benzo[*b*]oxocines **10e–g** by RCM using Grubbs' I catalyst (**6**) (Scheme 3, Table 2).[15,16] Migration of the olefin functionality during RCM (to form cyclic enol ethers) is again not observed.[17]



Scheme 3. Synthesis of **10a–g**: (i) $H_2C{=}CHCH_2Br$ or $H_2C{=}CH(CH_2)_2Br$ (1.5 equiv), NaH (2.0 equiv), TBAI (2.0 equiv), THF, 0→20 °C, 8–12 h; (ii) **6** (5 mol %), CH_2Cl_2 (1.5 equiv), 20 °C, 6–8 h.

In summary, we reported the synthesis of functionalized 2,5-dihydrobenzo[*b*]oxepins and 5,6-dihydro-2*H*-benzo[*b*]oxocines by combination of formal [3+3] cyclizations with the ring-closing metathesis.

3. Experimental section

3.1. General

Bruker TO 250 (250 MHz), Bruker ARX 300 (300 MHz) or Varian Inova 500 (500 MHz); δ=0.00 ppm for tetramethylsilane, δ=2.04 ppm for acetone-d_6, δ=7.26 ppm for deuterochloroform ($CDCl_3$). Characterization of the signal fragmentations: s=singlet, d=doublet, dd=doublet of doublet, ddd=doublet of a double doublet, t=triplet, q=quartet, quint=quintet, sixt=sextet, sept=septet, m=multiplet, br=broadly. Spectra were evaluated according to first order rule. Equipment: Bruker AM 250 (62.9 MHz), Bruker ARX 300 (75 MHz) or Bruker Advance 600 (150 MHz); δ=128.00 ppm for acetone-d_6, δ=77.00 ppm for $CDCl_3$. The multiplicity of the carbon atoms was determined by the DEPT 135 and APT (APT=Attached Proton Test) techniques and quoted as CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms. Characterization of the signal fragmentations: quart=quartet, the

multiplicity of the signals was determined by the DEPT recording technology and/or the APT recording technology. Mass spectroscopy: APPM MS40, Varian MAT CH 7, MAT 731, Finnigan MAT 95 spectrometer (EI, 70 eV), Finnigan LC-Q (ESI). High-resolution mass spectroscopy: Finnigan MAT 95 or Varian MAT 311, Bruker FT CIR. Infrared spectroscopy (IR): Bruker IFS 66 (FTIR), Nicolet 205 FTIR; KBr and/or KAP; abbreviations for signal allocations: w=weak, m=middle, s=strong, br=broad. UV–vis spectroscopy: Perkin–Elmer UV–vis/NIR Lambda 19, as solvent CH_3CN was used. Elementary analyses: Microanalytical laboratory of the University of Greifswald (Leco CHN CHNS-932). Melting points: Microheating table HMK 67/1825 Kuestner (Büchi apparatus). Melting points are uncorrected. Column chromatography: chromatographic separation took place at Merck silica gel 60 (0.063–0.200 mm, 70–230 mesh) as normal and/or at Macherey silica gel 60 (0.040–0.063 mm, 200–400 mesh) as flash chromatography. TLC: Merck DC finished foils, silica gel 60 F_{254} on aluminium foil and Macherey finished foils Alugram® Sil G/UV_{254}. Detection under UV light with 254 nm and/or 366 nm without dipping reagent, as well as with anisic aldehyde sulfuric acid dip reagent (1 mL of anisic aldehyde dissolved in 100 mL of a stock solution of 85% methanol, 14% acetic acid and 1% sulfuric acid).

3.2. General procedure for the synthesis of 3a,b and 8a–g

To a CH_2Cl_2 solution of **1a**,**b** and **7a–d** or 1,1,3,3-tetramethoxypropane (**2**) was dropwise added $TiCl_4$ at −78 °C under argon atmosphere. The solution was stirred at −78 °C for 30 min and was subsequently allowed to warm to 20 °C within 18 h. To the solution was added a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4×100 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc).

3.2.1. Ethyl 3-allyl-2-hydroxybenzoate (3a). Starting with **1a** (1.570 g, 5.0 mmol), $TiCl_4$ (0.945 g, 5.0 mmol), 1,1,3,3-tetramethoxypropane (0.821 g, 5.0 mmol) and CH_2Cl_2 (10 mL), **3a** was isolated by column chromatography (*n*-hexane/EtOAc=20:1) as a colourless oil (0.464 g, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.41 (t, J=7.2 Hz, 3H, OCH_2CH_3), 3.44 (d, J=6.6 Hz, 2H, CH_2=$CHCH_2$), 4.42 (q, J=7.1 Hz, 2H, OCH_2CH_3), 5.05–5.12 (m, 2H, CH_2=$CHCH_2$), 5.95–6.08 (m, 1H, CH_2=$CHCH_2$), 6.82 (t, J=7.8 Hz, 1H, Ar), 7.31 (dd, J=6.0, 1.5 Hz, 1H, Ar), 7.75 (dd, J=6.3, 1.7 Hz, 1H, Ar), 11.14 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2 (CH_3), 33.6, 61.4 (CH_2), 112.2 (C), 115.8 (CH_2), 118.6, 127.9 (CH), 128.5 (C), 135.6, 136.2 (CH), 159.6, 170.6 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3139 (m, br), 2983 (m), 1672 (s), 1614 (m), 1449 (s), 1303 (s), 1248 (s), 1150 (s), 1025 (s), 760 (s). UV–vis (CH_3CN, nm): λ_{max} (log ε)=209.3 (4.47), 242.4 (3.92), 309.7 (3.63). MS (EI, 70 eV): m/z (%)=206 (M^+, 38), 160 (43), 132 (100), 103 (34), 77 (41), 51 (16). Anal. Calcd for $C_{12}H_{14}O_3$: C 69.88, H 6.79; found: C 69.31, H 7.04.

3.2.2. Ethyl 3-(but-3-enyl)-2-hydroxybenzoate (3b). Starting with **1b** (3.286 g, 10 mmol), $TiCl_4$ (1.89 g, 10 mmol), 1,1,3,3-tetramethoxypropane (1.642 g, 10 mmol) and CH_2Cl_2 (25 mL), **3b** was isolated by column chromatography (*n*-hexane/EtOAc=20:1) as a colourless oil (1.177 g, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.41 (t, J=7.2 Hz, 3H, OCH_2CH_3), 2.38 (q, J=7.8 Hz, 2H, CH_2CH_2CH=CH_2), 2.75 (t, J=7.8 Hz, 2H, CH_2CH_2CH=CH_2), 4.43 (q, J=7.2 Hz, 2H, OCH_2CH_3), 4.95–5.07 (m, 2H, CH_2=$CHCH_2$), 5.81–5.94 (m, 1H, CH_2=$CHCH_2$), 6.80 (t, J=7.8 Hz, 1H, Ar), 7.31 (dd, J=7.3, 1.2 Hz, 1H, Ar), 7.72 (dd, J=7.8, 1.8 Hz, 1H, Ar), 11.1 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2 (CH_3), 26.2, 33.5, 61.4 (CH_2), 112.1 (C), 114.5 (CH_2), 119.2 (CH), 127.1 (C), 128.2, 134.4, 138.6 (CH), 159.2, 171.2 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3100 (m, br), 2981 (m), 2937 (m), 1669 (s), 1612 (m), 1448 (m), 1400 (m), 1375 (m), 1316 (s), 1256 (s), 1194 (s), 1125 (m), 1027 (m), 913 (m), 763 (m). MS (EI, 70 eV): m/z (%)=220 (M^+, 12), 179 (33), 134 (100), 106 (34), 91 (19), 77 (25). HRMS (EI, 70 eV) calcd for $C_{13}H_{16}O_3$ ([M^+]): m/z=220.10994, found: m/z=220.10953.

3.2.3. Ethyl 3-allyl-2-hydroxy-4,6-dimethylbenzoate (8a). Starting with **1a** (1.257 g, 4.0 mmol), $TiCl_4$ (0.760 g, 4.0 mmol) in 10 mL of CH_2Cl_2 and **7a** (0.680 g, 4.0 mmol), **8a** was isolated by column chromatography (*n*-hexane/EtOAc=20:1) as a colourless oil (0.338 g, 44%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.42 (t, J=7.2 Hz, 3H, OCH_2CH_3), 2.25 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 3.43 (m, J=1.5 Hz, 2H, CH_2=$CHCH_2$), 4.42 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.89–4.99 (m, J=15.5, 10.4, 1.7 Hz, 2H, CH_2=$CHCH_2$), 5.93 (m, J=5.2, 1.5 Hz, 1H, CH_2=$CHCH_2$), 6.55 (s, 1H, CH, Ar), 11.75 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 19.6, 23.9 (CH_3), 30.1, 61.4 (CH_2), 109.8 (C), 114.4 (CH_2), 123.8 (C), 124.7, 135.7 (CH), 138.5, 143.6, 160.8, 172.2 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2979 (m), 2934 (m), 1654 (s), 1616 (m), 1449 (m), 1396 (s), 1268 (s), 1173 (s), 1031 (m), 847 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=216.7 (4.41), 253.2 (3.98), 315.6 (3.57). MS (EI, 70 eV): m/z (%)=234 (M^+, 29), 188 (34), 173 (24), 160 (53), 145 (27), 114 (9), 91 (11), 28 (100). HRMS (EI, 70 eV) calcd for $C_{14}H_{18}O_3$: m/z=234.1256 ([M^+]), found: m/z=234.1256±2 ppm.

3.2.4. Ethyl 3-allyl-2-hydroxy-4,5,6-trimethylbenzoate (8b). Starting with **1a** (1.257 g, 4.0 mmol) and **7b** (0.745 g, 4.0 mmol) in 10 mL of CH_2Cl_2 and $TiCl_4$ (0.760 g, 4.0 mmol), **8b** was isolated by column chromatography (*n*-hexane/EtOAc=30:1) as a colourless oil (0.520 g, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.41 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.17 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.50 (m, J=1.18 Hz, 2H, CH_2=$CHCH_2$), 4.43 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.95 (m, J=15.5, 11.5, 1.8 Hz, 2H, CH_2=$CHCH_2$), 5.98 (m, J=5.5, 1.3 Hz, 1H, CH_2=$CHCH_2$), 11.51 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 16.1, 16.9, 19.2 (CH_3), 30.5, 61.4 (CH_2), 111.6 (C), 114.4 (CH_2), 123.4, 127.2 (C), 135.6, 136.1 (CH), 142.3, 156.9, 172.0 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2981 (m), 2931 (m), 1654 (s), 1600 (m), 1456 (s), 1403 (s), 1374 (s), 1312 (s), 1260 (s), 1196 (s), 1045 (m), 1019 (m), 910 (m), 806 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=217.1 (4.38), 256.1 (3.94), 320.9 (3.57). MS (EI, 70 eV): m/z (%)=248 (M^+, 58), 202 (55), 187 (40), 174 (100), 159 (65), 91 (18), 28 (12). HRMS (ESI^+) calcd for $C_{15}H_{20}O_3$ [M^++1]:

m/*z*=249.14907; found: *m*/*z*=249.14867. Anal. Calcd for $C_{15}H_{20}O_3$: C 72.55, H 8.18; found: C 72.13, H 7.67.

3.2.5. Ethyl 3-allyl-4,6-diethyl-2-hydroxybenzoate (8c). Starting with **1a** (1.257 g, 4.0 mmol), **7c** (0.800 g, 4.0 mmol) in 10 mL of CH_2Cl_2 and $TiCl_4$ (0.760 g, 4.0 mmol), **8c** was isolated by column chromatography (*n*-hexane/EtOAc=50:1) as a colourless oil (0.320 g, 31%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.17 (t, *J*=7.4 Hz, 6H, 2CH_3CH$_2$), 1.42 (t, *J*=7.1 Hz, 3H, OCH$_2$CH_3), 2.60 (q, *J*=7.5 Hz, 2H, CH$_3$CH_2), 2.92 (q, *J*=7.4 Hz, 2H, CH$_3$CH_2), 3.44 (m, *J*=2.4, 1.7 Hz, 2H, CH$_2$=CHCH_2), 4.43 (q, *J*=7.2 Hz, 2H, OCH_2CH$_3$), 4.99 (m, *J*=10.0, 1.7 Hz, 2H, CH_2=CHCH$_2$), 5.97 (m, *J*=1.3 Hz, 1H, CH$_2$=C*H*CH$_2$), 6.59 (s, 1H, CH, Ar), 11.66 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 15.1, 16.3 (CH$_3$), 26.1, 29.7, 29.8, 61.1 (CH$_2$), 109.1 (C), 114.4 (CH$_2$), 121.8 (CH), 123.2 (C), 136.5 (CH), 145.0, 149.4, 160.8, 172.0 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3078 (w), 2974 (m), 2879 (w), 1978 (w), 1654 (s), 1614 (m), 1401 (s), 1317 (m), 1266 (s), 1167 (m), 1019 (w), 909 (w), 865 (w). UV–vis (CH$_3$CN, nm): λ_{max} (log ε)=217.0 (4.44), 254.4 (4.02), 315.9 (3.63). MS (EI, 70 eV): *m*/*z* (%)=263 (M$^+$+1, 6), 262 (M$^+$, 52), 216 (100), 201 (51), 173 (99), 159 (67), 73 (36), 28 (94).

3.2.6. Ethyl 2-allyl-9,10-dihydro-3-hydroxy-1-methylphenanthrene-4-carboxylate (8d). Starting with **1a** (1.89 g, 6.0 mmol), **7d** (1.56 g, 6.0 mmol) in 15 mL of CH_2Cl_2 and $TiCl_4$ (1.14 g, 6.0 mmol), **8d** was isolated by column chromatography (*n*-hexane/EtOAc=30:1) as a colourless oil (0.820 g, 43%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.00 (t, *J*=7.1 Hz, 3H, OCH$_2$CH_3), 2.28 (s, 3H, CH$_3$), 2.65 (m, *J*=5.5, 1.2 Hz, 2H, CH$_2$), 2.81 (m, *J*=6.8 Hz, 2H, CH$_2$), 3.55 (m, *J*=2.5, 1.8 Hz, 2H, CH$_2$=CHCH_2), 4.16 (q, *J*=7.1 Hz, 2H, OCH_2CH$_3$), 4.96–5.04 (m, *J*=6.0, 1.8 Hz, 2H, CH_2=CHCH$_2$), 5.96 (m, *J*=5.8, 1.4 Hz, 1H, CH$_2$=C*H*CH$_2$), 7.09–7.24 (m, 4H, Ar), 9.95 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.4, 15.9 (CH$_3$), 25.7, 29.2, 30.7, 61.2 (CH$_2$), 109.1 (C), 114.8 (CH$_2$), 123.8, 125.2 (C), 125.3 (CH), 126.8 (C), 126.9, 129.2 (CH), 130.5, 134.7, 135.6 (C), 135.7 (CH), 140.2, 156.3, 172.1 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3217 (br, w), 3072 (m), 2980 (m), 2899 (m), 1661 (s), 1597 (m), 1442 (s), 1401 (s), 1375 (s), 1315 (s), 1255 (s), 1191 (s), 1123 (m), 1054 (m), 1018 (m), 911 (m), 785 (s). UV–vis (CH$_3$CN, nm): λ_{max} (log ε)=203.9 (4.49), 231.9 (4.39), 279.9 (3.94), 340.9 (3.89). MS (EI, 70 eV): *m*/*z* (%)=322 (M$^+$, 2), 276 (3), 248 (5), 105 (8), 78 (8), 74 (29), 32 (23), 28 (100). HRMS (ESI$^+$) calcd for $C_{21}H_{22}O_3$ [M$^+$+1]: *m*/*z*=323.16472; found: 323.16442. Anal. Calcd for $C_{15}H_{20}O_3$: C 78.23, H 6.88; found: C 78.42, H 7.60.

3.2.7. Ethyl 3-(but-3-enyl)-2-hydroxy-4,5,6-trimethylbenzoate (8e). Starting with **1b** (1.97 g, 6.0 mmol) and **7b** (1.12 g, 6.0 mmol) in 15 mL of CH_2Cl_2 and $TiCl_4$ (1.14 g, 6.0 mmol), **8e** was isolated by column chromatography (*n*-hexane/EtOAc=30:1) as a colourless oil (0.735 g, 47%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.41 (t, *J*=7.1 Hz, 3H, OCH$_2$CH_3), 2.16 (s, 3H, CH$_3$), 2.19–2.26 (m, 2H, CH$_2$=CHCH_2CH$_2$), 2.27 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$), 2.80 (m, *J*=6.9, 2.1 Hz, 2H, CH$_2$=CHCH$_2$CH_2), 4.43 (q, *J*=7.1 Hz, 2H, OCH_2CH$_3$), 4.95–5.10 (m, *J*=9.5, 17.1, 1.6 Hz, 2H, CH_2=CHCH$_2$CH$_2$), 5.92 (m, *J*=5.2 Hz, 1H, CH$_2$=C*H*CH$_2$), 10.74 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 16.1, 16.9, 19.2 (CH$_3$), 26.2, 33.3, 61.4 (CH$_2$), 111.2 (C), 114.3 (CH$_2$), 125.8, 127.1, 135.1 (C), 138.8 (CH), 141.6, 157.0, 172.1 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3075 (m), 2979 (s), 2932 (s), 1651 (s), 1599 (s), 1446 (s), 1403 (s), 1374 (s), 1312 (s), 1254 (s), 1196 (s), 1117 (m), 1045 (s), 1023 (m), 911 (m), 806 (m). UV–vis (CH$_3$CN, nm): λ_{max} (log ε)=217.2 (4.37), 256.6 (3.92), 321.4 (3.54). MS (EI, 70 eV): *m*/*z* (%)=262 (M$^+$, 16), 221 (24), 175 (100), 146 (8), 91 (15), 79 (16), 28 (30). HRMS (ESI$^+$) calcd for $C_{16}H_{22}O_3$ [M$^+$+1]: *m*/*z*=263.16472; found: *m*/*z*=263.16413.

3.2.8. Ethyl 3-(but-3-enyl)-4,6-diethyl-2-hydroxybenzoate (8f). Starting with **1b** (0.985 g, 3.0 mmol) and **7c** (0.600 g, 3.0 mmol) in 8 mL of CH_2Cl_2 and $TiCl_4$ (0.569 g, 3.0 mmol), **8f** was isolated by column chromatography (*n*-hexane/EtOAc=50:1) as a colourless oil (0.415 g, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.20 (t, *J*=7.4 Hz, 6H, 2CH_3CH$_2$), 1.42 (t, *J*=7.1 Hz, 3H, OCH$_2$CH_3), 2.28 (m, 2H, CH$_2$=CHCH_2CH$_2$), 2.60 (q, *J*=7.5 Hz, 2H, CH$_3$CH_2), 2.73 (m, *J*=6.5, 1.5 Hz, 2H, CH$_2$=CHCH$_2$CH_2), 2.91 (q, *J*=7.4 Hz, 2H, CH$_3$CH_2), 4.43 (q, *J*=7.1 Hz, 2H, OCH_2CH$_3$), 4.95–5.09 (m, *J*=10.1, 15.4, 1.2 Hz, 2H, CH_2=CHCH$_2$CH$_2$), 5.92 (m, *J*=6.5, 3.4 Hz, 1H, CH$_2$=C*H*CH$_2$CH$_2$), 6.57 (s, 1H, CH, Ar), 11.65 (s, 1H, OH). ^{13}C NMR: δ=14.0, 15.2, 16.3 (CH$_3$), 25.4, 26.3, 29.7, 33.5, 61.3 (CH$_2$), 109.0 (C), 114.3 (CH$_2$), 121.8 (CH), 125.6 (C), 138.9 (CH), 144.4, 148.9, 161.0, 172.0 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3077 (w), 2973 (s), 2936 (m), 1652 (s), 1614 (m), 1454 (w), 1399 (s), 1376 (m), 1318 (m), 1260 (s), 1171 (m), 1022 (w), 847 (w). UV–vis (CH$_3$CN, nm): λ_{max} (log ε)=217.1 (4.46), 254.9 (4.02), 316.4 (3.61). MS (EI, 70 eV): *m*/*z* (%)=277 (M$^+$+1, 6), 276 (M$^+$, 7), 235 (23), 189 (100), 91 (6), 79 (6), 32 (20), 28 (89). HRMS (ESI$^+$) calcd for $C_{17}H_{24}O_3$ [M$^+$+1]: *m*/*z*=277.18037; found: *m*/*z*=277.18001. Anal. Calcd for $C_{17}H_{24}O_3$: C 73.88, H 8.75; found C 73.35, H 8.58.

3.2.9. Ethyl 2-(but-3-enyl)-9,10-dihydro-3-hydroxy-1-methylphenanthrene-4-carboxylate (8g). Starting with **1b** (2.63 g, 8.0 mmol) and **7d** (2.08 g, 8.0 mmol) in 20 mL of CH_2Cl_2 and $TiCl_4$ (1.52 g, 8.0 mmol), **8g** was isolated by column chromatography (*n*-hexane/EtOAc=30:1) as a colourless solid (0.874 g, 33%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.02 (t, *J*=7.1 Hz, 3H, OCH$_2$CH_3), 2.27 (m, *J*=2.5 Hz, 2H, CH$_2$=CHCH_2CH$_2$), 2.29 (s, 3H, CH$_3$), 2.65 (m, *J*=5.7 Hz, 2H, CH$_2$), 2.81 (m, *J*=5.3 Hz, 2H, CH$_2$), 2.86 (m, *J*=2.5 Hz, 2H, CH$_2$=CHCH_2), 4.16 (q, *J*=7.1 Hz, 2H, OCH_2CH$_3$), 4.98–5.12 (m, *J*=10.2, 15.1, 1.8 Hz, 2H, CH_2=CHCH$_2$CH$_2$), 5.95 (m, 1H, CH$_2$=C*H*CH$_2$CH$_2$), 7.09 (m, 1H, Ar), 7.14–7.25 (m, 3H, Ar), 9.93 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.4, 16.0 (CH$_3$), 25.7, 26.3, 29.2, 33.2, 61.2 (CH$_2$), 108.9 (C), 114.5 (CH$_2$), 125.3, 126.8, 126.9 (CH), 127.7 (C), 129.2 (CH), 130.5, 134.3, 134.7, 137.6 (C), 138.6 (CH), 139.6, 156.5, 172.2 (C). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ: 9.93 (s, 1H, OH), 7.24 (dd, $^3J_{10,11}$=7.3 Hz, $^4J_{10,12}$=1.6 Hz, 1H, H-10), 7.20–7.13 (m, 2H, H-11,12), 7.08 (dd, $^3J_{12,13}$=7.3 Hz, $^4J_{11,13}$=1.6 Hz, 1H, H-13), 5.96 (m, 1H, H-17), 5.10 (dq, $^3J_{17,18a}$=17.0 Hz, 1H, H-18a), 5.00 (dq, $^3J_{17,18b}$=10.0 Hz, 1H, H-18b), 4.17 (q, 2H, CH_2CH$_3$), 2.86 (m, 2H, H-15), 2.81 (m, 2H, H-8), 2.64 (m, 2H, H-7), 2.30 (s, 3H,

Me), 2.29 (m, 2H, H-16), 1.00 (t, 3H, $^3J_{CH_2,CH_3}$ = 7.3 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ: 172.2 (CO), 156.5 (C-3), 139.6 (C-5), 138.6 (C-17), 137.6 (C-9), 134.8 (C-14), 134.3 (C-1), 130.5 (C-6), 129.2 (C-13), 127.7 (C-4), 126.9, 126.8 (C-10,11), 125.3 (C-12), 114.5 (C-18), 109.0 (C-2), 61.2 (CH_2CH_3), 33.2 (C-16), 29.2 (C-8), 26.3 (C-15), 25.7 (C-7), 16.0 (Me), 13.4 (CH_2CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$=3429 (br, m), 2981 (m), 2898 (m), 1660 (s), 1443 (m), 1398 (m), 1373 (m), 1315 (s), 1251 (s), 1197 (s), 1026 (m), 910 (w), 762 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=203.1 (4.53), 231.8 (4.39), 280.2 (3.94), 341.2 (3.89). MS (EI, 70 eV): *m*/*z* (%)=336 (M^+, 8), 275 (5), 249 (24), 114 (9), 79 (8), 74 (18), 32 (24), 28 (100). HRMS (ESI^+) calcd for $C_{22}H_{24}O_3$ [M^++1]: *m*/*z*=337.18037; found: *m*/*z*=337.18044.

3.3. General procedure for the synthesis of salicylates 4a,b and 9a–g

To a mixture of NaH and of *n*-Bu_4NI was simultaneously added a THF solution of **3a**,**b** or **8a–g** and of allyl bromide or homoallyl bromide at 0 °C under argon atmosphere. The pale yellow coloured solution was stirred at 0 °C and was allowed to warm to 20 °C within 8–12 h. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc=20:1).

3.3.1. Ethyl 3-allyl-2-(allyloxy)benzoate (4a). Starting with **3a** (0.300 g, 1.46 mmol) in 20 mL of THF, NaH (0.077 g, 3.2 mmol), *n*-Bu_4NI (1.182 g, 3.2 mmol) and allyl bromide (0.440 g, 3.2 mmol), **4a** was isolated as a yellow oil (0.308 g, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.39 (t, *J*=7.2 Hz, 3H, OCH_2CH_3), 3.46 (d, *J*=6.6 Hz, 2H, CH_2=$CHCH_2$), 4.37 (q, *J*=7.2 Hz, 2H, OCH_2CH_3), 4.42–4.46 (m, 2H, CH_2=$CHCH_2O$), 4.81 (dt, *J*=5.7, 1.4 Hz, 1H, CH_2=$CHCH_2Ar$), 5.03–5.10 (m, 1H, CH_2=$CHCH_2Ar$), 5.27 (tquint, *J*=10.5, 1.4 Hz, 1H, CH_2=$CHCH_2O$), 5.35–5.45 (m, 1H, CH_2=$CHCH_2O$), 5.90–6.15 (m, 2H, 2×CH_2=C*H*), 7.11 (dt, *J*=7.8, 1.5 Hz, 1H, Ar), 7.34–7.39 (ddd, *J*=7.5, 3.6, 1.8 Hz, 1H, Ar), 7.66–7.72 (ddd, *J*=7.5, 7.5, 1.8 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3 (CH_3), 33.8, 65.8, 75.6, 116.3, 117.4 (CH_2), 118.6 (C), 123.7 (CH), 125.4 (C), 129.7, 133.8, 134.5, 136.8 (CH), 157.1, 166.1 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2927 (m), 1724 (s), 1645 (w), 1452 (m), 1417 (m), 1290 (m), 1258 (s), 1219 (w), 1136 (s), 1099 (w), 992 (m), 922 (w). MS (EI, 70 eV): *m*/*z* (%)=246 (M^+, 1), 204 (64), 191 (22), 179 (41), 159 (91), 145 (30), 131 (100), 115 (31), 103 (58), 91 (22), 77 (44). HRMS (EI, 70 eV) calcd for $C_{15}H_{18}O_3$ ([M^+]): *m*/*z*=246.1250; found: *m*/*z*=246.1241.

3.3.2. Ethyl 2-(allyloxy)-3-(but-3-enyl)benzoate (4b). Starting with **3b** (0.500 g, 2.27 mmol) in 30 mL of THF, NaH (0.120 g, 5.0 mmol), *n*-Bu_4NI (1.847 g, 5.0 mmol) and allyl bromide (0.605 g, 5.0 mmol), **4b** was isolated as a yellow oil (0.496 g, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.38 (t, *J*=7.2 Hz, 3H, OCH_2CH_3), 2.25 (m, 2H, CH_2CH_2CH=CH_2), 2.72 (m, 2H, CH_2CH_2CH=CH_2), 4.37 (q, *J*=7.2 Hz, 2H, OCH_2CH_3), 4.44 (m, 2H, CH_2=$CHCH_2O$), 4.95–5.10 (m, 2H, CH_2=$CHCH_2CH_2$), 5.25–5.45 (m, 2H, CH_2=$CHCH_2O$), 5.80–6.12 (m, 2H, CH_2=C*H*CH_2CH_2, CH_2=C*H*CH_2O), 7.08 (dt, *J*=7.8, 1.5 Hz, 1H, Ar), 7.32–7.38 (ddd, *J*=7.5, 3.6, 1.8 Hz, 1H, Ar), 7.64–7.71 (ddd, *J*=7.5, 7.5, 1.8 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2 (CH_3), 26.4, 34.5, 61.2, 75.8, 114.6, 116.7 (CH_2), 117.5 (C), 122.9 (CH), 125.2 (C), 128.9, 133.9, 134.6, 138.4 (CH), 155.7, 167.2 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2928 (m), 1725 (s), 1644 (m), 1556 (w), 1456 (m), 1415 (m), 1288 (m), 1257 (s), 1145 (m), 1099 (w), 991 (m), 919 (m). MS (EI, 70 eV): *m*/*z* (%)=260 (M^+, 32), 219 (65), 203 (5), 174 (100), 148 (10), 103 (17), 87 (25), 76 (55). HRMS (EI, 70 eV) calcd for $C_{16}H_{20}O_3$ ([M^+]): *m*/*z*=260.14124; found: *m*/*z*=260.14095.

3.3.3. Ethyl 3-allyl-2-(allyloxy)-4,6-dimethylbenzoate (9a). Starting with **8a** (0.285 g, 1.22 mmol, 1.0 equiv) in 15 mL of THF, NaH (0.059 g, 2.44 mmol, 2.0 equiv), *n*-Bu_4NI (0.797 g, 2.44 mmol, 2.0 equiv) and allyl bromide (0.220 g, 1.83 mmol, 1.5 equiv), **9a** was isolated as a colourless oil (0.285 g, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.37 (t, *J*=7.1 Hz, 3H, OCH_2CH_3), 2.24 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.42 (m, *J*=1.8 Hz, 2H, CH_2=$CHCH_2Ar$), 4.37 (q, *J*=7.1 Hz, 2H, OCH_2CH_3), 4.39 (m, *J*=1.5 Hz, 2H, CH_2=$CHCH_2O$), 4.86–4.93 (m, *J*=15.3, 10.2, 1.8 Hz, 2H, CH_2=$CHCH_2Ar$), 5.34–5.41 (m, *J*=10.4, 15.5, 1.6 Hz, 2H, CH_2=$CHCH_2O$), 5.88–5.93 (m, *J*=5.4 Hz, 1H, CH_2=C*H*CH_2), 5.99–6.03 (s, *J*=5.3 Hz, 1H, CH_2=C*H*CH_2O), 6.80 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3, 19.0, 19.4 (CH_3), 30.5, 61.1, 76.0, 115.2, 116.8 (CH_2), 126.8 (C), 127.8 (CH), 128.9 (C), 133.9 (CH), 134.0 (C), 136.1 (CH), 140.1, 154.4, 168.6 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3081 (m), 2981 (s), 2928 (s), 2870 (m), 1726 (s), 1642 (m), 1609 (m), 1666 (m), 1453 (s), 1411 (s), 1297 (s), 1270 (s), 1150 (s), 1108 (s), 1067 (s), 1041 (s), 992 (s), 918 (s), 864 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=202.9 (4.59), 276.4 (3.89). MS (EI, 70 eV): *m*/*z* (%)=275.5 (M^++1, 11), 274.5 (M^+, 62), 233 (24), 232 (26), 229 (36), 228 (17), 201 (12), 188 (19), 187 (100), 173 (20), 161 (34), 160 (36), 159 (31), 145 (18), 91 (16), 41 (20), 29 (11). Anal. Calcd for $C_{17}H_{22}O_3$: C 74.42, H 8.08; found: C 74.41, H 7.91.

3.3.4. Ethyl 3-allyl-2-(allyloxy)-4,5,6-trimethylbenzoate (9b). Starting with **8b** (0.179 g, 0.72 mmol, 1.0 equiv) in 10 mL of THF, NaH (0.035 g, 1.44 mmol, 2.0 equiv), *n*-Bu_4NI (0.471 g, 1.44 mmol, 2.0 equiv) and allyl bromide (0.130 g, 1.08 mmol, 1.5 equiv), **9b** was isolated as a colourless oil (0.195 g, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.37 (t, *J*=7.1 Hz, 3H, OCH_2CH_3), 2.16 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.46 (m, *J*=1.9 Hz, 2H, CH_2=$CHCH_2Ar$), 4.33 (m, *J*=1.4 Hz, 2H, CH_2=$CHCH_2O$), 4.36 (q, *J*=7.0 Hz, 2H, OCH_2CH_3), 4.85–5.04 (m, *J*=15.4, 10.3, 1.8 Hz, 2H, CH_2=$CHCH_2Ar$), 5.18–5.39 (m, *J*=10.5, 15.5, 1.6 Hz, 2H, CH_2=$CHCH_2O$), 5.95–5.98 (m, 1H, CH_2=C*H*CH_2Ar), 5.99–6.04 (m, 1H, CH_2=C*H*CH_2O). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 15.9, 16.4, 17.3 (CH_3), 30.8, 61.2, 76.1, 115.2, 116.7 (CH_2), 127.6, 128.8, 131.6, 131.8 (C), 133.9, 136.5 (CH), 138.4, 151.6, 169.3 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2982 (m), 2931 (m), 1728 (s), 1445 (m), 1418 (m), 1273 (s), 1189 (s), 1045 (s), 917 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=202.9 (4.58), 279.4 (2.96). MS (EI, 70 eV): *m*/*z* (%)=289 (M^++1, 10), 288 (M^+, 59), 247 (27), 201 (100), 174 (34), 159 (23), 91 (19), 41 (23), 28 (4). Anal. Calcd for $C_{18}H_{24}O_3$: C 74.96, H 8.39; found: C 74.34, H 8.50.

3.3.5. Ethyl 3-allyl-2-(allyloxy)-4,6-diethylbenzoate (9c). Starting with **8c** (0.200 g, 0.76 mmol, 1.0 equiv) in 10 mL THF, NaH (0.036 g, 1.52 mmol, 2.0 equiv), *n*-Bu_4NI (0.497 g, 1.52 mmol, 2.0 equiv) and allyl bromide (0.137 g, 1.14 mmol, 1.5 equiv), **9c** was isolated as a colourless oil (0.180 g, 78%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.20 (t, J=7.5 Hz, 6H, $2CH_3CH_2$), 1.36 (t, J=7.2 Hz, 3H, OCH_2CH_3), 2.56–2.64 (q, J=7.5 Hz, 4H, $2CH_3CH_2$), 3.43 (m, J=1.8 Hz, 2H, CH_2=CHCH_2Ar), 4.34 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.39 (m, 2H, CH_2=CHCH_2O), 4.87–4.99 (m, J=11.6, 8.7, 1.8 Hz, 2H, CH_2=CHCH_2Ar), 5.18–5.41 (m, J=8.9, 15.5, 1.5 Hz, 2H, CH_2=CHCH_2O), 5.89–6.06 (m, 2H, CH_2=CHCH_2Ar, CH_2=CHCH_2O), 6.86 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 15.1, 15.5 (CH_3), 25.5, 26.4, 29.9, 61.1, 75.9, 115.1, 116.6 (CH_2), 124.4 (CH), 126.3, 128.3 (C), 133.9, 136.9 (CH), 140.3, 146.0, 154.2, 168.8 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2972 (m), 2934 (w), 1728 (s), 1641 (w), 1459 (w), 1414 (w), 1277 (m), 1149 (m), 1027 (w), 918 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=203.4 (4.57). MS (EI, 70 eV): m/z (%)=302 (M^+, 12), 261 (18), 215 (44), 173 (11), 41 (15), 32 (21), 28 (100). HRMS (EI, 70 eV) calcd for $C_{19}H_{26}O_3$: m/z=302.18819; found: m/z=302.18775.

3.3.6. Ethyl 2-allyl-3-(allyloxy)-9,10-dihydro-1-methylphenanthrene-4-carboxylate (9d). Starting with **8d** (0.322 g, 1.00 mmol, 1.0 equiv) in 15 mL of THF, NaH (0.048 g, 2.0 mmol, 2.0 equiv), *n*-Bu_4NI (0.653 g, 2.00 mmol, 2.0 equiv) and allyl bromide (0.181 g, 1.5 mmol, 1.5 equiv), **9d** was isolated as a slight yellow oil (0.280 g, 77%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.23 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.26 (s, 3H, CH_3), 2.73–2.78 (m, 4H, $2CH_2$), 3.54 (m, J=1.9 Hz, 2H, CH_2=CHCH_2Ar), 4.29 (q, J=7.2 Hz, 2H, OCH_2CH_3), 4.46 (m, J=2.5, 1.5 Hz, 2H, CH_2=CHCH_2O), 4.91–5.09 (m, J=22.3, 17.2, 8.5, 1.7 Hz, 2H, CH_2=CHCH_2Ar), 5.21–5.44 (m, J=15.5, 8.8, 1.7 Hz, 2H, CH_2=CHCH_2O), 6.05 (m, 2H, CH_2=CHCH_2Ar, CH_2=CHCH_2O), 7.18–7.23 (m, 3H, Ar), 7.55 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.9, 16.0 (CH_3), 25.8, 29.1, 31.0, 61.4, 76.3, 115.6, 116.7 (CH_2), 124.6 (C), 126.1, 126.4, 127.37, 127.40 (CH), 130.9, 131.7, 133.7, 133.9 (C), 134.3 (CH), 136.2 (C), 137.2 (CH), 138.5, 153.4, 169.6 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2979 (w), 2933 (w), 1725 (s), 1641 (w), 1408 (w), 1285 (w), 1189 (m), 1022 (w), 918 (w), 764 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=210.7 (4.49), 268.7 (4.15), 295.3 (3.78), 303.8 (3.78). MS (EI, 70 eV): m/z (%)=363 (M^++1, 1), 362 (M^+, 7), 275 (11), 248 (7), 215 (7), 32 (22), 28 (100). HRMS (EI, 70 eV) calcd for $C_{24}H_{26}O_3$ ([M^+]): m/z=362.18729; found: m/z=362.18764.

3.3.7. Ethyl 3-(but-3-enyl)-2-(allyloxy)-4,5,6-trimethylbenzoate (9e). Starting with **8e** (0.325 g, 1.31 mmol, 1.0 equiv) in 20 mL of THF, NaH (0.063 g, 2.62 mmol, 2.0 equiv), *n*-Bu_4NI (0.855 g, 2.62 mmol, 2.0 equiv) and allyl bromide (0.235 g, 1.95 mmol, 1.5 equiv), **9e** was isolated as a slight yellow oil (0.300 g, 76%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.37 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.16 (s, 3H, CH_3), 2.17–2.26 (m, 2H, CH_2=CHCH_2CH$_2$), 2.22 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.74 (m J=6.0, 1.5 Hz, 2H, CH_2=CHCH_2CH_2), 4.35–4.40 (m, 4H, OCH_2CH_3, CH_2=CHCH_2O), 4.97–5.10 (m, J=10.1, 17.1, 1.5 Hz, 2H, CH_2=CHCH_2CH$_2$), 5.19–5.43 (m, J=10.5, 15.5, 1.7 Hz, 2H, CH_2=CHCH_2O), 5.86–5.99 (m, J=5.9 Hz, 1H, CH_2=CHCH_2CH$_2$), 6.00–6.06 (m, J=5.2 Hz, 1H, CH_2=CHCH_2O). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 15.9, 16.4, 17.2 (CH_3), 26.5, 34.2, 61.1, 76.0, 114.5, 116.7 (CH_2), 127.5, 131.1, 131.4, 131.8 (C), 133.9 (CH), 137.5 (C), 138.3 (CH), 151.5, 169.3 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2981 (m), 2932 (m), 1727 (s), 1449 (m), 1423 (m), 1279 (s), 1189 (s), 1046 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=203.1 (4.50), 279.9 (2.79). MS (EI, 70 eV): m/z (%)=303 (M^++1, 5), 302 (M^+, 48), 261 (38), 215 (100), 189 (17), 175 (47), 146.5 (16), 91 (30), 41 (52), 28 (49). HRMS (ESI^+) calcd for $C_{19}H_{26}O_3$ [M^++1]: m/z=303.19602; found: m/z=303.19603. Anal. Calcd for $C_{19}H_{26}O_3$: C 75.46, H 8.67; found: C 75.80, H 8.46.

3.3.8. Ethyl 2-(allyloxy)-3-(but-3-enyl)-4,6-diethylbenzoate (9f). Starting with **8f** (0.350 g, 1.28 mmol, 1.0 equiv) in 20 mL of THF, NaH (0.061 g, 2.56 mmol, 2.0 equiv), *n*-Bu_4NI (0.836 g, 2.56 mmol, 2.0 equiv) and allyl bromide (0.230 g, 1.91 mmol, 1.5 equiv), **9f** was isolated as a colourless oil (0.330 g, 82%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.23 (t, J=7.1 Hz, 6H, $2CH_3CH_2$), 1.37 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.26 (m, 2H, CH_2=CHCH_2CH$_2$), 2.54–2.61 (q, J=7.5 Hz, 4H, $2CH_3CH_2$), 2.69 (m, 2H, CH_2=CHCH$_2$CH_2), 4.35 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.42 (m, J=1.5 Hz, 2H, CH_2=CHCH_2O), 4.96–5.20 (m, J=9.3, 15.3, 1.5 Hz, 2H, CH_2=CHCH$_2$CH$_2$), 5.24–5.44 (m, J=8.9, 15.5, 1.5 Hz, 2H, CH_2=CHCH$_2$O), 5.89–6.02 (m, 2H, CH_2=CHCH$_2$CH$_2$, CH_2=CHCH$_2$O), 6.84 (s, 1H, CH, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2, 15.5 ($2CH_3$), 25.8 ($2CH_2$), 26.3, 34.7, 61.1, 75.7, 114.5, 116.6 (CH_2), 124.5 (CH), 126.2, 130.8 (C), 133.9, 138.5 (CH), 139.9, 145.3, 154.3, 168.8 (C). UV–vis (CH_3CN, nm): λ_{max} (log ε)=203.5 (4.61), 278.5 (3.06). IR (KBr, cm^{-1}): $\tilde{\nu}$=2972 (m), 2935 (w), 1727 (s), 1458 (w), 1414 (w), 1282 (m), 1149 (m), 917 (m). MS (EI, 70 eV): m/z (%)=316 (M^+, 28), 275 (69), 229 (100), 189 (45), 105 (14), 91 (28), 70 (55), 41 (95), 28 (88). HRMS (ESI^+) calcd for $C_{20}H_{28}O_3$ [M^++1]: m/z=317.21167; found: m/z=317.21222. Anal. Calcd for $C_{20}H_{28}O_3$: C 75.91, H 8.92; found: C 75.72, H 8.72.

3.3.9. Ethyl 3-(allyloxy)-2-(but-3-enyl)-9,10-dihydro-1-methylphenanthrene-4-carboxylate (9g). Starting with **8g** (0.336 g, 1.00 mmol, 1.0 equiv) in 15 mL of THF, NaH (0.048 g, 2.00 mmol, 2.0 equiv), *n*-Bu_4NI (0.653 g, 2.00 mmol, 2.0 equiv) and allyl bromide (0.181 g, 1.50 mmol, 1.5 equiv), **9g** was isolated as a colourless oil (0.362 g, 96%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.24 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.27 (m, 2H, CH_2=CHCH_2CH$_2$), 2.31 (s, 3H, CH_3), 2.70–2.83 (m, 6H, CH_2=CHCH$_2$CH_2, C_6H_4(CH_2)$_2$), 4.27 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.48 (m, 2H, CH_2=CHCH_2O), 4.99–5.08 (m, J=10.2, 15.4, 1.5 Hz, 2H, CH_2=CHCH$_2$CH$_2$), 5.39–5.47 (m, J=10.5, 15.5, 1.6 Hz, 2H, CH_2=CHCH$_2$O), 5.87–5.98 (m, J=6.5 Hz, 1H, CH_2=CHCH$_2$CH$_2$), 6.01–6.13 (m, J=5.3 Hz, 1H, CH_2=CHCH$_2$O), 7.17–7.51 (m, 3H, Ar), 7.52 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.9, 15.9 (CH_3), 25.9, 26.8, 29.1, 34.1, 61.4, 76.3, 114.7, 116.8 (CH_2), 124.6 (C), 126.1, 126.4, 127.32, 127.33 (CH), 131.4, 133.6, 133.7 (C), 133.9 (CH), 134.4, 136.3 (C), 138.2 (CH), 138.4, 153.3, 169.7 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3075 (m), 2978 (s), 2900 (s), 1724 (s), 1643 (m), 1557

(m), 1444 (m), 1409 (m), 1286 (m), 1187 (m), 1109 (m), 1024 (m), 989 (m), 916 (m), 760 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=210.1 (4.57), 268.2 (4.25), 304.8 (3.88). MS (EI, 70 eV): *m*/*z* (%)=377 (M^++1, 26), 376 (M^+, 100), 335 (92), 307 (32), 249 (53), 221 (27), 178 (39), 85 (25), 57 (26), 41 (62), 28 (80). HRMS (ESI^+) calcd for $C_{25}H_{28}O_3$ [M^++1]: *m*/*z*=377.21167; found: *m*/*z*=377.21185.

3.4. General procedure for the synthesis of products 5a,b and 10a–g

To a CH_2Cl_2 solution of **4a**,**b** or **9a**–**g** was added a CH_2Cl_2 solution of catalyst **6** under argon atmosphere. After stirring for 6–8 h at 20 °C under argon atmosphere, the solution was exposed to air and concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc=25:1). The product should be stored at ca. 0 °C or below.

3.4.1. Ethyl 2,5-dihydrobenzo[*b*]oxepin-9-carboxylate (5a). Starting with **4a** (0.123 g, 0.5 mmol) in 10 mL of CH_2Cl_2 and **6** (0.021 g, 0.025 mmol), **5a** was isolated as a colourless oil (0.108 g, 99%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.39 (t, *J*=7.2 Hz, 3H, OCH_2CH_3), 3.48 (m, *J*=3.0 Hz, 2H, CH_2), 4.38 (q, *J*=7.2 Hz, 2H, OCH_2CH_3), 4.69–4.72 (m, *J*=2.4 Hz, 2H, CH_2), 5.44–5.48 (m, 1H, CH), 5.81–5.88 (m, 1H, CH), 7.03–7.08 (dt, *J*=7.8, 1.8 Hz, 1H, Ar), 7.23–7.27 (m, 1H, Ar), 7.62–7.68 (ddd, *J*=6.9, 6.9, 1.8 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.1 (CH_3), 31.2, 60.8, 70.9 (CH_2), 118.1 (C), 123.5 (CH), 125.2 (C), 127.4, 128.9, 129.9, 132.0 (CH), 156.3 (C), 165.8 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=2932 (m), 1723 (s), 1465 (m), 1290 (s), 1216 (m), 1170 (w), 1137 (s), 1085 (m), 1056 (w), 1023 (w), 989 (w), 761 (w). MS (EI, 70 eV): *m*/*z* (%)=218 (M^+, 64), 189 (15), 173 (100), 145 (42), 91 (28), 75 (15). HRMS (EI, 70 eV) calcd for $C_{13}H_{14}O_3$ ([M^+]): *m*/*z*=218.09429; found: *m*/*z*=218.09471.

3.4.2. Ethyl 5,6-dihydro-2*H*-benzo[*b*]oxocine-10-carboxylate (5b). Starting with **4b** (0.130 g, 0.5 mmol) in 10 mL of CH_2Cl_2 and **6** (0.021 g, 0.025 mmol), **5b** was isolated as a colourless oil (0.087 g, 75%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.37 (t, *J*=7.2 Hz, 3H, OCH_2CH_3), 2.68 (m, 2H, CH_2), 2.93 (m, *J*=6.2 Hz, 2H, CH_2), 4.38 (q, *J*=7.2 Hz, 2H, OCH_2CH_3), 4.70 (m, 2H, CH_2), 5.35–5.41 (m, *J*=3.0, 1.2 Hz, 1H, CH), 5.71–5.78 (m, *J*=3.0, 1.5 Hz, 1H, CH), 7.05 (dt, *J*=7.8, 1.8 Hz, 1H, Ar), 7.23–7.27 (m, 1H, Ar), 7.65 (ddd, *J*=6.9, 6.9, 1.8 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3 (CH_3), 28.0, 30.2, 61.2, 73.3 (CH_2), 118.2 (C), 123.5 (CH), 125.2 (C), 127.3, 129.1, 131.8, 133.9 (CH), 157.1 (C), 166.3 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=2982 (m), 2932 (m), 1725 (s), 1668 (w), 1452 (m), 1285 (s), 1216 (m), 1186 (m), 1142 (w), 1075 (m), 1023 (m), 763 (w). MS (EI, 70 eV): *m*/*z* (%)=232 (M^+, 52), 203 (5), 187 (100), 159 (42), 91 (35), 75 (12). HRMS (EI, 70 eV) calcd for $C_{14}H_{16}O_3$ ([M^+]): *m*/*z*=232.10994; found: *m*/*z*=232.11039.

3.4.3. Ethyl 8,6-dimethyl-2,5-dihydrobenzo[*b*]oxepin-9-carboxylate (10a). Starting with **9a** (0.260 g, 0.95 mmol, 1.0 equiv) in 18 mL of CH_2Cl_2 and **6** (0.039 g, 0.047 mmol, 5 mol %, dissolved in 2 mL of CH_2Cl_2), **10a** was isolated as a colourless oil (0.210 g, 99%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.38 (t, *J*=7.1 Hz, 3H, OCH_2CH_3), 2.26 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.44 (m, *J*=1.9 Hz, 2H, CH_2), 4.39 (q, *J*=7.1 Hz, 2H, OCH_2CH_3), 4.63 (m, *J*=1.5 Hz, 2H, CH_2), 5.46 (m, *J*=5.2, 1.4 Hz, 1H, CH), 5.83 (m, 1H, CH), 6.76 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3, 18.9, 19.8 (CH_3), 25.7, 60.9, 71.4 (CH_2), 124.9 (CH), 126.1 (C), 127.5, 127.8 (CH), 133.5 (2C), 136.6, 152.2, 168.1 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3438 (w), 2979 (s), 2930 (s), 1726 (s), 1609 (s), 1456 (s), 1387 (m), 1293 (s), 1270 (s), 1223 (m), 1149 (s), 1091 (s), 1046 (s), 862 (m), 653 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=205.8 (4.25), 263.1 (3.62), 301.8 (3.27). MS (EI, 70 eV): *m*/*z* (%)=247 (M^++1, 9), 246 (M^+, 77), 201 (92), 200 (100), 199 (47), 183 (35), 173 (23), 172 (63), 171 (24), 157 (53), 129 (41), 128 (31), 114 (21), 45 (18), 31 (41). Anal. Calcd for $C_{15}H_{18}O_3$: C 73.15, H 7.36; found: C 73.03, H 6.96.

3.4.4. Ethyl 6,7,8-trimethyl-2,5-dihydrobenzo[*b*]oxepin-9-carboxylate (10b). Starting with **9b** (0.140 g, 0.50 mmol, 1.0 equiv) in 10 mL of CH_2Cl_2 and **6** (0.021 mg, 0.025 mmol, 5 mol %, dissolved in 1 mL of CH_2Cl_2), **10b** was isolated as a colourless oil (0.121 g, 93%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.38 (t, *J*=7.2 Hz, 3H, OCH_2CH_3), 2.17 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.51 (m, *J*=1.8 Hz, 2H, CH_2), 4.40 (q, *J*=7.1 Hz, 2H, OCH_2CH_3), 4.61 (m, *J*=2.4 Hz, 2H, CH_2), 5.42 (m, *J*=6.1, 1.2 Hz, 1H, CH), 5.82–5.89 (m, *J*=2.3 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3, 16.2, 16.3, 17.3 (CH_3), 26.0, 61.0, 71.6 (CH_2), 125.3 (CH), 126.7 (C), 127.8 (CH), 131.1, 131.4, 133.9, 134.8, 152.2, 168.9 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3451 (br, m), 2982 (s), 2932 (s), 1730 (s), 1673 (s), 1587 (s), 1453 (s), 1386 (m), 1309 (s), 1278 (s), 1189 (s), 1101 (s), 1043 (s), 735 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=205.6 (4.25), 301.6 (3.43). MS (EI, 70 eV): *m*/*z* (%)=261 (M^++1, 10), 260 (M^+, 81), 215 (45), 214 (40), 186 (41), 171 (55), 143 (22), 129 (13), 128 (20), 45 (16), 32 (20), 31 (31), 28 (100). HRMS (ESI^+) calcd for $C_{16}H_{20}O_3$ [M^++1]: *m*/*z*=261.14907; found: *m*/*z*=261.14879.

3.4.5. Ethyl 6,8-diethyl-2,5-dihydrobenzo[*b*]oxepin-9-carboxylate (10c). Starting with **9c** (0.120 g, 0.397 mmol, 1.0 equiv) in 5 mL of CH_2Cl_2 and **6** (0.014 g, 0.017 mmol, 5 mol %, dissolved in 0.5 mL of CH_2Cl_2), **10c** was isolated as a colourless oil (0.099 g, 91%). ^1H NMR ($CDCl_3$, 300 MHz): δ=1.18 (t, *J*=7.4 Hz, 3H, CH_3CH_2), 1.23 (t, *J*=7.5 Hz, 3H, CH_3CH_2), 1.38 (t, *J*=7.1 Hz, 3H, OCH_2CH_3), 2.63 (m, *J*=7.4 Hz, 4H, $2CH_3CH_2$), 3.44 (m, *J*=2.0 Hz, 2H, CH_2), 4.38 (q, *J*=7.1 Hz, 2H, OCH_2CH_3), 4.63 (m, *J*=2.3 Hz, 2H, CH_2), 5.46 (m, *J*=7.3, 1.4 Hz, 1H, CH), 5.85 (m, *J*=5.7 Hz, 1H, CH), 6.79 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3, 15.2, 15.6 (CH_3), 25.5 (CH_2), 26.3, 26.9 (CH_3), 61.3, 71.5 (CH_2), 124.7, 125.1, 127.9 (CH), 128.5, 133.2, 139.9, 142.9, 153.7, 168.7 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2981 (m), 2930 (m), 1655 (s), 1600 (m), 1446 (m), 1403 (s), 1312 (s), 1260 (s), 1195 (s), 1116 (w), 1045 (m), 910 (w), 806 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=204.4 (4.41), 299.8 (3.43). MS (EI, 70 eV): *m*/*z* (%)=274 (M^+, 12), 259 (3), 229 (4), 213 (7), 186 (7), 171 (9), 128 (6), 32 (22), 28 (100).

3.4.6. Ethyl 5,6,8,11-tetrahydro-7-methylphenanthro[3,2-*b*]oxepin-13-carboxylate (10d). Starting with **9d**

(0.250 g, 0.688 mmol, 1.0 equiv) in 12 mL of CH_2Cl_2 and **6** (0.028 g, 0.034 mmol, 5 mol %, dissolved in 1 mL of CH_2Cl_2), **10d** was isolated as a colourless oil (0.185 g, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.27 (t, J=7.2 Hz, 3H, OCH_2CH_3), 2.31 (s, 3H, CH_3), 2.72–2.80 (m, J=4.1, 2.5 Hz, 4H, $C_6H_4(CH_2)_2$), 3.58 (m, J=2.1 Hz, 2H, CH_2), 4.34 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.70 (m, J=2.3 Hz, 2H, CH_2), 5.49 (m, J=11.3 Hz, 1H, CH), 5.90 (m, 1H, CH), 7.18–7.24 (m, 3H, Ar), 7.53 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.1, 15.9 (CH_3), 26.0, 26.2, 29.2, 61.3, 71.9 (CH_2), 123.8 (C), 125.0, 126.0 (CH), 126.2, 126.4 (C), 126.5, 127.3, 127.9, 128.0 (CH), 131.1, 133.5, 133.7, 138.3, 153.8, 169.3 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2977 (w), 2935 (w), 1722 (s), 1446 (w), 1280 (m), 1194 (s), 1071 (w), 1026 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=209.4 (4.48), 269.2 (4.16), 303.2 (3.90). MS (EI, 70 eV): m/z (%)=335 (M^++1, 23), 334 (M^+, 100), 320 (18), 319 (37), 289 (27), 260 (34), 245 (24), 202 (22), 29 (32). HRMS (ESI^+) calcd for $C_{22}H_{22}O_3$ [M^++1]: m/z=335.16472; found: m/z=335.16511.

3.4.7. Ethyl 7,8,9-trimethyl-5,6-dihydro-2*H*-benzo[*b*]oxocine-10-carboxylate (10e). Starting with **9e** (0.243 g, 0.804 mmol, 1.0 equiv) in 16 mL of CH_2Cl_2 and **6** (0.035 g, 0.040 mmol, 5 mol %, dissolved in 1 mL of CH_2Cl_2), **10e** was isolated as a colourless oil (0.166 g, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.37 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.13 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.68 (m, J=5.5, 1.2 Hz, 2H, CH_2), 2.94 (m, J=6.2 Hz, 2H, CH_2), 4.38 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.71 (m, J=1.3 Hz, 2H, CH_2), 5.33–5.39 (m, J=3.0, 1.3 Hz, 1H, CH), 5.69–5.76 (m, J=3.0, 1.5 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3, 16.0, 16.1, 17.3 (CH_3), 28.0, 28.2, 61.1, 73.2 (CH_2), 125.2 (CH), 127.5, 130.4, 131.2, 131.4 (C), 131.6 (CH), 136.9, 150.8, 169.5 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2981 (m), 2932 (m), 1727 (s), 1449 (m), 1423 (m), 1279 (s), 1189 (s), 1046 (m), 98 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=203.1 (4.50), 279.9 (2.79). MS (EI, 70 eV): m/z (%)=275 (M^++1, 15), 274 (M^+, 100), 229 (39), 187 (53), 175 (31), 146.5 (28), 91 (31), 28 (47). HRMS (ESI^+) calcd for $C_{17}H_{22}O_3$ [M^++1]: m/z=275.16472; found: m/z=275.16444.

3.4.8. Ethyl 7,9-diethyl-5,6-dihydro-2*H*-benzo[*b*]oxocine-10-carboxylate (10f). Starting with **9f** (0.265 g, 0.837 mmol, 1.0 equiv) in 16 mL of CH_2Cl_2 and **6** (0.035 g, 0.042 mmol, 5 mol %, dissolved in 1 mL of CH_2Cl_2), **10f** was isolated as a colourless oil (0.220 g, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.20 (t, J=7.5 Hz, 6H, $2CH_3CH_2$), 1.37 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.56 (q, J=7.5 Hz, 4H, $2CH_3CH_2$), 2.68 (m, J=7.0, 1.2 Hz, 2H, CH_2), 2.92 (m, J=6.3, 2.3 Hz, 2H, CH_2), 4.38 (q, J=7.1 Hz, 2H, OCH_2CH_3), 4.70 (m, J=1.4 Hz, 2H, CH_2), 5.37–5.43 (m, J=3.0, 1.2 Hz, 1H, CH), 5.73–5.77 (m, J=1.6 Hz, 1H, CH), 6.82 (s, 1H, CH, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.3, 14.9, 15.5 (CH_3), 26.2, 26.2, 27.0, 27.8, 60.9, 73.1 (CH_2), 124.3, 125.5 (CH), 126.6, 129.9 (C), 131.9 (CH), 139.7, 144.8, 153.6, 168.9 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=2968 (s), 2935 (s), 2875 (m), 1726 (s), 1606 (m), 1562 (m), 1454 (m), 1415 (m), 1282 (s), 1245 (s), 1148 (s), 1100 (s), 1072 (s), 877 (w), 707 (w). UV–vis (CH_3CN, nm): λ_{max} (log ε)=203.7 (2.44), 277.5 (3.07). MS (EI, 70 eV): m/z (%)=288 (M^+, 4), 234 (18), 188 (18), 163 (5), 91 (6), 32 (24), 28 (100). HRMS (ESI^+) calcd for $C_{18}H_{24}O_3$ [M^++1]: m/z=289.18037; found: m/z=289.18049.

3.4.9. Ethyl 6,8,9,12-tetrahydro-7-methyl-5*H*-phenanthro[3,2-*b*]oxocine-14-carboxylate (10g). Starting with **9g** (0.300 g, 0.797 mmol, 1.0 equiv) in 19 mL of CH_2Cl_2 and **6** (0.033 g, 0.0398 mmol, 5 mol %, dissolved in 1 mL of CH_2Cl_2), **10g** was isolated as a colourless oil (0.180 g, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.23 (t, J=7.2 Hz, 3H, OCH_2CH_3), 2.24 (s, 3H, CH_3), 2.26 (m, 2H, CH_2), 2.67–2.78 (m, 4H, $C_6H_4(CH_2)_2$), 3.00 (m, J=1.3 Hz, 2H, CH_2), 4.30 (q, J=7.1 Hz, 2H, OCH_2CH_3), 5.41 (m, J=6.2, 1.3 Hz, 1H, CH), 5.75 (m, J=5.7, 1.7 Hz, 1H, CH), 7.17–7.25 (m, 3H, Ar), 7.54 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.9, 15.7 (CH_3), 26.0, 28.10, 28.14, 29.2, 61.3, 73.7 (CH_2), 124.4 (C), 125.4, 126.1, 126.4, 127.25, 127.29, 131.2 (CH), 131.6, 132.8, 133.85, 133.98, 135.7, 138.4, 152.7 (C), 169.8 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3432 (br, m), 2978 (w), 2890 (w), 1723 (s), 1450 (w), 1283 (m), 1188 (s), 1159 (w), 1023 (m). UV–vis (CH_3CN, nm): λ_{max} (log ε)=209.3 (4.50), 268.2 (4.18), 304.9 (3.84). MS (EI, 70 eV): m/z (%)=348 (M^+, 2), 125 (1), 40 (3), 32 (29), 28 (100). HRMS (ESI^+) calcd for $C_{25}H_{28}O_3$ ([M^++1]): m/z=349.18037; found: m/z=349.18032.

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