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ORIGINAL PAPER

Synthesis of new functionalized alizarins from alizarin, acetylenic esters, and phosphorus nucleophiles

Issa Yavari · Leila Azad · Tayebeh Sanaeishoar

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Abstract The 1:1 intermediate generated by the addition of triphenylphosphine to dialkyl acetylenedicarboxylates is trapped by alizarin to produce alkyl 6,11-dihydro-12-hydroxy-2,6,11-trioxo-2*H*-naphtho[2,3-*g*]chromene-4-carboxylates in good yields. When ethyl propiolate was used, the reaction afforded ethyl 6,11-dihydro-6,11-dioxoanthra[1,2-*d*][1,3]-dioxole-2-acetate. The reaction of dialkyl acetylenedicarboxylates, alizarin, and trialkyl phosphites produced dialkyl 2-(dialkoxyphosphoryl)-3-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)succinates.

Keywords Alizarin · Acetylenic esters · Triphenylphosphine · Trialkyl phosphites

Introduction

Alizarin (1,2-dihydroxyanthraquinone) is the parent compound for a large palette of anthraquinone dyes. Hydroxy-substituted 9,10-anthraquinones are important in the dye industry, biology, and pharmaceutical chemistry. Alizarin derivatives have been the subject of many studies [1, 2]. In recent years, the reactions of phenols [3–5], dihydroxybenzenes [6, 7], and 1,5-dihydroxyanthraquinone [8] with the zwitterionic intermediates derived from triphenylphosphine (Ph_3P) and dialkyl acetylenedicarboxylates have been reported.

In continuation of our current interest in the development of new routes to heterocyclic and carbocyclic systems [9–14], we report a simple one-pot synthesis of functionalized alizarin derivatives. Thus, the reaction of alizarin with dialkyl acetylenedicarboxylates in the presence of Ph_3P produced functionalized dihydro-2*H*-naphtho[2,3-*g*]-chromenes in good yields. When ethyl propiolate was used, the reaction afforded ethyl 6,11-dihydro-6,11-dioxoanthra[1,2-*d*][1,3]-dioxole-2-acetate. The reaction of dialkyl acetylenedicarboxylates, alizarin, and trialkyl phosphites produced phosphorylated alizarins.

I. Yavari (✉) · L. Azad · T. Sanaeishoar
Department of Chemistry, Science and Research Branch, Islamic Azad University, Ponak, Tehran, Iran
e-mail: yavarisa@modares.ac.ir

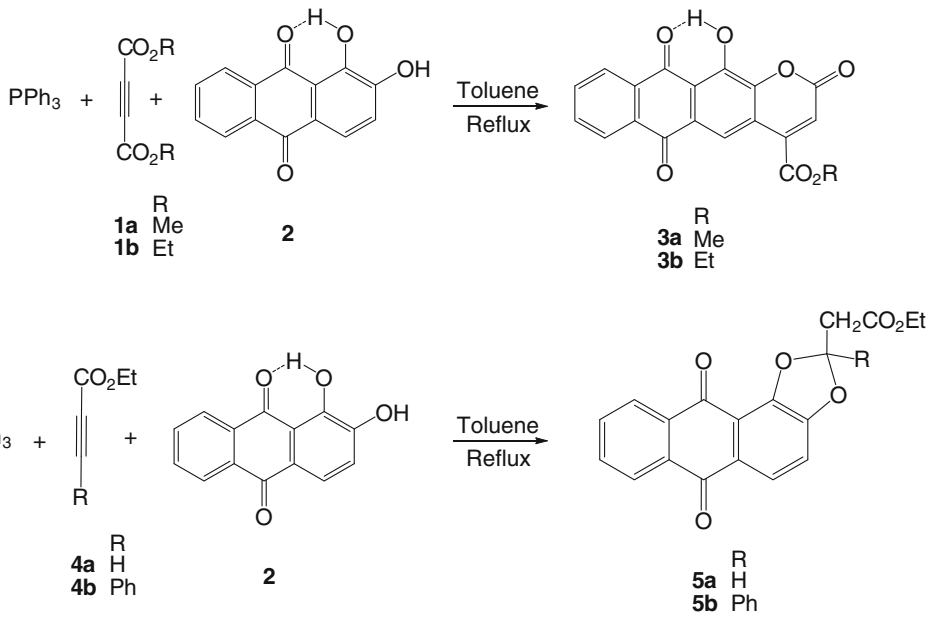
Results and discussion

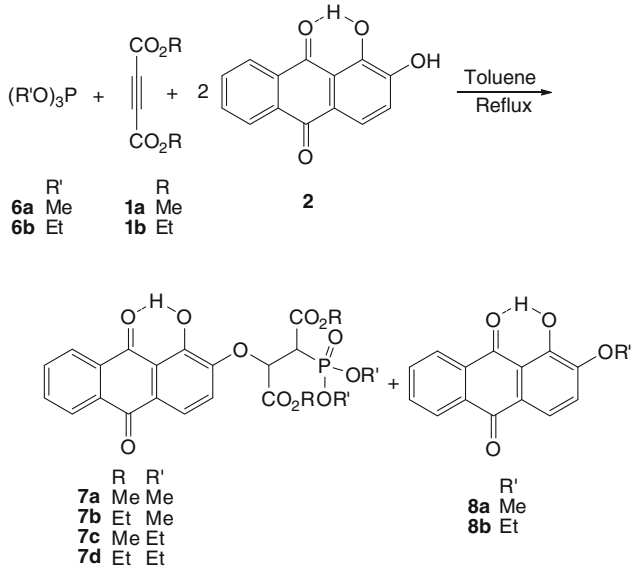
The reaction of alizarin, dialkyl acetylenedicarboxylates **1**, and Ph_3P in toluene proceeded smoothly under reflux and afforded alkyl 6,11-dihydro-12-hydroxy-2,6,11-trioxo-2*H*-naphtho[2,3-*g*]chromene-4-carboxylates **3a**, **3b** in good yields. When ethyl propiolate (**4a**) and ethyl phenylpropiolate (**4b**) were employed as the acetylenic component, the reaction produced ethyl 6,11-dihydro-6,11-dioxoanthra[1,2-*d*][1,3]-dioxole-2-acetate (**5a**) and ethyl 6,11-dihydro-6,11-dioxo-2-phenylanthra[1,2-*d*][1,3]-dioxole-2-acetate (**5b**), respectively (Scheme 1).

The reaction of alizarin with **1** in the presence of trialkyl phosphites **6** in toluene under reflux produced dialkyl 2-(dialkoxyphosphoryl)-3-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)succinates **7a**–**7d**, together with 2-alkoxy-1-hydroxyanthracene-9,10-diones **8a**, **8b** (Scheme 2). Compounds **8** have been reported previously [15].

The structures of compounds **3**, **5**, and **7** were deduced from their high-field ^1H and ^{13}C NMR, IR, and UV-Vis absorption spectral data. The mass spectra of these compounds exhibited molecular ion peaks at the appropriate *m*/*z* values. The ^{31}P NMR spectra of phosphonates **7** confirmed the presence of phosphonate groups.

Scheme 1





Scheme 2

The ^{1}H NMR spectrum of **3a** in $CDCl_3$ exhibited a singlet at $\delta = 4.10$ ppm for the methoxy protons along with resonances at 7.88–8.40 ppm for the aromatic protons. The OH proton appears as a singlet at 13.05 ppm, as a result of strong intramolecular hydrogen bonding. The ^{13}C NMR spectrum of **3a** showed 19 distinct resonances in agreement with the proposed structure. The ^{1}H and ^{13}C NMR spectra of **3b** were similar to those of **3a** except for the alkoxy moieties, which exhibited characteristic signals with appropriate chemical shifts.

The ^{1}H NMR spectrum of **5a** in $CDCl_3$ showed two signals at $\delta = 1.30$ and 4.25 ppm for the ethoxy protons, along with resonances at 7.14–8.33 ppm for the aromatic protons. The ^{13}C NMR spectrum of **5a** showed 19 resonances in agreement with the proposed structure.

The ^{1}H NMR spectrum of **7a** showed two doublets for the two diastereotopic methoxy ($\delta = 3.55$ ppm, $^{3}J_{HP} = 11.1$ Hz and $\delta = 3.65$ ppm, $^{3}J_{HP} = 11.1$ Hz) groups. The two singlets at 3.88 and 4.14 ppm belong to the ester methoxy protons. Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of **7a**–**7d**, it helps in the assignment of the signals by long-range coupling with ^{1}H and ^{13}C nuclei.

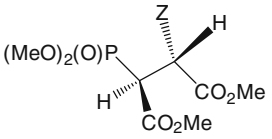
Observation of $^{3}J_{HH} = 11.6$ Hz for the vicinal methine protons in **7a** indicates the dominance of the anti-arrangement. Since compound **7a** possesses two stereogenic centers, two diastereoisomers with anti-HCCH arrangements are possible (Scheme 3). The observation of $^{3}J_{CP} = 21$ Hz for the carbonyl carbon atom of the CO_2Me group is in agreement with the (2*S*,3*R*) or (2*R*,3*S*) diastereoisomer.

In conclusion, we have reported a one-pot synthesis of functionalized dihydro-2*H*-naphtho[2,3-*g*]chromenes from alizarin and dialkyl acetylenedicarboxylates in the presence of Ph_3P. When ethyl propiolate was used, the reaction led to ethyl 6,11-dihydro-6,11-dioxoanthra[1,2-*d*][1,3]-dioxole-2-acetate. The reaction of dialkyl acetylenedicarboxylates, alizarin, and trialkyl phosphites produced phosphorylated dialkyl 3-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)succinates.

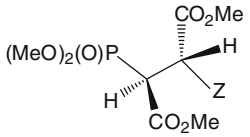
Experimental

All chemicals used in this study were purchased from Merck and were used without further purification. Melting

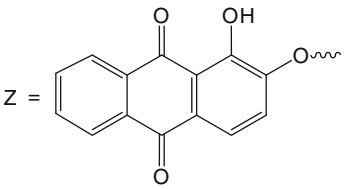
Scheme 3



(2*S*,3*R*)-**7a** or (2*R*,3*S*)-**7a**



(2*S*,3*S*)-**7a** or (2*R*,3*R*)-**7a**



points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C and H were performed using a Heraeus CHN-O-Rapid analyzer. UV spectra were taken on a Shimadzu UV-160A spectrometer. The experimental data were in good agreement with the calculated values. ^{1}H and ^{13}C NMR spectra ($CDCl_3$) were measured with a Bruker DRX-300 Avance spectrometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Mass spectra were recorded on a Finnigan-Mat 8430 spectrometer operating at an ionization potential of 70 eV. Chromatography columns were prepared from Aldrich silica gel (70–230 mesh).

General procedure for the preparation of compounds ***3***

To a stirred solution of 0.26 g of Ph_3P (1 mmol) and 0.22 g of alizarin (1 mmol) in 5 cm^3 of toluene was added dropwise a mixture of the dialkyl acetylenedicarboxylate (1 mmol) in 2 cm^3 of toluene at r.t. The reaction mixture was then refluxed for 24 h. The product was filtered and washed with cold Et_2O.

Methyl 6,11-dihydro-12-hydroxy-2,6,11-trioxo-2H-naphtho[2,3-g]chromene-4-carboxylate (**3a**, $C_{19}H_{10}O_7$)
Green powder; yield: 0.33 g (95%); m.p.: 248–250 °C; UV (EtOH, 95%): λ_{max} (ε) = 403 (6,105) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu}$ = 3,405 (OH), 1,735 (C=O) cm^{-1}; EI–MS: *m/z* = 350 (M^+, 10), 321 (15), 291 (100), 262 (35), 239 (41), 210 (11); ^{1}H NMR ($CDCl_3$): δ = 4.11 (3H, s, MeO), 7.19 (1H, s, CH), 7.87–7.90 (2H, m, CH), 8.33–8.39 (2H, m, CH), 8.73 (1H, s, CH), 13.04 (1H, s, OH) ppm; ^{13}C NMR ($CDCl_3$): δ = 54.3 (MeO), 117.6 (C), 117.7 (CH), 121.3 (C), 123.5 (CH), 127.9 (CH), 128.3 (CH), 128.9 (C), 133.5 (C), 134.7 (C), 134.8 (CH), 135.8 (CH), 142.2 (C), 147.5 (C–O), 151.2 (C–O), 158.2, 163.2, 181.1, 189.9 (4 C=O) ppm.

Ethyl 6,11-dihydro-12-hydroxy-2,6,11-trioxo-2H-naphtho[2,3-g]chromene-4-carboxylate (**3b**, $C_{20}H_{12}O_7$)
Green powder; yield: 0.34 g (94%); m.p.: 224–226 °C; UV (EtOH, 95%): λ_{max} (ε) = 400 (6,080) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu}$ = 3,410 (OH), 1,737 (C=O) cm^{-1}; EI–MS: *m/z* = 364 (M^+, 9), 335 (17), 291 (100), 262 (38), 239 (43), 210 (8); ^{1}H NMR ($CDCl_3$): δ = 1.52 (3H, t, $^3J_{HH}$ = 7.1 Hz, Me), 4.55 (2H, q, $^3J_{HH}$ = 7.1 Hz, CH_2O), 7.17 (1H, s, CH), 7.84–7.91 (2H, m, CH), 8.31–8.39 (2H, m, CH), 8.73 (1H, s, CH), 13.02 (1H, s, OH) ppm; ^{13}C NMR ($CDCl_3$): δ = 14.5 (Me), 63.5 (CH_2O), 117.3 (C), 117.8 (CH), 121.2 (C), 123.3 (CH), 127.6 (CH), 128.1 (CH), 128.5 (C), 133.5 (C), 134.1 (C), 134.8 (CH), 135.8 (CH), 142.6 (C), 147.6 (C–O), 151.1 (C–O), 158.2, 163.3, 181.2, 189.9 (4C=O) ppm.

General procedure for the preparation of compounds ***5***

To a stirred solution of 0.26 g of Ph_3P (1 mmol) and 0.22 g of alizarin (1 mmol) in 5 cm^3 of toluene was added dropwise a mixture of the propiolate ester (1 mmol) in 2 cm^3 of toluene at r.t. The reaction mixture was then refluxed for 24 h. The solvent was removed under reduced pressure, and the residue was separated on silica gel column chromatography (Merck 230–400 mesh) using hexane-AcOEt (3:1) as eluent.

Ethyl 6,11-dihydro-6,11-dioxoanthra[1,2-d][1,3]-dioxole-2-acetate (**5a**, $C_{19}H_{14}O_6$)
Yellow powder; yield: 0.23 g (97%); m.p.: 139–141 °C; UV (EtOH, 95%): λ_{max} (ε) = 410 (4,110) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu}$ = 1,732 (C=O), 1,224 (C–O) cm^{-1}; EI–MS: *m/z* = 338 (M^+, 8), 293 (18), 239 (100), 132 (8), 57 (21); ^{1}H NMR ($CDCl_3$): δ = 1.30 (3H, t, $^3J_{HH}$ = 7.1 Hz, Me), 3.16 (2H, (AB)X system, J_{AB} = 16 Hz, J_{AX} = 6.5 HZ, J_{BX} = 3.5 Hz, CH_2), 4.25 (2H, q, $^3J_{HH}$ = 7.1 Hz, CH_2O), 6.88 (1H, dd, ^3J = 6.5 Hz, ^3J = 3.5 Hz, CH), 7.15 (1H, d, $^3J_{HH}$ = 8 Hz, CH), 7.77–7.83 (2H, m, CH), 8.00 (1H, d, $^3J_{HH}$ = 8 Hz, CH), 8.26–8.35 (2H, m, CH) ppm; ^{13}C NMR ($CDCl_3$): δ = 14.3 (Me), 45.4 (CH_2), 61.4 (CH_2O), 99.6 (CH), 119.4 (CH), 124.2 (CH), 127.4 (CH), 127.6 (CH), 127.7 (C), 130.1 (C), 134.0 (C), 134.2 (CH), 134.3 (CH), 134.4 (C), 148.2 (C–O), 154.3 (C–O), 167.2, 182.0, 182.0 (3C=O) ppm.

Ethyl 6,11-dihydro-6,11-dioxo-2-phenylanthra-[1,2-d][1,3]-dioxole-2-acetate (**5b**, $C_{25}H_{18}O_6$)
Yellow powder; yield: 0.30 g (73%); m.p.: 145–147 °C; UV (EtOH, 95%): λ_{max} (ε) = 409 (3,514) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu}$ = 1,740 (C=O), 1,226 (C–O) cm^{-1}; EI–MS: *m/z* = 414 (M^+, 7), 369 (17), 239 (100), 132 (20), 77 (34); ^{1}H NMR ($CDCl_3$): δ = 1.52 (3H, t, $^3J_{HH}$ = 7.1 Hz, Me), 3.45 (2H, ABq, J_{AB} = 10.5 Hz, $\Delta\nu_{AB}$ = 6 Hz, CH_2), 4.07 (2H, q, $^3J_{HH}$ = 7.1 Hz, CH_2O), 7.16 (1H, d, $^3J_{HH}$ = 8 Hz, CH), 7.35–7.47 (5H, m, CH), 7.69–7.73

(2H, m, CH), 7.76–7.81 (1H, m, CH), 7.98 (1H, d, $^3J_{HH} = 8$ Hz, CH), 8.26–8.32 (1H, m, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 45.4 (CH_2), 61.4 (CH_2O), 112.8 (C), 117.0 (CH), 119.3 (CH), 124.3 (CH), 125.4 (2CH), 127.3 (CH), 127.6 (CH), 127.7 (C), 129.0 (2CH), 130.1 (C), 134.0 (C), 134.2 (CH), 134.3 (CH), 134.4 (C), 139.0 (C), 148.2 (C–O), 154.3 (C–O), 167.2, 182.0, 182.0 (3C=O) ppm.

*General procedure for the preparation of compounds **7** and **8***

To a stirred solution of trialkyl phosphite (1 mmol) and 0.44 g of alizarin (2 mmol) in 5 cm^3 of toluene was added dropwise a mixture of the dialkyl acetylenedicarboxylate (1 mmol) in 2 cm^3 of toluene at r.t. The reaction mixture was then refluxed for 24 h. The precipitate (compound **8**) was filtered and washed with cold Et_2O. Then, the mother liquid was evaporated under reduced pressure to give a residue, which was separated on silica gel column chromatography (Merck 230–400 mesh) using hexane-AcOEt (1:1) as eluent to afford compound **7**.

Dimethyl 2-(dimethoxyphosphoryl)-3-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)butanedioate
(**7a**, $C_{22}H_{21}O_{11}P$)
Yellow powder; yield: 0.33 g (67%); m.p.: 137–139 °C; UV (EtOH, 95%): λ_{max} (ε) = 413 (2,350) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu} = 1{,}739$ (C=O), 1,273 (P=O) cm^{-1}; EI–MS: $m/z = 492$ (M^+, 3), 477 (9), 463 (100), 249 (29), 240 (51), 224 (14), 167 (10), 132 (8), 109 (7), 31 (55); ^{1}H NMR ($CDCl_3$): $\delta = 3.55$ (3H, d, $^3J_{HP} = 11.1$ Hz, MeO), 3.65 (3H, d, $^3J_{HP} = 11.1$ Hz, MeO), 3.88 (3H, s, MeO), 4.06 (1H, dd, $^3J_{HH} = 11.6$ Hz, $^2J_{HP} = 21.2$ Hz, CH), 4.14 (3H, s, MeO), 4.75 (1H, dd, $^3J_{HH} = 11.6$ Hz, $^3J_{HP} = 6.4$ Hz, CH), 7.80-7.84 (4H, m, CH), 8.27-8.39 (2H, m, CH), 12.95 (1H, s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 45.9$ (d, $^1J_{CP} = 130.4$ Hz, CH), 46.4 (d, $^2J_{CP} = 4.0$ Hz, CH), 53.0 (MeO), 53.2 (MeO), 53.8 (d, $^2J_{PC} = 7.77$ Hz, MeO), 54.2 (d, $^2J_{PC} = 6.21$ Hz, MeO), 117.4 (C), 122.2 (CH), 127.2 (CH), 127.7 (CH), 127.8 (CH), 133.6 (C), 134.1 (C), 134.3 (CH), 135.2 (CH), 136.3 (C), 152.5 (C–O), 155.5 (C–O), 169.3 (d, $^2J_{CP} = 6.0$ Hz, C=O), 171.8 (d, $^3J_{CP} = 21.0$ Hz, C=O), 181.8 (C=O), 189.4 (C=O) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 22.47$ ppm.

Diethyl 2-(dimethoxyphosphoryl)-3-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)butanedioate
(**7b**, $C_{24}H_{25}O_{11}P$)
Yellow powder; yield: 0.34 g (67%); m.p.: 145–148 °C; UV (EtOH, 95%): λ_{max} (ε) = 412 (2,455) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu} = 1{,}740$ (C=O), 1,275 (P=O) cm^{-1}; EI–MS: $m/z = 520$ (M^+, 8), 505 (11), 491 (100), 276 (30), 251 (14), 240 (50), 178 (10), 146 (7), 109 (8), 31 (56); ^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 1.35 (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 3.60 (3H, d, $^3J_{HP} = 11.1$ Hz, MeO), 3.65 (3H, d, $^3J_{HP} = 11.1$ Hz, MeO), 4.07-4.38 (5H, m, CH_2O, CH), 4.78 (1H, dd, $^3J_{HH} = 11.8$ Hz, $^3J_{HP} = 6.7$ Hz, CH), 7.79-7.86 (4H, m, CH), 8.28-8.35 (2H, m, CH), 12.95 (1H, s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 14.4 (Me), 46.2 (d, $^1J_{CP} = 130.0$ Hz, CH), 46.3 (d, $^2J_{CP} = 4.0$ Hz, CH), 53.3 (d, $^2J_{PC} = 6.7$ Hz, MeO), 53.7 (d, $^2J_{PC} = 7.2$ Hz, MeO), 61.3 (CH_2O), 62.2 (CH_2O), 117.3 (C), 122.0 (CH), 127.2 (CH), 127.7 (CH), 127.8 (CH), 133.6 (C), 134.1 (C), 134.3 (CH), 135.2 (CH), 136.7 (C), 152.7 (C–O), 155.6 (C–O), 168.7 (d, $^2J_{CP} = 6.9$ Hz, C=O), 171.4 (d, $^3J_{CP} = 20.9$ Hz, C=O), 181.9 (C=O), 189.5 (C=O) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 22.71$ ppm.

Diethyl 2-(dimethoxyphosphoryl)-3-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)butanedioate
(**7c**, $C_{24}H_{25}O_{11}P$)
Yellow powder; yield: 0.34 g (67%); m.p.: 130–132 °C; UV (EtOH, 95%): λ_{max} (ε) = 415 (2,990) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu} = 1{,}738$ (C=O), 1,265 (P=O) cm^{-1}; EI–MS: $m/z = 520$ (M^+, 5), 491 (100), 293 (33), 240 (55), 224 (15), 167 (9), 137 (7), 45 (80), 29 (65); ^{1}H NMR ($CDCl_3$): $\delta = 1.14$ (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 1.46 (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 3.65 (3H, s, MeO), 3.87 (3H, s, MeO), 3.88-4.10 (3H, m, CH_2O, CH), 4.29–4.63 (2H, m, CH_2O), 4.75 (1H, dd, $^3J_{HH} = 11.6$ Hz, $^3J_{HP} = 6.2$ Hz, CH), 7.79–7.86 (4H, m, CH), 8.28–8.34 (2H, m, CH), 12.98 (1H, s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 14.4 (Me), 46.2 (d, $^1J_{CP} = 131.0$ Hz, CH), 46.3 (d, $^2J_{CP} = 4.1$ Hz, CH), 53.0 (MeO), 53.4 (MeO), 62.8 (d, $^2J_{PC} = 6.2$ Hz, CH_2O), 63.3 (d, $^2J_{PC} = 6.9$ Hz, CH_2O), 117.5 (C), 122.1 (CH), 127.2 (CH), 127.7 (CH), 127.8 (CH), 133.5 (C), 134.1 (C), 134.3 (CH), 135.3 (CH), 136.3 (C), 152.5 (C–O), 155.5 (C–O), 169.4 (d, $^2J_{CP} = 6.7$ Hz, C=O), 171.5 (d, $^3J_{CP} = 21.2$ Hz, C=O), 181.7 (C=O), 189.4 (C=O) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 22.69$ ppm.

Diethyl 2-(diethoxyphosphoryl)-3-(9,10-dihydro-1-hydroxy-9,10-dioxoanthracen-2-yloxy)butanedioate
(**7d**, $C_{26}H_{29}O_{11}P$)
Yellow powder; yield: 0.36 g (65%); m.p.: 127–125 °C; UV (EtOH, 95%): λ_{max} (ε) = 414 (3,100) nm (mol^{-1} cm^2); IR (KBr): $\bar{\nu} = 1{,}734$ (C=O), 1,255 (P=O) cm^{-1}; EI–MS: $m/z = 548$ (M^+, 7), 519 (100), 276 (26), 251 (15), 240 (56), 178 (11), 137 (8), 146 (9), 45 (87), 29 (63); ^{1}H NMR ($CDCl_3$): $\delta = 1.11$ (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 1.21 (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 1.33 (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 1.50 (3H, t, $^3J_{HH} = 7.1$ Hz, Me), 3.78-4.22 (5H, m, CH_2O, CH), 4.33 (2H, q, $^3J_{HH} = 7.1$ Hz, CH_2O), 4.43 (2H, q, $^3J_{HH} = 7.1$ Hz, CH_2O), 4.79 (1H, dd, $^3J_{HH} = 11.7$ Hz, $^3J_{HP} = 6.3$ Hz, CH), 7.77–7.87 (4H, m, CH), 8.25–8.37 (2H, m, CH), 12.98 (1H, s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 14.4 (Me), 15.0 (Me), 15.0 (Me), 46.2 (d,

$^{1}J_{CP} = 132.0$ Hz, CH), 46.3 (d, $^{2}J_{CP} = 4.1$ Hz, CH), 62.1 (CH_2O), 62.2 (CH_2O), 63.1 (d, $^{2}J_{PC} = 7.1$ Hz, CH_2O), 63.3 (d, $^{2}J_{PC} = 7.8$ Hz, CH_2O), 117.4 (C), 122.1 (CH), 127.1 (CH), 127.7 (CH), 127.8 (CH), 133.5 (C), 134.1 (C), 134.3 (CH), 135.2 (CH), 136.7 (C), 152.7 (C–O), 155.6 (C–O), 168.7 (d, $^{2}J_{CP} = 6.5$ Hz, C=O), 171.4 (d, $^{3}J_{CP} = 21.0$ Hz, C=O), 181.8 (C=O), 189.6 (C=O) ppm; ^{31}P NMR ($CDCl_3$): $\delta = 22.67$ ppm.

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