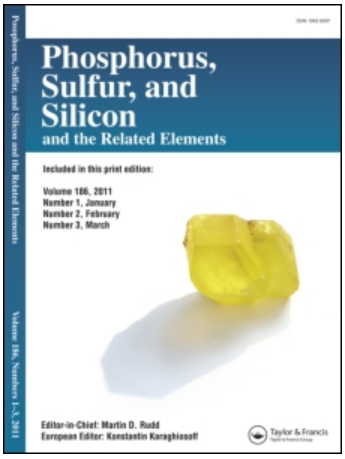

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Regioselective Synthesis of Novel Functionalized Phosphanylidene Anthra[2,1-b]furan Derivatives Under Solvent-Free Conditions

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REGIOSELECTIVE SYNTHESIS OF NOVEL FUNCTIONALIZED PHOSPHANYLIDENE ANTHRA[2,1-b]FURAN DERIVATIVES UNDER SOLVENT-FREE CONDITIONS

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A convenient and efficient, regioselective, solvent-free procedure has been developed to react 2,6-dihydroxyanthraquinone, dialkyl acetylenedicarboxylates, and triphenylphosphine in one-pot, to afford novel phosphanylidene anthracenyl derivatives 3a-c, which at 90°C due to intramolecular nucleophilic attack formed novel phosphanylidene anthra[2,1-b]furans 4a–c in good yield.

Keywords 2,6-Dihydroxyanthraquinone; hydroxyfuran; phosphanylidene anthracenyls; triphenyl phosphine

INTRODUCTION

The building blocks in organic pigments are molecules that determine, directly or indirectly, important performance properties of them.[1] From the beginning of modern structural theory of organic chemistry, quinones have been intimately associated with the chemistry of aromatic compounds.[2,3] Hydroxyanthraquinones (HAQs) as dyes, liquid crystals, and key intermediates with a variety of biological effects, such as interesting antitumor and antiviral activities and pharmaceutical properties,[4–12] could serve as a nucleophile in a three-component reaction such as the reaction of 2,6-dihydroxyanthraquinon (2,6-DHAQ), triphenylphosphine (PPh_3), and dialkyl acetylene dicarboxylates in one-pot and under solvent-free conditions to produce some novel phosphanylidene anthracenyl (**3a–c**) and phosphanylidene anthra[2,1-b]furan derivatives (**4a–c**).

Although the synthesis of stable phosphorus ylides, coumarins, and chromones via solvent-mediated reactions of phenols and naphthols,[13,14] and under solvent free conditions[15–22] were also reported previously, DHAQ-mediated reactions do not frequently produce anthra [2,1-b] furan derivatives, and 2-hydroxyfuran as a known tautomer of 2-furanone was also not commonly detected in the solution. Actually, stable 2-hydroxyfuran derivatives were reported only in limited numbers of studies.[22,23]

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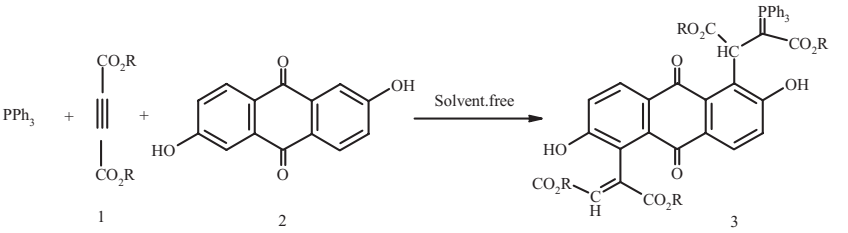
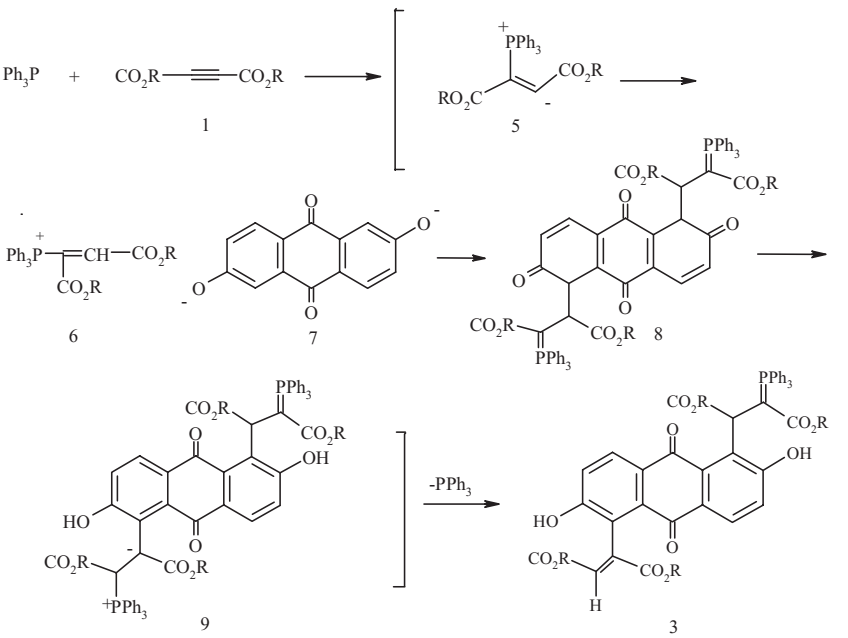
In this context, and in continuation of our current interest in the application of PPh_3 and activated acetylenes in organic synthesis,[24–32] the current study sought to obtain stable anthra[2,1-b]furans with a 2-hydroxyfuran moiety. Therefore, under solvent-free conditions, as an optimal alternative for the insoluble HAQs such as 2,6-DHAQ, some novel phosphanylidene anthracenyl derivatives (**3a–c**) have been synthesized (Scheme 1).

Even with considerable stability of **3a–c** at room temperature, an intramolecular nucleophilic attack occurred under solvent-free conditions by heating at 90°C for 2 h, and novel phosphanylidene anthra[2,1-b]furan derivatives **4a–c** (Scheme 2) were produced.



1,3	R	% Yields of 3
a	Me	85
b	Et	80
c	ipr	68

Scheme 1 Functionalized phosphanylidene anthracenyl derivatives **3a–c**.



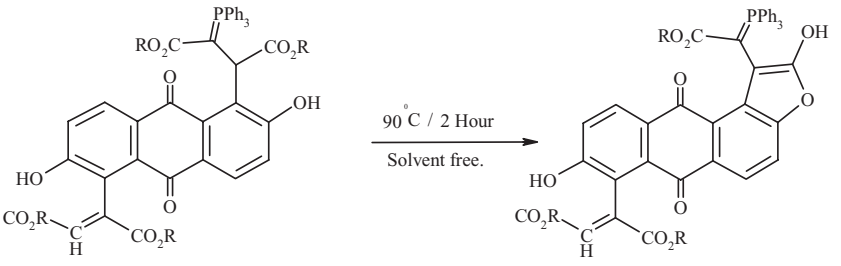
Scheme 2 Plausible mechanism for formation of **3**.

RESULTS AND DISCUSSION

The reaction of activated acetylenes **1** with PPh_3 in the presence of 2,6-DHAQ **2** under solvent-free conditions led to the corresponding functionalized dialkyl (*E*)-2-{2,6-dihydroxy-5-[3-alkoxy-1-(alkoxycarbonyl)-3-oxo-(1,1,1-triphenyl-λ^5-phosphanylidene)propyl]-9,10-dioxo-9,10-dihydro-2-anthracenyl}-2-butenedioate **3a–c** (Scheme 1) in less than 20 min. The structures of compounds **3a–c** were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data.

The ^{1}H NMR of the products **3** exhibited a C=CH proton signal at about 7.0–7.4 ppm. Additionally, the carbons of C=CH moiety in ^{13}C NMR spectra appear in 127 ppm, which is in agreement with the *E* configuration for the vinyl moiety.[6] The mechanism for the reaction between PPh_3 and **1** in the presence of **2** in a possible explanation is proposed in Scheme 2.[17,33,34] It is reasonable to assume that the zwitterionic intermediate[35] **5** formed from PPh_3 and dialkyl acetylenedicarboxylate is protonated by 2,6-DHAQ to furnish intermediate **6**, which then is attacked by the conjugate base **7** to produce ylide **8.** This intermediate undergoes proton transfer to furnish the 1,3-diionic structure **9**, which is converted to the final product by loss of PPh_3.

In spite of the considerable stability of **3a–c** at room temperature, novel, highly functionalized dialkyl (*E*)-2-{2,8-dihydroxy-1-[2-alkoxy-2-oxo-1-(1,1,1-triphenyl-λ^5-phosphanylidene)ethyl]-6,11-dioxo-6,11-dihydroanthra[2,1-b]furan-7-yl}-2-butenedioates **4a–c** were produced under solvent-free conditions in good yields by heating at 90°C for 2 h (Scheme 3).



3 4

4	R	%Yields of 4
a	Me	65
b	Et	62
c	iPr	59

Scheme 3 Phosphanylidene anthra[2,1-b]furan derivatives **4a–c**.

The structures of compounds **4a–c** were also deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data. For example the ^{1}H NMR spectrum of **4a** exhibited three singlets for the methoxy groups arising from the two methoxy groups on *E* butanedioate (as discussed above for **3**) and a methoxy group on furan moiety (Scheme 3). In ^{13}C NMR, the carbons of the furan moiety on **4a** appeared at 105.2 (d, $^2J_{PC}$ 12.0 Hz, C), 128.6 (d, $^3J_{PC}$ 11.7 Hz, C), 134.3 (d, $^4J_{PC}$ 2.6 Hz, C), and 166.2 (d, $^3J_{PC}$ 18.9 Hz, C), and the carbons of methoxy groups appeared at 50.6, 52.0, and 52.2.

Table I Summarized fluorescence spectroscopic data for **2**, **3a–c**, and **4a–c**

Compound*	$\lambda_{abs\ (nm)}$	ε ($M^{-1}cm^{-1}$)	$\lambda_{ex\ (nm)}$	$\lambda_{em\ (nm)}$
2	350	0.84×10^4	230	448
3a	380	1.8×10^4	230	441
3b	376	1.48×10^4	230	440
3c	370	1.4×10^4	230	438
4a	344	1.39×10^4	230	491
4b	340	1.28×10^4	230	488
4c	334	1.2×10^4	230	480

$\lambda_{abs:}$ Maximum absorption wavelength for peaks and; ε: corresponding molar absorption coefficient; λ_{ex}: maximum excitation wavelength and shoulders; λ_{em}: maximum emission and shoulders.

*The concentrations for all compounds are 1.9×10^{-4} mol lit^{-1}.

These reactions are regioselective, since ortho CH of the anthraquinone moieties revealed two doublets at δ 7.02 to 7.92 ppm, with $^3J_{HH}$ 7.0–8.1 Hz in the ^{1}H NMR spectra for **3a–c** and **4a–c**.

The fluorescence properties of the reactant **2** (2,6-DHAQ) and initial and final products were evaluated by means of fluorescence spectroscopy, and showed that the maximum intensity of fluorescence emission (λ_{max}) was found in the 456 ± 20 nm region (Table I).

EXPERIMENTAL

2,6-DHAQ, dialkyl acetylenedicarboxylates, and PPh_3 were obtained from Fluka (Buchs, Switzerland) and used without further purification. Melting points were measured on a Buchi melting point B-545 apparatus. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured at 500, 125.7, and 202.4 MHz, respectively, on a Bruker 500-Avance FT-NMR instrument with DMSO as solvent. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Perkin Elmer Spectrum One BX FT-IR spectrometer. Luminescence spectra were measured on a Luminescence spectrometer, Perkin-Elmer Ls5. UV/vis spectra were recorded on an UV/vis spectrophotometer, Cecil CE 9200.

General Procedure for the Preparation of Compounds 3

The 2,6-dihydroxyanthraquinone (1 mmol) and triphenylphosphine (2 mmol) were mixed and grinded for 2 min, and then dimethyl acetylenedicarboxylate was added dropwise (2 mmol) over a period of 10 min. The reaction mixture was allowed to stand at room temperature for 8 min. The products **3a–c** were purified by silica gel thin layer chromatography using n-hexane:EtOAc (1:1) as eluent.

Dimethyl (E)-2-{2,6-Dihydroxy-5-[3-methoxy-1-(methoxy carbonyl)-3-oxo-(1,1,1-triphenyl-λ^5-phosphanylidene)propyl]-9,10-dioxo-9,10-dihydro-2-anthracenyl}-2-butenedioate (3a). Yellow powder; yield (85%); mp 200–202°C; IR (KBr) (υ_{max}/cm^{-1}): 3437 (OH); 2947 (CH=); 1749, 1738, 1684, and 1641 (C=O). ^{1}H NMR (500 MHz, DMSO): δ_H 3.08 (3H, S, OCH_3); 3.30 (3H, S, OCH_3); 3.52 (3H, S, OCH_3); 3.70 (3H, S, OCH_3); 3.78 (1H, d, $^3J_{PH}$ 13.5 Hz, CH); 7.01 (1H, S, CH); 7.02 (2H, d, $^3J_{HH}$ 7.9 Hz, 2CH); 7.59–7.65 (15 H, m, PPh_3); 7.76 (2H, d, $^3J_{HH}$ 7.9 Hz, 2CH); 10.99 and 11.06 (2H, S, 2OH). ^{13}C NMR (125.7 MHz, DMSO): δ_C 50.1, 51.4, 51.5 and

51.9 ($4OCH_3$); 70.0 (d, $^1J_{PC}$ 118.1 Hz, C); 86.8 (d, $^2J_{PC}$ 11.8 Hz, CH); 107.3 (d, $^3J_{PC}$ 10.6 Hz, C); 116.6 (C); 123.4 (d, $^1J_{PC}$ 91.7 Hz, C); 127.5 (CH); 127.7 (CH); 127.8 (CH); 130.0 (d, $^3J_{PC}$ 12.5 Hz, C); 132.6 (C); 133.1 (C); 133.9 (CH); 134.2 (d, $^2J_{PC}$ 10.5 Hz, C); 134.6 (CH); 134.8 (C); 134.9 (C); 135.0 (d, $^4J_{PC}$ 2.6 Hz, C); 136.1 (C); 160.8 (d, $^2J_{PC}$ 12.5 Hz, C); 162.5 (d, $^3J_{PC}$ 5.2 Hz, C); 167.1 (C), 167.6 (C); 167.8 (C); 168.6 (C); 188.2 (C); 194.7 (C). ^{31}P NMR (202.4 MHz, DMSO): δ_p 20.69. Anal. Calcd for $C_{44}H_{35}O_{12}P$ (786): C, 67.17; H, 4.45%. Found C, 67.10; H, 4.38%.

Diethyl (E)-2-{2,6-Dihydroxy-5-[3-ethoxy-1-(ethoxy carbonyl)-3-oxo-(1,1, 1-triphenyl-λ^5-phosphanylidene)propyl]-9,10-dioxo-9,10-dihydro-2-anthracen yl}-2-butenedioate (3b). Deep yellow powder; yield (80%); mp 173–175°C; IR (KBr) (υ_{max}/cm^{-1}): 3434 (OH); 2919 (CH=); 1736, 1729, 1692 and 1657 (C=O). ^{1}H NMR (500 MHz, DMSO): δ_H 0.78 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3); 0.88 (3H, t, $^3J_{HH}$ 7.1Hz, CH_3); 1.22 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3); 1.36 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3); 3.57 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2); 3.77 (1H, d, $^3J_{PH}$ 13.8 Hz, CH); 3.78 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2); 3.90 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2); 4.04 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2); 7.02 (1H, S, CH); 7.03 (2H, d, $^3J_{HH}$ 8.1 Hz, 2CH); 7.23–7.73 (15H, m, PPh_3); 7.78 (2H, d, $^3J_{HH}$ 8.1 Hz, 2CH); 10.97 and 11.06 (2H, S, 2OH). ^{13}C NMR (125.7 MHz, DMSO): δ_C 13.1, 13.9 and 14.0 and 14.1 ($4CH_3$); 58.6, 60.6, 61.4 and 61.5 ($4OCH_2$); 69.2 (d, $^1J_{PC}$ 116.7 Hz, C); 88.3 (d, $^2J_{PC}$ 10.1 Hz, CH); 106.0 (d, $^3J_{PC}$ 9.8 Hz, C); 117.1 (C); 122.5 (d, $^1J_{PC}$ 90.8 Hz, C); 127.1 (CH); 127.4 (CH); 127.6 (CH); 129.3 (d, $^3J_{PC}$ 12.5 Hz, C_{meta}); 131.8 (CH), 131.9 (*C*); 132.0 (C); 132.8 (C); 133.1 (CH); 133.4 (*C*); 133.5 (d, $^2J_{PC}$ 9.6 Hz, C); 133.7 (d, $^2J_{PC}$ 3.0 Hz, C); 134.1 (C); 163.2 (d, $^2J_{PC}$ 11.12 Hz, C); 165.1 (d, $^3J_{PC}$ 6.2 Hz, C); 166.5 (C); 167.3 (C); 168.5 (C); 169.6 (C); 188.3 (C) 194.7(C). ^{31}P NMR (202.4 MHz, DMSO): δ_p 20.61. Anal. Calcd for $C_{48}H_{43}O_{12}P$ (842): C, 68.41; H, 5.10%. Found C, 68.36; H, 5.01%.

Diisopropyl (E)-2-{2,6-Dihydroxy-5-[3-isopropoxy-1-(isopropoxy carbon yl)-3-oxo-(1,1,1-triphenyl-λ^5-phosphanylidene)propyl]-9,10-dioxo-9,10-dihydro-2-anthracenyl}-2-butenedioate (3c). Pale yellow powder; yield (68%); mp 166–168°C; IR (KBr) (υ_{max}/cm^{-1}): 3434 (OH); 2980 (CH=); 1732, 1721, 1693 and 1660 (C=O). ^{1}H NMR (500 MHz, DMSO): δ_H 0.79 (6H, d, $^3J_{HH}$ 6.0 Hz, $2CH_3$); 1.05 (6H, d, $^3J_{HH}$ 6.0 Hz, $2CH_3$); 1.30 (6H, d, $^3J_{HH}$ 6.0 Hz, $2CH_3$); 1.56 (6H, d, $^3J_{HH}$ 6.0 Hz, $2CH_3$) 3.70 (1H, d, $^3J_{PH}$ 15.0 Hz, CH); 4.38 (1H, m, OCH); 4.82 (1H, m, OCH); 4.94 (1H, m, OCH); 5.36 (1H, m, OCH); 7.01 (1H, S, CH); 7.08 (2H, d, $^3J_{HH}$ 7.8 Hz, 2CH); 7.12–7.90 (15 H, m, PPh_3); 7.94 (2H, d, $^3J_{HH}$ 7.8 Hz, 2CH); 11.82 and 12.64 (2H, S, 2OH). ^{13}C NMR (125.7 MHz, DMSO): δ_C 21.2, 21.57, 21.8 and 21.9 ($8CH_3$); 66.5, 69.2, 70.5 and 70.55 (4OCH); 70.1 (d, $^1J_{PC}$ 116.0 Hz, C); 84.6 (d, $^2J_{PC}$ 10.2 Hz, CH); 104.5 (d, $^3J_{PC}$ 9.5 Hz, C); 116.9 (C); 122.5 (d, $^1J_{PC}$ 91.0 Hz, C); 127.2 (CH); 127.5 (CH); 127.6 (CH); 128.8 (d, $^3J_{PC}$ 12.5 Hz, C); 129.4 (CH); 131.5 (C); 132.0 (C); 132.1 (C); 132.2 (CH); 133.0 (C); 133.1 (d, $^2J_{PC}$ 9.8 Hz, C); 134.1 (d, $^4J_{PC}$ 2.8 Hz, C); 134.2 (C); 160.1 (d, $^2J_{PC}$ 11.7 Hz, C); 163.7 (d, $^3J_{PC}$ 5.0 Hz, C); 166.1 (C); 166.3 (C); 166.9 (C); 167.8 (C); 188.1 (C); 194.7 (C). ^{31}P NMR (202.4 MHz, DMSO): δ_p 21.01. Anal. Calcd for $C_{52}H_{51}O_{12}P$ (898): C, 69.48; H, 5.68%. Found C, 69.39; H, 5.73%.

General Procedure for the Preparation of Compounds 4

3a–c were heated at 90°C for 2 h in the solid phase under solvent-free conditions. The reaction mixture was allowed to stand at room temperature for 8 min. The products

4a–c were purified by silica gel thin layer chromatography using n-hexane:EtOAc (1:1) as eluent.

Dimethyl (E)-2-{2,8-Dihydroxy-1-[2-methoxy-2-oxo-1-(1,1,1-triphenyl-λ^5-phosphanylidene)ethyl]-6,11-dioxo-6,11-dihydroanthra[2,1-b]furan-7-yl}-2-butenedioate (4a). Orange powder; yield (65%); mp 173–175°C; IR (KBr) (υ_{max}/cm^{-1}): 3435(OH); 2953(CH=); 1740, 1662 and 1640 (C=O). ^{1}H NMR (500 MHz, DMSO): δ_H 3.00, 3.33 and 3.85 (9H, S, 3OCH$_3$); 7.03 (1H, S, CH); 7.04 (2H, d, $^3J_{HH}$ 7.0 Hz, 2CH); 7.29–7.75 (15 H, m, PPh$_3$); 7.78 (2H, d, $^3J_{HH}$ 7.0 Hz, 2CH); 11.05 and 11.11 (2H, S, 2OH). ^{13}C NMR(125.7 MHz, DMSO): δ_C 50.6; 52.0 and 52.2 (3OCH$_3$); 51.0 (d,$^1J_{PC}$ 117.1 Hz, C); 105.2 (d, $^2J_{PC}$ 12.1 Hz, C); 116.8 (C); 123.4 (d, $^1J_{PC}$ 91.8 Hz, C); 127.3 (CH); 127.6 (CH); 127.7 (CH); 128.5 (d, $^3J_{PC}$ 12.7 Hz, C); 128.7 (d, $^3J_{PC}$ 11.8 Hz, C); 131.5 (CH); 132.0 (C); 132.2 (C); 132.9 (C); 133.1 (CH); 133.4 (C); 134.1(d, $^2J_{PC}$ 9.6 Hz, C); 134.4 (d, $^4J_{PC}$ 2.6 Hz, C); 135.1 (C); 163.7 (d, $^2J_{PC}$ 11.8 Hz, C); 165.1 (d, $^4J_{PC}$ 2.6 Hz, C); 166.2 (d, $^3J_{PC}$ 19.6 Hz, C); 166.8 (C); 167.5 (C); 188.2 (C); 194.2 (C). ^{31}P NMR (202.4 MHz, DMSO): δ_p 21.49. Anal. Calcd for $C_{43}H_{31}O_{11}P$ (754): C, 68.43; H, 4.11%. Found C, 68.35; H, 4.02%.

Diethyl (E)-2-{2,8-Dihydroxy-1-[2-ethoxy-2-oxo-1-(1,1,1-triphenyl-λ^5-phosphanylidene)ethyl]-6,11-dioxo-6,11-dihydroanthra[2,1-b]furan-7-yl}-2-butenedioate (4b). Deep yellow powder; yield (62%); mp 150–152°C; IR (KBr) (υ_{max}/cm^{-1}): 3432 (OH); 2924 (CH=); 1728, 1678 and 1630 (C=O). ^{1}H NMR(500 MHz, DMSO): δ_H 0.70, 1.43 and 1.49 (9H, d, $^3J_{HH}$ 7.1 Hz, 3CH$_3$); 3.49, 4.38 and 4.45 (6H, q, $^3J_{HH}$ 7.1 Hz, 3OCH$_2$); 7.00 (1H, S, CH); 7.02 (2H, d, $^3J_{HH}$ 7.1 Hz, 2CH); 7.05–7.75 (15 H, m, PPh$_3$); 7.79 (2H, d, $^3J_{HH}$ 7.1 Hz, 2CH); 11.12 and 11.20 (2H, S, 2OH). ^{13}C NMR (125.7 MHz, DMSO): δ_C 13.1, 14.3 and 14.7 (3CH$_3$); 50.6 (d, $^1J_{PC}$ 117.0 Hz, C); 58.7, 62.0 and 62.6 (3OCH$_2$); 105.0 (d, $^2J_{PC}$ 12.0 Hz, C); 117.1 (C); 122.4 (d, $^1J_{PC}$ 90.8 Hz, C); 127.0 (CH); 127.2 (CH); 127.5 (CH); 127.9 (d, $^3J_{PC}$ 12.5 Hz, C); 128.4 (d, $^3J_{PC}$ 12.4 Hz, C); 131.1 (CH); 131.9 (C); 132.2 (C); 132.5 (C); 132.8 (CH); 133.1 (C); 133.3 (d, $^2J_{PC}$ 9.6 Hz, C); 133.6 (d, $^4J_{PC}$ 3.0 Hz, C); 134.2 (C); 164.0 (d, $^2J_{PC}$ 11.12 Hz, C); 165.2 (d, $^4J_{PC}$ 2.8 Hz, C); 165.8(d, $^3J_{PC}$ 18.7 Hz, C); 167.1 (C); 188.3 (C); 194.1(C). ^{31}P NMR (202.4 MHz, DMSO): δ_p 21.17. Anal. Calcd for $C_{46}H_{37}O_{11}P$ (796): C, 69.34; H, 4.65%. Found C, 69.25; H, 4.59%.

Diisopropyl (E)-2-{2,8-Dihydroxy-1-[2-isopropoxy-2-oxo-1-(1,1,1-triphenyl-λ^5-phosphanylidene)ethyl]-6,11-dioxo-6,11-dihydroanthra[2,1-b]furan-7-yl}-2-butenedioate (4c). Yellow powder; yield (59%); mp 146–148°C. IR (KBr) (υ_{max}/cm^{-1}): 3432 (OH); 2985 (CH=); 1724, 1673 and 1641 (C=O). ^{1}H NMR (500 MHz, DMSO): δ_H 0.71 (6H, d, $^3J_{HH}$ 6.0 Hz, 2CH$_3$); 1.65 (6H, d, $^3J_{HH}$ 6.0 Hz, 2CH$_3$); 1.75 (6H, d, $^3J_{HH}$ 6.0 Hz, 2CH$_3$); 4.30 (1H, m, OCH); 5.33 (1H, m, OCH); 5.49 (1H, m, OCH); 7.01 (1H, S, CH); 7.07 (2H, d, $^3J_{HH}$ 7.0 Hz, 2CH); 7.10–7.90 (15 H, m, PPh$_3$); 7.93 (2H, d, $^3J_{HH}$ 7.0 Hz, 2CH); 12.68 and 12.74 (2H, S, 2OH). ^{13}C NMR(125.7 MHz, DMSO): δ_C 21.3, 22.5 and 22.9 (6CH$_3$); 50.9 (d,$^1J_{PC}$ 116.0 Hz, C); 66.6, 70.5 and 71.2 (3OCH); 104.8 (d, ^{2}J$_{PC}$ 11.8Hz, C); 116.6 (C); 122.5 (d, $^1J_{PC}$ 91.0 Hz, C); 127.1 (CH); 127.3 (CH); 127.4 (CH); 127.8 (d, $^3J_{PC}$ 12.5 Hz, C); 128.5 (d, $^3J_{PC}$ 12.0 Hz, C); 129.4 (CH); 130.6 (C); 131.8 (C); 132.1 (C); 132.6 (CH); 132.9 (C); 133.1 (d, $^2J_{PC}$ 9.8 Hz, C); 133.6 (d, $^4J_{PC}$ 2.8 Hz, C); 134.1 (C); 163.0 (d, $^2J_{PC}$ 11.6 Hz, C); 165.3 (d, $^4J_{PC}$ 2.8 Hz, C); 166.8 (d, $^2J_{PC}$18.5 Hz, C); 167.5 (C); 188.1 (C); 194.2 (C). ^{31}P NMR (202.4 MHz, DMSO): δ_p 21.95. Anal. Calcd for $C_{49}H_{43}O_{11}P$ (838): C, 70.17; H, 5.13%. Found C, 70.10; H, 5.17%.

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