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Reaction between naphthols and dimethyl acetylenedicarboxylate in the presence of phosphites. Synthesis of stable oxa-2λ^5-phosphaphenanthrenes, and benzochromene derivatives

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The reaction of dimethyl acetylenedicarboxylate (DMAD) with 2-naphthol in the presence of trimethyl or triphenyl phosphite leads to stable dimethyl oxa-2λ^5-phosphaphenanthrene derivatives in good yields. The reaction of DMAD and trimethyl phosphite in the presence of 1-naphthol or 8-hydroxyquinoline leads to dimethyl 2-(dimethoxyphosphoryl)-3-(1-hydroxy-2-naphthyl)succinate or dimethyl 2-(dimethoxyphosphoryl)-3-(8-hydroxyquinolin-7-yl)-succinate in excellent yields. Using triethyl phosphite and DMAD in the presence of 2-naphthol or 1-naphthol produces methyl 3-oxo-2,3-dihydro-1*H*-benzo[*f*]chromene-1-carboxylate or methyl 2-oxo-3,4-dihydro-2*H*-benzo[*h*]-chromene-4-carboxylate in excellent yields.

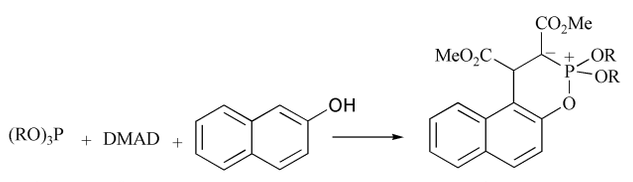
Introduction

Organophosphorus compounds, *i.e.* those bearing a carbon atom directly bound to a phosphorus atom, are synthetic targets of interest, not least because of their value for a variety of industrial, biological, and chemical synthetic uses.[1–3] As a result, a large number of methods have appeared describing novel syntheses of organophosphorus compounds. There are many studies on the reaction between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source such as alcohol or phenol.[4–6] We describe herein the reaction of dimethyl acetylenedicarboxylate (DMAD) with a trivalent phosphorus nucleophile such as trimethyl phosphite, triethyl phosphite, or triphenyl phosphite in the presence of phenolic compounds such as 1-naphthol, 2-naphthol, or 8-hydroxyquinoline.

Results and discussion

2-Naphthol

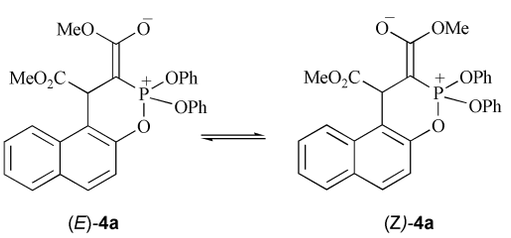
The reaction of DMAD and 2-naphthol in the presence of trimethyl or triphenyl phosphite leads to 4*H*-1-oxa-2λ^5-phosphaphenanthrene-3,4-dicarboxylate derivatives **4** in high yields (Scheme 1).



1,4	R	%Yield of 4
a	Ph	90
b	Me	85

Scheme 1

The structures of **4a** and **4b** were determined on the basis of their ^{1}H, ^{13}C, and ^{31}P NMR spectra, IR spectra, elemental analyses, and mass spectrometric data. The ^{1}H NMR spectrum of **4a** in $CDCl_3$ shows four singlets at δ = 3–4 ppm for the methoxy protons and two doublets at δ = 5.48 ($^3J_{PH}$ = 34 Hz) and 5.55 ($^3J_{PH}$ = 33 Hz), for the methine proton, along with multiplets at δ = 6.98–9.20 for the aromatic protons. At ambient temperature, the ^{1}H NMR spectrum of **4a** in $CDCl_3$ exhibits two sets of methoxy resonances at 3.21 and 3.72 ppm and at 3.09 and 3.77 ppm with a relative intensity ratio of *ca.* 3 : 1. As the temperature was increased, broadening of the signals occurred (coalescence temperature, 320 ± 1 K), and only one set of resonances at δ = 3.25 and 3.65 ppm was observed at 333 K. Although an extensive line-shape analysis in relation to the dynamic ^{1}H NMR effect observed for **4a** was not undertaken, the variable temperature spectra allowed the calculation of the free energy barrier for the dynamic NMR process in **4a**. From coalescence of the O–Me proton resonances and using the expression, $k = \pi\Delta\nu/\sqrt{2}$, the first-order rate constant (k) for the dynamic NMR effect in **4a** was calculated to be 133 s^{-1} at 320 K. Application of the absolute rate theory with a transmission coefficient of 1 gives a free-energy of activation ($\Delta G^{\#}$) of 65.5 ± 2 kJmol^{-1}, where all known sources of errors are estimated and included.[7] These results were rationalized on the basis of the presence of geometrical isomers (*E*)-**4a** and (*Z*)-**4a** (see Scheme 2) that undergo rapid interconversion at 333 K.



(*E*)-**4a** (*Z*)-**4a**

Scheme 2

The *E*–*Z* isomerism of ylides possessing a carbonyl group at the α-position has been observed previously.[8–10] Further evidence for the presence of an ylide ester group in **4a** was the observation of a strong low-frequency carbonyl absorption at 1667 cm^{-1} in the IR spectrum.[8] The other ester carbonyl absorption in **4a** appears at 1722 cm^{-1}.

The ^{13}C and ^{31}P NMR spectra of **4a** also confirmed the presence of two rotational isomers at ambient temperature. Thus, the ^{13}C NMR spectrum consisted of two sets of signals that comprised more than 50 resonances in total. Characteristic carbonyl resonances appear clearly at δ = 168.40 (d, $^2J_{PC}$ = 17 Hz), 169.40 (d, $^2J_{PC}$ = 18 Hz), 173.13, and 173.32 ppm, whereas the ylide carbon atom exhibits resonances at δ = 41.10 (d, $^1J_{PC}$ =

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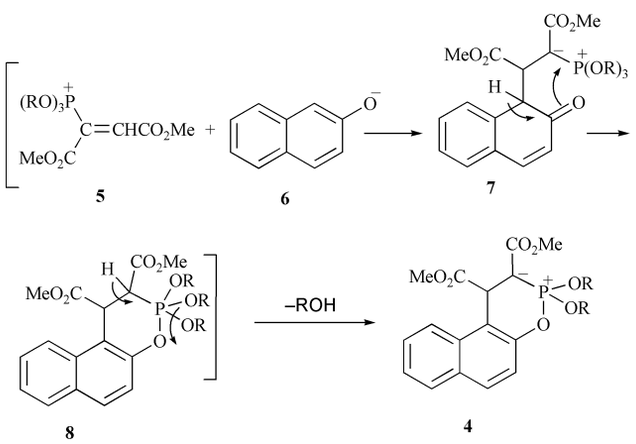
225 Hz) and 41.15 (d, $^1J_{CP}$ = 223 Hz) ppm. The observed $^1J_{CP}$ values are typical of an α-ylide ester.[11] The double bond character of the C–P bond and the presence of three electronegative oxo substituents on the phosphorus atom increases the $^1J_{CP}$ value.[11] Evidence for the presence of an oxaphosphaphenanthrene skeleton in **4a** was shown by the ^{13}C signals at δ = 118.22 (d, $^3J_{CP}$ = 6 Hz) and 118.50 (d, $^3J_{CP}$ = 6 Hz) for the CH groups of the naphthalene moiety and at δ = 148.13 (d, $^2J_{CP}$ = 8 Hz) for the C–O carbon of naphthalene. The observed coupling constants are consistent with the existence of a single bond between the oxygen atom of the naphthol moiety and the phosphorus atom. The two phenyl groups are diastereotopic and exhibited two sets of signals. Two ^{31}P NMR signals were found at δ = 39.81 and 41.54 ppm.

The ^{1}H and ^{13}C NMR spectra of **4b** were similar to those for **4a** except for the phosphoranyl moiety. The ^{1}H NMR spectrum of **4b** also exhibits two rotational isomers at ambient temperature.

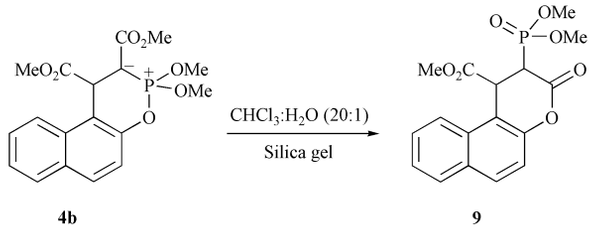
Although we have not yet established the mechanism of the reaction between DMAD and phosphites in the presence of 2-naphthol in an experimental manner, a possible explanation is proposed in Scheme 3.



Scheme 3

On the basis of the well established chemistry of phosphorus nucleophiles[2,3] it is reasonable to assume that ylide **4** results from initial addition of the phosphite to DMAD with subsequent protonation of the reactive 1 : 1 adduct, followed by attack of the carbon atom of the anion of 2-naphthol **6** to cation **5** to generate ylide **7**, which isomerises under the reaction conditions employed to produce the oxaphosphorane **8**. Elimination of ROH from **8** leads to product **4**.

Hydrolysis–lactonization of **4b** in a mixture of $CHCl_3$: H_2O (20 : 1) on silica gel gave methyl 2-(dimethoxyphosphoryl)-3-oxo-2,3-dihydro-1*H*-benzo[*f*]chromene-1-carboxylate **9** (Scheme 4). The IR spectrum of the reaction mixture showed



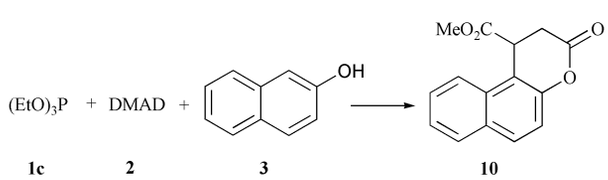
Scheme 4

the disappearance of the carbonyl absorption of the ester group of **4b** at 1652 cm^{-1} and appearance of a new absorption band at 1760 cm^{-1} for the lactone carbonyl group. The other ester carbonyl absorption in **9** was observed at 1730 cm^{-1}. The ^{1}H NMR spectrum of **9** displayed two doublets at δ = 3.10 ($^3J_{PH}$ = 11 Hz) and 3.82 ($^3J_{PH}$ = 11 Hz) for the P–OMe protons, along with a singlet at δ = 3.70 for the ester methoxy protons and two doublets at δ = 3.91 ($^2J_{PH}$ = 25 Hz) and 5.11 ($^3J_{PH}$ = 13 Hz) for the methine protons. The aromatic moiety showed four doublets and two triplets for the CH protons. The ^{13}C and ^{31}P NMR spectra of **9** are consistent with the proposed structure (see Experimental section).

Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra[10] of **9**, it helps in the assignment of the signals by long-range coupling with ^{1}H and ^{13}C nuclei (see Experimental section). Of particular interest are the three-bond carbon–phosphorus coupling constants, $^3J_{CP}$, which provide information on the P–C–C–C torsion angles. The $^3J_{CP}$ depends on the conformation, as expected, *transoid* coupling being larger than *cisoid* coupling. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and penta-coordinate phosphorus.[9] The observation of $^3J_{CP}$ = 21 Hz for the ester *C*=O group in **9** is in agreement with the *anti* arrangement of the P–CH–CH–C(O) moiety. The $^3J_{CP}$ for the α-carbon of the naphthalene moiety is less than 1 Hz, which corresponds to a *gauche* arrangement. The lack of observable couplings between vicinal methine protons is also consistent with a H–C–C–H dihedral angle of about 90°.[11] The coupling constants discussed above are in agreement with the *anti* arrangement of the CO_2Me and $PO(OMe)_2$ groups.

Hydrolysis of **4a** under similar conditions as used for **4b** led to a complex mixture of products.

The reaction between triethyl phosphite **1c**, DMAD **2**, and 2-naphthol **3** quantitatively gave product **10** (Scheme 5).



Scheme 5

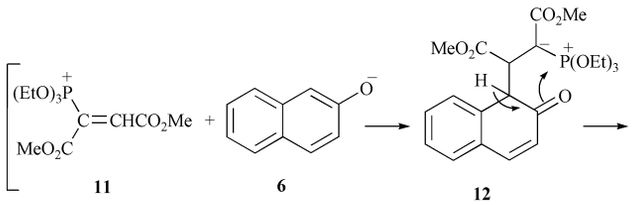
The IR spectrum of **10** exhibited the ester and lactone carbonyl groups at 1711 and 1752 cm^{-1}, respectively. The ^{1}H NMR spectrum of **10** showed a double doublet at δ = 2.82 ($^2J_{HH}$ = 16 Hz, $^3J_{HH}$ = 6 Hz) for one of the methylene protons. The other methylene proton displayed a doublet ($^2J_{HH}$ = 16 Hz) at δ = 3.25 ppm. The methine proton showed a doublet ($^3J_{HH}$ = 6 Hz) at δ = 4.60 ppm. The coupling constants observed for this AMX system are consistent with a conformation in which the H–C–C–H dihedral angles for the CH–CH_2 moiety are expected to be about 90° and 30°.[11] The ^{13}C NMR spectrum of **10** displayed 15 distinct resonances in agreement with the proposed structure.

A possible mechanism for the formation of compound **10** is shown in Scheme 6. The oxaphosphorane **13** is formed using similar steps as shown for oxaphosphorane **8** in Scheme 3. However, since the ethoxide anion is a weaker leaving group, cleavage of the phosphorus–oxygen bond of the naphthol residue becomes favorable, giving dimethyl succinate **16**. Lactonization of this hydroxy ester gave product **10**.

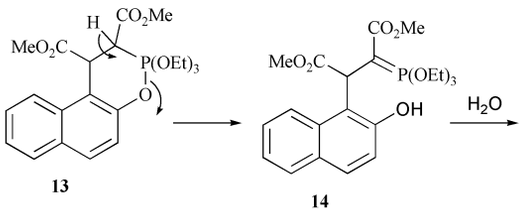
1-Naphthol

The reaction of DMAD **2** and trimethyl phosphite **1b** in the presence of 1-naphthol **17** gave dimethyl 2-(dimethoxyphosphoryl)-3-(1-hydroxy-2-naphthyl)succinate **18** in 96% yield (Scheme 7).

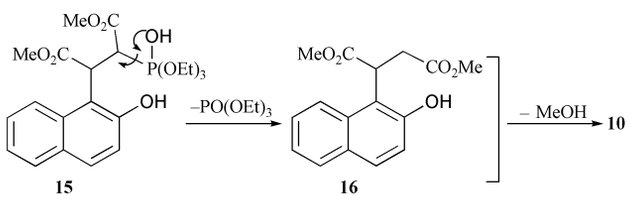
The ^{1}H NMR spectrum of **18** displayed signals for vicinal methine protons at δ = 3.88 and 4.99, which appeared as two sets of double doublets with $^2J_{HP}$ and $^3J_{HP}$ values of 21 and 9 Hz, respectively. The methoxy groups of the phosphoranyl moiety are diastereotopic and show two separate doublets at δ = 2.85 and 3.67. The hydroxy proton was observed as a broad



11 **6** **12**

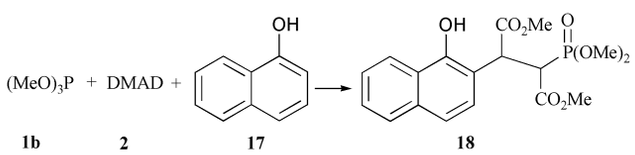


13 **14**



15 **16** **10**

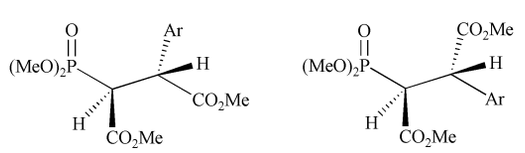
Scheme 6



1b **2** **17** **18**

Scheme 7

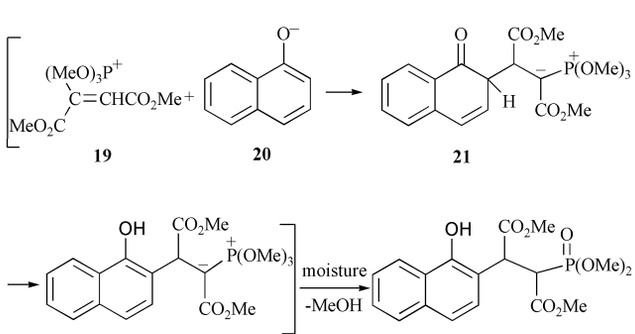
singlet at δ = 8.47 which disappeared with addition of D_2O. Observation of $^3J_{HH}$= 12 Hz for the vicinal methine protons in **18** indicates the dominance of the *anti* arrangement. Since compound **18** possesses two stereogenic centers, two diastereomers with *anti* HCCH arrangements are possible (Scheme 8). The observation of $^3J_{CP}$ = 22 Hz for the CO_2Me group and $^3J_{CP}$ = 0 Hz for the *C* of the naphthalene moiety is in agreement with the (2*R*,3*S*) or (2*S*,3*R*) diastereoisomer.



(2*R*,3*S*)-**18** or (2*S*,3*R*)-**18** (2*S*,3*S*)-**18** or (2*R*,3*R*)-**18**

Scheme 8

A proposed mechanism for the formation of compound **18** is shown in Scheme 9.

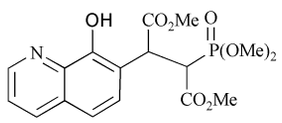


19 **20** **21** **22** **18**

Scheme 9

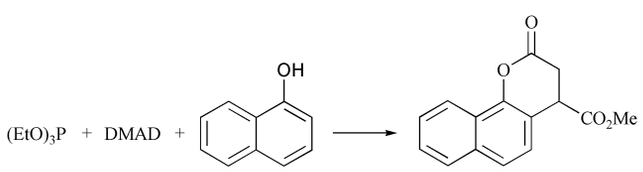
Ylide **21** is produced in the same way as shown for ylide **7** (Scheme 3) and isomerises, under the reaction conditions employed, to ylide **22**. Hydrolysis of **22** leads to phosphoranyl derivative **18**.

The reaction of 8-hydroxyquinoline and trimethyl phosphite **1b** in the presence of DMAD **2** gave dimethyl 2-(dimethoxyphosphoryl)-3-(8-hydroxyquinolin-7-yl)succinate **23** in 77% yield. As for compound **18**, the $^3J_{HH}$ and $^3J_{CP}$ coupling constants in compound **23** are also in agreement with (2*R*,3*S*) and (2*S*,3*R*) geometries.



23

Although the reaction of triphenyl phosphite, DMAD, and 1-naphthol leads to a complex mixture, reaction of DMAD **2** and triethyl phosphite **1c** in the presence of 1-naphthol **17** produces methyl 2-oxo-3,4-dihydro-2*H*-benzo[*h*]chromene-4-carboxylate **24** in excellent yield (Scheme 10). The spectroscopic data for carboxylate **24** is very similar to those for compound **10** (see Experimental section).



1c **2** **17** **24**

Scheme 10

Carboxylate **24** is possibly produced through an ylide intermediate similar to **22** (Scheme 9). However, due to steric reasons, hydrolysis of this intermediate occurs on the phosphorus atom and leads to a succinate derivative, which is lactonized to produce **24**.

In conclusion, we have found that the reaction of DMAD with trimethyl phosphite or triphenyl phosphite in the presence of 2-naphthol leads to a facile synthesis of some functionalized oxaphosphaphenanthrenes. The reaction of 1-naphthol with DMAD and trimethyl phosphite produces, stereoselectively, a 3-oxo-2,3-dihydrobenzochromene derivative in high yield. The addition reaction of triethyl phosphite, DMAD, and 1-naphthol or 2-naphthol leads quantitatively to benzochromene derivatives. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modification.

Experimental

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN–O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively. ^1H, ^{13}C, and ^{31}P spectra were obtained for solutions in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. All the chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

Dimethyl 2,2-diphenoxy-4*H*-1-oxa-2λ^5-phosphaphenanthrene-3,4-dicarboxylate (4a)

To a magnetically stirred solution of 0.28 g dimethyl acethylenedicarboxylate **2** (2 mmol) and 0.29 g 2-naphthol **3** (2 mmol) in 20 cm^3 CH_2Cl_2 was added 0.62 g triphenyl phosphite **1a** (2 mmol) at room temperature. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the residue was crystallized from diethyl ether. The product **4a** was obtained as colorless crystals, mp 178–180 °C, 0.90 g, yield 90%. IR (KBr) (ν_{max}/cm^{-1}): 1667, and 1722 (2 C=O). Anal. calcd for $C_{28}H_{23}O_7P$ (502.4): C, 66.93; H, 4.61. Found: C, 66.9; H, 4.7%. NMR data for the major isomer (75%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.21 and 3.72 (6 H, 2 s, 2 Me), 5.55 (1 H, d, $^3J_{HP}$ 33 Hz, CH), 6.98–9.20 (16 H, m, 16 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 41.10 (d, $^1J_{CP}$ 225 Hz, C), 41.37 (d, $^2J_{CP}$ 9 Hz, CH), 50.32 and 52.06 (2 OMe), 118.22 (d, $^3J_{PC}$ 6 Hz, CH of $C_{10}H_6$), 120.54 (d, $^3J_{CP}$ 4 Hz, 2 CH_{ortho} of Ph), 120.83 (d, $^3J_{PC}$ 9 Hz, C of $C_{10}H_6$), 121.50 (d, $^3J_{PC}$ 4 Hz, 2 CH_{ortho} of Ph), 124.10 and 125.56 (2 CH of $C_{10}H_6$), 125.92 and 126.14 (2 CH_{para} of Ph), 127.49 and 128.43 (2 CH of $C_{10}H_6$), 129.71 (m, 4 CH_{meta} of Ph groups), 129.79 (CH of $C_{10}H_6$), 131.13 and 131.33 (2 C of $C_{10}H_6$), 148.13 (d $^2J_{PC}$ 8 Hz, C–O of $C_{10}H_6$), 149.96 (m, 2 CH_{ipso} of Ph groups), 168.40 (d, $^2J_{PC}$ 17.3 Hz, C=O), 173.32 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 41.54. NMR data for the minor isomer (25%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.09 and 3.77 (6 H, 2 s, 2 Me), 5.48 (1 H, d $^3J_{HP}$ 34 Hz, CH), 6.98–9.20 (16 H, m, 16 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 41.15 (d, $^1J_{CP}$ 223 Hz, C), 41.30 (d, $^2J_{CP}$ 9 Hz, CH), 50.72 and 52.00 (2 OMe), 118.50 (d, $^3J_{PC}$ 6 Hz, CH of $C_{10}H_6$), 120.54 (d, $^3J_{CP}$ 4 Hz, 2 CH_{ortho} of Ph), 120.99 (d, $^3J_{PC}$ 9.4 Hz, C of $C_{10}H_6$), 121.50 (d, $^3J_{PC}$ 4 Hz, 2 CH_{ortho} of Ph), 123.83, and 125.00 (2 CH of $C_{10}H_6$), 125.92 and 126.05 (2 CH_{para} of Ph), 127.70 and 128.53 (2 CH of $C_{10}H_6$), 129.71 (m, 4 CH_{meta} of Ph groups), 129.79 (CH of $C_{10}H_6$), 131.13 and 131.33 (2 C of $C_{10}H_6$), 148.13 (d, $^2J_{PC}$ 8 Hz, C–O of $C_{10}H_6$), 149.96 (m, 2 CH_{ipso} of Ph groups), 169.40 (d, $^2J_{PC}$ 18 Hz, C=O), 173.13 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 39.81. MS, *m*/*z* (%): 502 ($M^{+\bullet}$, 5), 444 (35), 273 (26), 181 (51), 151 (100).

Dimethyl 2,2-dimethoxy-4*H*-1-oxa-2λ^5-phosphaphenanthrene-3,4-dicarboxylate (4b)

The procedure for preparation of **4b** was similar to that for **4a**. Colorless crystals, mp 128–130 °C, 0.64 g, yield 85%. IR (KBr) (ν_{max}/cm^{-1}): 1652, and 1722 (2 C=O). Anal. calcd for $C_{18}H_{19}O_7P$ (378.3): C, 57.15; H, 5.06. Found: C, 57.2; H, 5.1%. NMR data for the major isomer (75%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.61 and 3.70 (6 H, 2 s, 2 Me), 3.65 (3 H, d, $^3J_{PH}$ 13 Hz, OMe), 4.07 (3 H, d, $^3J_{PH}$ 13 Hz, OMe), 5.65 (1 H, d, $^3J_{HP}$ 31 Hz, CH), 7.26 (d, $^3J_{HH}$ 9 Hz, CH), 7.45 (1 H, t, $^3J_{HH}$ 9 Hz, CH), 7.59 (1 H, t, $^3J_{HH}$ 9 Hz), 7.73 (1 H, d, $^3J_{HH}$ 9 Hz, CH), 7.79 (1 H, d, $^3J_{HH}$ 9 Hz, CH), 8.39 (1 H, d, $^3J_{HH}$ 9 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 39.20 (d, $^1J_{CP}$ 222 Hz, C), 41.37 (d, $^2J_{CP}$ 9 Hz, CH), 50.37 and 52.21 (2 OMe), 55.33 (d, $^2J_{PC}$ 6 Hz, P–OMe), 55.65 (d, $^2J_{PC}$ 5 Hz, P–OMe), 118.35 (d, $^3J_{PC}$ 6 Hz, CH), 121.29 (d, $^3J_{PC}$ 9.1 Hz, C), 124.40, 125.43, 127.38, 128.40 and 129.79 (5 CH), 131.13 and 131.31 (2 C), 148.58 (d, $^2J_{PC}$ 8 Hz, C–O), 169.20 (d, $^2J_{PC}$ 18 Hz, C=O), 174.92 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 42.53. NMR data for the minor isomer (25%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.57 and 3.72 (6 H, 2 s, 2 Me), 3.76 (3 H, d, $^3J_{PH}$ 13 Hz, OMe), 4.12 (3 H, d, $^3J_{PH}$ 13 Hz, OMe), 5.56 (1 H, d $^3J_{HP}$ 32 Hz, CH), 7.26 (1H, d, $^3J_{HH}$ 9 Hz, CH), 7.45 (1 H, t, $^3J_{HH}$ 9 Hz, CH), 7.59 (1 H, t, $^3J_{HH}$ 9 Hz), 7.73 (1 H, d, $^3J_{HH}$ 9 Hz, CH), 7.79 (1 H, d, $^3J_{HH}$ 9 Hz, CH), 8.32 (1 H, d, $^3J_{HH}$ 9 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 39.31 (d, $^1J_{CP}$ 222 Hz, C), 40.96 (d, $^2J_{CP}$ 9 Hz, CH), 50.37 and 52.17 (2 OMe), 55.81 (d, $^3J_{PC}$ 6 Hz, P–OMe), 55.83 (d, $^3J_{PC}$ 5 Hz, P–OMe), 118.69 (d, $^3J_{PC}$ 5.7 Hz, CH), 120.96 (d, $^3J_{PC}$ 9 Hz, C), 124.10, 125.43, 127.38, 128.53 and 129.79 (5 CH), 131.06 and 131.17 (2 C), 148.58 (d, $^2J_{PC}$ 8 Hz, C–O), 169.60 (d, $^2J_{PC}$ 22 Hz, C=O), 174.57 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 41.04. MS, *m*/*z* (%): 378 ($M^{+\bullet}$, 11), 332 (29), 319 (45), 273 (59), 168 (80), 139 (100).

Methyl 2-(dimethoxyphosphoryl)-3-oxo-2,3-dihydro-1*H*-benzo-[*f*]chromene-1-carboxylate (9)

A mixture of 0.76 g **4b** (2 mmol), 2 g silica gel, 20 cm^3 CH_2Cl_2 and 1 cm^3 water was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the residue was passed through a short column of silica gel using dichloromethane as eluent. The solvent was removed under reduced pressure and the residue was crystallized from diethyl ether. The product **6** was obtained as a white powder, mp 183–186 °C, 0.71 g, yield 97%. IR (KBr) (ν_{max}/cm^{-1}): 1730, and 1760 (2 C=O). Anal. calcd for $C_{17}H_{17}O_7P$ (364.3): C, 56.05; H, 4.70. Found: C, 56.2; H, 4.7%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.10 (3 H, d, $^3J_{PH}$ 11 Hz, OMe), 3.70 (3 H, s, OMe), 3.82 (3 H, d, $^3J_{PH}$ 11 Hz, OMe), 3.91 (1 H, d $^2J_{PH}$ 25 Hz, CH), 5.11 (1 H, d, $^3J_{PH}$ 13 Hz, CH), 7.26 (d, $^3J_{HH}$ 9 Hz, CH), 7.49 (1 H, t, $^3J_{HH}$ 9 Hz, CH), 7.59 (1 H, t, $^3J_{HH}$ 9 Hz), 7.73 (1 H, d, $^3J_{HH}$ 9 Hz, CH), 7.79 (1 H, d, $^3J_{HH}$ 9 Hz, CH), 8.32 (1 H, $^3J_{HH}$ 9 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 39.30 (d, $^2J_{CP}$ 5 Hz, CH), 41.09 (d, $^1J_{CP}$ 129 Hz, CH), 53.22 (OMe), 53.75 (m, 2 P–OMe), 110.79 (C), 117.12, 123.53, 125.66, 128.12, 128.68 (5 CH), 130.90 (C), 131.10 (CH), 131.13 (C), 149.70 (C), 162.30 (d, $^2J_{PC}$ 6 Hz, C=O), 170.47 (d, $^3J_{PC}$ 21 Hz, C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 20.10. MS, *m*/*z* (%): 364 ($M^{+\bullet}$, 9), 332 (63), 273 (75), 255 (78), 168 (93), 139 (100), 109 (95).

Methyl 3-oxo-2,3-dihydro-1*H*-benzo[*f*]chromene-1-carboxylate (10)

To a magnetically stirred solution of 0.28 g dimethyl acethylenedicarboxylate **2** (2 mmol) and 0.29 g 2-naphthol **3** (2 mmol) in 20 cm^3 CH_2Cl_2 was added 0.33 g triethyl phosphite **1c** (2 mmol) at room temperature. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the residue was crystallized from diethyl ether (0.49 g, yield 96%). mp 151–152 °C, IR (KBr) (ν_{max}/cm^{-1}): 1711, and 1752 (2 C=O). Anal. calcd for $C_{15}H_{12}O_4$ (256.3): C, 70.31; H, 4.72. Found: C, 70.1; H, 4.7%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.82 (1 H, dd, $^2J_{HH}$ 16 Hz, $^3J_{HH}$ 6 Hz, HCH), 3.25 (1 H, d, $^2J_{HH}$ 16 Hz, HCH), 3.65 (3 H, s, OMe), 4.60 (1 H, d, $^3J_{HH}$ 6 Hz, CH), 7.26 (1 H, d, $^3J_{HH}$ 9 Hz, CH), 7.49 (1 H, t, $^3J_{HH}$ 8 Hz, CH), 7.59 (1 H, t, $^3J_{HH}$ 8 Hz), 7.73 (1 H, d, $^3J_{HH}$ 8 Hz, CH), 7.79 (1 H, d $^3J_{HH}$ 8 Hz, CH), 8.32 (1 H, $^3J_{HH}$ 9 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 31.37 (CH_2), 37.87 (CH), 52.84 (OMe), 112.73 (C), 117.70, 123.27, 125.42, 127.75, 128.76, and 130.65 (6 CH), 130.90, 131.00, and 149.96 (3 C), 166.16 and 171.22 (2 C=O). MS, *m*/*z* (%): 256 ($M^{+\bullet}$, 15), 196 (100), 168 (41).

Dimethyl 2-(dimethoxyphosphoryl)-3-(1-hydroxy-2-naphthyl)-succinate (18)

To a magnetically stirred solution of 0.28 g dimethyl acethylenedicarboxylate **2** (2 mmol) and 0.29 g 1-naphthol **17** (2 mmol) in 20 cm^3 CH_2Cl_2 was added 0.25 g trimethyl phosphite **1b** (2 mmol) at room temperature. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the residue was crystallized from diethyl ether. The product **18** was obtained as colorless crystals, mp 173–185 °C, 0.76 g, yield 96%. IR (KBr) (ν_{max}/cm^{-1}): 3230 (OH), 1724 (C=O). Anal. calcd for $C_{18}H_{21}O_8P$ (396.3): C, 54.55; H, 5.34. Found: C, 54.4; H, 5.3%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.85 (3 H, d, $^3J_{HP}$ 11 Hz, OMe), 3.60 (3 H, s, OMe), 3.67 (3 H, d, $^3J_{HP}$ 11 Hz, OMe), 3.82 (3 H, s, OMe), 3.88 (1 H, dd, $^2J_{HP}$ 21 Hz, $^3J_{HH}$ 12 Hz, CH), 4.99 (1 H, dd, $^3J_{HH}$ 12 Hz, $^3J_{HP}$ 9 Hz, CH), 7.10–8.42 (6 H, m, 6 CH), 8.47 (1 H, s, OH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 44.04 (CH), 48.51 (d, $^1J_{PC}$ 135 Hz, CH), 52.79 (OMe), 52.86 (d, $^2J_{PC}$ 7 Hz, OMe), 53.05 (OMe), 53.97 (d, $^2J_{PC}$ 7

Hz, OMe), 116.92 (C), 121.78 and 123.42 (2 CH), 124.60 (C), 125.74, 126.82 and 127.20 (3 CH), 127.67 (C), 134.20 (CH), 150.50 (C), 168.24 (d, $^{2}J_{PC}$ 5 Hz, C=O), 173.01 (d, $^{3}J_{PC}$ 22 Hz, C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 18.56. MS, *m*/*z* (%): 396 ($M^{+\bullet}$, 42), 305 (82), 273 (100), 168 (87), 139 (72).

Dimethyl 2-(dimethoxyphosphoryl)-3-(8-hydroxyquinolin-7-yl)-succinate (23)

The procedure for the preparation of **23** was the same as that for **18**. Brown powder, mp 152–155 °C, 0.61 g, yield 77%. IR (KBr) (ν_{max}/cm^{-1}): 3235 (OH), 1737 (C=O). Anal. calcd for $C_{17}H_{20}NO_8P$ (397.3): C, 51.39; H, 5.07; N, 3.53. Found: C, 51.3; H, 5.0; N, 3.4%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.41 (3 H, d, $^{3}J_{HP}$ 11 Hz, OMe), 3.45 (3 H, d, $^{3}J_{HP}$ 11 Hz, OMe), 3.52 (3 H, s, OMe), 3.86 (3 H, s, OMe), 4.25 (1 H, dd, $^{2}J_{HP}$ 21 Hz, $^{3}J_{HH}$ 12 Hz, CH), 4.89 (1 H, dd, $^{3}J_{HH}$ 12 Hz, $^{3}J_{HP}$ 8 Hz, CH), 7.36 (1 H, d $^{3}J_{HH}$ 9 Hz, CH), 7.44 (1 H, dd, $^{3}J_{HH}$ 8 Hz, $^{3}J_{HH}$ 3 Hz, CH), 7.54 (1 H, d, $^{3}J_{HH}$ 9 Hz, CH), 8.19 (1 H, $^{3}J_{HH}$ 8 Hz, CH), 8.81 (1 H, d, $^{3}J_{HH}$ 3 Hz, CH), 8.47 (1 H, br s, OH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 45.50 (CH), 45.92 (d, $^{1}J_{PC}$ 131 Hz, CH), 52.65 and 53.07 (2 OMe), 53.13, and 53.65 (2 d, $^{2}J_{PC}$ 7 Hz, 2 P–OMe), 116.93 (C), 117.61, and 122.06 (2 CH), 127.95 (CH), 129.37 (C), 136.13 (CH), 138.01 (C), 148.24 (CH), 150.37 (C), 169.27 (d, $^{2}J_{PC}$ 6 Hz, C=O), 172.49 (d, $^{3}J_{PC}$ 21 Hz, C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 26.01. MS, *m*/*z* (%): 397 ($M^{+\bullet}$, 7), 288 (39), 274 (47), 256 (100), 170 (83).

Methyl 2-oxo-3,4-dihydro-2*H*-benzo[*h*]chromene-4-carboxylate (24)

The procedure for the preparation of **24** was the same as that for **10**. White powder, mp 127–129 °C, 0.49 g, yield 96%., IR (KBr) (ν_{max}/cm^{-1}): 1721 and 1757 (2 C=O). Anal. calcd for $C_{15}H_{12}O_4$ (256.3): C, 70.31; H, 4.72. Found: C, 70.2; H, 4.7%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.9 (1 H, dd, $^{2}J_{HH}$ 16 Hz, $^{3}J_{HH}$ 7 Hz, HCH), 3.25 (1 H, dd, $^{2}J_{HH}$ 16 Hz, $^{3}J_{HH}$ 3 Hz, HCH), 3.74 (3 H, s, OMe), 4.1 (1 H, dd, $^{3}J_{HH}$ 7 Hz, $^{3}J_{HH}$ 3 Hz, CH), 7.34–8.30 (6 H, m, 6 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 31.33 (CH_2), 41.44 (CH), 52.84 (OMe), 113.85 (C), 121.40 (CH), 123.73 (C), 124.38, 125.18, 126.84, 127.24 and 127.58 (5 CH), 134.08 and 146.98 (2 C), 166.05 and 171.33 (2 C=O). MS, *m*/*z* (%): 256 ($M^{+\bullet}$, 20), 196 (100), 168 (96), 141 (96), 139 (42).

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