A three-component reaction between trialkyl phosphites or triphenylphosphine, dimethyl acetylenedicarboxylate and *N*-aryl-3-hydroxynaphthalene–2-carboxamide

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A three-component reaction between dimethyl acetylenedicarboxylate (DMAD) and trialkyl phosphites in the presence of *N*-aryl-3-hydroxynaphthalene-2-carboxamide leads to dialkyl 2-(dimethoxyphosphoryl)-3-[2-hydroxy-3-(arylcarbamyl)naphthalen-1-yl] succinate in excellent yields. A similar reaction with triphenylphosphine, instead of phosphites, produces dimethyl 2-[2-hydroxy-3-(arylcarbamoyl)naphthalen-1-yl]maleates. In the absence of triphenylphosphine or phosphite, DMAD adds to *N*-aryl-3-hydroxynaphthalene-2-carboxamide to produce alkyl 2-(alkoxycarbonylmethyl)-4-oxo-3-aryl-3,4-dihydro-2*H*-naphtho[2,3-*e*][1,3]oxazine-2-carboxylates in good yields.

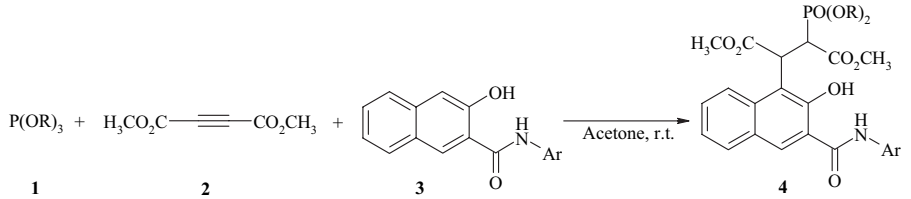
Keywords: dimethyl acetylenedicarboxylate, thialkyl phosphites; *N*-aryl-3-hydroxynaphthalene-2-carboxamide, stereoselective synthesis, triphenylphosphine

The nucleophilic addition of trialkyl phosphites to electron-deficient triple bonds leads to a highly reactive zwitterionic intermediate, which may be trapped by various electrophiles. There have been many studies on the reactions between trivalent phosphorus nucleophiles and unsaturated carbonyl compounds in the presence of a proton source such as an alcohol.[1] The reaction of trimethyl phosphite with dimethyl acetylenedicarboxylate (DMAD) in the presence of alcohols is reported to produce phosphite ylide derivatives which are stable at low temperatures, but converted to phosphonate derivatives by warming or by treatment with water.[2] The reaction of trimethyl phosphite with DMAD in the presence of 2-naphthol has been reported to afford stable dimethyl oxa-2,5-phosphaphenanthrene derivatives in good yields.[3] In continuation of our previous work on three-component reactions between trivalent phosphorus nucleophiles, acetylenic esters and organic acidic compounds,[4-8] we report herein the results of our study on the reaction between acetylenic esters and trialkyl phosphites or triphenylphosphine in the presence of *N*-aryl-3-hydroxynaphthalene-2-carboxamides.

Reaction of DMAD with trimethyl (or triethyl or tributyl) phosphite in the presence of N-phenyl (or 2-methylphenyl) (3-hydroxynaphthalene-2-carboxamide leads to dialkyl 2-(dimethoxyphosphoryl)-3-[2-hydroxy-3-(arylcarbamyl) naphthalen-1-yl] succinates in excellent yields (Scheme 1).

The ^{1}H NMR spectrum of **4a** exhibits two sharp lines at δ = 3.61 and 3.93 ppm for the protons of two methoxy groups. Two methoxy groups of phosphoryl moiety are diastereotopic and appear as two doublets at 3.37 and 3.45 ppm ($^3J_{HP}$ = 11H$_Z$). The ^{1}H NMR spectrum of **4a** also exhibits signals for vicinal methine protons at δ = 4.23 and 5.49 ppm as two sets of doublet of doublets, with $^2J_{HP}$ = 21 H$_Z$, $^3J_{HP}$ = 6 H$_Z$ and $^3J_{HH}$ = 11 H$_Z$. The vicinal proton–proton coupling constants can be obtained from the Karplus equation.[9,10] Typically, J_{gauche} varies between 1.5 and 5 H$_Z$ and J_{anti} between 10 and 14 H$_Z$. Observation of $^3J_{HH}$ = 11 H$_Z$ for vicinal protons in compound **4a** indicates an anti arrangement for these centres. Since compound **4a** possesses two stereogenic centres, two diastereomers with anti HCCH arrangements are possible (Scheme 2). The three-bond carbon–phosphorus coupling, $^3J_{CP}$, depends on configuration, as expected, transoid couplings being larger than cisoid ones.[11] The observation for $^3J_{CP}$ of 19 H$_Z$ for the ester carbonyl carbon, is in agreement with the (2*R,* 3*S*)-**4a** and its mirror image (2*S,* 3*R*)-**4a** geometries. The NMR spectra of compounds **4b–f** also show only (2*R,* 3*R*) isomer and its enantiomer.

It is reasonable to assume that compounds **4** result from the initial addition of trimethyl phosphite to DMAD and subsequent protonation of the 1:1 adduct by *N*-aryl-3-hydroxynaphthalene–2-carboxamide **3** (Scheme 3). Then,



1 **2** **3** **4**

4	Ar	R	Yield*(%)
a	Ph	Me	93
b	Ph	Et	89
c	Ph	Bu	91
d	2-Me-C$_6$H$_4$	Me	95
e	2-Me-C$_6$H$_4$	Et	93
f	2-Me-C$_6$H$_4$	Bu	90

*Isolated yield

Scheme 1

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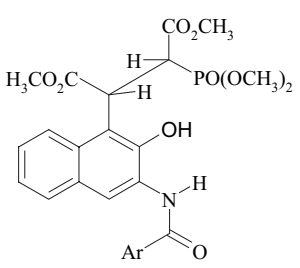
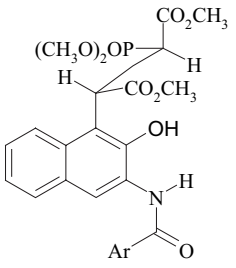


(2*S*, 3*R*)-**4a**



(2*R*, 3*S*)-**4a**

Scheme 2

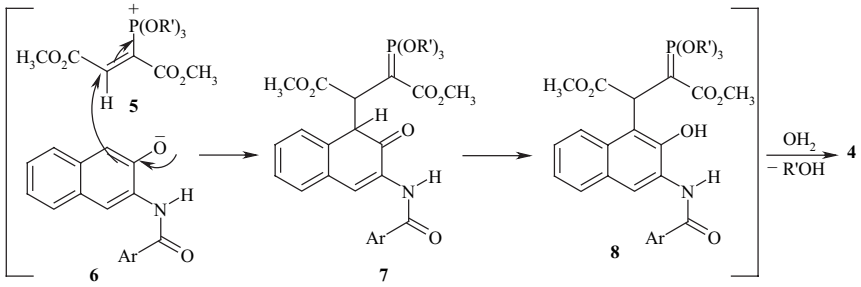
the positively charged ion **5** is attacked by the anion **6** to form ylide **7** that then tautomerises and is hydrolysed to phosphonate **4**.

The reaction of acetylenic ester **9** with triphenylphosphine (**8**) in the presence of *N*-aryl 3-hydroxynaphthalene-2-carboxamide **3** leads to dialkyl 2-[2-hydroxy-3-(arylcarbamoyl)naphthalen-1-yl]but-2-enedioate **10** in excellent yields (Scheme 4).

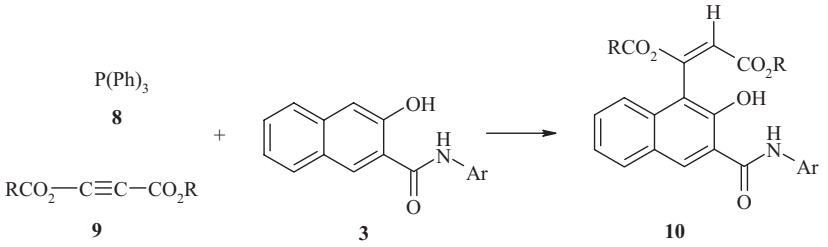
The ^{1}H NMR spectrum of **10a** exhibits three sharp lines at δ = 3.74, 3.83 and 6.44 ppm for the protons of two methoxy groups and olefinic proton, respectively. Two single signals are observed at 10.17 and 12.33 ppm that disappeared after addition of a few drops of D_2O to d_6-DMSO solution of compound **10a**. These signals are related to OH and NH protons. Aromatic protons resonate between 7.21 and 8.75 ppm as multiplets. The chemical shift of 6.44 ppm of the olefinic proton in the ^{1}H NMR spectrum of compound **10a** is consistent with the *E*-geometry of the carbon–carbon double bond.[13] ^{13}C NMR spectra of compound **10a** shows 21 distinct signals, which is consistent with the proposed structure.

It is reasonable to assume that compound **10** results from the initial addition of triphenylphosphine **2** to acetylenic ester **9** and subsequent protonation of the 1:1 adduct by *N*-aryl-3-hydroxynaphthalene–2-carboxamide **3** (Scheme 5). Then, the positively charged ion **11** is attacked by the anion **6** to form ylide **12** that loses triphenylphosphine to produce compound **10**.

When acetylenic ester **9** was treated with *N*-aryl 3-hydroxynaphthalene-2-carboxamide **3** in the absence of triphenylphospline the addition product alkyl 2-(alkoxy-



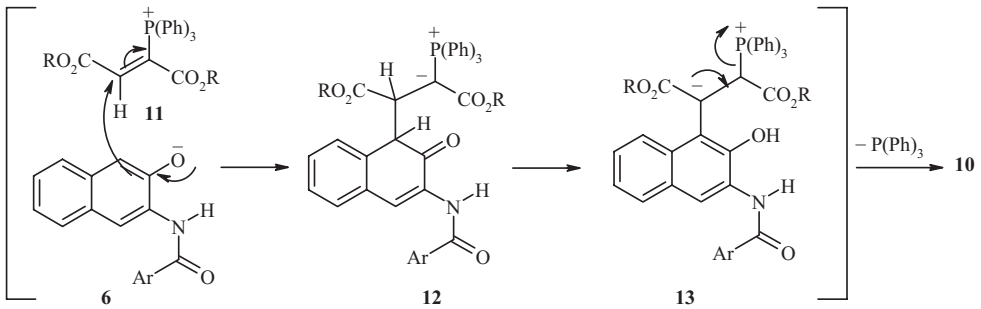
Scheme 3



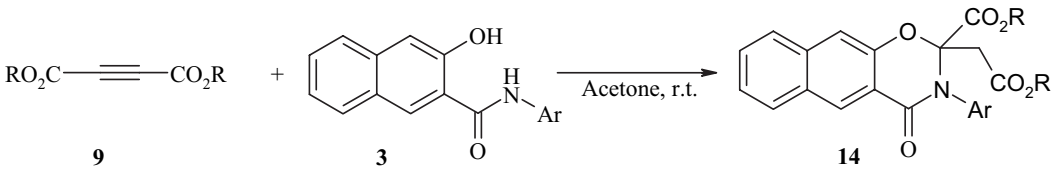
10	Ar	R	Yield*(%)
a	Ph	Me	92
b	Ph	Et	90
c	Me-C_6H_4	Me	90
d	Me-C_6H_4	Et	89

*isolated yields

Scheme 4



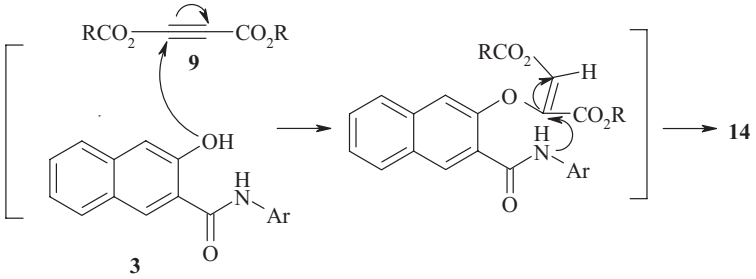
Scheme 5



14	Ar	R	Yield*(%)
a	Ph	Me	92
b	Ph	Et	87
c	2-Me-C_6H_4	Me	93
d	2-Me-C_6H_4	Et	90

*Isolated yield

Scheme 6



Scheme 7

carbonylmethyl)-4-oxo-3-aryl-3,4-dihydro-2*H*-naphtho[2,3-*e*][1,3]oxazine-2-carboxylate **14** was obtained in good yield (Scheme 6).

The ^{1}H NMR spectrum of **14a** exhibits two sharp lines at δ = 3.74 and 3.83 ppm for the protons of two methoxy groups. The methylene protons resonate at 3.28 ppm as an AB-quartet (δ_1 = 3.24, δ_2 = 3.32, $^2J_{HH}$ = 16 Hz). Aromatic protons resonate between 7.21 and 8.75 ppm as multiplets. The IR spectrum of compound **14a** does not show the stretching absorption bonds related to OH or NH bonds.

Compound **14** is probably produced by the addition of *N*-aryl 3-hydroxynaphthalene-2-carboxamide **3** to ecetylenic ester **9** as shown in Scheme 7.

In summary functionalised phosphonates may be prepared by a simple, one-pot, three-component reaction between DMAD, aryl 3-hydroxynaphthalene–2-carboxamides, and trialkyl phosphites. The addition reaction between acetylenic esters and *N*-aryl-3-hydroxynaphthalene-2-carboxamides catalysed by triphenylphosphine produces dialkyl 2-[2-hydroxy-3-(arylcarbamoyl)naphthalen-1-yl]-but-2-enedioates in good yields. In the absence of triphenylphosphine *N*-aryl-3-hydroxynaphthalene-2-carboxamides add to acetylenic esters to produce alkyl 2-(alkoxycarbonylmethyl)-4-oxo-3-aryl-3,4-dihydro-2*H*-naphtho[2,3-*e*][1,3]oxazine-2-carboxylates in excellent yields. The present method carries the advantage that the reaction is performed under neutral conditions and starting materials can be mixed without any activation or modification.

Experimental

Melting points were determined with an electrothermal 9100 apparatus. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyser. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionisation potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX-500 Avance spectrometer at solutions in d_6-DMSO using TMS as internal standard or 85% H_3PO_4 as external standard. The chemicals used in this work purchased from fluka (Buchs, Switzerland) and were used without further purification.

Dimethyl 2-(dimethoxyphosphoryl)-3-[2-hydroxy-3-(phenylcarbamoyl) naphthalen-1-yl]succinate **(4a)**

General procedure for preparation of compounds **4a–f**

To a magnetically stirred solution of 0.53 g *N*-phenyl-3-hydroxynaphthalene–2-carboxamide **3** (2 mmol) and 0.28 g DMAD (2 mmol) in 10,ml acetone was added a mixture of 0.25 g trimethyl phosphite **1** (2 mmol) in 2 ml acetone at room temperature. The reaction mixture was then allowed to stir for 24 h. The solvent was evaporated at reduced pressure. The residue was precipitated in a solution of diethyl ether–hexane. The solid was filtered and washed with diethyl ether to give the pure product.

White powder, yield 0.96 g (93%), m.p. 177–180°C, IR (KBr) (ν_{max} cm^{-1}): 3245 OH and NH), 1727 (C=O, ester), 1642 (C=O, amide). Analyses: Calcd. for $C_{25}H_{26}NO_9P$: C, 58.25; H, 5.08; N, 2.72%. Found: C, 58.34; H, 4.93; N,2.80. MS (*m/z*,%): 515 (5). ^{1}H NMR (500 MHz, d_6-DMSO): δ 3.37 and 3.45 (6 H, 2d, $^3J_{HP}$ = 11 Hz, 2 $POCH_3$), 3.61 and 3.93 (6 H, 2 s, 2 OCH_3), 4.70 (1 H, dd, $^2J_{HP}$ = 21 Hz, $^3J_{HH}$ = 11 H_Z, CH), 5.33 (1 H, dd, $^3J_{HP}$ = 6 Hz, $^3J_{HH}$ = 11 H_Z, CH), 7.16–8.15 (10 H, m, aromatic),). 9.09 and 12.66 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, d_6-DMSO–Me_4Si): δ 41.95 (d, $^2J_{cp}$ = 2 H_Z, P–C–*C*), 43.95 (d, $^1J_{cp}$ = 131 H_Z, P-*C*), 53.17 and 53.28 (2 OCH_3), 66.32 and 66.58 (2 d, $^2J_{cp}$ = 7 H_Z, 2 POCH_3), 116.21, 116.77, 123.04, 123.83, 125.86, 127.40, 129.16, 130.26, 135.76 and 156.55 (naphthol moiety), 121.89, 122.81, 129.30, 137.34 (phenyl moiety), 169.00 (C=O), 170.43 (d, $^2J_{CP}$ = 6 H_Z, C=O), 173.49 (d, $^3J_{CP}$ = 21 H_Z, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 19.94.

Dimethyl 2-(diethoxyphosphoryl)-3-[2-hydroxy-3-(phenylcarbamoyl) naphthalen-1-yl]succinate **(4b):** White powder, yield 0.97 g (89%), m.p. 185–188°C, IR (KBr) (ν_{max} cm^{-1}): 3255(OH),1729 (C=O, ester),1643 (C=O, amide). Analyses: Calcd. for $C_{27}H_{30}NO_9P$: C, 59.67; H, 5.56; N, 2.58%. Found: C, 59.72; H, 5.48; N, 2.60. MS (*m/z*,%): 543 (11). ^{1}H NMR (500 MHz, d_6-DMSO): δ 0.87 and 0.93 (6 H, t, 2 CH_3), 3.71–3.76(4 H, m, 2 $POCH_2$), 3.50 and 3.82 (6 H, 2 s, 2 OCH_3), 4.54 (1 H, dd, $^2J_{HP}$ = 21 Hz, $^3J_{HH}$ = 11 H_Z, CH), 5.21 (1 H, dd, $^3J_{HP}$ = 6 Hz, $^3J_{HH}$ = 11 H_Z, CH), 7.13–8.57 (10 H, m, aromatic), 9.91 and 12.43 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, d_6-DMSO-Me_4Si): δ 16.08 and 16.22 (2 *C*H_3), 41.93 (d, $^2J_{cp}$

= 2 H_Z, P–C–*C*), 43.78 (d, $^1J_{cp}$ = 131 H_Z, P-*C*), 53.28 and 53.60 (2 O*C*H_3), 61.73 and 62.38 (2 d, $^2J_{cp}$ = 7 H_Z, 2 PO*C*H_2), 116.27, 117.77, 123.33, 123.80, 125.52, 127.46, 129.43, 130.76, 136.06 and 156.09 (naphthol moiety), 121.80, 122.77, 129.54, 137.31 (phenyl moiety), 169.27(C=O), 170.16(d, $^2J_{CP}$ = 6 H_Z, C=O), 173.03 (d, $^3J_{CP}$ = 21 H_Z, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 19.80.

Dimethyl 2-(dibutoxyphosphoryl)-3-[2-hydroxy-3-(phenylcarbamoyl) naphthalen-1-yl]succinate **(4c):** White powder, yield 1.12 g (91%), m.p. 190–193°C, IR (KBr) (ν_{max} cm^{-1}): 3250 (OH),1724 (C=O, ester), 1641 (C=O, amide). Analyses: Calcd. for $C_{31}H_{38}NO_9P$: C, 62.10; H, 6.39; N, 2.34%. Found: C, 62.18; H, 6.30; N, 2.42. MS (*m/z*,%): 599 (7). ^{1}H NMR (500 MHz, d_6-DMSO): δ 0.83 (6 H, t, 2 CH_3), 0.93 (4 H, sextet, 2 CH_2), 1.32(4 H, quintet, 2 CH_2), 3.71–3.86 (4 H, m, 2 POCH_2), 3.60 and 3.92 (6 H, 2 s, 2 OCH_3), 4.72 (1 H, dd, $^2J_{HP}$ = 21 Hz, $^3J_{HH}$ = 11 H_Z, CH), 5.34 (1 H, dd, $^3J_{HP}$ = 6 Hz, $^3J_{HH}$ = 11 H_Z, CH), 7.12–8.56 (10 H, m, aromatic), 9.06 and 12.64 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, d_6-DMSO-Me_4Si): δ 13.94 and 14.02 (2 *C*H_3), 18.87 and 18.96 (2CH_2), 32.32 and 32.64 (2 d, $^3J_{CP}$ = 7 Hz, 2 CH_2), 42.12 (d, $^2J_{cp}$ = 2 H_Z, P–C–*C*), 44.82 (d, $^1J_{cp}$ = 131 H_Z, P-*C*), 53.11 and 53.38 (2 O*C*H_3), 66.53 and 66.91 (2 d, $^2J_{cp}$ = 7 H_Z, 2 PO*C*H_2), 116.22, 117.01, 123.27, 123.71, 125.78, 127.47, 129.04, 130.17, 135.86 and 156.61 (naphthol moiety), 121.50, 122.82, 129.29 and 137.39 (phenyl moiety), 169.01 (C=O), 170.16(d, $^2J_{CP}$ = 6 H_Z, C=O), 172.92 (d, $^3J_{CP}$ = 21 H_Z, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 21.65.

Dimethyl 2-(dimethoxyphosphoryl)-3-[2-hydroxy-3-(2-methylphenyl-carbamoyl)naphthalen-1-yl]succinate **(4d):** White powder, yield 1.03 g (95%), m.p. 194–197°C, IR (KBr) (ν_{max} cm^{-1}): 3200(OH), 1729(C=O, ester), 1641(C=O, amide). Analyses: Calcd. for $C_{26}H_{28}NO_9P$: C, 58.98; H, 5.33; N, 2.65%. Found: C, 59.45; H, 5.22; N, 2.73. MS (*m/z*,%): 529 (6). ^{1}H NMR (500 MHz, d_6-DMSO): δ 2.34 (3 H, s, C*H*$_3$), 3.13 and 3.43 (6 H, 2d, $^3J_{HP}$ = 11 Hz, 2 POCH_3), 3.60 and 3.90 (6 H, 2 s, 2 OCH_3), 4.62 (1 H, dd, $^2J_{HP}$ = 21 Hz, $^3J_{HH}$ = 11 H_Z, CH), 5.32 (1 H, dd, $^3J_{HP}$ = 6 Hz, $^3J_{HH}$ = 11 H_Z, CH), 7.17–8.21 (9 H, m, aromatic), 8.90 and 12.61 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, d_6-DMSO–Me_4Si): δ 18.46 (*C*H_3), 41.95 (d, $^2J_{cp}$ = 2 H_Z, P–C–*C*), 43.95 (d, $^1J_{cp}$ = 131 H_Z, P–*C*), 53.17 and 53.28 (2 O*C*H_3), 66.32 and 66.58 (2 d, $^2J_{cp}$ = 7 H_Z, 2 PO*C*H_3), 116.13, 117.14, 123.20, 124.08, 126.49, 127.47, 129.00, 130.36, 135.06 and 156.49 (naphthol moiety), 127.34, 127.43, 129.21, 131.10, 133.31 and 135.89 (phenyl moiety), 169.23 (C=O), 170.30 (d, $^2J_{CP}$ = 6 H_Z, C=O), 173.31 (d, $^3J_{CP}$ = 21 H_Z, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 20.71.

Dimethyl2-(diethoxyphosphoryl)-3-[2-hydroxy-3-(2-methylphenyl-carbamoyl)naphthalen-1-yl]succinate **(4e):** White powder, yield 1.05 g (93%), m.p. 175–178°C, IR (KBr) (ν_{max} cm^{-1}): 3195 (OH), 1725 (C=O, ester),1642 (C=O, amide). Analyses: Calcd. for $C_{28}H_{32}NO_9P$: C, 60.32; H, 5.79; N, 2.51%. Found: C, 60.48; H, 5.70; N, 2.55. MS (*m/z*,%): 557 (9). ^{1}H NMR (500 MHz, d_6-DMSO): δ 0.96 and 1.11 (6 H, t, 2 CH_3), 2.36 (3 H, s, C*H*$_3$), 3.72–3.82 (4 H, m, 2 POCH_2), 3.61 and 3.91 (6 H, 2 s, 2 OCH_3), 4.62 (1 H, dd, $^2J_{HP}$ = 21 Hz, $^3J_{HH}$ = 11 H_Z, CH), 5.34 (1 H, dd, $^3J_{HP}$ = 6 Hz, $^3J_{HH}$ = 11 H_Z, CH), 7.15–8.72 (9 H, m, aromatic), 8.95 and 12.50 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, d_6-DMSO-Me_4Si): δ 16.34 and 16.48 (2*C*H_3),18.43(*C*H_3),42.09(d,$^2J_{cp}$=2H_Z,P-C-*C*),44.23(d,$^1J_{cp}$=131H_Z, P-*C*), 53.14 and 53.43 (2 O*C*H_3), 62.66 and 62.88 (2 d, $^2J_{cp}$ = 7 H_Z, 2 PO*C*H_2), 116.29, 117.53, 123.69, 124.12, 126.10, 127.45, 129.70, 130.87, 135.01 and 156.40 (naphthol moiety), 127.17, 127.37, 130.13, 131.15, 133.62 and 136.08 (phenyl moiety), 169.12 (C=O), 170.49(d, $^2J_{CP}$ = 6 H_Z, C=O), 173.17 (d, $^3J_{CP}$ = 21 H_Z, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 20.31.

Dimethyl2-(dibutoxyphosphoryl)-3-[2-hydroxy-3-(2-methylphenyl-carbamoyl)naphthalen-1-yl]succinate **(4f):** White powder, yield 1.10 g (90%), m.p. 181–184°C, IR (KBr) (ν_{max} cm^{-1}): 3150 (OH), 1727 (C=O, ester), 1640 (C=O, amide). Analyses: Calcd. for $C_{32}H_{40}NO_9P$: C, 62.63; H, 6.57; N, 2.28%. Found: C, 62.70; H, 6.47; N, 2.30. MS (*m/z*,%): 613 (8). ^{1}H NMR (500 MHz, d_6-DMSO): δ 0.82 (6 H, t, 2 CH_3), 0.91 (4 H, sextet, 2 CH_2), 1.29 (4 H, quintet, 2 CH_2), 2.35 (3 H, s, C*H*$_3$), 3.70–3.78 (4 H, m, 2 POCH_2), 3.60 and 3.89 (6 H, 2 s, 2 OCH_3), 4.63 (1 H, dd, $^2J_{HP}$ = 21 Hz, $^3J_{HH}$ = 11 H_Z, CH), 5.34 (1 H, dd, $^3J_{HP}$ = 6 Hz, $^3J_{HH}$ = 11 H_Z, CH), 7.13–8.76 (9 H, m, aromatic), 8.80 and 12.47 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, d_6-DMSO-Me_4Si): δ 13.96 and 14.00 (2 *C*H_3), 18.46 (*C*H_3), 18.85 and 18.93 (2CH_2), 32.66 and 32.58 (2 d, $^3J_{CP}$ = 7 Hz, 2 CH_2), 42.11 (d, $^2J_{cp}$ = 2 H_Z, P–C–*C*), 44.63 (d, $^1J_{cp}$ = 131 H_Z, P–*C*), 53.09 and 53.42 (2 O*C*H_3), 66.32 and 66.57 (2 d, $^2J_{cp}$ = 7 H_Z, 2 PO*C*H_2), 116.24, 117.50, 123.61, 124.08, 126.14, 127.47, 129.66, 130.83, 135.06 and 156.43 (naphthol moiety), 127.15, 127.38, 130.13, 131.13, 134.01 and 136.05 (phenyl moiety), 169.10 (C=O), 170.45(d, $^2J_{CP}$ = 6 H_Z, C=O), 173.46 (d, $^3J_{CP}$ = 21 H_Z, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 21.37

General procedure for preparation of compounds **10a–d**

Dimethyl 2-[2-hydroxy-3-(phenylcarbamoyl)naphthalen-1-yl]-but-2-enedioate (**10a**)*:* To a magnetically stirred solution of 0.53 g of phenyl (3-hydroxynaphthalene)–2-carboxamide (2 mmol) and 0.28 g of DMAD (2 mmol) in 10 ml acetone was added a mixture of 0.53 g triphenylphosphine (2 mmol) in 2 ml acetone at room temperature. The reaction mixture was then allowed to stir for 24 h. The solvent was evaporated at reduced pressure. The residue was precipitated in a solution of diethyl ether-hexane. The solid was filtered and washed with diethyl ether to give the pure product.

Yellow powder, yield 92%, m.p. 179–181°C, IR (KBr) (ν_{max} cm^{-1}): 3305 OH), 1722 (C=O, ester), 1692 (C=O, amide). MS (*m/z*,%): 405 (7). ^{1}H NMR (500 MHz, δ, $CDCl_3$): 3.74 and 3.83 (6 H, 2 s, 2 OCH_3), 6.44 (1 H, s, CH), 7.21–8.75 (10 H, m, aromatic),). 10.17 and 12.33 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 51.78 and 52.06 (2 O*C*H_3), 130.17 (C), 139.20 (C), 117.21, 118.01, 124.46, 125.44, 127.24, 129.87, 129.95, 130.46, 135.40 and 155.09 (naphthol moiety), 122.00, 123.91, 129.21, 138.09 (phenyl moiety), 165.77 (C=O), 167.12 (C=O), 169.08 (C=O). Anal. Calcd. for $C_{23}H_{19}NO_6$: C, 68.14; H, 4.72; N, 3.46%. Found: C, 68.5; H, 4.45; N,3.65%.

Diethyl 2-[2-hydroxy-3-(phenylcarbamoyl)naphthalen-1-yl]-but-2-enedioate (**10b**)**:** Yellow powder, yield 90%, m.p. 168–170°C, IR (KBr) (ν_{max} cm^{-1}): 3390(OH), 1704 (C=O, ester), 1683 (C=O, amide). MS (*m/z*,%): 433 (10). ^{1}H NMR (500 MHz,,δ, $CDCl_3$): 1.24 and 1.35 (6 H, 2t, 2 CH_3), 4.18 and 4.31(4 H, 2q, 2 OCH_2), 6.42 (1 H, s, CH), 7.21–8.57 (10 H, m, aromatic), 10.17 and 12.31 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 13.71 and 13.94 (2 *C*H_3), 61.02 and 61.26 (2 O*C*H_2), 130.20 (C), 139.28 (C), 117.24, 118.26, 124.42, 125.42, 127.24, 129.78, 129.93, 130.39, 135.46 and 155.09 (naphthol moiety), 121.98, 124.00, 129.20, 138.12 (phenyl moiety), 165.34(C=O), 166.64(C=O), 169.24 (C=O). Anal. Calcd. for $C_{25}H_{23}NO_6$: C, 69.27; H, 5.35; N, 3.23%. Found: C, 69.40; H, 5.25; N, 3.3%.

Dimethyl 2-[2-hydroxy-3-(2-methylphenylcarbamoyl)naphthalen-1-yl]-but-2-enedioate (**10c**)**:** Yellow powder, yield 90%, m.p. 163–165°C, IR (KBr) (ν_{max} cm^{-1}): 3375 (OH), 1713 (C=O, ester), 1642 (C=O, amide). MS (*m/z*,%): 419 (9). ^{1}H NMR (500 MHz, δ, $CDCl_3$): 2.94 (3 H, s, C*H*$_3$), 3.51 and 3.73 (6 H, 2 s, 2 OCH_3), 6.45 (1 H, s, CH), 7.26–8.87 (9 H, m, aromatic), 10.11 and 12.41 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 17.81(*C*H_3), 51.45 and 52.59 (2 O*C*H_3), 129.90 (C), 138.85 (C), 116.69, 117.26, 123.61, 123.99, 126.66, 127.26, 128.90, 130.94, 135.39 and 154.52 (naphthol moiety), 127.05, 127.17, 129.04, 131.40, 133.03 and 135.40 (phenyl moiety), 164.66 (C=O), 166.73(C=O), 169.52 (C=O). Anal. Calcd. for $C_{24}H_{21}NO_6$: C, 68.73; H, 5.05; N, 3.34%. Found: C, 68.9; H, 4.95; N, 3.4%.

Diethyl 2-[2-hydroxy-3-(2-methylphenylcarbamoyl)naphthalen-1-yl]-but-2-enedioate (**10d**)**:** Yellow powder, yield 89%, m.p. 154–156°C, IR (KBr) (ν_{max} cm^{-1}): 3320(OH), 1719(C=O, ester), 1648(C=O, amide). MS (*m/z*,%): 447 (6). ^{1}H NMR (500 MHz, δ, $CDCl_3$): 0.99 and 1.28 (6 H, 2t, 2 CH_3), 2.50 (3 H, s, C*H*$_3$), 4.38 and 4.50 (4 H, 2q, 2 OCH_2), 6.30 (1 H, s, CH), 7.17–8.52 (9 H, m, aromatic), 9.03 and 11.80 (2 H, 2 s, NH and OH). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 14.09 and 14.46 (2 *C*H_3), 18.43 (*C*H_3), 61.13 and 62.80 (2 O*C*H_2), 131.04 (C), 140.42 (C), 117.02, 117.83, 122.86, 124.28, 125.25, 127.30, 129.54, 131.63, 135.60 and 154.00 (naphthol moiety), 126.37, 127.09, 129.69, 132.17, 134.84 and 138.11 (phenyl moiety), 165.13 (C=O), 166.68 (C=O), 168.66 (C=O). Anal. Calcd. for $C_{26}H_{25}NO_6$: C, 69.79; H, 5.63; N, 3.13%. Found: C, 69.9; H, 5.5; N,3.2%.

General procedure for preparation of compounds **14a–d**

Dimethyl 2-(methoxycarbonylmethyl)-4-oxo-3-phenyl-3,4-dihydro-2H-naphtho[2,3-e][1,3]oxazine-2-carboxylate (**14a**): A mixture of 0.53 g of *N*-phenyl-3-hydroxynaphthalene)–2-carboxamide (2 mmol) and 0.28 g of DMAD (2 mmol) in 10 ml acetone was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was purified by silica gel (Merck silica gel 60, 230–400 mesh) column chromatography using hexane-ethyl acetate as eluent. The solvent was removed under reduced pressure to afford the product.

Yellow powder, yield 92%, m.p. 161–163°C, IR (KBr) (ν_{max} cm^{-1}): 3458 (OH), 1744 (C=O, ester), 1673 (C=O, amide). MS (*m/z*,%): 405 (8). ^{1}H NMR (500 MHz,,δ, $CDCl_3$): 3.28 (2 H, AB quartet, $^2J_{HH}$ = 16 H_Z, CH_2), 3.42 and 3.72 (6 H, 2 s, 2 OCH_3), 7.46–8.59 (11 H, m, aromatic). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 42.84 (*C*H_2), 52.37 and 53.92 (2 O*C*H_3), 91.57 (C), 112.70, 118.48, 129.24, 129.47, 129.70, 129.98, 130.02, 131.24, 136.84 and 151.31(naphthol moiety), 125.69, 127.40, 130.85, 137.14 (phenyl moiety), 162.44 (C=O), 167.87 (C=O), 168.83 (C=O). Anal. Calcd. for $C_{23}H_{19}NO_6$: C, 68.14; H, 4.72; N, 3.46%. Found: C, 68.3; H, 4.70; N, 3.5%.

Diethyl 2-(methoxycarbonylmethyl)-4-oxo-3-phenyl-3,4-dihydro-2H-naphtho[2,3-e][1,3]oxazine-2-carboxylate (**14b**)**:** Yellow powder, yield 87%, m.p. 126–128°C, IR (KBr) (ν_{max} cm^{-1}): 3465 (OH), 1727 (C=O, ester),1673 (C=O, amide). MS (*m/z*,%): 433 (9). ^{1}H NMR (500 MHz, δ, $CDCl_3$): 1.05 and 1.11 (6 H, 2t, 2 CH_3), 3.27 (2 H, AB quartet, $^2J_{HH}$ = 16 H_Z, CH_2), 3.78–4.18 (4 H, m, 2 OCH_2), 7.47–8.53 (11 H, m, aromatic). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 13.62 and 13.67 (2CH_3), 42.38 (*C*H_2), 60.93 and 62.75 (2 O*C*H_2), 91.78 (C), 112.56, 119.21, 129.05, 129.23, 129.78, 129.92, 130.12, 131.43, 137.13 and 151.65(naphthol moiety), 125.71, 127.36, 131.64, 137.42 (phenyl moiety), 161.86 (C=O), 166.97 (C=O), 168.05 (C=O). Anal. Calcd. for $C_{25}H_{23}NO_6$: C, 69.27; H, 5.35; N, 3.23%. Found: C, 69.4; H, 5.24; N, 3.3%.

Dimethyl 2-(methoxycarbonylmethyl)-4-oxo-3-o-tolyl-3,4-dihydro-2H-naphtho[2,3-e][1,3]oxazine-2-carboxylate (**14c**)**:** Yellow powder, yield 93%, m.p. 158–160°C, IR (KBr) (ν_{max} cm^{-1}): 3470 (OH), 1730 (C=O, ester), 1675(C=O, amide). MS (*m/z*,%): 419 (9). ^{1}H NMR (500 MHz, δ, $CDCl_3$): 2.84 (3 H, s, C*H*$_3$), 3.30 (2 H, AB quartet, $^2J_{HH}$ = 16 H_Z, CH_2), 3.36 and 3.71 (6 H, 2 s, 2 OCH_3), 7.46–8.55 (10 H, m, aromatic). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 17.90 (*C*H_3), 42.40 (*C*H_2), 60.95 and 62.77 (2 O*C*H_3), 91.80 (C), 112.74, 119.21, 125.72, 126.81, 129.06, 129.95, 130.18, 131.36, 137.13 and 151.65(naphthol moiety), 127.37, 129.25, 131.12, 131.66, 136.41 and 138.21 (phenyl moiety), 161.61 (C=O), 168.06 (C=O), 169.04 (C=O). Anal. Calcd. for $C_{24}H_{21}NO_6$: C, 68.73; H, 5.05; N, 3.34%. Found: C, 68.8; H, 4.9; N, 3.4%.

Diethyl 2-(methoxycarbonylmethyl)-4-oxo-3-o-tolyl-3,4-dihydro-2H-naphtho[2,3-e][1,3]oxazine-2-carboxylate (**14d**)**:** Yellow powder, yield 90%, m.p. 125–127°C, IR (KBr) (ν_{max} cm^{-1}): 3430 (OH), 1745 (C=O, ester), 1681 (C=O, amide). MS (*m/z*,%): 447 (6). ^{1}H NMR (500 MHz,,δ, $CDCl_3$): 1.14 and 1.16 (6 H, 2t, 2 CH_3), 2.34 (3 H, s, C*H*$_3$), 3.10 (2 H, AB quartet, $^2J_{HH}$ = 16 H_Z, CH_2), 3.76–4.25 (4 H, m, 2 OCH_2), 7.29–8.62 (10 H, m, aromatic). ^{13}C NMR (125.8 MHz, δ, $CDCl_3$): 14.26 and 14.30 (2CH_3), 18.69 (*C*H_3), 42.30 (*C*H_2), 61.60 and 63.21 (2 O*C*H_2), 91.81 (C), 112.76, 118.90, 125.65, 127.41, 129.58, 129.94, 130.02, 131.29, 137.16 and 151.88(naphthol moiety), 127.21, 129.22, 130.83, 131.41, 136.16 and 138.04 (phenyl moiety), 161.92 (C=O), 167.35 (C=O), 168.50 (C=O). *Anal*. Calcd. for $C_{26}H_{25}NO_6$: C, 69.79; H, 5.63; N, 3.13%. Found: C, 69.9; H, 5.6; N, 3.2%.

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References

1 D.E.C. Corbridge, *Phosphorus an Outline of the Chemistry Biochemistry and Uses*, 5th edn, Elsevier, Amsterdam, 1995.
2 A.W. Johnson, W.C. Kaska, A.O. Starzewski and D.A. Dixon, *Ylides and Imines of Phosphorus*, John Wiley & Sons, 1993, pp.386-387.
3 I. Yavari and M. Anary-Abbasinejad, *Org. Biomo.l Chem.,* 2003, **3**, 560.
4 M. Anary-Abbasinejad and N. Ascarrian, *J Chem Res.*, 2007, 11.
5 M. Anary-Abbasinejad, N. Rostami, A. Parhami and A. Hassanabadi*, J. Chem. Res.,* 2007, 257.
6 M. Anary-Abbasinejad, A. Hassanabadi and H. Anaraki-Ardakani, *J. Chem. Res.*, 2007, 455.
7 M. Anary-Abbasinejad and A. Hassanabadi, *J. Chem. Res.*, 2007, 475.
8 M. Anary-Abbasinejad, H. Anaraki-Ardakani, A. Dehghan, A. Hassanabadi and M.R. Seyedmir, *J. Chem. Res., 2007*, in press.
9 M. Karplus, *J. Am. Chem. Soc.*, 1963, **88**, 2870.
10 C.A.G. Haasnot, F.A.A.M. De Leeuww and C. Altona, *Tetrahedron*, 1980, **36**, 2783.
11 E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy,* 3rd edn, VCH New York, 1990, p. 250.