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Efficient synthesis of functionalized spiro-2,5-dihydro-1,2-λ5-oxaphospholes

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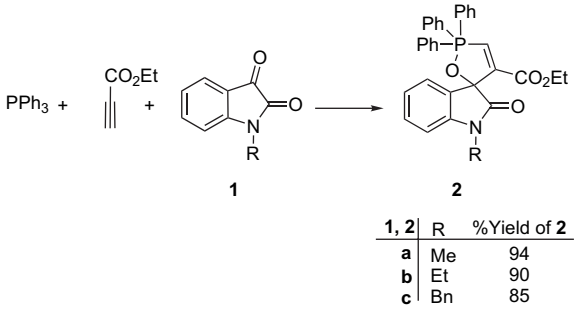
Abstract—The reaction of ethyl propiolate with triphenylphosphine (Ph_3P) in the presence of *N*-alkylisatins led to ethyl 2,2,2-triphenyl-2,5-dihydro-1,2-λ5-oxaphosphole-4-carboxylate-spiro-1-alkyl-1,3-dihydro-2*H*-indol-2-ones in good yield. The reaction of dialkyl acetylenedicarboxylates with Ph_3P in the presence of *N*-alkylisatins led to dialkyl 2,2,2-triphenyl-2,5-dihydro-1,2-λ5-oxaphosphole-3,4-dicarboxylate-spiro-1-alkyl-1,3-dihydro-2*H*-indol-2-ones and alkyl 4-(alkoxy)-5-oxo-2,5-dihydro-3-furancarboxylate-spiro-1-alkyl-1,3-dihydro-2*H*-indol-2-ones.

1. Introduction

Organophosphorus compounds are widely used in organic synthesis.[1] In recent years there has been increasing interest in the synthesis of organophosphorus compounds, that is, those bearing a carbon atom bound directly to a phosphorus atom. This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial, and synthetic uses. A large number of methods have appeared describing novel syntheses of organophosphorus compounds.[1–4] The successful attack by nucleophilic trivalent phosphines on a carbon atom is facilitated when the latter is conjugated with a carbonyl group, or when it is part of an otherwise activated unsaturated bond.[1–10]

2. Results and discussion

The reaction of Ph_3P with ethyl propiolate in the presence of *N*-alkylisatins led to ethyl 2,2,2-triphenyl-2,5-dihydro-1,2-λ5-oxaphosphole-4-carboxylate-spiro-1-alkyl-1,3-dihydro-2*H*-indol-2-ones **2** in 85–94% yield (Scheme 1).



1, 2	R	%Yield of 2
a	Me	94
b	Et	90
c	Bn	85

Scheme 1.

The structures of compounds **2a–c** were apparent from their mass spectra, which displayed in each case, the molecular ion peak at the appropriate *m*/*z* values. The ^1H and ^{13}C NMR spectroscopic data, as well as IR spectra, are in agreement with the proposed structures. The ^1H NMR spectrum of **2a** exhibited a singlet at δ=3.25 ppm arising from the NMe proton. The carbonyl groups' resonances in the ^{13}C NMR spectra of **2a** appear at δ=168.4 ($^3J_{CP}$=21.2 Hz) and 169.7 ppm. The ^{31}P NMR signal of **2a** was found at δ=−50.35 ppm. The mass spectrum of **2a** displayed the molecular ion peak at *m*/*z*=521, which is consistent with the 1:1:1 adduct of Ph_3P, ethyl propiolate, and *N*-methylisatin.

Mechanistically, it is conceivable that the reaction involves the initial formation of a 1,3-dipolar intermediate **3** between triphenylphosphine and ethyl propiolate, which reacts with the carbonyl group of *N*-alkylisatin to produce **4**. Cyclization of this zwitterionic intermediate leads to the spiro compound **2** (Scheme 2).

The reaction of Ph_3P and dialkyl acetylenedicarboxylates **5** in the presence of *N*-alkylisatins **1** proceeds smoothly in CH_2Cl_2 at ambient temperature to produce **6** and **7** in about 3:1 ratio (Scheme 3).

The reactions were carried out by mixing the acetylenic ester **5** with **1** and then Ph_3P was added slowly. The reactions were complete within 24 h. The structures of compounds **6** and **7** were apparent from their mass spectra, which displayed in each case, the molecular ion peak at appropriate *m*/*z* values.

Keywords: Ethyl propiolate; Triphenylphosphine; *N*-Alkylisatins; Oxaphosphole; Dialkyl acetylenedicarboxylates; Spiro butenolides.
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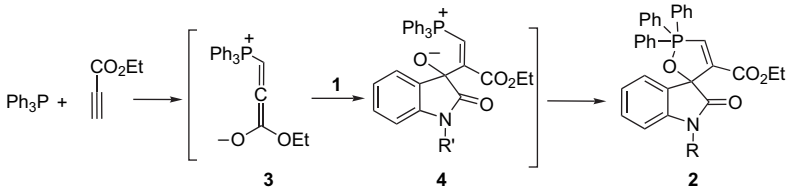
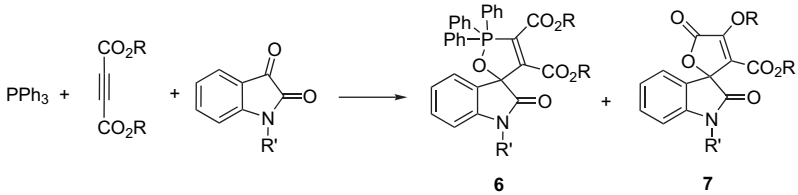


Scheme 2.



5	R
a	Me
b	Et

1	R'
a	Me
b	Bn
c	Et

6, 7	R	R'	% Yield	6:7 ratio
a	Me	Me	75	3:1
b	Et	Me	75	3:1
c	Me	Bn	70	7:3
d	Et	Bn	75	3:1
e	Me	Et	70	7:3
f	Et	Et	70	7:3

Scheme 3.

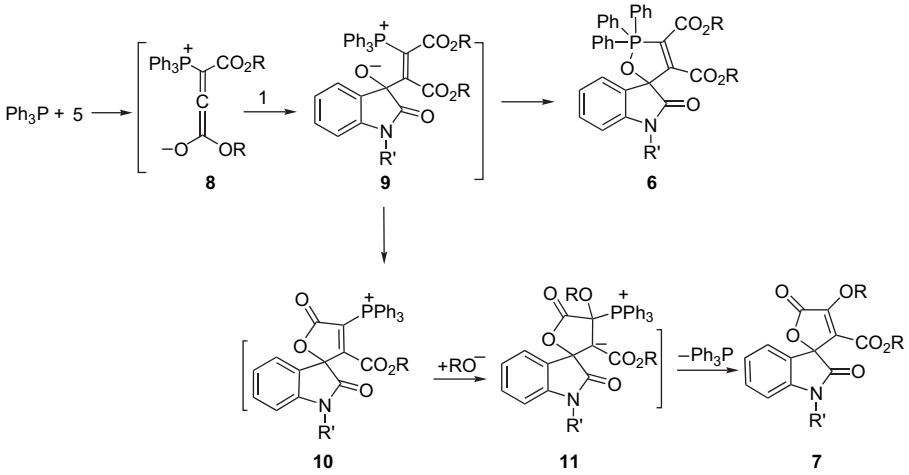
The ^{1}H and ^{13}C NMR spectroscopic data, as well as IR spectra, are in agreement with the proposed structures.

The ^{1}H NMR spectrum of **6a** exhibited three singlets readily recognized as arising from the NMe (δ=3.27 ppm) and two methoxy (δ=3.69 and 3.98 ppm) protons. The carbonyl resonances in the ^{13}C NMR spectrum of **6a** appear at 163.0 (d, $^{2}J_{CP}$=24.2 Hz), 168.4 (d, $^{3}J_{CP}$=21.2 Hz), and 169.7 ppm. The ^{31}P NMR signal of **6a** was found at δ=−79.45 ppm. The mass spectrum of **6a** displayed the molecular ion peak at *m*/*z*=565, which is consistent with the 1:1:1 adduct of Ph_3P, DMAD, and *N*-methylisatin.

The ^{1}H NMR spectrum of **7a** exhibited three singlets for NMe (δ=3.26 ppm) and methoxy (δ=3.58 and 4.35 ppm) protons. The carbonyl groups' resonances in the ^{13}C NMR spectrum of **7a** appear at δ 160.5, 165.4, and 169.9 ppm. The mass spectrum of **7a** displayed the molecular ion peak at *m*/*z*=303.

A tentative mechanism for this transformation is proposed in Scheme 4. It is conceivable that the reaction involves the initial formation of a 1,3-dipolar intermediate **8** between Ph_3P and the acetylenic compound,[7] which reacts with the carbonyl group of *N*-alkylisatin to produce **9**. Cyclization of this zwitterionic intermediate leads to the spiro compound **6**. Another pathway may be envisaged, involving intermediate **10** and its subsequent conversion to the spiro butenolide **7** (see Scheme 4).

In summary, the reaction of ethyl propiolate with *N*-alkylisatins in the presence of Ph_3P led to ethyl 2,2,2-triphenyl-2,5-dihydro-1,2-λ^{5}-oxaphosphole-4-carboxylate-spiro-1-alkyl-1,3-dihydro-2*H*-indol-2-ones of potential synthetic interest. Under similar conditions, dialkyl acetylenedicarboxylates react with *N*-alkylisatins to produce dialkyl 2,2,2-triphenyl-2,5-dihydro-1,2-λ^{5}-oxaphosphole-3,4-dicarboxylate-spiro-1-alkyl-1,3-dihydro-2*H*-indol-2-ones and alkyl 4-(alkoxy)-5-oxo-2,5-dihydro-3-furancarboxylate-spiro-1-alkyl-



Scheme 4.

1,3-dihydro-2*H*-indol-2-ones in nearly 3:1 ratio. The present procedure has the advantage that the reaction is performed under neutral conditions, and the starting material can be used without any activation or modification.

3. Experimental

3.1. General

Ethyl propiolate, Ph_3P, and **5** were obtained from *Fluka* and were used without further purification. Alkylisatins were prepared according to the literature procedure.[11] Mp: *Electrothermal-9100* apparatus. IR spectra: *Shimadzu IR-460* spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra: Bruker DRX-500 Avance instrument; in $CDCl_3$ at 500.1, 125.7, and 202.4 MHz, respectively; δ in parts per million, J in hertz. EIMS (70 eV): Finnigan-MAT-8430 mass spectrometer, in *m*/*z*. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer.

3.2. General procedure for the preparation of compounds 2a–c

To a stirred solution of ethyl propiolate (2 mmol) and *N*-alkylisatin (2 mmol) in CH_2Cl_2 (15 mL) was added Ph_3P (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 separated by silica gel (Merck 230–400 mesh) column chromatography using hexane–ethyl acetate mixture as an eluant.

3.2.1. Ethyl 1,2-dihydro-2-oxo-1-methyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-4-carboxylate (2a). Yellow crystals, mp 210–212 °C, 0.98 g, yield 94%. IR (KBr) (ν_{max}/cm^{-1}): 1726, 1682, 1459, 1110, 1031, and 1009. MS, *m*/*z* (%): 521 (M$^+$, 5), 476 (66), 278 (85), 243 (64), 201 (62), 111 (34), 169 (100), 45 (100). Anal. Calcd for $C_{32}H_{28}NO_4P$ (521.5): C, 73.69; H, 5.41; N, 2.69. Found: C, 73.70; H, 5.40; N, 2.70%. ^1H NMR: δ 1.25 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 3.25 (3H, s, NMe), 4.17 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 6.89 (1H, d, $^2J_{HP}$=22.7 Hz, CH), 7.09 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.32 (1H, t, $^3J_{HH}$=7.3 Hz, CH), 7.42 (1H, d, $^3J_{HH}$=7.3 Hz, CH), 7.48 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.52–7.78 (15H, m, 15CH). ^{13}C NMR: δ 14.3 (Me), 28.1 (NMe), 61.7 (OCH_2), 91.2 (d, $^2J_{CP}$=49.1 Hz, C_{ipso}), 116.7 (CH), 120.3 (CH), 123.6 (CH), 128.1 (CH), 128.6 (d, $^3J_{CP}$=10.2 Hz, C), 129.2 (d, $^3J_{CP}$=21.1 Hz, 6CH), 129.4 (3CH), 131.9 (d, $^2J_{CP}$=31.9 Hz, CH), 135.1 (d, $^1J_{CP}$=230.1 Hz, 3C), 149.3 (d, $^1J_{CP}$=192.3 Hz, CH), 150.4 (C), 157.3 (d, $^2J_{CP}$=19.3 Hz, C), 168.4 (d, $^3J_{CP}$=21.2 Hz, C=O), 169.7 (d, $^3J_{CP}$=17.4 Hz, C=O). ^{31}P NMR: δ −50.35.

3.2.2. Ethyl 1,2-dihydro-2-oxo-1-ethyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-4-carboxylate (2b). Yellow powder, mp 196–198 °C, 0.96 g, yield 90%. IR (KBr) (ν_{max}/cm^{-1}): 1727, 1680, 1450, 1100, 1029, and 1010. MS, *m*/*z* (%): 535 (M$^+$, 15), 490 (74), 461 (54), 278 (68), 257 (62), 175 (34), 74 (46), 45 (94). Anal. Calcd for $C_{33}H_{30}NO_4P$ (535.6): C, 74.01; H, 5.65; N, 2.62. Found: C, 74.00; H, 5.60; N, 2.60%. ^1H NMR: δ 1.24 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.37 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 4.13 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.35 (2H, m, CH_2), 6.75 (1H, d, $^2J_{PH}$=25.4 Hz, CH), 7.34 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.42 (1H, t, $^3J_{HH}$=7.2 Hz, CH), 7.50 (1H, d, $^3J_{HH}$=7.3 Hz, CH), 7.73 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.45–7.84 (15H, m, 15CH). ^{13}C NMR: δ 13.3 (Me), 14.0 (Me), 38.4 (CH_2), 62.1 (OCH_2), 93.2 (d, $^2J_{CP}$=35.4 Hz, C_{ipso}), 118.3 (CH), 120.4 (CH), 124.2 (CH), 127.4 (CH), 127.9 (d, $^3J_{CP}$=8.0 Hz, C), 128.4 (d, $^3J_{CP}$=21.1 Hz, 6CH), 129.1 (3CH), 132.0 (d, $^2J_{CP}$=31.9 Hz, 6CH), 135.4 (d, $^1J_{CP}$=226.5 Hz, 3C), 144.1 (d, $^1J_{CP}$=194.1 Hz, CH), 149.2 (C), 154.2 (d, $^2J_{CP}$=15.4 Hz, C), 166.5 (d, $^3J_{CP}$=21.2 Hz, C=O), 168.7 (d, $^3J_{CP}$=19.8 Hz, C=O). ^{31}P NMR: δ −52.42.

3.2.3. Ethyl 1,2-dihydro-2-oxo-1-benzyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-4-carboxylate (2c). Pale yellow crystals, mp 223–225 °C, 1.01 g, yield 85%. IR (KBr) (ν_{max}/cm^{-1}): 1730, 1685, 1462, 1210, 1054, and 1022. MS, *m*/*z* (%): 597 (M$^+$, 10), 506 (70), 319 (64), 278 (64), 217 (62), 91 (96), 45 (100). Anal. Calcd for $C_{38}H_{32}NO_4P$ (597.65): C, 76.37; H, 5.40; N, 2.34. Found: C, 76.40; H, 5.40; N, 2.35%. ^1H NMR: δ 1.23 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 4.24 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.82 (2H, m, CH_2), 6.94 (1H, d, $^2J_{PH}$=20.8 Hz, CH), 7.15 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.26–7.29 (3H, m, 3CH), 7.34 (2H, d, $^3J_{HH}$=7.2 Hz, 2CH), 7.37 (1H, t, $^3J_{HH}$=7.2 Hz, CH), 7.44 (1H, d, $^3J_{HH}$=7.3 Hz, CH), 7.45–7.80 (16H, m, 16CH). ^{13}C NMR: δ 14.1 (Me), 49.2 (CH_2), 61.4 (OCH_2), 91.7 (d, $^2J_{CP}$=30.2 Hz, C_{ipso}), 117.4 (CH), 120.0 (CH), 122.4 (2CH), 123.9 (CH), 125.8 (CH), 127.9 (2CH), 128.2 (CH), 128.6 (d, $^3J_{CP}$=9.4 Hz, C), 129.1 (d, $^3J_{CP}$=18.5 Hz, 6CH), 129.9 (3CH), 132.4 (d, $^2J_{CP}$=28.4 Hz, 6CH), 135.6 (C), 137.4 (d, $^1J_{CP}$=230.2 Hz, 3C), 145.4 (d, $^1J_{CP}$=201.3 Hz, CH), 150.4 (C), 157.1 (d, $^2J_{CP}$=16.2 Hz, C), 169.5 (d, $^3J_{CP}$=23.5 Hz, C=O), 170.1 (d, $^3J_{CP}$=20.1 Hz, C=O). ^{31}P NMR: δ −59.58.

3.3. General procedure for the preparation of compounds 6a–f and 7a–f

To a stirred solution of dialkyl acetylenedicarboxylate (2 mmol) and *N*-alkylisatin (2 mmol) in CH_2Cl_2 (15 mL) was added Ph_3P (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 separated by silica gel (Merck 230–400 mesh) column chromatography using hexane–ethyl acetate mixture as an eluant.

3.3.1. Dimethyl 1,2-dihydro-2-oxo-1-methyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-3,4-dicarboxylate (6a). Pale yellow crystals, mp 195–197 °C, 0.85 g, yield 75%. IR (KBr) (ν_{max}/cm^{-1}): 1752, 1732, 1672, 1478, 1135, 1097, and 1019. MS, *m*/*z* (%): 565 (M$^+$, 15), 533 (85), 502 (72), 403 (54), 278 (96), 161 (38), 146 (88), 31 (100). Anal. Calcd for $C_{33}H_{28}NO_6P$ (565.56): C, 70.08; H, 4.99; N, 2.48. Found: C, 70.10; H, 5.00; N, 2.45%. ^1H NMR: δ 3.27 (3H, s, NMe), 3.69 (3H, s, OMe), 3.98 (3H, s, OMe), 6.91 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.08 (1H, t, $^3J_{HH}$=7.3 Hz, CH), 7.11 (1H, d, $^3J_{HH}$=7.3 Hz, CH), 7.43 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.47–7.84 (15H, m, 15CH). ^{13}C NMR: δ 26.9 (NMe), 51.7 (OMe), 52.3 (OMe), 90.1 (d, $^2J_{CP}$=51.2 Hz, C_{ipso}), 116.7 (CH), 120.3 (CH), 123.6 (CH), 128.1 (CH), 128.6 (d, $^3J_{CP}$=22.4 Hz, C), 129.2 (d, $^3J_{CP}$=21.1 Hz, 6CH), 129.4 (3CH), 131.9 (d, $^2J_{CP}$=31.9 Hz, 6CH), 135.1 (d, $^1J_{CP}$=230.1 Hz,

3C), 149.3 (C), 150.4 (d, $^1J_{CP}$=192.3 Hz, C), 163.0 (d, $^2J_{CP}$=24.2 Hz, C=O), 165.1 (C), 168.4 (d, $^3J_{CP}$=21.2 Hz, C=O), 169.7 (C=O). ^{31}P NMR: δ −79.45.

3.3.2. Diethyl 1,2-dihydro-2-oxo-1-methyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-3,4-dicarboxylate (6b). Yellow powder, mp 190–192 °C, 0.89 g, yield 75%. IR (KBr) (ν_{max}/cm^{-1}): 1727, 1720, 1643, 1478, 1166, 1086, and 1004. MS, *m*/*z* (%): 593 (M$^+$, 10), 548 (82), 503 (76), 315 (54), 278 (96), 161 (46), 146 (88), 45 (100). Anal. Calcd for $C_{35}H_{32}NO_6P$ (593.6): C, 70.82; H, 5.43; N, 2.36. Found: C, 70.80; H, 5.40; N, 2.35%. ^{1}H NMR: δ 1.23 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.48 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 3.25 (3H, s, NMe), 3.84 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.08 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 6.95 (1H, t, $^3J_{HH}$=7.2 Hz, CH), 7.08 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.33 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.35–7.72 (16H, m, 16CH). ^{13}C NMR: δ 13.0 (Me), 13.2 (Me), 26.4 (NMe), 61.4 (OCH_2), 62.4 (OCH_2), 92.0 (d, $^2J_{CP}$=49.5 Hz, C_{ipso}), 116.2 (CH), 119.5 (CH), 122.9 (CH), 127.9 (CH), 128.4 (d, $^3J_{CP}$=23.9 Hz, C), 130.1 (d, $^3J_{CP}$=20.1 Hz, 6CH), 130.5 (3CH), 132.0 (d, $^2J_{CP}$=32.9 Hz, 6CH), 134.9 (d, $^1J_{CP}$=230.1 Hz, 3C), 149.2 (C), 150.4 (d, $^1J_{CP}$= 195.3 Hz, C), 162.9 (d, $^2J_{CP}$=23.6 Hz, C=O), 166.1 (C), 168.2 (d, $^3J_{CP}$=23.2 Hz, C=O), 169.2 (C=O). ^{31}P NMR: δ −75.45.

3.3.3. Dimethyl 1,2-dihydro-2-oxo-1-benzyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-3,4-dicarboxylate (6c). Pale yellow crystals, mp 178–180 °C, 0.89 g, yield 70%. IR (KBr) (ν_{max}/cm^{-1}): 1725, 1720, 1642, 1472, 1165, 1090, and 1012. MS, *m*/*z* (%): 641 (M$^+$, 10), 610 (84), 579 (74), 368 (54), 278 (96), 237 (46), 146 (88), 91 (96), 31 (100). Anal. Calcd for $C_{39}H_{32}NO_6P$ (641.66): C, 73.00; H, 5.03; N, 2.18. Found: C, 73.00; H, 5.05; N, 2.20%. ^{1}H NMR: δ 3.75 (3H, s, OMe), 4.11 (3H, s, OMe), 4.80 (1H, d, $^2J_{HH}$=15.6 Hz, CH), 5.01 (1H, d, $^2J_{HH}$=15.6 Hz, CH), 7.15 (1H, d, $^3J_{HH}$=7.4 Hz, CH), 7.30 (1H, t, $^3J_{HH}$=7.5 Hz, CH), 7.36 (1H, d, $^3J_{HH}$=7.5 Hz, CH), 7.38 (2H, t, $^3J_{HH}$=7.5 Hz, 2CH), 7.45 (2H, t, $^3J_{HH}$=7.7 Hz, 2CH), 7.54 (2H, d, $^3J_{HH}$=7.5 Hz, 2CH), 7.62–7.84 (15H, m, 15CH). ^{13}C NMR: δ 46.2 (NCH_2), 51.4 (OMe), 52.2 (OMe), 89.3 (d, $^2J_{CP}$=47.8 Hz, C_{ipso}), 116.5 (CH), 119.1 (CH), 123.4 (2CH), 123.6 (CH), 125.9 (CH), 127.7 (2CH), 128.3 (CH), 128.5 (d, $^3J_{CP}$=24.2 Hz, C), 128.9 (d, $^3J_{CP}$=20.1 Hz, 6CH), 130.2 (3CH), 132.4 (d, $^2J_{CP}$=34.2 Hz, 6CH), 135.9 (C), 136.2 (d, $^1J_{CP}$=234.5 Hz, 3C), 148.4 (C), 151.2 (d, $^1J_{CP}$=190.1 Hz, C), 162.4 (d, $^2J_{CP}$=26.5 Hz, C=O), 164.8 (C), 167.5 (d, $^3J_{CP}$=20.3 Hz, C=O), 169.5 (C=O). ^{31}P NMR: δ −44.2.

3.3.4. Diethyl 1,2-dihydro-2-oxo-1-benzyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-3,4-dicarboxylate (6d). Yellow crystals, mp 196–198 °C, 1.00 g, yield 75%. IR (KBr) (ν_{max}/cm^{-1}): 1730, 1723, 1642, 1472, 1165, 1090, and 1014. MS, *m*/*z* (%): 669 (M$^+$, 15), 624 (82), 579 (74), 391 (52), 278 (96), 237 (46), 146 (88), 91 (96), 45 (100). Anal. Calcd for $C_{41}H_{36}NO_6P$ (669.71): C, 73.53; H, 5.42; N, 2.09. Found: C, 73.50; H, 5.40; N, 2.10%. ^{1}H NMR: δ 0.84 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.48 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 3.84 (2H, q, $^3J_{HH}$= 7.2 Hz, OCH_2), 4.08 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.74 (1H, d, $^2J_{HH}$=15.2 Hz, CH), 4.96 (1H, d, $^2J_{HH}$=15.2 Hz, CH), 6.91 (1H, d, $^3J_{HH}$=7.8 Hz, CH), 7.05 (1H, t, $^3J_{HH}$=7.5 Hz, CH), 7.13 (1H, d, $^3J_{HH}$=7.5 Hz, CH), 7.26–7.33 (15H, m, 15CH), 7.28 (2H, t, $^3J_{HH}$=8.1 Hz, 2CH), 7.34 (2H, t, $^3J_{HH}$=7.7 Hz, 2CH), 7.41 (2H, d, $^3J_{HH}$=7.5 Hz, 2CH). ^{13}C NMR: δ 13.4 (Me), 13.6 (Me), 44.6 (NCH_2), 61.1 (OCH_2), 62.4 (OCH_2), 88.4 (d, $^2J_{CP}$=43.9 Hz, C_{ipso}), 117.7 (CH), 120.0 (CH), 122.6 (2CH), 123.2 (CH), 126.7 (CH), 127.5 (2CH), 128.2 (CH), 128.8 (d, $^3J_{CP}$=25.1 Hz, C), 129.5 (d, $^3J_{CP}$=19.6 Hz, 6CH), 129.8 (3CH), 131.8 (d, $^2J_{CP}$=31.4 Hz, 6CH), 135.2 (C), 136.8 (d, $^1J_{CP}$=236.2 Hz, 3C), 149.2 (C), 150.1 (d, $^1J_{CP}$=198.6 Hz, C), 161.1 (d, $^2J_{CP}$=23.1 Hz, C=O), 165.7 (C), 167.3 (d, $^3J_{CP}$=18.7 Hz, C=O), 170.4 (C=O). ^{31}P NMR: δ −46.41.

3.3.5. Dimethyl 1,2-dihydro-2-oxo-1-ethyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-3,4-dicarboxylate (6e). Yellow crystals, mp 184–186 °C, 0.81 g, yield 70%. IR (KBr) (ν_{max}/cm^{-1}): 1722, 1720, 1638, 1452, 1194, 1066, and 1004. MS, *m*/*z* (%): 579 (M$^+$, 15), 548 (52), 517 (46), 301 (86), 278 (96), 175 (64), 146 (86), 31 (100). Anal. Calcd for $C_{34}H_{30}NO_6P$ (579.59): C, 70.46; H, 5.22; N, 2.42. Found: C, 70.50; H, 5.20; N, 2.40%. ^{1}H NMR: δ 1.36 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 3.56 (3H, s, OMe), 3.86 (3H, s, OMe), 4.39 (2H, q, $^3J_{HH}$=7.2 Hz, NCH_2), 7.32 (1H, d, $^3J_{HH}$=7.2 Hz, CH), 7.41 (1H, t, $^3J_{HH}$= 7.3 Hz, CH), 7.46 (1H, d, $^3J_{HH}$=7.3 Hz, CH), 7.51–7.84 (15H, m, 15CH), 7.76 (1H, d, $^3J_{HH}$=7.2 Hz, CH). ^{13}C NMR: δ 13.4 (Me), 38.2 (CH_2), 51.3 (OMe), 52.3 (OMe), 91.4 (d, $^2J_{CP}$=54.3 Hz, C_{ipso}), 118.7 (CH), 120.2 (CH), 124.5 (CH), 127.4 (CH), 128.2 (d, $^3J_{CP}$=21.4 Hz, C), 128.9 (d, $^3J_{CP}$=20.4 Hz, 6CH), 129.1 (3CH), 131.7 (d, $^2J_{CP}$=33.4 Hz, 6CH), 135.4 (d, $^1J_{CP}$=229.8 Hz, 3C), 148.4 (C), 151.4 (d, $^1J_{CP}$=196.4 Hz, C), 163.1 (d, $^2J_{CP}$=26.3 Hz, C=O), 165.4 (C), 168.2 (d, $^3J_{CP}$=21.9 Hz, C=O), 169.1 (C=O). ^{31}P NMR: δ −69.15.

3.3.6. Diethyl 1,2-dihydro-2-oxo-1-ethyl-spiro-[3*H*-indol-2,2,2-triphenyl-2,5-dihydro-1,2-λ^5-oxaphosphole]-3,4-dicarboxylate (6f). Orange powder, mp 192–194 °C, 0.84 g, yield 70%, IR (KBr) (ν_{max}/cm^{-1}): 1720, 1717, 1643, 1457, 1178, 1094, and 1019. MS, *m*/*z* (%): 607 (M$^+$, 5), 562 (34), 517 (18), 329 (84), 278 (88), 178 (56), 146 (76), 45 (100). Anal. Calcd for $C_{36}H_{34}NO_6P$ (607.64): C, 71.16; H, 5.64; N, 2.31. Found: C, 71.20; H, 5.60; N, 2.30%. ^{1}H NMR: δ 1.22 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.25 (3H, t, $^3J_{HH}$= 7.2 Hz, Me), 1.27 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 4.15 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.27 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.54 (2H, q, $^3J_{HH}$=7.2 Hz, NCH_2), 7.30 (1H, d, $^3J_{HH}$= 7.2 Hz, CH), 7.36 (1H, t, $^3J_{HH}$=7.3 Hz, CH), 7.42 (1H, d, $^3J_{HH}$=7.3 Hz, CH), 7.54–7.80 (15H, m, 15CH), 7.75 (1H, d, $^3J_{HH}$=7.2 Hz, CH). ^{13}C NMR: δ 13.2 (Me), 13.9 (Me), 14.2 (Me), 36.4 (NCH_2), 61.7 (OCH_2), 62.4 (OCH_2), 86.3 (d, $^2J_{CP}$=49.6 Hz, C_{ipso}), 118.4 (CH), 121.2 (CH), 124.0 (CH), 127.9 (CH), 128.6 (d, $^3J_{CP}$=22.5 Hz, C), 129.2 (d, $^3J_{CP}$=19.8 Hz, 6CH), 129.4 (3CH), 132.0 (d, $^2J_{CP}$=32.4 Hz, 6CH), 135.1 (d, $^1J_{CP}$=235.1 Hz, 3C), 149.3 (C), 150.4 (d, $^1J_{CP}$=194.2 Hz, C), 163.0 (d, $^2J_{CP}$=26.4 Hz, C=O), 165.1 (C), 168.4 (d, $^3J_{CP}$=23.7 Hz, C=O), 169.7 (C=O). ^{31}P NMR: δ −70.54.

3.3.7. Methyl 1,2-dihydro-2-oxo-1-methyl-spiro-[3*H*-indol-4-(methoxy)-5-oxo-2,5-dihydro]-3-furancarboxylate (7a). Yellow crystals, mp 154–156 °C, 0.15 g, yield 25%. IR

(KBr) (ν_{max}/cm^{-1}): 1770, 1732, and 1696. MS, *m/z* (%): 303 (M^+, 5), 272 (96), 241 (52), 161 (58), 157 (34), 142 (22), 31 (100). Anal. Calcd for $C_{15}H_{13}NO_6$ (303.27): C, 59.41; H, 4.32; N, 4.62. Found: C, 59.40; H, 4.30; N, 4.60%. ^{1}H NMR: δ 3.26 (3H, s, NMe), 3.58 (3H, s, OMe), 4.35 (3H, s, OMe), 6.91 (1H, d, $^3J_{HH}$=7.8 Hz, CH), 7.05 (1H, dd, $^3J_{HH}$=7.5, 7.5 Hz, CH), 7.12 (1H, d, $^3J_{HH}$=7.4 Hz, CH), 7.13 (1H, dd, $^3J_{HH}$=7.5, 7.4 Hz, CH). ^{13}C NMR: δ 26.9 (NMe), 52.2 (OMe), 60.3 (OMe), 77.0 (C_{ipso}), 109.0 (CH), 119.2 (C), 122.9 (C), 123.3 (CH), 124.2 (CH), 131.7 (CH), 144.9 (CN), 149.3 (C), 160.5 (C=O), 165.4 (C=O), 169.9 (C=O).

3.3.8. Ethyl 1,2-dihydro-2-oxo-1-methyl-spiro-[3*H*-indol-4-(ethoxy)-5-oxo-2,5-dihydro]-3-furancarboxylate (7b). Yellow crystals, mp 160–162 °C, 0.16 g, yield 25%. IR (KBr) (ν_{max}/cm^{-1}): 1775, 1722, and 1648. MS, *m/z* (%): 331 (M^+, 15), 286 (94), 241 (56), 175 (54), 157 (36), 45 (100). Anal. Calcd for $C_{17}H_{17}NO_6$ (331.32): C, 61.63; H, 5.17; N, 4.23. Found: C, 61.60; H, 5.20; N, 4.20%. ^{1}H NMR: δ 1.26 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.41 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 3.45 (3H, s, NMe), 3.66 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.03 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 6.53 (1H, d, $^3J_{HH}$=7.8 Hz, CH), 7.04 (1H, dd, $^3J_{HH}$=7.5, 7.5 Hz, CH), 7.08 (1H, d, $^3J_{HH}$=7.4 Hz, CH), 7.32 (1H, dd, $^3J_{HH}$=7.5, 7.4 Hz, CH). ^{13}C NMR: δ 13.3 (Me), 13.9 (Me), 32.3 (NMe), 60.4 (OCH_2), 69.6 (OCH_2), 86.7 (C_{ipso}), 111.3 (CH), 116.1 (C), 121.7 (C), 127.7 (CH), 128.3 (CH), 129.3 (C), 144.5 (C), 145.6 (C), 159.8 (C=O), 160.2 (C=O), 167.6 (C=O).

3.3.9. Methyl 1,2-dihydro-2-oxo-1-benzyl-spiro-[3*H*-indol-4-(methoxy)-5-oxo-2,5-dihydro]-3-furancarboxylate (7c). The procedure for the preparation of **7c** was similar to that for **7a**. Pale yellow crystals, mp 165–167 °C, 0.22 g, yield 30%. IR (KBr) (ν_{max}/cm^{-1}): 1779, 1719, and 1643. MS, *m/z* (%): 379 (M^+, 10), 348 (66), 317 (68), 237 (82), 146 (78), 91 (100), 31 (100). Anal. Calcd for $C_{21}H_{17}NO_6$ (379.37): C, 66.49; H, 4.52; N, 3.69. Found: C, 66.50; H, 4.50; N, 3.70%. ^{1}H NMR: δ 3.48 (3H, s, OMe), 4.37 (3H, s, OMe), 4.78 (1H, d, $^2J_{HH}$=15.7 Hz, CH), 5.08 (1H, d, $^2J_{HH}$=15.7 Hz, CH), 6.78 (1H, d, $^3J_{HH}$=7.9 Hz, CH), 7.03 (1H, t, $^3J_{HH}$=7.5 Hz, CH), 7.13 (1H, d, $^3J_{HH}$=7.5 Hz, CH), 7.28 (2H, t, $^3J_{HH}$=8.1 Hz, 2CH), 7.35 (2H, t, $^3J_{HH}$=7.7 Hz, 2CH), 7.38 (2H, d, $^3J_{HH}$=7.5 Hz, 2CH). ^{13}C NMR: δ 44.7 (CH_2), 52.2 (OMe), 60.5 (OMe), 81.7 (C_{ipso}), 110.2 (CH), 119.0 (C), 123.1 (C), 123.5 (CH), 124.4 (2CH), 127.5 (2CH), 127.9 (C), 128.9 (2CH), 131.7 (CH), 144.1 (C), 149.8 (C), 160.5 (C=O), 165.9 (C=O), 170.2 (C=O).

3.3.10. Ethyl 1,2-dihydro-2-oxo-1-benzyl-spiro-[3*H*-indol-4-(ethoxy)-5-oxo-2,5-dihydro]-3-furancarboxylate (7d). Pale yellow crystals, mp 152–154 °C, 0.20 g, yield 25%. IR (KBr) (ν_{max}/cm^{-1}): 1770, 1730, and 1656. MS, *m/z* (%): 407 (M^+, 15), 362 (62), 317 (84), 237 (82), 170 (78), 91 (100), 45 (100). Anal. Calcd for $C_{23}H_{21}NO_6$ (407.42): C, 67.81; H, 5.20; N, 3.44. Found: C, 67.80; H, 5.20; N, 3.40%. ^{1}H NMR: δ 0.82 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.47 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 3.82 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.11 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.70 (1H, d, $^2J_{HH}$=15.7 Hz, CH), 4.95 (1H, d, $^2J_{HH}$=15.7 Hz, CH), 6.78 (1H, d, $^3J_{HH}$=7.8 Hz, CH), 7.03 (1H, t, $^3J_{HH}$=7.5 Hz, CH), 7.13 (1H, d, $^3J_{HH}$=7.5 Hz, CH), 7.28 (2H, t, $^3J_{HH}$=8.1 Hz, 2CH), 7.34 (2H, t, $^3J_{HH}$=7.7 Hz, 2CH), 7.37 (2H, d, $^3J_{HH}$=7.5 Hz, 2CH). ^{13}C NMR: δ 13.5 (Me), 15.3 (Me), 44.7 (NCH_2), 62.4 (OCH_2), 69.5 (OCH_2), 81.8 (C_{ipso}), 109.9 (CH), 119.3 (C), 123.4 (C), 123.5 (CH), 124.4 (2CH), 127.5 (2CH), 127.9 (C), 128.1 (2CH), 131.6 (CH), 144.2 (C), 149.5 (C), 156.9 (C=O), 165.7 (C=O), 170.4 (C=O).

3.3.11. Methyl 1,2-dihydro-2-oxo-1-ethyl-spiro-[3*H*-indol-4-(methoxy)-5-oxo-2,5-dihydro]-3-furancarboxylate (7e). Pale yellow crystals, 0.19 g, yield 30%, mp 159–161 °C. IR (KBr) (ν_{max}/cm^{-1}): 1779, 1727, and 1643. MS, *m/z* (%): 317 (M^+, 15), 286 (68), 255 (64), 175 (82), 142 (78), 31 (100). Anal. Calcd for $C_{16}H_{15}NO_6$ (317.29): C, 60.57; H, 4.76; N, 4.41. Found: C, 60.55; H, 4.70; N, 4.40%. ^{1}H NMR: δ 1.29 (3H, t, $^3J_{HH}$=7.1 Hz, Me), 3.57 (3H, s, OMe), 3.73–3.88 (2H, m, NCH_2), 4.35 (3H, s, OMe), 6.91 (1H, d, $^3J_{HH}$=7.8 Hz, CH), 7.05 (1H, dd, $^3J_{HH}$=7.5, 7.5 Hz, CH), 7.12 (1H, d, $^3J_{HH}$=7.4 Hz, CH), 7.13 (1H, dd, $^3J_{HH}$=7.5, 7.4 Hz, CH). ^{13}C NMR: δ 12.6 (Me), 35.9 (CH_2), 52.6 (OMe), 60.9 (OMe), 82.5 (C_{ipso}), 109.6 (CH), 119.5 (C), 123.5 (C), 123.6 (CH), 124.6 (CH), 132.2 (CH), 144.4 (CN), 149.9 (C), 160.9 (C=O), 166.0 (C=O), 167.0 (C=O).

3.3.12. Ethyl 1,2-dihydro-2-oxo-1-ethyl-spiro-[3*H*-indol-4-(ethoxy)-5-oxo-2,5-dihydro]-3-furancarboxylate (7f). Orange powder, mp 170–172 °C, 0.21 g, yield 30%. IR (KBr) (ν_{max}/cm^{-1}): 1776, 1728, and 1642. MS, *m/z* (%): 345 (M^+, 5), 300 (68), 255 (68), 175 (82), 170 (28), 45 (100). Anal. Calcd for $C_{18}H_{19}NO_6$ (345.35): C, 62.60; H, 5.55; N, 4.06. Found: C, 62.60; H, 5.50; N, 4.10%. ^{1}H NMR: δ 0.97 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.07 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 1.27 (3H, t, $^3J_{HH}$=7.2 Hz, Me), 3.85 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.15 (2H, q, $^3J_{HH}$=7.2 Hz, OCH_2), 4.61–4.81 (2H, m, NCH_2), 6.21 (1H, d, $^3J_{HH}$=7.3 Hz, CH), 6.63 (1H, t, $^3J_{HH}$=7.5 Hz, CH), 6.81 (1H, d, $^3J_{HH}$=7.5 Hz, CH), 7.02 (1H, t, $^3J_{HH}$=7.5 Hz, CH). ^{13}C NMR: δ 12.0 (Me), 13.4 (Me), 13.5 (Me), 35.5 (NCH_2), 62.0 (OCH_2), 69.2 (OCH_2), 81.5 (C_{ipso}), 108.9 (CH), 119.2 (C), 123.0 (C), 123.3 (CH), 124.3 (CH), 131.5 (CH), 143.9 (C), 149.1 (C), 159.8 (C=O), 165.6 (C=O), 169.6 (C=O).

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