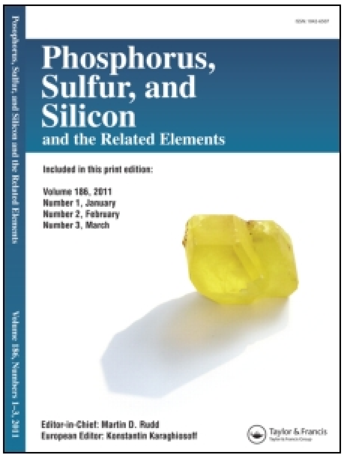

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A Facile One-Pot Synthesis of Highly-Functionalized Stable Heterocyclic Phosphorus Ylides in Aqueous Media

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A FACILE ONE-POT SYNTHESIS OF HIGHLY-FUNCTIONALIZED STABLE HETEROCYCLIC PHOSPHORUS YLIDES IN AQUEOUS MEDIA

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Phthalimide or succinimide undergo a reaction with dialkyl acetylenedicarboxylates and triphenylphosphine to produce highly-functionalized stable heterocyclic phosphorus ylides in good yields in water-tetrahydrofuran (6:1). This methodology is of interest because of the use of water as solvent, thus minimizing the cost, operational hazards, and environmental pollution.

Keywords: Heterocyclic phosphorus ylides; dialkyl acetylenedicarboxylate

INTRODUCTION

Recently, organic reactions in water have attracted much attention because water is the most readily available solvent and safe.[1] In the course of our investigations to develop the synthesis of organophosphorus compounds,[2] we found that a combination of water-tetrahydrofuran (6:1) as solvent provides an efficient system for one-pot synthesis of heterocyclic phosphorus ylides. This system involved three component reaction of triphenylphosphine, dialkyl acetylenedicarboxylates, and NH-acids. The synthesis and chemistry of organophosphorus compounds, that is, those bearing a carbon atom bounded directly to a phosphorus atom have attracted considerable attention in recent years.[3–6] This interest has resulted from the recognition of the value of such compounds for a variety of industrial and chemical synthetic uses. Several

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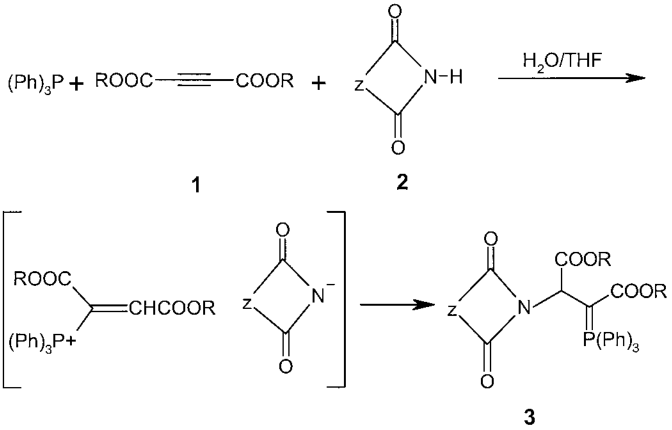
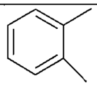
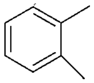
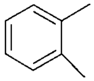
methods have been developed for preparation of phosphorus ylides. This ylides are usually prepared by treatment of a phosphonium salt with a base and these salts are usually prepared from the phosphine and an alkyl halide.[7,8] We now report a simple and an efficient route for the synthesis of stable heterocyclic phosphorus ylides **3** using triphenylphosphine, dialkyl acetylenedicarboxylates **1** in the presence of NH-acids, such as phthalimide or succinimide in water-tetrahydrofuran (6:1) in good yields.

RESULTS AND DISCUSSION

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles[9–12] it is reasonable to assume that phosphorus ylides **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid **2**. Then the positively charged ion is attacked by the nitrogen atom of the conjugate base of the NH-acid to form phosphoranes **3** (Scheme 1).

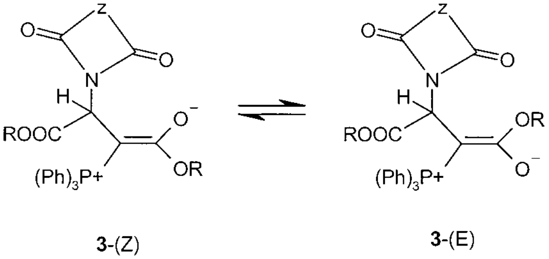


3	R	Z	3	R	Z
a	Me		d	Me	CH_2CH_2
b	Et		e	Et	CH_2CH_2
			f	i-Pr	CH_2CH_2
c	i- Pr				

SCHEME 1

The structures of compounds **3a–f** were deduced from their high-field ^{1}H and ^{13}C NMR and IR spectral data. The nature of these compounds as 1:1:1 adducts was apparent from their mass spectra which displayed fairly weak molecular ion peaks at *m/z* = 551, 579, 607, 503, 531, and 559 respectively. Initial fragmentations involve loss of the complete side chain or partially loss of the side chains and scission of the heterocyclic ring system.

The ^{1}H and ^{13}C NMR spectral data of the phosphoranes **3a–f** exhibited a mixture of two rotational isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in **3**-(E) and **3**-(Z) geometrical isomer is low on the NMR time scale at ambient temperature (Scheme 2).



SCHEME 2

The 500 MHz ^{1}H NMR spectra of compound **3a** displayed four sharp lines ($\delta = 3.14, 3.60, 3.69$, and 3.71) arising from methoxy protons along with signals for methine protons at $\delta = 4.77$ and 4.81 ppm, which appear as two doublets ($^3J_{PH} = 15.5$ Hz) and ($^3J_{PH} = 14.5$ Hz), respectively, for the major and minor geometrical isomer. The ^{13}C NMR spectrum of **3a** exhibited 27 distinct resonances that are in agreement with the mixture of two rotational isomers. Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of **3a**, it helps in assignment of the signals by long-range couplings with the ^{1}H and ^{13}C nuclei (see Experimental section).

The ^{1}H and ^{13}C NMR spectra of **3b** and **3c** are similar to those of **3a**, except for the ester groups, which exhibited characteristic resonances with appropriate chemical shifts (see Experimental section). The ^{1}H and ^{13}C NMR spectral data for compounds (**3c–f**) are consistant with the geometrical isomers. The structural assignments made on the basis of the ^{1}H and ^{13}C NMR spectra of compounds (**3a–f**) were supported by the IR spectra. The carbonyl region of the spectra exhibited four distinct absorption bands for each compound (see Experimental section). Of special interest is the ester absorption at 1780–1641 cm^{-1} for these compounds. Conjugation with the negative charge appears to be a plausible factor in the reduction of the wave numbers of the carbonyl absorption bands.

CONCLUSION

Functionalized phosphorus ylides **3a–f** may be considered as potentially useful synthetic intermediates.[3,7] The procedure described here could be considered as an acceptable method for the preparation of phosphoranes with variable functionalities in aqueous media. We have shown that the condensation reaction of triphenylphosphine with dialkyl acetylenedicarboxylates in the presence of strong NH-acids efficiently occurs in water, providing a convenient and rapid synthesis of stable heterocyclic ylides as synthetic intermediates. Although the reaction can be carried out in organic solvents and gave a similar result, we selected water as the medium of choice because it offers some advantages, including its low cost, non-inflammability, and more importantly, that it is not toxic.

EXPERIMENTAL

Dialkyl acetylenedicarboxylats, phthalimide, succinimide, and triphenylphosphine were obtained from Merck Chemical Co. and were used without further purification. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were measured on a Mattson 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125.77 MHz respectively. Mass spectra were recorded on a MS-QP2000A Shimadzu mass spectrometer operating at an ionization potential of 70 eV.

Preparation of Dimethyl 2-(Phthalimido)-3-(triphenylphosphoranylidene)-butanedioate 3a

General Procedure

At ambient temperature dimethyl acetylenedicarboxylate (0.24 ml, 2 mmol) was added dropwise to a stirred emulsion of triphenylphosphine (0.53 g, 2 mmol) and phthalimide (0.3 g, 2 mmol) in a 7 ml mixture of water-tetrahydrofuran (6:1). After the addition was complete (approximately 5 min) the mixture was stirred for another 30 min and then 1 ml ethylacetate added and it was subsequently filtered. The solid collected in the filter was washed throughly with ethylacetate to give a white powder. (0.89 g, m.p. 184–186°C, yield 80%); IR (KBr) (ν_{max}, cm^{-1}): 1780, 1769, 1741, and 1647(C=O). MS, *m/z* (%): 551 (M^+,2), 520 (5), 492 (100), 405 (20), 345 (10), 262 (85), 230 (25), 183 (90). Major isomer, **3a**-(Z) (53%), ^{1}H NMR: δ 3.14 and 3.71 (6H, 2s, 2 OCH_3), 4.77 (1H, d, $^3J_{PH}$ 15.5 Hz, P=C–CH), 7.42–7.73 (38H, m, arom).* ^{13}C NMR: δ 37.87 (d, $^1J_{PC}$ 130.6 Hz, P=C), 49.16 and 52.90 (2 OCH_3), 55.11 (d, $^2J_{PC}$ 17.3 Hz, P=C–CH), 123.06 (CH), 127.19 (d, $^1J_{PC}$ 85.6 Hz, C^{ipso}), 128.90 (d, $^3J_{PC}$ 12.2 Hz, C^{meta}), 132.16 (C^{para}), 133.60 (CH), 133.71 (C), 133.75 (d, $^2J_{PC}$ 9.9 Hz, C^{ortho}), 167.65 (4 C=O),* 169.30 (d, $^2J_{PC}$ 13.2 Hz, C=O), 171.54 (d, $^3J_{PC}$ 7.5 Hz, C=O).

Minor isomer, **3a**-(E) (47%), ^{1}H NMR: δ 3.60 and 3.69 (6H, 2s, 2 OCH_3), 4.81 (1H, d, $^3J_{PH}$ 14.5 Hz, P=C–CH). ^{13}C NMR: δ 39.07 (d, $^1J_{PC}$ 138.9 Hz, P=C), 50.53 and 52.64 (2 OCH_3), 54.49 (d, $^2J_{PC}$ 16.9 Hz, P=C–CH), 123.04 (CH), 126.11 (d, $^1J_{PC}$ 85.5 Hz, C^{ipso}), 128.93 (d, $^3J_{PC}$ 12.3 Hz, C^{meta}), 132.14 (C^{para}), 132.33 (C), 132.44 (CH), 133.77 (d, $^2J_{PC}$ 10.0 Hz, C^{ortho}), 171.23 (d, $^2J_{PC}$ 18.1 Hz, C=O), 171.59 (d, $^3J_{PC}$ 5.9 Hz, C=O).

Diethyl 2-(Phthalimido)-3-(triphenylphosphoranylidene)-butanedioate 3b

(0.93 g, m.p. 196–198°C, yield 81%); IR (KBr) (ν_{max}, cm^{-1}): 1776, 1766, 1742, and 1643 (C=O). MS, *m/z* (%): 574 (M^+,3), 534 (5), 506 (100), 434 (18), 359 (5), 287 (16), 262 (30), 183 (38). Major isomer, **3b**-(Z) (57%), ^{1}H NMR; δ 0.48 (3H, t, $^3J_{HH}$ 7.0 Hz, CH_3), 1.24 (3H, t, $^3J_{HH}$ 6.1 Hz. CH_3), 4.09–4.28 (4H, m, 2CH_2), 4.82 (1H, d, $^3J_{PH}$ 16.5 Hz, P=C–CH), 7.42–7.76 (38H, m, arom).* ^{13}C NMR: δ 13.99 and 14.19 (2CH_3), 36.98 (d, $^1J_{PC}$ 130.7 Hz, P=C), 55.16 (d, $^2J_{PC}$ 17.5 Hz, P=C–CH), 57.53 and 61.39 (2 OCH_2), 122.87 (CH), 127.29 (d, $^1J_{PC}$ 91.8 Hz, C^{ipso}), 128.67 (d, $^3J_{PC}$ 12.1 Hz, C^{meta}), 131.98 (C^{para}), 133.43 (CH), 133.53 (C), 133.74 (d, $^2J_{PC}$ 9.8 Hz, C^{ortho}), 167.54 (4 C=O),* 168.62 (d, $^2J_{PC}$ 13.1 Hz, C=O), 170.85 (d, $^3J_{PC}$ 8.1 Hz, C=O).

Minor isomer, **3b**-(E) (43%), ^{1}H NMR: δ 1.18 (3H, t, $^3J_{HH}$ 6.9 Hz, CH_3), 1.31 (3H, t, $^3J_{HH}$ 7.0 Hz, CH_3), 3.66–3.84 (4H, m, 2CH_2), 4.80 (1H, d, $^3J_{PH}$ 17.8 Hz, P=C–CH). ^{13}C NMR: δ 14.17 and 14.79 (2CH_3), 38.75 (d, $^1J_{PC}$ 139.1 Hz, P=C), 54.50 (d, $^2J_{PC}$ 17.3 Hz, P=C–CH), 58.52 and 61.26 (2 OCH_2) 122.85 (CH), 126.64 (d, $^1J_{PC}$ 92.3 Hz, C^{ipso}), 128.73 (d, $^3J_{PC}$ 11.5 Hz, C^{meta}), 131.92 (C^{para}), 132.25 (C), 132.34 (CH), 133.66 (d, $^2J_{PC}$ 9.7 Hz, C^{ortho}), 170.78 (d, $^2J_{PC}$ 11.2 Hz, C=O), 170.97 (d, $^3J_{PC}$ 7.1 Hz, C=O).

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*For two rotamers.

Diisopropyl 2-(Phthalimido)-3-(triphenylphosphoranylidene)–butanedioate 3c

(0.75 g, m.p. 157–160°C, yield 68%); IR (KBr) (ν_{max}, cm^{-1}): 1778, 1765, 1743, and 1641 (C=O). MS, *m/z* (%): 607 (M^+,2), 548 (5), 520 (100), 478 (25), 461 (10), 434 (27), 262 (80), 182 (40). Major isomer, **3c**-(Z) (71%), ^{1}H NMR: δ 0.41 (3H, d, $^3J_{HH}$ 6.0 Hz, CH_3), 0.75 (3H, d, $^3J_{HH}$ 6.1 Hz, CH_3), 1.25 (3H, d, $^3J_{HH}$ 5.8 Hz, CH_3), 1.29 (3H, d, $^3J_{HH}$ 6.0 Hz, CH_3), 4.75 (1H, d, $^3J_{PH}$ 16.8 Hz, P=C—CH), 4.82 (1H, m, CH), 5.07 (1H, m, CH), 7.44–7.77 (38H, m, arom).* ^{13}C NMR: δ 21.50, 21.67, 21.91 and 22.09 (4CH_3), 36.68 (d, $^1J_{PC}$ 130.7 Hz, P=C), 55.43 (d, $^2J_{PC}$ 17.5 Hz, P=C—CH), 64.29 and 68.87 (2 OCH), 122.85 (CH), 127.50 (d, $^1J_{PC}$ 91.7 Hz, C^{ipso}), 128.57 (d, $^3J_{PC}$ 12.1 Hz, C^{meta}), 131.90 (C^{para}), 133.33 (CH), 133.44 (C), 133.77 (d, $^3J_{PC}$ 9.8 Hz, C^{ortho}), 167.53 (2 C=O), 167.71 (d, $^2J_{PC}$ 12.9 Hz, C=O), 170.34 (d, $^3J_{PC}$ 12.2 Hz, C=O).

Minor isomer, **3c**-(E) (29%), ^{1}H NMR: δ 1.15 (3H, d $^3J_{HH}$ 5.9 Hz, CH_3), 1.19 (3H, d, $^3J_{HH}$ 6.0 Hz, CH_3), 1.24 (3H, d, $^3J_{HH}$ 5.9 Hz, CH_3), 1.33 (3H, d, $^3J_{HH}$ 5.9 Hz, CH_3), 4.66 (1H, d, $^3J_{PH}$ 17.9 Hz, P=C—CH), 4.90 (1H, m, CH), 4.98 (1H, m, CH). ^{13}C NMR: δ 21.64, 21.98, 22.14, and 22.68 (4CH_3), 38.77 (d, $^1J_{PC}$ 130.6 Hz, P=C), 54.63 (d, $^2J_{PC}$ 18.2 Hz, P=C—CH), 65.54 and 68.85 (2 OCH), 122.79 (CH), 126.90 (d, $^1J_{PC}$ 91.9 Hz, C^{ipso}), 128.63 (d, $^3J_{PC}$ 11.9 Hz, C^{meta}), 131.81 (C^{para}), 132.33 (C), 132.41 (CH), 133.69 (d, $^2J_{PC}$ 11.0 Hz, C^{ortho}), 167.46 (2 C=O), 170.02 (d, $^2J_{PC}$ 11.6 Hz, C=O), 170.39 (d, $^3J_{PC}$ 11.9 Hz, C=O).

Dimethyl 2-(Succinimido)-3-(triphenylphosphoranylidene)–butanedioate 3d

(0.7 g, m.p. 178–180°C, yield 70%); IR (KBr) (ν_{max}, cm^{-1}): 1779, 1765, 1716, and 1641 (C=O). MS, *m/z* (%): 503 (M^+,2), 472 (5), 444 (100), 405 (20), 345 (10), 287 (15), 262 (45), 183 (58). Major isomer, **3d**-(Z) (57%), ^{1}H NMR: δ 2.51 (4H, d, $^2J_{HH}$ 7.8 Hz, 2CH_2), 3.06 and 3.66 (6H, 2s, 2 OCH_3), 4.64 (1H, d, $^3J_{PH}$ 16.1 Hz, P=C—CH), 7.45–7.68 (30H, m, arom).* ^{13}C NMR: δ 28.07 and 28.05 (2CH_2), 36.46 (d, $^1J_{PC}$ 130.6 Hz, P=C), 49.05 and 52.80 (2 OCH_3), 55.41 (d, $^2J_{PC}$ 14.1 Hz, P=C—CH), 127.11 (d, $^1J_{PC}$ 84.9 Hz, C^{ipso}), 128.84 (d, $^3J_{PC}$ 11.7 Hz, C^{meta}), 132.16 (C^{para}), 133.76 (d, $^2J_{PC}$ 9.8 Hz, C^{ortho}), 169.09 (d, $^2J_{PC}$ 12.9 Hz, C=O), 170.94 (d, $^3J_{PC}$ 10.1 Hz, C=O), 176.32 (2C=O).

Minor isomer, **3d**-(E) (43%), ^{1}H NMR: δ 2.53 (4H, d, $^2J_{HH}$ 7.7 Hz, 2CH_2), 3.55 and 3.64 (6H, 2s, 2 OCH_3), 4.67 (1H, d, $^3J_{PH}$ 19.4 Hz, P=C—CH). ^{13}C NMR: δ 28.09 and 28.10 (2CH_2), 37.21 (d, $^1J_{PC}$ 131.7 Hz, P=C), 50.52 and 52.58 (2 OCH_3), 55.02 (d, $^2J_{PC}$ 18.0 Hz, P=C—CH), 126.38 (d, $^1J_{PC}$ 84.7 Hz, C^{ipso}), 128.92 (d, $^3J_{PC}$ 9.9 Hz, C^{meta}), 132.17 (C^{para}), 133.79 (d, $^2J_{PC}$ 9.8 Hz, C^{ortho}), 168.97 (d, $^2J_{PC}$ 11.2 Hz, C=O), 171.04 (d, $^3J_{PC}$ 9.8 Hz, C=O), 176.26 (2C=O).

Diethyl 2-(Succinimido)-3-(triphenylphosphoranylidene)–butanedioate 3e

(0.65 g, m.p. 163–164°C, yield 61%); IR (KBr) (ν_{max}, cm^{-1}): 1775, 1766, 1717, and 1647 (C=O). MS, *m/z* (%): 531 (M$^+$,3), 486 (5), 458 (85), 433 (18), 359 (15), 287 (17), 261 (100), 183 (70). Major isomer, **3e**-(Z) (64%), ^{1}H NMR: δ 0.38 (3H, t, $^3J_{HH}$ 7.0 Hz, CH$_3$), 1.19 (3H, t, $^3J_{HH}$ 7.1 Hz, CH$_3$), 2.52 (4H, d, $^2J_{HH}$ 6.2 Hz, 2CH$_2$), 3.97–4.23 (4H, m, 2CH$_2$), 4.63 (1H, d, $^3J_{PH}$ 16.0 Hz, P=C–CH), 7.42–7.69 (30H, m, arom).* ^{13}C NMR: δ 13.91 and 14.13 (2CH$_3$), 28.01 and 28.08 (2CH$_2$), 36.22 (d, $^1J_{PC}$ 130.8 Hz, P=C), 55.51 (d, $^2J_{PC}$ 17.9 Hz, P=C–CH), 57.48 and 61.36 (2 OCH$_2$), 127.22 (d, $^1J_{PC}$ 91.9 Hz, C^{ipso}), 128.71 (d, $^3J_{PC}$ 12.8 Hz, C^{meta}), 131.96 (C^{para}), 133.74 (d, $^2J_{PC}$ 9.9 Hz, C^{ortho}), 168.47 (d, $^2J_{PC}$ 16.4 Hz, C=O), 170.36 (d, $^3J_{PC}$ 9.9 Hz, C=O), 176.26 (2C=O).

Minor isomer, **3e**-(E) (36%), ^{1}H NMR: δ 1.12 (3H, t, $^3J_{HH}$ 6.9 Hz, CH$_3$), 1.25 (3H, t, $^3J_{HH}$ 7.6 Hz, CH$_3$), 2.51 (4H, d, $^2J_{HH}$ 6.3 Hz, 2CH$_2$), 3.54–3.71 (4H, m, 2CH$_2$), 4.61 (1H, d, $^3J_{PH}$ 17.8 Hz, P=C–CH). ^{13}C NMR: δ 14.00 and 14.78 (2CH$_3$), 29.67 and 29.69 (2CH$_2$), 37.92 (d, $^1J_{PC}$ 131.1 Hz, P=C), 55.06 (d, $^2J_{PC}$ 17.7 Hz, P=C–CH), 58.52 and 61.19 (2 OCH$_2$), 126.60 (d, $^1J_{PC}$ 92.1 Hz, C^{ipso}), 128.61 (d, $^3J_{PC}$ 12.4 Hz, C^{meta}), 131.94 (C^{para}), 133.66 (d, $^2J_{PC}$ 10.7 Hz, C^{ortho}), 165.22 (d, $^2J_{PC}$ 17.9 Hz, C=O), 170.30 (d, $^3J_{PC}$ 10.1 Hz, C=O), 176.13 (2C=O).

Diisopropyl 2-(Succinimido)-3-(triphenylphosphoranylidene)–butanedioate 3f

(0.61 g, m.p. 150–152°C, yield 55%); IR (KBr) (ν_{max}, cm^{-1}): 1770, 1764, 1718, and 1645 (C=O). MS, *m/z* (%): 559 (M$^+$,4), 500 (7), 472 (90), 430 (21), 386 (15), 287 (22), 262 (82), 183 (100). Major isomer, **3f**-(Z) (75%), ^{1}H NMR: δ 0.38 (3H, d, $^3J_{HH}$ 5.4 Hz, CH$_3$), 0.59 (3H, d, $^3J_{HH}$ 5.4 Hz, CH$_3$), 1.18 (3H, d, $^3J_{HH}$ 4.4 Hz, CH$_3$), 1.19 (3H, d, $^3J_{HH}$ 4.5 Hz, CH$_3$), 2.51 (4H, d, $^2J_{HH}$ 6.0 Hz, 2CH$_2$), 4.51 (1H, d, $^3J_{PH}$ 16.1 Hz, P=C–CH), 4.70 (1H, m, CH), 4.96 (1H, m, CH), 7.46–7.71 (30H, m, arom).* ^{13}C NMR: δ 21.59, 21.83, 22.04, and 22.12 (4CH$_3$), 28.07 and 28.09 (2CH$_2$), 35.89 (d, $^1J_{PC}$ 130.8 Hz, P=C), 55.92 (d, $^2J_{PC}$ 18.5 Hz, P=C–CH), 64.30 and 68.97 (2 OCH), 127.51 (d, $^1J_{PC}$ 91.8 Hz, C^{ipso}), 128.64 (d, $^3J_{PC}$ 12.2 Hz, C^{meta}), 132.01 (C^{para}), 133.92 (d, $^2J_{PC}$ 9.7 Hz, C^{ortho}), 167.62 (d, $^2J_{PC}$ 12.9 Hz, C=O), 169.99 (d, $^3J_{PC}$ 9.7 Hz, C=O), 176.33 (2C=O).

Minor isomer, **3f**-(E) (25%), ^{1}H NMR: δ 1.09 (3H, d, $^3J_{HH}$ 4.4 Hz, CH$_3$), 1.14 (3H, d, $^3J_{HH}$ 5.0 Hz, CH$_3$), 1.16 (3H, d, $^3J_{HH}$ 5.4 Hz, CH$_3$), 1.25 (3H, d, $^3J_{HH}$ 4.6 Hz, CH$_3$), 2.53 (4H, d, $^2J_{HH}$ 6.1 Hz, 2CH$_2$), 4.47 (1H, d, $^3J_{PH}$ 17.9 Hz, P=C–CH), 4.81 (1H, m, CH), 4.88 (1H, m, CH). ^{13}C NMR: δ 21.77, 21.85, 22.11, and 22.25 (4CH$_3$), 28.05 and 28.11 (2CH$_2$), 37.19 (d, $^1J_{PC}$ 131.9 Hz, P=C), 55.27 (d, $^2J_{PC}$ 18.7 Hz, P=C–CH), 65.59 and

68.99 (2 OCH), 126.95 (d, $^1J_{PC}$ 92.4 Hz, C^{ipso}), 128.69 (d, $^3J_{PC}$ 12.1 Hz, C^{meta}), 131.93 (C^{para}), 133.88 (d, $^2J_{PC}$ 9.8 Hz, C^{ortho}), 164.70 (d, $^2J_{PC}$ 15.1 Hz, C=O), 169.55 (d, $^3J_{PC}$ 9.8 Hz, C=O), 176.08 (2C=O).

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