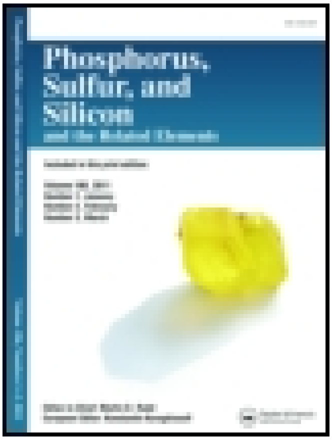

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# Synthesis of New Phosphorous Ylides Containing Urethane Derivatives

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# Synthesis of New Phosphorous Ylides Containing Urethane Derivatives

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*The readily available (DMAD& DEAD) and triphenylphosphine undergo facile reaction with several urethanes such as methyl–N-phenylcarbamate, ethyl-N-phenylcarbamate, phenyl-N-phenylcarbamate, phenyl-N-(2-methylphenyl) carbamate and phenyl –N(3-methylphenyl)carbamate, to give crystalline phosphorus ylides in good yields. The overall sequence from a 1:1:1 reaction provides a simple and efficient rout to functionalized urethanes.*

**Keywords** Acetylenic esters; phosphorus compounds; urethanes

## INTRODUCTION

The urethanes have attracted considerable attention since they have been extensively used in organic synthesis polyurethanes during the past 60 years.[1–4] Although the properties and synthesis of these compounds have been widely studied, the closely related highly functionalized urethane derivatives containing phosphorous ylide moiety are unknown so far. Recently, our interest focused on the synthesis of phosphorous ylides that could be transformed into versatile compounds.[5–8] Our aim of this study is to prepare new urethanes containing the ylide moiety from the reaction of carbamate derivatives with acetylenic esters in the presence of triphenylphosphine as a good nucleophile.[9–12]

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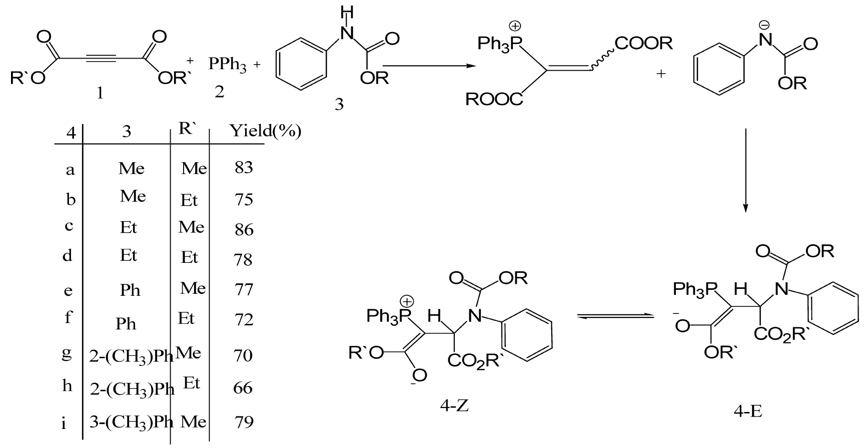

| 4 | 3 | R` | Yield(%) |
|---|---|---|---|
| a | Me | Me | 83 |
| b | Me | Et | 75 |
| c | Et | Me | 86 |
| d | Et | Et | 78 |
| e | Ph | Me | 77 |
| f | Ph | Et | 72 |
| g | $2-(CH_3)Ph$ | Me | 70 |
| h | $2-(CH_3)Ph$ | Et | 66 |
| i | $3-(CH_3)Ph$ | Me | 79 |

**SCHEME 1**

## RESULTS AND DISCUSSION

The synthesis of compounds **4a–i** was accomplished in accordance with the reaction depicted in Scheme 1. The starting compounds, carbamate derivatives **3a–i** were prepared according to the procedure, which was reported in the literature. The reaction of compounds **3a–i** with dialkyl acetylenedicarboxylate in the presence of $Ph_3P$ gave the stable phosphorus ylides **4a–i**.

A plausible mechanism of the reaction and formation of the final products is depicted in Scheme 1. The structures of compounds **4a–i** were deduced from their high- field $^1H$, $^{13}C$ NMR, and IR spectral data. The $^1H$ and $^{13}C$ NMR spectroscopic data for compounds **4a–i** exhibit 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 **4-(E)** and **4-(Z)** geometrical isomer is low on the NMR time scale at ambient temperature. The structure of rotamers, which were found in ylides, have been previously established and reported in the literature.[13,14]

The $^1H$ NMR spectrum of 4a showed six sharp lines ($\delta = 2.83$, 3.0, 3.42, 3.45, 3.7, 3.86 ppm) due to the methoxy protons, along with signals for methine protons at $\delta = 4.92$ and 4.96 which appear as two doublets ($^3J_{PH} = 16.2$Hz) and ($^3J_{PH} = 18$Hz), respectively, for major and minor geometrical isomers. The aromatic region appeared as a multiplet at 7.26–7.59 ppm. The $^{13}C$ NMR spectrum of **4a** is in agreement with the mixture of two rotamers. Although the presence of the $^{31}P$ nucleus complicates both the $^1H$ and $^{13}C$ NMR spectra of the compounds **4a-i** but it does help us to obtain some valuable information by long-range spin-spin coupling constants $^{31}P$ with $^{1}H$ and $^{13}C$ nuclei.

The $^{1}H$ and $^{13}C$ NMR spectroscopic data for compound **4b** are similar to those of **4a**, except for the ester groups, which exhibited characteristic resonances with appropriate chemical shifts.

The NMR spectral data for compounds (**4c–i**) are consistent with the phosphorane structure.

The structural assignments made for the phosphorane **4a–i** based on the $^{1}H$, $^{13}C$ NMR, and their IR spectra.

The carbonyl group region of the spectrum exhibited two absorption bands for each compound, the conjugation of one ester group with the negative charge is a plausible factor in reduction of the wave number of one carbonyl absorption band.

## CONCLUSION

In conclusion, we have demonstrated that the readily available acetylenedicarboxylates in the presence of triphenylphosphine undergoes facile reaction with urethane, providing a convenient and rapid synthesis of urethane derivatives containing the ylide moiety.

## EXPERIMENTAL

Dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, phenylisocyanate, o-cresol, and m-cresol were obtained from Merck Co. and were used without further purification.

Melting points were obtained on a Gallenkamp melting point apparatus and were uncorrected. IR spectra were measured on a Mattson 1000 FT-IR spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were reported on a BRUKER DRX-500 AVANCE spectrometer at 500.13 and 125.77 MHz, respectively.

### Dimethyl-2-[(methoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ5-phosphonylidene)succinate 4a

Dimethyl acetylenedicarboxylate or diethyl acetylenedicarboxylate (2 mmol, 0.24 ml) was added dropwise to a magnetically stirred solution of triphenylphosphine (2 mmol, 0.53 g) and urethane (2 mmol) in a 15 ml mixture of ethyl acetate-petroleum ether (4:1) at an ambient temperature After the addition was complete the mixture was stirred for an additional 6 h and then filtered.

The filtrate was washed thoroughly with mixture of ethyl acetate-petroleum ether to give a white powder. (0.92g, m.p. 156–158°C, yield 83%); IR (KBr) ($\nu_{max}$, cm$^{-1}$):1756, 1645, and 1617 (C=O). m.p.

Major isomer, **4a**-(E) (57.2%), $^1$H NMR: $\delta$ 3.09, 3.45, and 3.77 (9H, 3s, 3OCH$_3$), 4.92(1H, d, $^3J_{PH}$ = 16.2 Hz, P=C—CH)*, 7.26–7.59 (40H, m, arm)*. $^{13}$C NMR: $\delta$ 40.87 (d, $^1J_{PC}$ = 135.8 Hz, P=C), 49.35, 52.03, and 52.34(3OCH$_3$), 61.12(d, $^2J_{PC}$ = 17.0Hz, P=C—CH), 126.65, and 127.35 (2CH)*,126.27 (d, $^1J_{PC}$ = 91.9Hz, $C^{ipso}$), 128.53 (d, $^3J_{PC}$ = 12.4Hz, $C^{meta}$), 131.24 (1C)*, 132.04 (d, $^4J_{PC}$ = 4.0Hz, $C^{para}$), 133.79 (d, $^2J_{PC}$ = 9.8Hz, $C^{ortho}$), 139.14 and 155.78 (2C), 168.4 (C=O), 169.99 (d, $^2J_{PC}$ = 17.8Hz, C=O) *, 173.50 (d, $^3J_{PC}$ = 3.7Hz, C=O).*

Minor isomer, **4a**-(Z) (42.8%), 1H NMR: $\delta$ 2.87, 3.42, and 3.86 (9H, 3s, 3OCH$_3$), $^{13}$C NMR: 38.65 (d, $^1J_{PC}$ = 136.6Hz, P=C), 48.70, 52.28 and 52.43(3OCH$_3$), 61.96 (d, $^2J_{PC}$ = 16.6Hz, P=C—CH), 126.13 (d, $^1J_{PC}$ = 96.8Hz, $C^{ipso}$), 128.63 (d, $^3J_{PC}$ = 12.4Hz, $C^{meta}$), 131.94 (d, $^4J_{PC}$ = 3.60Hz, $C^{para}$), 133.56 (d, $^2J_{PC}$ = 9 .7Hz, $C^{ortho}$), 139.41, and 155.44 (2C), 168.51 (C=O).

## Diethyl-2-[(methoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ5-phosphonylidene)succinate 4b

(0.87g, m.p. 170–173°C, yield 75%); IR (KBr) ($\nu_{max}$, cm$^{-1}$):1750, 1651, and 1621 (C=O).

Major isomer, **4b**-(E) (51.1%), $^1$H NMR: $\delta$ 0.30 and 1.33 (6H,2t, CH$_3$), 3.34 (3H, s, OCH$_3$), 3.39, and 4.21 (4H,2q, OCH$_2$-), 4.90 (1H, d, $J_{PH}$ = 16.4 Hz, P=C—CH)*, 7.23–7.62 (40H, m, arm)*. $^{13}$C NMR: $\delta$ 13.9 and 14.3 (2CH$_3$), 40.72 (d, $^1J_{PC}$ = 134.7Hz, P=C), 52.40(OCH$_3$), 57.37 and 60.81 (2OCH$_2$-), 61.12(d, $^2J_{PC}$ = 17.0Hz, P=C—CH), 126.15 (d, $^1J_{PC}$ = 91.3Hz, $C^{ipso}$), 127.39, and 127.56 (2C)*, 128.44 (d, $^3J_{PC}$ = 12.2Hz, $C^{meta}$), 131.43 (1C)*, 132.04 (d, $^4J_{PC}$ = 2.6Hz, $C^{para}$), 133.67 (d, $^2J_{PC}$ = 9.7Hz, $C^{ortho}$), 139.51, and 155.81(2C), 167.97 (C=O), 168.82 (d, $^2J_{PC}$ = 18.0Hz, C=O)*, 172.68 (d, $^3J_{PC}$ = 13.6Hz, C=O)*.

Minor isomer, **4b**-(Z) (49.9%), 1H NMR: $\delta$ 0.94, and 1.36 (6H, 2t, CH$_3$), 3.37 (3H, s, OCH$_3$), 3.43 and 4.26 (4H, 2q, OCH$_2$-),$^{13}$C NMR: 14.28 and 14.45 (2CH$_3$), 38.42 (d, $^1J_{PC}$ = 127.8Hz, P=C), 52.40 (OCH$_3$), 57.91 and 60.12 (2OCH$_2$-), 61.96 (d, $^2J_{PC}$ = 16.6Hz, P=C—CH), 126.13 (d, $^1J_{PC}$ = 91.9Hz, $C^{ipso}$), 128.56 (d, $^3J_{PC}$ = 12.3Hz, $C^{meta}$), 131.97 (d, $^4J_{PC}$ = 2.7Hz, $C^{para}$), 133.80 (d, $^2J_{PC}$ = 9.8Hz, $C^{ortho}$), 139.22, and 155.49 (2C), 167.86 (C=O).

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*For two rotamers

## Dimethyl-2-[(ethoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ5-phosphonylidene)succinate 4c

(0.99g, m.p. 150–151°C, yield 86%); IR (KBr) ($\nu_{\max}$, cm$^{-1}$): 1754, 1650, and 1619 (C=O).

Major isomer, **4c**-(E) (53.1%), $^1$H NMR: $\delta$ 1.1 (CH$_3$)*, 2.88 and 3.77 (3H, 2s, OCH$_3$), 3.97 (4H,m, OCH$_2$-)*, 4.90 (1H, d, $J_{PH}$ = 1 6.3 Hz, P=C–CH)*, 7.26–7.58 (40H, m, arm)*. $^{13}$C NMR: $\delta$ 14.53 (CH$_3$)*, 40.77 (d, $^1J_{PC}$ = 135.1Hz, P=C), 49.40 (OCH$_2$-) 52.03(OCH$_3$), 61.03(OCH$_3$), 61.95(d, $^2J_{PC}$ = 16.5Hz, P=C–CH)*, 125.93, 126.75 and 126.64 (C)*, 126.61 (d, $^1J_{PC}$ = 90.6 Hz, C$^{ipso}$), 128.64 (d, $^3J_{PC}$ = 12.3Hz, C$^{meta}$), 131.20 (1C)*, 132.03(d, $^4J_{PC}$ = 2.6Hz, C$^{para}$), 133.78 (d, $^2J_{PC}$ = 9.9Hz, C$^{ortho}$), 139.25 and 155.36(2C), 168.56 (C=O), 169.98 (d, $^2J_{PC}$ = 18.8Hz, C=O)*, 173.54 (d, $^3J_{PC}$ = 6.8Hz, C=O)*. Minor isomer, **4c**-(Z) (46.9%), 1H NMR: $\delta$ 3.1 and 3.90 (3H, 2s, OCH$_3$), 3.43 and 4.26 (4H, 2q, OCH$_2$-),$^{13}$C NMR: 38.61 (d, $^1J_{PC}$ = 129.5Hz, P=C), 48.75 (OCH$_2$-), 52.32 (OCH$_3$), 60.94 (OCH$_3$), 126.26 (d, $^1J_{PC}$ = 92.1Hz, C$^{ipso}$), 128.54 (d, $^3J_{PC}$ = 12.3Hz, C$^{meta}$), 131.93 (d, $^4J_{PC}$ = 2.5Hz, C$^{para}$), 133.55 (d, $^2J_{PC}$ = 9.7Hz, C$^{ortho}$), 139.49 and 154.99 (2C), 168.45(C=O).

## Diethyl-2-[(ethoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ5-phosphonylidene)succinate 4d

(0.96 g, m.p. 155–156°C, yield 78%); IR (KBr) ($\nu_{\max}$, cm$^{-1}$):1754, 1660, and 1625 (C=O).

Major isomer, **4d**-(E) (50.3%), $^1$H NMR: $\delta$ 0.29, 0.95, and 1.33 (9H, 3t, CH$_3$), 3.33, 3.92, and 4.20 (6H,3q, OCH$_2$-), 4.91 (1H, d, $J_{PH}$ = 16.4 Hz, P=C–CH)*, 7.23–7.61 (40H, m, arm)*. $^{13}$C NMR: $\delta$ 13.89, 14.30, and 14.57 (3CH$_3$), 40.62 (d, $^1J_{PC}$ = 134.8Hz, P=C), 57.38, 60.92, and 61.14 (3OCH$_2$-), 61.89(d, $^2J_{PC}$ = 16.6Hz, P=C–CH)*, 125.96,126.71, and 127.34 (3C)*, 126.51 (d, $^1J_{PC}$ = 91.9Hz, C$^{ipso}$), 128.55 (d, $^3J_{PC}$ = 12.3Hz, C$^{meta}$), 131.43 (1C)*, 131.86 (d, $^4J_{PC}$ = 2.7Hz, C$^{para}$), 133.67 (d, $^2J_{PC}$ = 9.7Hz, C$^{ortho}$), 139.33 and 155.40(2C), 168.00 (C=O), 169.28 (d, $^2J_{PC}$ = 18.8Hz, C=O)*, 172.82 (d, $^3J_{PC}$ = 4.9Hz, C=O)*.

Minor isomer, **4d**-(Z) (49.7%), 1H NMR: $\delta$ 0.97, 0.98, and 1.34 (9H, 3t, CH$_3$), 3.68, 4.1, and 4.38 (6H, q, OCH$_2$-), 3.43 and 4.26 (4H, 2q, OCH$_2$-), $^{13}$C NMR: 14.28, 14.39 and 14.45 (3CH$_3$), 38.61 (d, $^1J_{PC}$ = 133.6Hz, P=C),52.40 (OCH$_3$), 57.92, 60.87, and 60.97 (3OCH$_2$-), 126.84 (d, $^1J_{PC}$ = 91.3Hz, C$^{ipso}$), 128.43 (d, $^3J_{PC}$ = 12.3Hz, C$^{meta}$), 131.94 (d, $^4J_{PC}$ = 2.7Hz, C$^{para}$), 133.79 (d, $^2J_{PC}$ = 9.8Hz, C$^{ortho}$), 139.61 and 155.06 (2C), 167.90 (C=O).

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*For two rotamers

## Dimethyl-2-[(phenoxycarbonyl)anilino]-3-(1,1,1-triphenyl-$\lambda$5-phosphonylidene)succinate 4e

(0.98g, m.p. 140–142°C, yield 77%); IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1755, 1660, and 1616 (C=O).

Major isomer, **4e**-(E) (53.5%), $^1$H NMR: $\delta$ 2.91 and 3.8 (6H, 2s, OCH$_3$), 5.02(1H, d, J$_{PH}$ = 19.9 Hz, P=C—CH), 6.92–7.63 (50H, m, arm)*. $^{13}$C NMR: $\delta$ 40.66(d, $^1$J$_{PC}$ = 135.4Hz, P=C)*, 49.46 and 52.20(2OCH$_3$), 61.69(1H, d, $^2$J$_{PC}$ = 17.4Hz, P=C—CH), 121.42 and 121.46 (2C$^{ortho}$,OPh)*, 124.72, 127.50, 127.79, and 131.14 (4CH)*, 126.15 (d, $^1$J$_{PC}$ = 92.0Hz, C$^{ipso}$), 127.39 and 127.56 (4CH)* 128.75 (d, $^3$J$_{PC}$ = 12.2Hz, C$^{meta}$), 131.43 (1C)*, 132.18 (d, $^4$J$_{PC}$ = 2.6Hz, C$^{para}$), 133.78 (d, $^2$J$_{PC}$ = 9.9Hz, C$^{ortho}$), 139.51, 151.67, 153.65 and 155.81 (4C), 168.51(C=O), 169.99 (d, $^2$J$_{PC}$ = 16.7Hz, C=O)*, 173.17 (d, $^3$J$_{PC}$ = 16.4Hz, C=O)*.

Minor isomer, **4e**-(Z) (46.5%), 1H NMR: $\delta$ 3.1 and 3.9 (6H,2s, OCH$_3$), 5.04 (1H, d, J$_{PH}$ = 17.7), $^{13}$C NMR: 14.28 and 14.45 (2CH$_3$), 48.84 and 52.50 (2OCH$_3$), 62.63 (d, $^2$J$_{PC}$ = 16.9Hz, P=C—CH), 126.47 (d, $^1$J$_{PC}$ = 87.7Hz, C$^{ipso}$), 128.65(d, $^3$J$_{PC}$ = 11.8Hz, C$^{meta}$), 129.80, 139.15, 151.68, and 153.66(4C), 132.08 (d, $^4$J$_{PC}$ = 2.7Hz, C$^{para}$), 133.58 (d, $^2$J$_{PC}$ = 9.8Hz, C$^{ortho}$), 139.22 and 155.49 (2C), 168.62 (C=O).

## Diethyl-2-[(phenoxycarbonyl)anilino]-3-(1,1,1-triphenyl-$\lambda$5-phosphonylidene)succinate 4f

(0.96g, m.p. 160–161°C, yield 72%); IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1748, 1650, and 1617 (C=O).

Major isomer, **4f**-(E) (69.0%), $^1$H NMR: $\delta$ 0.32 and 1.36 (6H,2t, CH$_3$), 3.34 and 4.10 (4H,2q, OCH$_2$-), 5.02 (1H, d, J$_{PH}$ = 12.4 Hz, P=C—CH)*, 6.91–7.65 (50H, m, arm)*. $^{13}$C NMR: $\delta$ 13.9 and 14.3 (2CH$_3$), 40.50 (d, $^1$J$_{PC}$ = 135.0Hz, P=C)*, 57.48 and 60.33 (2OCH$_2$-), 60.99(d, $^2$J$_{PC}$ = 16.6Hz, P=C—CH)*, 121.41 and 121.47 (C$^{ortho}$, OPh)*, 124.66, 126.44, 127.70, and 131.31 (4CH)*, 126.40 (d, $^1$J$_{PC}$ = 89.8Hz, C$^{ipso}$), 128.65 (d, $^3$J$_{PC}$ = 12.7Hz, C$^{meta}$), 131.43 (4CH)*, 132.00 (d, $^4$J$_{PC}$ = 2.7Hz, C$^{para}$), 133.77 (d, $^2$J$_{PC}$ = 9.8Hz, C$^{ortho}$), 139.24 and 151.75(2C), 167.95 (C=O), 168.82 (d, $^2$J$_{PC}$ = 17.4Hz, C=O)*, 172.68 (d, $^3$J$_{PC}$ = 6.6Hz, C=O)*.

Minor isomer, **4f**-(Z) (31.0%), 1H NMR: $\delta$ 1.25 and 2.04 (6H, 2t, CH$_3$), 3.71 and 4.43 (4H, 2q, OCH$_2$-),$^{13}$C NMR: 14.28 and 14.45 (2CH$_3$), 38.42 (d, $^1$J$_{PC}$ = 127.8Hz, P=C), 57.48 and 60.12 (2OCH$_2$-), 61.96 (d, $^2$J$_{PC}$ = 16.6Hz, P=C—CH), 126.78 (d, $^1$J$_{PC}$ = 91.5Hz, C$^{ipso}$), 128.75 (d, $^3$J$_{PC}$ = 10.8Hz, C$^{meta}$), 132.08 (d, $^4$J$_{PC}$ = 2.6Hz, C$^{para}$), 133.79 (d, $^2$J$_{PC}$ = 9.9, C$^{ortho}$), 138.95 and 152.62 (2C), 168.05 (C=O).

*For two rotamers

## Dimethyl-2-{[(2-methylphenoxy)carbonyl]anilino}-3-(1,1,1-triphenyl-$\lambda$5-phosphonylidene) Succinate 4g

(0.95g, m.p. 130–132°C, yield 70%); IR (KBr) ($\nu_{max}$, cm$^{-1}$):1754, 1662, and 1618 (C=O).

Major isomer, **4g**-(E) (56.7%), $^{1}$H NMR: $\delta$ 2.06 ($CH_3$), 3.13 and 3.79 (6H, 2s, $OCH_3$), 4.99 (1H, d, $J_{PH}$ = 19.4 Hz, P=C—CH)*, 6.91–7.63 (48H, m, arm)*. $^{13}$C NMR: $\delta$ 16.17 ($CH_3$), 40.49 (d, $^{1}J_{PC}$ = 135.4Hz, P=C)*, 49.41 and 52.14 ($OCH_3$), 61.50(d, $^{2}J_{PC}$ = 16.1Hz, P=C—CH)*, 121.89, 125.01, 126.37, 127.21, 127.45, 127.74, and 131.30 (9CH)*, 126.18 (d, $^{1}J_{PC}$ = 92.0Hz, $C^{ipso}$), 128.72 (d, $^{3}J_{PC}$ = 12.2Hz, $C^{meta}$), 139.00, and 150.11 (3C)*, 132.07 (d, $^{4}J_{PC}$ = 2.5Hz, $C^{para}$), 133.77 (d, $^{2}J_{PC}$ = 9.8Hz, $C^{ortho}$), 68.84 (C=O), 170.02 (d, $^{2}J_{PC}$ = 17.1Hz, C=O)*, 172.97 (d, $^{3}J_{PC}$ = 13.7Hz, C=O)*.

Minor isomer, **4g**-(Z) (43.3%), 1H NMR: $\delta$ 2.03 ($CH_3$), 2.89 and 3.88 (6H, 2s, $OCH_3$), $^{13}$C NMR: 16.25 ($CH_3$), 48.79 and 52.40 ($OCH_3$), 126.66 (d, $^{1}J_{PC}$ = 91.8Hz, $C^{ipso}$), 128.63 (d, $^{3}J_{PC}$ = 11.7Hz, $C^{meta}$), 132.05 (d, $^{4}J_{PC}$ = 2.5Hz, $C^{para}$), 133.59 (d, $^{2}J_{PC}$ = 9.7Hz, $C^{ortho}$), 139.22 and 155.49 (2C), 168.58(C=O).

## Diethyl-2-{[(2-methylphenoxy)carbonyl] anilino}-3-(1,1,1-triphenyl-$\lambda$5-phosphonylidene)succinate 4h

(0.93g, m.p. 163–165°C, yield 66%); IR (KBr) ($\nu_{max}$, cm$^{-1}$): 1745, 1653, and 1622 (C=O).

Major isomer, **4h**-(E) (63.7%), $^{1}$H NMR: $\delta$ 0.30 and 1.25 (6H, 2t, $CH_3$), 2.06 (3H, m, $CH_3$)*, 3.34 and 4.11 (4H, 2q, $OCH_2$-), 5.08 (1H, d, $J_{PH}$ = 17.8Hz, P=C—CH)*, 6.90–7.66 (48H, m, arm)*. $^{13}$C NMR: $\delta$ 14.20, 14.32, and 16.32 ($3CH_3$), 40.42 (d, $^{1}J_{PC}$ = 132.7Hz, P=C), 57.45 and 60.35 ($2OCH_2$-), 61.48(d, $^{2}J_{PC}$ = 17.9Hz, P=C—CH), 121.89, 126.36, 126.60, 127.20, 129.86, 130.45, 130.57, and 131.51 (9CH)*, 124.96, 139.04 and 152.87 (3C)*, 126.41 (d, $^{1}J_{PC}$ = 92.0Hz, $C^{ipso}$), 128.65 (d, $^{3}J_{PC}$ = 12.3Hz, $C^{meta}$), 131.43 (1C)*, 132.01 (d, $^{4}J_{PC}$ = 2.5Hz, $C^{para}$), 133.77 (d, $^{2}J_{PC}$ = 10.1Hz, $C^{ortho}$), 167.94(C=O), 169.87 (d, $^{2}J_{PC}$ = 17.7Hz, C=O)*, 172.37 (d, $^{3}J_{PC}$ = 5.2Hz, C=O)*.

Minor isomer, **4h**-(Z) (36.3%), 1H NMR: $\delta$ 1.37 and 1.39 (6H, 2t, $CH_3$), 3.72 and 4.38 (4H, 2q, $OCH_2$-),$^{13}$C NMR: 14,40, 14.49, and 16.23 ($3CH_3$), 37.42 (d, $^{1}J_{PC}$ = 133.7Hz, P=C), 57.99 and 60.94 ($2OCH_2$-), 62.45 (d, $^{2}J_{PC}$ = 16.7Hz, P=C—CH), 126.86 (d, $^{1}J_{PC}$ = 91.8Hz, $C^{ipso}$), 128.54 (d, $^{3}J_{PC}$ = 12.3Hz, $C^{meta}$), 132.09 (d, $^{4}J_{PC}$ = 2.3Hz, $C^{para}$), 133.69(d, $^{2}J_{PC}$ = 10.0Hz, $C^{ortho}$), 139.22 and 155.49 (2C), 168.04(C=O).

*For two rotamers

### Dimethyl-2-{[(3-methylphenoxy)carbonyl]anilin}-3-(1, 1,1-triphenyl-λ5-phosphonylidene)succinate 4i

(1.07g, m.p. 125–127°C, yield 79%); IR (KBr) ($\nu_{max}$, $cm^{-1}$):1749, 1651, and 1619 (C=O).

Major isomer, **4i**-(E) (53.7%), $^1$H NMR: $\delta$ 2.27 (3H,s, $CH_3$)*, 3.13 and 3.80 (6H, 2s, $OCH_3$), 5.00 (1H, d, $J_{PH}$ = 19.9 Hz, P=C—CH), 6.73–7.62 (48H, m, arm)*. $^{13}$C NMR: $\delta$ 21.21 ($CH_3$), 40.67 (d, $^1J_{PC}$ = 133.2Hz, P=C), 48.83 and 52.19(2$OCH_3$), 61.59(d, $^2J_{PC}$ = 17.1Hz, P=C—CH), 118.36, 125.52, 126.41, 127.11, 127.47, 127.78, 131.13 and 151.33 (9CH)*, 122.07,138.91 and 153.75 (3C)*, 126.41(d, $^1J_{PC}$ = 92.0Hz, $C^{ipso}$), 128.73 (d, $^3J_{PC}$ = 12.2Hz, $C^{meta}$), 131.43 (1C)*, 132.16 (d, $^4J_{PC}$ = 2.5Hz, $C^{para}$), 133.78 (d, $^2J_{PC}$ = 9.8Hz, $C^{ortho}$), 168.50(C=O), 170.00 (d, $^2J_{PC}$ = 19.2Hz, C=O)*, 173.14 (d, $^3J_{PC}$ = 4.2Hz, C=O)*.

Minor isomer, **4i**-(Z) (46.3%), 1H NMR: $\delta$ 2.90 and 3.90 (6H, 2s, $OCH_3$), 5.03 (1H, d, $J_{PH}$ = 18.1 Hz, P=C—CH), $^{13}$C NMR: 37.39 (d, $^1J_{PC}$ = 136.0Hz, P=C), 49.47 and 52.50 (2$OCH_3$), 62.56 (d, $^2J_{PC}$ = 16.5Hz, P=C—CH), 126.57(d, $^1J_{PC}$ = 91.5Hz, $C^{ipso}$), 128.64 (d, $^3J_{PC}$ = 11.9Hz, $C^{meta}$), 132.05 (d, $^4J_{PC}$ = 2.7Hz, $C^{para}$), 133.58 (d, $^2J_{PC}$ = 9.6Hz, $C^{ortho}$), 139.22 and 155.49 (2C), 168.60 (C=O).

## REFERENCES

[1] H. Yeganeh, S. Jamshidi, and P. Hayati, *Eur. Polym. J.,* **42,** 17439 (2002).

[2] S. Dutta and N. Karak, *Prog. Org. Coat.,* **53,** 147 (2005).

[3] L. Wu, B. You, and D. Li, *J. Appl. Polym. Sci.,* **84,** 1620 (2002).

[4] J. Y. Kim, D. H. Shim, J. H. Ryu, G. H. Choi, and K. D. Suh, *J. Appl. Polym. Sci.,* **91**,3549 (2004).

[5] E. Tavakolinejad, K. Saidi, and M. R. Islami, *Phosphorus. Sulfur. Silicon. Relat. Elem.,* **180,** 1879 (2005).

[6] I. Yavari and M. R. Islami, *J. Chem. Res(s)*, **3,** 166 (1998).

[7] I. Yavari, M. R. Islami, and H. R. Bijanzadeh, *Tetrahedron,* **55,** 5547 (1999).

[8] M. R. Islami, I. Yavari, A. M. Tikdari, L. Ebrahimi, S. Razee, and H. R. Bjanzadeh, *Russ. Chem. Bull.*, **51,** 121, 2244 (2002).

[9] B. E. Maryanoff and A. B. Reitz, *Chem. Rew.*, **89,** 863 (1989).

[10] I. Yavari and R. Baharifar, *Tetrahedron Lett.*, **39,** 1051 (1998).

[11] M. R. Islami, Z. Hassani, H. Sheibani, B. Abdollahzadeh, and N. Etminan, *Tetrahedron,* **59,** 4993 (2003).

[12] M. Maghsoodlou, N. Hazeri, S. M. H. Khorassani, L. Saghatforoush, M. K. Rofouei, and M. Rezaie, *Arkivoc.*, **117** (xiii) (2006).

[13] M. R. Islami, J. Torghabeh, S. J. Fatemi, Z. Hassani, and A. Amiry, *Syn Lett.*, **10,** 1707 (2004).

[14] M. R. Islami, Z. Hassani, and K. Saidi, *Synth.Commun.*, **33,** 65 (2003).

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*For two rotamers