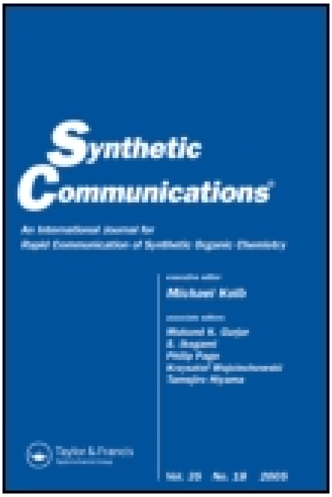

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Three-Component Reaction of Triphenylphosphine, Acetylenic Esters, and Arylsulfonyl Hydrazides or Aryl Hydrazines: An Efficient One-Pot Synthesis of Stable β-Nitrogen-Substituted Phosphorus Ylides

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Three-Component Reaction of Triphenylphosphine, Acetylenic Esters, and Arylsulfonyl Hydrazides or Aryl Hydrazines: An Efficient One-Pot Synthesis of Stable *β*-Nitrogen-Substituted Phosphorus Ylides

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Abstract: The three-component reaction between dialkyl acetylenedicarboxylates and triphenylphosphine in the presence of arylsulfonyl hydrazides or aryl hydrazines produces highly functionalized, salt-free phosphorus ylides in excellent yields.

Keywords: Acetylenic esters; Aryl hydrazines; Arylsulfonyl hydrazides; Phosphorus ylides; Triphenylphosphine

Phosphorus ylides are reactive systems that take part in many valuable reactions in organic synthesis.[1–7] Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of an appropriate phosphonium salt with a base; the corresponding phosphonium salts are usually obtained from the phosphine and an alkyl halide.[1,2] Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins.[1] The phosphonium salts are most often converted to the ylides by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. Reaction of acetylenic esters with triphenylphosphine in

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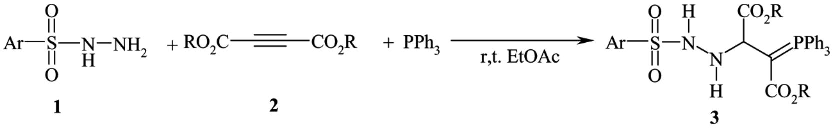
the presence of an organic acid has also been reported to produce phosphorus ylides.[8] In continuation of our work on the reaction between trivalent phosphorus nucleophiles and electron-deficient acetylenic compounds in the presence of organic N-H, O-H, or C-H acids,[9] we herein report an efficient synthetic route to stable phosphorus ylides using triphenylphosphine, dialkyl acetylenedicarboxylates, and arylsulfonyl hydrazides or aryl hydrazines. Thus, the reaction of the arylsulfonyl hydrazide **1** with the acetylenic ester **2** in the presence of triphenylphosphine leads to the corresponding ylide **3a** in good yields (Scheme 1).

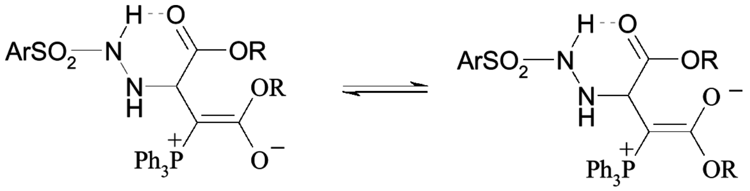
The mass spectra of the ylides **3** are fairly similar and display molecular ion peaks. The NMR spectra of ylides **3a–f** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and rotation about the C-C bond due to partial double bond character is slow on the NMR timescale at room temperature (Scheme 2).

The ^{1}H NMR spectrum of **3a** shows two sharp lines ($\delta = 3.06$, 3.73 ppm) for the methyl groups of the major isomer, along with a signal for the methine proton at 4.62 ppm, which appears as a doublet ($^3J_{PH} = 8.65$ Hz). Two single signals are observed at $\delta = 6.63$ and 6.68 ppm, which disappear after addition to $CDCl_3$ solution of **3a** a few drops of D_2O. These signals are related to two NH protons. The aromatic protons show multiplets at $\delta = 7.37$–7.99 ppm. The corresponding signals for the minor isomer appear at $\delta = 3.42$, 3.82 ppm for methyl



3	R	Ar	Yield [%]
a	Me	C_6H_5	90
b	Et	C_6H_5	95
c	Me	4-$CH_3C_6H_4$	92
d	Et	4-$CH_3C_6H_4$	93
e	Me	4-$NO_2C_6H_4$	90
f	Et	4-$NO_2C_6H_4$	94

Scheme 1. Three-component reaction between triphenylphosphine, acetylenic esters, and arylsulfonyl hydrazides.



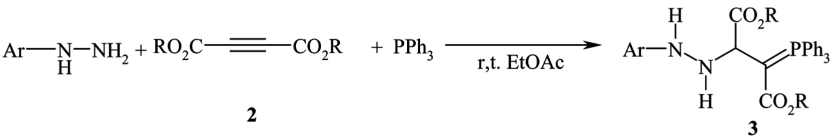
Scheme 2. Two rotational isomers for ylides **3a–f**.

groups and at $\delta = 4.39$ ppm ($^3J_{PH} = 8.7$ HZ,) for the methine proton. The ^{31}P NMR spectrum of compound **3a** displays two signals at 24.49 and 24.85 ppm for major and minor isomers, respectively. These shifts are similar to those observed for other stable phosphorus ylides.[10,11] The structural assignments made on the basis of the NMR spectra of compound **3a** are supported by its IR spectrum. The ester carbonyl groups exhibit absorption bands at 1736 and 1619cm^{-1}. The N-H stretching absorption bands appear at 3295–3150cm^{-1}.

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[1–7] it is reasonable to assume that ylides **3** result from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid. Then, the positively charged ion is attacked by the anion of the NH-acid to form the phosphorane **3**.

The three-component reaction of acetylenic esters, triphenylphosphine, and aryl hydrazines also leads to the similar phosphorus ylides **3g–i** (Scheme 3). As for ylides **3a–f**, the NMR spectra of ylides **3g–i** are consistent with the presence of two isomers.

In summary, phosphorus ylides may be prepared by a simple, one-pot, three-component reaction of dialkyl acetylenedicarboxylates,



2

3

3	R	Ar	Yield [%]
g	Me	2,4-$NO_2C_6H_3$	90
h	Me	4-$NO_2C_6H_4$	91
i	Et	4-$NO_2C_6H_4$	94

Scheme 3. Three-component reaction between triphenylphosphine, acetylenic esters, and aryl hydrazines.

triphenylphosphine, and arylsulfonyl hydrazides or aryl hydrazines. The present method has the advantage that not only the reaction is performed under neutral conditions but also the substances can be mixed without any activation or modification.

EXPERIMENTAL

All melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a Finnigan-Mat 8430 mass spectrometer operating at an ionization 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 a Bruker DRX-300 Avance spectrometer at 300.1, 75.46, and 121.49 MHz, respectively. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in $CDCl_3$ solution using TMS as internal standard (^{1}H, ^{13}C) or 85% H_3PO_4 as external standard (^{31}P). The chemicals used in this study were purchased from Fluka and were used without further purification.

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.52 g, 2 mmol) and arylsulfonyl hydrazide (2 mmol) in ethyl acetate (10 ml), a mixture of dialkyl acetylenedicarboxylate (2 mmol) in ethyl acetate (3 ml) was added dropwise at room temperature over 2 min. The reaction mixture was then stirred for 30 min, and the product was removed by filtration and washed with ethyl acetate (10 ml).

Dimethyl 2-[2-(Phenylsulfonyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3a)

Yield: 90%; colorless crystals; mp 119–120 °C. IR (KBr) (ν_{max}, cm^{-1}): 3295, 3150 (NH), 1736, 1619 (C=O). Calcd. for $C_{30}H_{29}N_2O_6PS$: C, 62.49; H, 5.07; N, 4.86%. Found: C, 62.52; H, 5.01; N, 4.87%. MS (m/z, %): 576 (M, 3). Major isomer (80%): ^{1}H NMR ($CDCl_3$): δ 3.06 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 4.62 (d, $^{3}J_{PH} = 8.65$ Hz, 1 H, P=C-CH), 6.63 (s, 1 H, NH), 6.68 (s, 1 H, NH), 7.37–7.99 (m, 40 H, arom)* (*for two conformational isomers). ^{13}C NMR ($CDCl_3$): δ 42.83 (d, $^{1}J_{PC} = 125$ Hz, C=P), 49.02, 52.16 (2 OCH_3), 60.41 (d, $^{2}J_{PC} = 14.6$ Hz, CH), 125.90 (d, $^{1}J_{PC} = 92.25$ Hz, C^{ipso}), 128.86 (d, $^{3}J_{PC} = 12.0$ Hz, C^{meta}), 132.03 (d, $^{4}J_{PC} = 2.4$ Hz, C^{para})*, 133.65 (d, $^{2}J_{PC} = 9.82$ Hz,

C^{ortho}), 128.10, 128.70, 132.66, 138.43 (CH, arom), 169.82 (d, $^2J_{PC} = 12.15$ Hz, C=O)*, 175.34 (d, $^3J_{PC} = 11.32$ Hz, C=O)*. ^{31}P NMR ($CDCl_3$): δ 24.49 Minor isomer (20%): ^{1}H NMR ($CDCl_3$): δ 3.42 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 4.39 (d, $^3J_{PH} = 8.7$ Hz, 1 H, P=C-CH), 6.57 (s, 1 H, NH), 6.88 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 41.16 (d, $^1J_{PC} = 122$ Hz, C=P), 49.96, 52.52 (2 OCH_3), 63.59 (d, $^2J_{PC} = 14.25$ Hz, CH), 125.34 (d, $^1J_{PC} = 91.5$ Hz, C^{ipso}), 128.43 (d, $^3J_{PC} = 11$ Hz, C^{meta}), 133.18 (d, $^2J_{PC} = 9.74$ Hz, C^{ortho}), 128.22, 128.34, 132.71, 139.01 (CH, arom). ^{31}P NMR ($CDCl_3$): δ 24.85.

Diethyl 2-[2-(Phenylsulfonyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3b)

Yield: 95%; colorless crystals; mp 133–134 °C. IR (KBr) (ν_{max}, cm^{-1}): 3335, 3150 (NH) 1735, 1619 (C=O). Calcd. for $C_{32}H_{33}N_2O_6PS$: C, 63.56; H, 5.50; N, 4.63%. Found: C, 63.61; H, 5.52; N, 4.58%. MS (m/z, %): 604 (M, 1). Major isomer (70%): ^{1}H NMR ($CDCl_3$): δ 0.40 (t, $^3J_{HH} = 7.05$ Hz, 3 H, CH_3), 1.27 (t, $^3J_{HH} = 7.11$ Hz, 3 H, CH_3), 3.59 (m, 2 H, OCH_2), 4.28 (m, 2 H, OCH_2), 4.68 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.25 (s, 1 H, NH), 6.87 (s, 1 H, NH) 7.39–7.93 (m, 40 H, arom)*. ^{13}C NMR ($CDCl_3$): δ 13.87, 14.28 ($2CH_3$), 41.83 (d, $^1J_{PC} = 126$ Hz, C=P), 57.56, 61.26 (2 OCH_2), 63.48 (d, $^2J_{PC} = 15.2$ Hz, CH), 126.16 (d, $^1J_{PC} = 92.25$ Hz, C^{ipso}), 128.65 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 132.06 (d, $^4J_{PC} = 2.2$ Hz, C^{para}), 133.75 (d, $^2J_{PC} = 9.83$ Hz, C^{ortho}), 128.11, 129.25, 132.60, 138.53 (CH, arom), 169.45 (d, $^2J_{PC} = 12.52$ Hz, C=O)*, 174.93 (d, $^3J_{PC} = 11$ Hz, C=O)*. ^{31}P NMR ($CDCl_3$): δ 23.41. Minor isomer (30%): ^{1}H NMR ($CDCl_3$) δ 0.45 (t, $^3J_{HH} = 7.08$ Hz, 3 H, CH_3), 1.35 (t, $^3J_{HH} = 7.11$ Hz, 3 H, CH_3), 3.81 (m, 2 H, OCH_2), 4.08 (m, 2 H, OCH_2), 4.71 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.22 (s, 1 H, NH), 6.71 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 14.03, 14.12 ($2CH_3$), 43.36 (d, $^1J_{PC} = 126$ Hz, C=P), 57.79, 61.34 (2 OCH_2), 63.72 (d, $^2J_{PC} = 15.2$ Hz, CH), 126.72 (d, $^1J_{PC} = 92$ Hz, C^{ipso}), 128.55 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 131.94 (d, $^4J_{PC} = 2.2$ Hz, C^{para}), 133.19 (d, $^2J_{PC} = 9.83$ Hz, C^{ortho}), 128.43, 129.81, 132.16, 138.57 (CH, arom). ^{31}P NMR ($CDCl_3$): δ 25.12.

Dimethyl 2-[2-((4-Methylphenyl)sulfonyl)hydrazino]-3 (triphenylphosphanylidene) Succinate (3c)

Yield: 92%; colorless crystals; mp 140–142 °C. IR (KBr) (ν_{max}, cm^{-1}): 3255, 3180 (NH), 1730, 1670 (C=O). Calcd. for $C_{31}H_{31}N_2O_6PS$: C, 63.04; H, 5.29; N, 4.74%. Found: C, 63.10; H, 5.21; N, 4.75%. MS (m/z, %): 590 (M, 1). Major isomer (80%): ^{1}H NMR (CDCl$_3$): δ 2.46 (s, 3 H, CH$_3$), 3.06 (s, 3 H, OCH$_3$), 3.73 (s, 3 H, OCH$_3$), 4.59 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.60 (s, 1 H, NH), 7.24 (s, 1 H, NH), 7.27–8.00 (m, 38 H, arom)*. ^{13}C NMR (CDCl$_3$): δ 21.60 (CH$_3$), 41.84 (d, $^1J_{PC} = 125.5$ Hz, C=P)*, 48.99, 52.11 (2 OCH$_3$), 63.55 (d, $^2J_{PC} = 14.2$ Hz, CH), 125.91 (d, $^1J_{PC} = 91.8$ Hz, C^{ipso}), 128.68 (d, $^3J_{PC} = 12.3$ Hz, C^{meta}), 132.13 (d, $^4J_{PC} = 2$ Hz, C^{para}), 133.76 (d, $^2J_{PC} = 9.75$ Hz, C^{ortho}), 128.14, 129.31, 135.39, 144.07 (CH, arom), 169.81 (d, $^2J_{PC} = 12.7$ Hz, C=O), 175.33 (d, $^3J_{PC} = 12.52$ Hz, C=O). ^{31}P NMR (CDCl$_3$): δ 23.79 Minor isomer (20%): ^{1}H NMR (CDCl$_3$): δ 1.65 (s, 3 H, CH$_3$), 3.42 (s, 3 H, OCH$_3$), 3.83 (s, 3 H, OCH$_3$), 4.37 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.28 (s, 1 H, NH), 6.88 (s, 1 H, NH). ^{13}C NMR (CDCl$_3$): δ 21.77 (CH$_3$), 49.90, 52.36 (2 OCH$_3$), 62.81 (d, $^2J_{PC} = 14.2$ Hz, CH), 125.31 (d, $^1J_{PC} = 91.8$ Hz, C^{ipso}), 128.44 (d, $^3J_{PC} = 12.3$ Hz, C^{meta}), 131.96 (d, $^4J_{PC} = 2$ Hz, C^{para}), 133.41 (d, $^2J_{PC} = 10$ Hz, C^{ortho}), 128.29, 129.73, 135.43, 144.12 (CH, arom), 169.86 (d, $^2J_{PC} = 12.7$ Hz, C=O), 175.65 (d, $^3J_{PC} = 12.50$ Hz, C=O). ^{31}P NMR (CDCl$_3$): δ 24.85.

Diethyl 2-[2-((4-Methylphenyl)sulfonyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3d)

Yield: 93%; colorless crystals; mp 150–152 °C. IR (KBr) (ν_{max}, cm^{-1}): 3285, 3170 (NH), 1733, 1625 (C=O). Calcd. for C$_{33}$H$_{35}$N$_2$O$_6$PS: C, 64.06; H, 5.70; N, 4.53%. Found: C, 64.11; H, 5.68; N, 4.55%. MS (m/z, %): 618 (M, 1). Major isomer (80%): ^{1}H NMR (CDCl$_3$): δ 0.40 (t, $^3J_{HH} = 7$ Hz, 3 H, CH$_3$), 1.26 (t, $^3J_{HH} = 7.08$ Hz, 3 H, CH$_3$), 2.45 (s, 3H, CH$_3$), 3.59 (m, 2 H, OCH$_2$), 4.11 (m, 2 H, OCH$_2$), 4.65 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.64 (s, 1 H, NH), 7.23 (s, 1 H, NH), 7.26–7.94 (m, 38 H, arom)*. ^{13}C NMR (CDCl$_3$): δ 13.89, 14.29 (2CH$_3$), 21.58 (CH$_3$), 41.99 (d, $^1J_{PC} = 126.3$ Hz, C=P), 57.50, 60.76 (2 OCH$_2$), 63.62 (d, $^2J_{PC} = 15$ Hz, CH), 126.15 (d, $^1J_{PC} = 92$ Hz, C^{ipso}), 128.60 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 132.09 (d, $^4J_{PC} = 2.3$ Hz, C^{para}), 133.67 (d, $^2J_{PC} = 9.82$ Hz, C^{ortho}), 128.16, 129.45, 135.49, 143.31 (CH, arom), 169.26 (d, $^2J_{PC} = 12.52$ Hz, C=O)*, 174.77 (d, $^3J_{PC} = 11.77$ Hz, C=O)*. ^{31}P NMR (CDCl$_3$): δ 23.64. Minor isomer (30%): ^{1}H NMR (CDCl$_3$) δ 1.05 (t, $^3J_{HH} = 6.95$ Hz, 3 H, CH$_3$), 1.35 (t, $^3J_{HH} = 7$ Hz, 3 H, CH$_3$), 2.41 (s, 3 H, CH$_3$), 3.65 (m, 2 H, OCH$_2$), 4.21 (m, 2 H, OCH$_2$) 4.41 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.65 (s, 1 H, NH), 6.86 (s, 1 H, NH). ^{13}C NMR (CDCl$_3$): δ 14.12, 14.87 (2CH$_3$), 21.61 (CH$_3$), 42.01 (d, $^1J_{PC} = 126.3$ Hz, C=P), 57.94, 61.22 (2 OCH$_2$), 62.90 (d, $^2J_{PC} = 15$ Hz, CH), 125.47 (d, $^1J_{PC} = 92$ Hz, C^{ipso}), 128.44

(d, $^3J_{PC} = 12$ Hz, C^{meta}), 131.99 (d, $^4J_{PC} = 2.3$ Hz, C^{para}), 133.14 (d, $^2J_{PC} = 10$ Hz, C^{ortho}), 128.28, 129.66, 135.52, 143.40, (CH, arom). ^{31}P NMR (CDCl$_3$): δ 24.14.

Dimethyl 2-[2-((4-nitrophenyl)sulfonyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3e)

Yield: 90%; colorless crystals; mp 142–1143 °C. IR (KBr) (ν_{max}, cm^{-1}): 3400, 3130 (NH), 1733, 1615 (C=O). Calcd. for $C_{30}H_{28}N_3O_8PS$: C, 57.97; H, 4.54; N, 6.76%. Found: C, 57.90; H, 4.48; N, 6.80%. MS (m/z, %): 621 (M, 1). Major isomer (80%): ^{1}H NMR (CDCl$_3$): δ, 3.07 (s, 3 H, OCH$_3$), 3.70 (s, 3 H, OCH$_3$), 4.88 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.87 (s, 1 H, NH), 7.18 (s, 1 H, NH), 7.33–8.28 (m, 38 H, arom)*. ^{13}C NMR (CDCl$_3$): δ 42.83 (d, $^1J_{PC} = 125.5$ Hz, C=P)*, 49.14, 52.34 (2 OCH$_3$), 63.42 (d, $^2J_{PC} = 14.5$ Hz, CH), 125.72 (d, $^1J_{PC} = 92$ Hz, Hz, C^{ipso}), 128.77 (d, $^3J_{PC} = 12.2$ Hz, C^{meta}), 132.12 (d, $^4J_{PC} = 2$ Hz, C^{para}), 133.73 (d, $^2J_{PC} = 10$ Hz, C^{ortho}), 123.90, 129.41, 144.44, 150.06 (CH, arom), 169.92 (d, $^2J_{PC} = 12.6$ Hz, C=O)*, 175.01 (d, $^3J_{PC} = 11.76$ Hz, C=O)*. ^{31}P NMR (CDCl$_3$): δ 25.49. Minor isomer (20%): ^{1}H NMR (CDCl$_3$): δ, 3.45 (s, 3 H, OCH$_3$), 3.82 (s, 3 H, OCH$_3$), 4.51 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.69 (s, 1 H, NH), 7.21 (s, 1 H, NH). ^{13}C NMR (CDCl$_3$): δ 51.86, 52.18, (2 OCH$_3$), 62.67 (d, $^2J_{PC} = 14.2$ Hz, CH), 126.40 (d, $^1J_{PC} = 92$ Hz, C^{ipso}), 128.94 (d, $^3J_{PC} = 12.3$ Hz, C^{meta}), 131.62 (d, $^4J_{PC} = 2$ Hz, C^{para}), 133.01 (d, $^2J_{PC} = 10$ Hz, C^{ortho}), 124.15, 129.76, 144.59, 150.32 (CH, arom). ^{31}P NMR (CDCl$_3$): δ 26.85.

Diethyl 2-[2-((4-Nitrophenyl)sulfonyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3f)

Yield: 94%; colorless crystals; mp 152–154 °C. IR (KBr) (ν_{max}, cm^{-1}): 3270, 3110 (NH), 1726, 1609, (C=O). Calcd. for $C_{32}H_{32}N_3O_8PS$: C, 59.16; H, 4.96; N, 6.47%. Found: C, 59.21; H, 4.94; N, 6.39%. MS (m/z, %): 649 (M, 1). Major isomer (80%): ^{1}H NMR (CDCl$_3$): δ 0.42 (t, $^3J_{HH} = 6.9$ Hz, 3 H, CH$_3$), 1.26 (t, $^3J_{HH} = 7.1$ Hz, 3 H, CH$_3$), 3.56 (m, 4 H, OCH$_2$)*, 4.14 (m, 4 H, OCH$_2$)*, 4.96 (d, $^3J_{PH} = 9.9$ Hz,1 H, P=C-CH), 6.60 (s, 1 H, NH), 7.19 (s, 1 H, NH), 7.24–8.2 (m, 38 H, arom)*. ^{13}C NMR (CDCl$_3$): δ 13.86, 14.25 (2CH$_3$), 42.43 (d, $^1J_{PC} = 126.3$ Hz, C=P), 57.70, 60.38 (2 OCH$_2$), 63.47 (d, $^2J_{PC} = 14$ Hz, CH), 126.07 (d, $^1J_{PC} = 91.8$ Hz, C^{ipso}), 128.65 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 132.03 (d, $^4J_{PC} = 2.1$ Hz, C^{para}), 133.66 (d, $^2J_{PC} = 9.83$ Hz, C^{ortho}), 123.75, 129.42, 144.68, 149.95 (CH, arom), 169.51 (d, $^2J_{PC} = 12.67$ Hz, C=O)*, 174.53 (d, $^3J_{PC} = 11.78$ Hz, C=O)*. ^{31}P NMR ($CDCl_3$): δ 24.27. Minor isomer (30%): ^{1}H NMR ($CDCl_3$) δ 1.06 (t, $^3J_{HH} = 7$ Hz, 3 H, CH_3), 1.32 (t, $^3J_{HH} = 7.1$ Hz, 3 H, CH_3), 4.54 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.57 (s, 1 H, NH), 7.16 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 13.84, 14.20 ($2CH_3$), 41.35 (d, $^1J_{PC} = 126.3$ Hz, C=P), 58.01, 60.84 (2 OCH_2), 62.96 (d, $^2J_{PC} = 15.2$ Hz, CH), 125.29 (d, $^1J_{PC} = 92$ Hz, C^{ipso}), 128.23 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 131.96 (d, $^4J_{PC} = 2.1$ Hz, C^{para}), 133.57 (d, $^2J_{PC} = 10$ Hz, C^{ortho}), 123.81, 129.03, 144.61, 149.84 (CH, arom). ^{31}P NMR ($CDCl_3$): δ 25.81.

Dimethyl 2-[2-(2,4-Dinitrophenyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3g)

Yield: 90%; colorless crystals; mp 153–155 °C. IR (KBr) (ν_{max}, cm^{-1}): 3350 (NH), 1734, 1616 (C=O). Calcd. for $C_{30}H_{29}N_4O_8P$: C, 59.60; H, 4.84; N, 9.27%. Found: C, 59.65; H, 4.78; N, 9.31%. MS (m/z, %): 604 (M, 3). Major isomer (75%): ^{1}H NMR ($CDCl_3$): δ 3.17 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 5.54 (d, $^3J_{PH} = 10.18$ Hz, 1 H, P=C-CH), 7.28–8.01 (m, 36 H, arom)*, 9.00 (s, 1 H, NH), 9.97 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 37.4 (d, $^1J_{PC} = 122$ Hz, C=P), 49.3, 52.34 (2 OCH_3), 62.28 (d, $^2J_{PC} = 14.52$ Hz, CH), 125.64 (d, $^1J_{PC} = 91.5$ Hz, C^{ipso}), 128.43 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 132.01 (d, $^4J_{PC} = 2.3$ Hz, C^{para}), 133.52 (d, $^2J_{PC} = 9.75$ Hz, C^{ortho}), 115.35, 123.84, 129.41, 132.14, 135.91, 149.4 (CH, arom), 165.38 (d, $^2J_{PC} = 12.32$ Hz, C=O)*, 169.95 (d, $^3J_{PC} = 11.52$ Hz, C=O)*. ^{31}P NMR ($CDCl_3$): δ 23.36. Minor isomer (25%): ^{1}H NMR ($CDCl_3$): δ 3.57 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 5.05 (d, $^3J_{PH} = 9.21$ Hz, 1 H, P=C-CH), 9.04 (s, 1 H, NH), 10.02 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 36.5 (d, $^1J_{PC} = 121.7$ Hz, C=P), 50.1, 53.42 (2 OCH_3), 62.53 (d, $^2J_{PC} = 14.52$ Hz, CH), 125.04 (d, $^1J_{PC} = 91$ Hz, C^{ipso}), 128.80 (d, $^3J_{PC} = 11.92$ Hz, C^{meta}), 132.41 (d, $^4J_{PC} = 2.2$ Hz, C^{para}), 133.40 (d, $^2J_{PC} = 10$ Hz, C^{ortho}), 115.48, 123.75, 129.91, 131.80, 136.42, 150.3 (CH, arom). ^{31}P NMR ($CDCl_3$): δ 23.43.

Dimethyl 2-[2-(4-Nitrophenyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3h)

Yield: 91%; colorless crystals; mp 148–150 °C. IR (KBr) (ν_{max}, cm^{-1}): 3335, 3300, (NH), 1779, 1637 (C=O). Analyses: calcd. for $C_{30}H_{29}N_3O_6P$: C, 64.51; H, 5.23; N, 7.52%. Found: C, 64.49; H, 5.29; N, 7.56%. MS (m/z, %): 558 (M, 5). Major isomer (80%): ^{1}H NMR ($CDCl_3$): δ 3.13

(s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 5.05 (d, $^3J_{PH} = 8.8$ Hz, 1 H, P=C-CH), 6.51–7.93 (m, 38 H, arom)*, 7.93 (s, 1 H, NH), 9.97 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 40.59 (d, $^1J_{PC} = 125$ Hz, C=P)*, 49.64, 52.69 (2 OCH_3), 62.34 (d, $^2J_{PC} = 14.52$ Hz, CH), 126.27 (d, $^1J_{PC} = 91.65$ Hz, C^{ipso}), 129.08 (d, $^3J_{PC} = 12.15$ Hz, C^{meta}), 132.67 (d, $^4J_{PC} = 2.7$ Hz, C^{para})*, 133.88 (d, $^2J_{PC} = 9.75$ Hz, C^{ortho}), 110.87, 126.49, 138.38, 155.74 (CH, arom), 170.73 (d, $^2J_{PC} = 12.82$ Hz, C=O)*, 175.87 (d, $^3J_{PC} = 11.25$ Hz, C=O)*. ^{31}P NMR ($CDCl_3$): δ 23.66. Minor isomer (20%): ^{1}H NMR ($CDCl_3$): δ 3.56 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 4.79 (d, $^3J_{PH} = 9.92$ Hz, 1 H, P=C-CH), 9.04 (s, 1 H, NH), 10.02 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 39.5 (d, $^1J_{PC} = 122$ Hz, C=P), 50.57, 52.51 (2 OCH_3), 61.87 (d, $^2J_{PC} = 15.2$ Hz, CH), 125.70 (d, $^1J_{PC} = 93.97$ Hz, C^{ipso}), 128.63 (d, $^3J_{PC} = 11$ Hz, C^{meta}), 134.10 (d, $^2J_{PC} = 9.74$ Hz, C^{ortho}), 110.57, 126.53, 138.27, 154.97 (CH, arom). ^{31}P NMR ($CDCl_3$): δ 23.92.

Diethyl 2-[2-(4-Nitrophenyl)hydrazino]-3-(triphenylphosphanylidene) Succinate (3i)

Yield: 94%; colorless crystals; mp 152–154 °C. IR (KBr) (ν_{max}, cm^{-1}): 3335, 3270 (NH), 1741, 1620 (C=O). Calcd. for $C_{32}H_{33}N_3O_6P$: C, 65.52; H, 5.67; N, 7.16%. Found: C, 65.61; H, 5.67; N, 7.22%. MS (m/z, %): 586 (M, 3). Major isomer (80%): ^{1}H NMR ($CDCl_3$): δ 0.44 (t, $^3J_{HH} = 7.08$ Hz, 3 H, CH_3), 1.31 (t, $^3J_{HH} = 7.08$ Hz, 3 H, CH_3), 3.66 (q, $^3J_{HH} = 7$ Hz, 2 H, OCH_2), 4.14 (q, $^3J_{HH} = 7$ Hz, 2 H, OCH_2), 5.29 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 6.55–7.93 (m, 38 H, arom)*, 9.00 (s, 1 H, NH), 9.97 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 14.38, 14.72 (2CH_3), 40.45 (d, $^1J_{PC} = 126$ Hz, C=P), 58.72, 61.83 (2 OCH_2), 62.42 (d, $^2J_{PC} = 14.63$ Hz, CH), 126.44 (d, $^1J_{PC} = 92$ Hz, C^{ipso}), 128.96 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 132.60 (d, $^4J_{PC} = 2.6$ Hz, C^{para})*, 133.94 (d, $^2J_{PC} = 9.82$ Hz, C^{ortho}), 110.88, 126.50, 138.26, 156.04 (CH, arom), 170.39 (d, $^2J_{PC} = 12.52$ Hz, C=O), 175.52 (d, $^3J_{PC} = 11$ Hz, C=O). ^{31}P NMR ($CDCl_3$): δ 23.74. Minor isomer (20%): ^{1}H NMR ($CDCl_3$) δ 0.49 (t, $^3J_{HH} = 7.08$ Hz, 3 H, CH_3), 1.19 (t, $^3J_{HH} = 7.08$ Hz, 3 H, CH_3), 3.33 (q, $^3J_{HH} = 7$ Hz, 2 H, OCH_2), 4.32 (q, $^3J_{HH} = 7$ Hz, 2 H, OCH_2), 5.05 (d, $^3J_{PH} = 9$ Hz, 1 H, P=C-CH), 9.00 (s, 1 H, NH), 9.97 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 14.76, 15.42, (2CH_3), 41.54 (d, $^1J_{PC} = 133$ Hz, C=P), 53.89, 58.72 (2 OCH_2), 61.83 (d, $^2J_{PC} = 14.63$ Hz, CH), 125.87 (d, $^1J_{PC} = 92$ Hz, C^{ipso}), 129.28 (d, $^3J_{PC} = 12$ Hz, C^{meta}), 134.17 (d, $^2J_{PC} = 9.82$ Hz, C^{ortho}), 110.50, 126.65, 138.49, 155.06 (CH, arom), 170.46 (d, $^2J_{PC} = 12.52$ Hz, C=O), 175.39 (d, $^3J_{PC} = 11$ Hz, C=O). ^{31}P NMR ($CDCl_3$): δ 25.12.

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