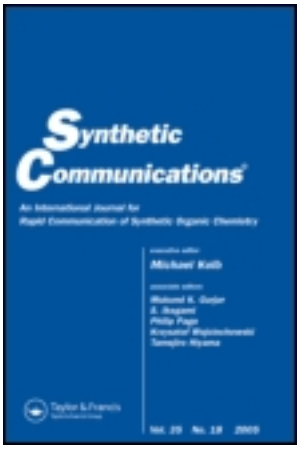

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Three-Component Reaction of Triphenylphosphine, Dialkyl Acetylenedicarboxylates, and Heterocyclic Rings and the Related Iminophosphoranes

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THREE-COMPONENT REACTION OF TRIPHENYLPHOSPHINE, DIALKYL ACETYLENEDICARBOXYLATES, AND HETEROCYCLIC RINGS AND THE RELATED IMINOPHOSPHORANES

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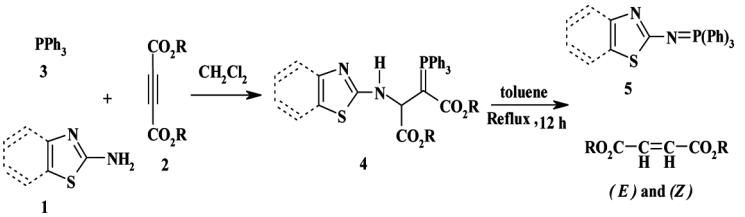
GRAPHICAL ABSTRACT



Abstract *Crystalline phosphorus ylides are obtained in excellent yields from the 1:1:1 addition reaction of triphenylphosphine, dialkyl acetylenedicarboxylate, and NH acids, such as 2-aminothiazole and 2-aminobenzothiazole. These stabilized phosphoranes undergo a smooth intramolecular reaction in boiling toluene to produce aryliminophosphoranes in excellent yields.*

Keywords Dialkyl acetylenedicarboxylates; iminophosphoranes; phosphorus ylides; thiazoles; triphenylphosphine

INTRODUCTION

Iminophosphoranes are important reagents and intermediates, recently, they have been used for the introduction of imine unit organic synthesis.[1,2] In the realm of ylide compounds and their value for a variety of industrial, biological, and chemical synthetic uses, phosphorus ylides are playing increasingly pivotal roles[3] They has provided chemists with exceptionally fertile ground for the design and development of new bond formation.[4] Since the pioneering work by Staudinger

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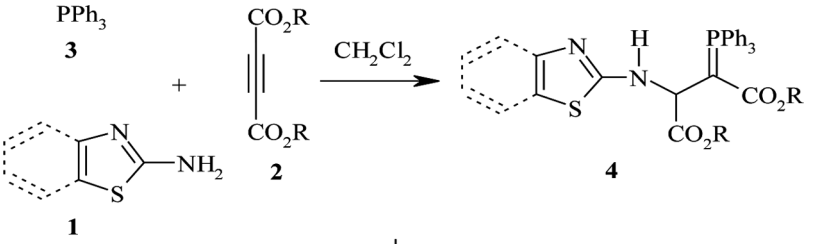
and Meyre in 1919,[5] on the preparation of iminophosphoranes, compounds of general structure R_3PNR, the synthetic application of phosphorus ylides to the preparation of various organic products has increased enormously, especially during the past three decades.[6] Several methods for the preparation of iminophophoranes have been developed.[7–9]

Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins.[10,11] Reaction of acetylenic esters with triphenylphosphine in the presence of an organic compound possessing an acidic hydrogen recently has been reported to produce phosphorus ylides.[12–14] In continuation of our work on the reaction between triphenylphosphine and acetylene diesters in the presence of organic N-H, O-H, or C-H acids,[15–21] we herein report an efficient synthetic route to stable phosphorus ylides using a three-component reaction of triphenylphosphine, dialkyl acetylenedicarboxylate (DAAD) and NH acids, such as 2-aminothiazole and 2-aminobenzothiazole. These stabilized phosphoranes undergo a smooth intramolecular reaction in boiling toluene to produce arylimino-phosphoranes **5** in excellent yields.

The reaction of the thiazoles **1** with DAAD **2** in the presence of triphenylphosphine **3** leads to the corresponding ylide **4** in good yields (Scheme 1).

The ylides **4a, b** were converted to iminophosphoranes **5a, b** when the reaction mixture was refluxed in toluene (Scheme 2).

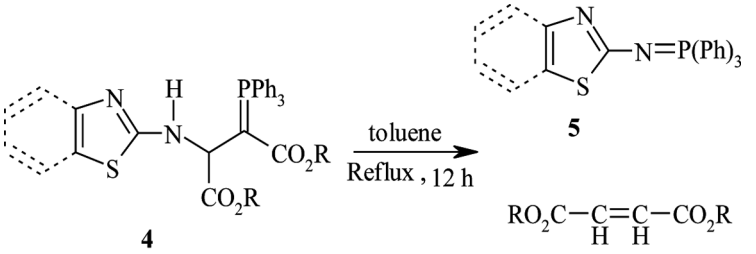
Because the rotation about the partial double bond in *E* and *Z* isomers is slow on the NMR time scale at ambient temperature (Scheme 3), the presence of a mixture of two geometrical isomers E and Z for compounds **4a–d** was proven by their ^{13}C NMR and ^{1}H NMR absorption. For example, ^{1}H NMR and ^{13}C NMR spectra of these compounds show four singlets for methyl hydrogens and four absorptions for carbonyl groups, respectively, which are indicative of the presence



4	R	Yield*(%)
a	Me	90
b	Me	95
c	Et	93
d	Et	90

*Isolated yields

Scheme 1. Three-component reaction of triphenylphosphine, DAADs, and thiazoles.



5	R	Yield*(%)
a	Me	92
b	Me	90

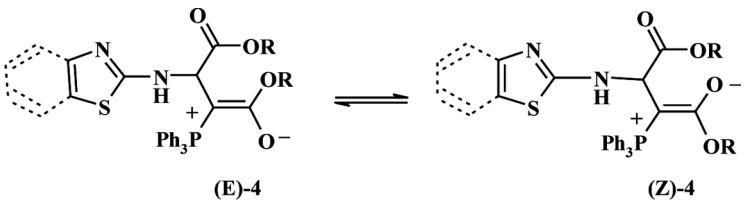
*Isolated yields

Scheme 2. Reaction mixture refluxed in toluene.

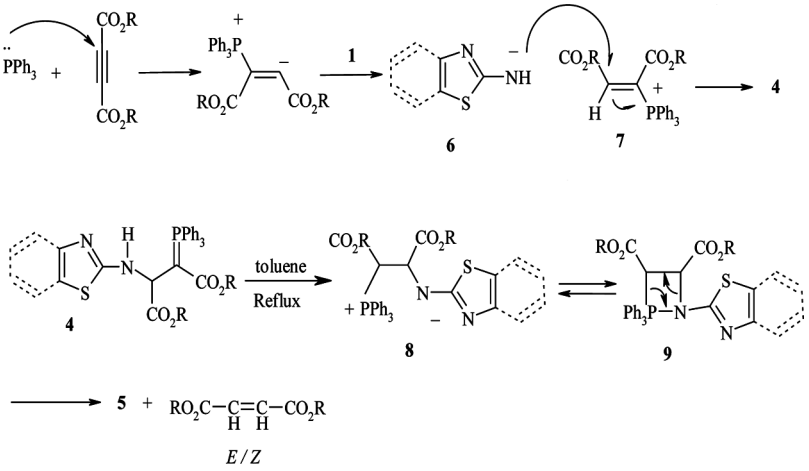
of two isomers. Presence of the ^{31}P nucleus helps in assignment of compounds **4a–d** by long-range spin–spin coupling constants of ^{31}P with ^{1}H and ^{13}C nuclei.

The mass spectrum of compound **4a** showed the molecular ion peak at 504. The ^{1}H NMR spectrum of compound **4a** shows four different sharp lines at $\delta = 3.11$, 3.07, 3.57, and 3.68 ppm, which are due to the methoxy protons and two doublet at 4.36 and 4.45 ($^{3}J_{PH} = 5$ Hz, $^{3}J_{HH} = 10$ Hz, P=C-CH) for methine proton, which is coupled with phosphorus atom and NH, two fairly broad signals at $\delta = 6.72$ and 6.91 ppm related to protons of N-H groups, and multiplets between 6.32 and 7.68 ppm for aromatic protons. The ^{13}C NMR of compound **4a** is in good agreement with the proposed structure of this compound. The ^{31}P NMR spectrum of compound **4a** consists of two signals at 23.09 and 23.15 ppm. This shift is similar to those observed for other stable phosphorus ylides.[22,23] The infrared (IR) spectrum showed an absorption bond at 3365 cm^{-1} for the NH group. The carbonyl stretching vibration was observed as strong absorption bonds at 1741 cm^{-1}.

The ^{1}H NMR spectrum of compound **5a** shows two doublet at 6.39 and 6.95 ($^{3}J_{HH} = 3.8$ Hz,) for thiazole protons and multiplets between 7.43 and 7.83 ppm for aromatic protons. The ^{13}C NMR spectrum of compound **5a** showed seven distinct resonances in agreement with the proposed structure. Signals of triphenylphosphine group appear at 129.05 ($^{2}J_{PC} = 12$ Hz), 129.28 (d, $^{1}J_{PC} = 100$ Hz), 132.60



Scheme 3. Two rotamers.



Scheme 4. Suggested mechanism for formation of ylides **4** and iminophosphoranes **5**.

(d, $^4J_{PC} = 3$ Hz), and 133.52 (d, $^3J_{PC} = 10$ Hz). The ^{31}P NMR spectrum of compound **5a** consists of one signal at 15.58 ppm.

It is reasonable to assume that ylide **4** results from the initial addition of triphenylphosphine to DAAD and subsequent protonation of the 1:1 adduct by the NH-acidic thiazole. The positively charged ion **7** is then attacked by the anion **6** to form the phosphorane **4.** In the ylide **4** in boiling toluene, the NH-proton shifts to the ylidic carbon and forms the phosphorus betaine **8**. This betaine can be in equilibrium with the azaphosphetane **9**. Formation of dimethyl fumarate and/or dimethyl maleate **4** confirms the proposed mechanism (Scheme 4).

In summary, we report herein that the three-component reaction of triphenylphosphine, DAAD, and NH acids, such as 2-aminothiazole and 2-aminobenzothiazole, produces functionalized phosphoranes in good yields. These stabilized phosphoranes undergo a smooth intramolecular reaction in boiling toluene to produce aryliminophosphoranes in excellent yields. The advantages of the reported method are simple available starting materials, short reaction time, simple workup, neutral reaction conditions, and good yields.

EXPERIMENTAL

Melting points were determined with an Electrothermal 9100 apparatus. Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer at the analytical laboratory of Islamic Azad University, Yazd branch. 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 Bruker DRX-500 Avance spectrometer at solution in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

General Procedure for Preparation of Compounds 4a–d

A mixture of dialkyl acetylenedicarboxylate (2 mmol) in dichloromethane (3 mL) was added dropwise to a magnetically stirred solution of triphenylphosphine (2 mmol) and thiazole (2 mmol) in dichloromethane (10 mL) at room temperature over 2 min. The reaction mixture was then stirred for 2 h. The resulted precipitate was filtered off and then recrystallized from 1:1 hexane–ethyl acetate.

General Procedure for Preparation of Compounds 5a, b

A mixture of **4** (1 mmol) in toluene (10 mL) was refluxed for 12 h. The solvent was removed under reduced pressure, and the residue was purified by silica-gel column chromatography using hexane–ethyl acetate as eluent. The solvent was removed under reduced pressure to afford the product.

Dimethyl 2-(Thiazole-2-ylamino)-3-(triphenyl-λ^5-phosphanylidene)-succinate (4a)

Yield: 90%; white powder; mp 152–154 °C. IR (KBr) (ν_{max}, cm^{-1}): 3365 (NH), 1741 (C=O, ester). Calcd. for ($C_{27}H_{25}N_2O_4PS$): C, 64.27; H, 4.99; N, 5.55;%. Found: C, 64.43; H, 4.86; N, 5.59%. MS (m/z, %): 504 (M, 11).

Major isomer (70%). ^{1}H NMR ($CDCl_3$): $\delta = 3.11$ (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 4.45 (1H, dd, $^3J_{HP} = 5$ Hz, $^3J_{HH} = 10$ Hz, P-C-CH), 6.91 (1H, d, $^3J_{HH} = 10$ Hz, NH), 6.32 (1H, d, $^3J_{HH} = 3.8$ Hz, CH of C_3H_2NS), 6.74 (1H, d, $^3J_{HH} = 3.8$ Hz, CH of C_3H_2NS) 7.26 –7.68 (15H, m, $3C_6H_5$).* (*For two conformational isomers.) ^{13}C NMR ($CDCl_3$): $\delta = 50.06$ (d, $^1J_{PC} = 123$ Hz, C=P), 58.20 (d, $^2J_{PC} = 13$ Hz, CH), 49.46, 52.66 (2 OCH_3), 106.78, 139.09, 174.15 (3C C_3H_2NS), 126.99 (d, $^1J_{PC} = 92$ Hz), 129.03 ($^2J_{PC} = 12$ Hz), 132.29 (d, $^4J_{PC} = 3$ Hz), 134.23 (d, $^3J_{PC} = 10$ Hz). 169.34 (d, $^2J_{PC} = 12$ Hz, C=O),* 170.49 (d, $^3J_{PC} = 12$ Hz, C=O).* ^{31}P NMR ($CDCl_3$): δ 23. 15.

Minor isomer (30%). ^{1}H NMR ($CDCl_3$): $\delta = 3.07$ (3H, s, OCH_3), 3.57 (3H, s, OCH_3), 4.36 (1H, dd, $^3J_{HP} = 5$ Hz, $^3J_{HH} = 10$ Hz, P-C-CH), 6.72 (1H, d, $^3J_{HH} = 10$ Hz, NH), 6.25 (1H, d, $^3J_{HH} = 3.8$ Hz, CH of C_3H_2NS), 6.43 (1H, d, $^3J_{HH} = 3.8$ Hz, CH of C_3H_2NS). ^{13}C NMR ($CDCl_3$): $\delta = 50.16$ (d, $^1J_{PC} = 123$ Hz, C=P), 58.34 (d, $^2J_{PC} = 13$ Hz, CH), 49.38, 52.71 (2 OCH_3), 107.14, 139.01, 174.17 (3C C_3H_2NS), 126.75 (d, $^1J_{PC} = 92$ Hz), 129.18 ($^2J_{PC} = 12$ Hz), 132.43 (d, $^4J_{PC} = 3$ Hz), 134.05 (d, $^3J_{PC} = 10$ Hz). ^{31}P NMR ($CDCl_3$): δ 23.09.

Dimethyl 2-(Benzothiazole-2-ylamino)-3-(triphenyl-λ^5-phosphanylidene)-succinate (4b)

Yield: 93%; white powder; mp 157–159 °C. IR (KBr) (ν_{max}, cm^{-1}): 3390 (NH), 1744 (C=O, ester). Calcd. for ($C_{31}H_{27}N_2O_4PS$): C, 67.14; H, 4.91; N, 5.05%. Found: C, 67.28; H, 4.97; N, 4.96%. MS (m/z, %): 554 (M, 7).

Major isomer (60%). ^{1}H NMR ($CDCl_3$): $\delta = 3.28$ (3H, s, OCH_3), 3.56 (3H, s, OCH_3), 4.52 (1H, dd, $^3J_{HP} = 5$ Hz, $^3J_{HH} = 10$ Hz, P-C-CH), 6.88 (1H, d, $^3J_{HH} = 10$ Hz, NH), 6.99–8.23 (19H, m, aromatic).* (*For two conformational isomers.)

^{13}C NMR ($CDCl_3$): δ = 50.12 (d, $^1J_{PC}$ = 123 Hz, C=P), 58.37 (d, $^2J_{PC}$ = 13 Hz, CH), 49.57, 52.73 (2 OCH_3), 118.41, 121.26, 121.44, 125.92, 133.03, 153.08, 174.12 (7C benzothiazole), 129.66 ($^2J_{PC}$ = 12 Hz), 127.68 (d, $^1J_{PC}$ = 92 Hz), 131.39 (d, $^4J_{PC}$ = 3 Hz), 133.03 (d, $^3J_{PC}$ = 10 Hz), 168.96 (d, $^2J_{PC}$ = 12 Hz, C=O),* 171.08 (d, $^3J_{PC}$ = 12 Hz, C=O).* ^{31}P NMR ($CDCl_3$): δ 22.45.

Minor isomer (40%). ^1H NMR ($CDCl_3$): δ = 2.94 (3H, s, OCH_3), 3.53 (3H, s, OCH_3), 4.46 (1H, dd, $^3J_{HP}$ = 5 Hz, $^3J_{HH}$ = 10 Hz, P-C-CH), 6.86 (1H, d, $^3J_{HH}$ = 10 Hz, NH), ^{13}C NMR ($CDCl_3$): δ = 50.10 (d, $^1J_{PC}$ = 123 Hz, C=P), 58.42 (d, $^2J_{PC}$ = 13 Hz, CH), 49.60, 52.69 (2 OCH_3), 118.45, 121.20, 121.32, 125.87, 133.08, 153.12, 174.00 (7C benzothiazole), 129.45 ($^2J_{PC}$ = 12 Hz), 127.61 (d, $^1J_{PC}$ = 92 Hz), 131.32 (d, $^4J_{PC}$ = 3 Hz), 133.09 (d, $^3J_{PC}$ = 10 Hz). ^{31}P NMR ($CDCl_3$): δ 23.49.

Diethyl 2-(Thiazole-2-ylamino)-3-(triphenyl-λ^5-phosphanylidene)-succinate (4c)

Yield: 95%; white powder; mp 168–170 °C. IR (KBr) (ν_{max}, cm^{-1}): 3386 (NH), 1748 (C=O, ester). Calcd. for ($C_{29}H_{29}N_2O_4PS$): C, 65.40; H, 5.49; N, 5.26%. Found: C, 65.51; H, 5.40; N, 5.18%. MS (*m/z*, %): 532 (M, 4).

Major isomer (75%). ^1H NMR ($CDCl_3$): δ = 1.23 and 1.35 (6H, 2t $^3J_{HH}$ = 7 Hz, 2 CH_3), 3.36 and 4.25 (4H, 2q $^3J_{HH}$ = 7 Hz, 2 OCH_2), 4.62 (1H, dd, $^3J_{HP}$ = 5 Hz, $^3J_{HH}$ = 10 Hz, P-C-CH), 6.92 (1H, d, $^3J_{HH}$ = 10 Hz, NH), 6.30 (1H, d, $^3J_{HH}$ = 3.8 Hz, CH of C_3H_2NS), 6.77 (1H, d, $^3J_{HH}$ = 3.8 Hz, CH of C_3H_2NS) 7.13–7.72 (15H, m, $3C_6H_5$).* (*For two conformational isomers.) ^{13}C NMR ($CDCl_3$): δ = 13.50 and 13.81 (2 CH_3), 49.95 (d, $^1J_{PC}$ = 123 Hz, C=P), 57,76 (d, $^2J_{PC}$ = 13 Hz, CH), 62.07 and 62.31 (2 OCH_2), 107.19, 138.87, 174.35 (3C C_3H_2NS), 127.16 (d, $^1J_{PC}$ = 92 Hz), 129.27 ($^2J_{PC}$ = 12 Hz), 132.47 (d, $^4J_{PC}$ = 3 Hz), 134.07 (d, $^3J_{PC}$ = 10 Hz). 168.89 (d, $^2J_{PC}$ = 12 Hz, C=O)*, 171.32 (d, $^3J_{PC}$ = 12 Hz, C=O).* ^{31}P NMR ($CDCl_3$): δ 22.75.

Minor isomer (25%). ^1H NMR ($CDCl_3$): δ = 1.17 and 1.33 (6H, 2t $^3J_{HH}$ = 7 Hz, 2 CH_3), 3.52 and 4.20 (4H, 2q $^3J_{HH}$ = 7 Hz, 2 OCH_2), 4.69 (1H, dd, $^3J_{HP}$ = 5 Hz, $^3J_{HH}$ = 10 Hz, P-C-CH), 6.70 (1H, d, $^3J_{HH}$ = 10 Hz, NH), 6.18 (1H, d, $^3J_{HH}$ = 3.8 Hz, CH of C_3H_2NS), 6.79 (1H, d, $^3J_{HH}$ = 3.8 Hz, CH of C_3H_2NS). ^{13}C NMR ($CDCl_3$): δ = 13.52 and 13.78 (2 CH_3), 49.90 (d, $^1J_{PC}$ = 123 Hz, C=P), 57.86 (d, $^2J_{PC}$ = 13 Hz, CH), 62.01 and 62.16 (2 OCH_2), 107.08, 138.94, 174.30 (3C C_3H_2NS), 127.47 (d, $^1J_{PC}$ = 92 Hz), 129.36 ($^2J_{PC}$ = 12 Hz), 132.56 (d, $^4J_{PC}$ = 3 Hz), 134.23 (d, $^3J_{PC}$ = 10 Hz). ^{31}P NMR ($CDCl_3$): δ 22.83.

Diethyl 2-(Benzothiazole-2-ylamino)-3-(triphenyl-λ^5-phosphanylidene)-succinate (4d)

Yield: 90%; white powder; mp 163–165 °C. IR (KBr) (ν_{max}, cm^{-1}): 3360 (NH), 1735 (C=O, ester). Calcd. for ($C_{33}H_{31}N_2O_4PS$): C, 68.03; H, 5.36; N, 4.81%. Found: C, 68.15; H,5.21; N, 4.77%. MS (*m/z*, %): 582 (M, 9).

Major isomer (70%). ^1H NMR ($CDCl_3$): δ = 1.20 and 1.42 (6H, 2t $^3J_{HH}$ = 7 Hz, 2 CH_3), 3.47 and 4.18 (4H, 2q $^3J_{HH}$ = 7 Hz, 2 OCH_2), 4.69 (1H, dd,

$^3J_{HP} = 5$ Hz, $^3J_{HH} = 10$ Hz, P-C-CH), 6.99 (1H, d, $^3J_{HH} = 10$ Hz, NH), 7.13–7.71 (19H, m, aromatic).* (*For two conformational isomers).^{13}C NMR ($CDCl_3$): $\delta = 14.08$ and 14.27 (2 CH_3), 49.83 (d, $^1J_{PC} = 123$ Hz, C=P), 57.78 (d, $^2J_{PC} = 13$ Hz, CH), 62.29 and 62.46 (2 OCH_2), 117.15, 121.22, 121.68, 125.75, 133.16, 153.02, 173.89 (7C benzothiazole), 129.46 ($^2J_{PC} = 12$ Hz), 127.61 (d, $^1J_{PC} = 92$ Hz), 131.45 (d, $^4J_{PC} = 3$ Hz), 133.18 (d, $^3J_{PC} = 10$ Hz), 168.78 (d, $^2J_{PC} = 12$ Hz, C=O)*, 170.56 (d, $^3J_{PC} = 12$ Hz, C=O).* ^{31}P NMR ($CDCl_3$): δ 23.06.

Minor isomer (30%). ^{1}H NMR ($CDCl_3$): $\delta = 1.14$ and 1.34 (6H, 2t, $^3J_{HH} = 7$ Hz, 2 CH_3), 3.35 and 4.01 (4H, 2q $^3J_{HH} = 7$ Hz, 2 OCH_2), 4.37 (1H, dd, $^3J_{HP} = 5$ Hz, $^3J_{HH} = 10$ Hz, P-C-CH), 6.92 (1H, d, $^3J_{HH} = 10$ Hz, NH), ^{13}C NMR ($CDCl_3$): $\delta = 13.56$ and 14.06 (2 CH_3), 50.03 (d, $^1J_{PC} = 123$ Hz, C=P), 57,60 (d, $^2J_{PC} = 13$ Hz, CH), 61.95 and 62.37 (2 OCH_2), 117.25, 121.20, 121.64, 125.71, 133.29, 153.19, 173.97 (7C benzothiazole), 129.11 ($^2J_{PC} = 12$ Hz), 127.89 (d, $^1J_{PC} = 92$ Hz), 131.68 (d, $^4J_{PC} = 3$ Hz), 133.29 (d, $^3J_{PC} = 10$ Hz), ^{31}P NMR ($CDCl_3$): δ 23.19.

N-(Thiazole-2-yl)triphenyl Iminophosphorane (5a)

Yield: 92%; white powder; mp 141–143 °C. IR (KBr) (ν_{max}, cm^{-1}): 1492, 1435, 1306, 1234, 1100. Calcd. for ($C_{21}H_{17}N_2PS$): C, 69.98; H, 4.75; N, 7.77%. Found: C, 69.80; H, 4.90; N, 7.73%. MS (m/z, %): 360 (M, 100). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.39$ (1H, d, $^3J_{HH} = 3.8$ Hz, CH of C_3H_2NS), 6.95 (1H, d, $^3J_{HH} = 3.8$ Hz, CH of C_3H_2NS,) 7.43–7.83 (15H, m, $3C_6H_5$) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 109.26$, 138.99, 174.36 (3C C_3H_2NS), 129.05 ($^2J_{PC} = 12$ Hz), 129.28 (d, $^1J_{PC} = 100$ Hz), 132.60 (d, $^4J_{PC} = 3$ Hz), 133.52 (d, $^3J_{PC} = 10$ Hz). ^{31}P NMR ($CDCl_3$): 15.58 (Ph_3P=N) ppm.

N-(Benzothiazole-2-yl)triphenyl Iminophosphorane (5b)

Yield: 90%; white powder; mp 158–160 °C. IR (KBr) (ν_{max}, cm^{-1}): 1591, 1494, 1438, 1298, 1210, 1106. Calcd. for ($C_{25}H_{19}N_2PS$): C, 73.15; H, 4.67; N, 6.82%. Found: C, 73.30; H, 4.75; N, 6.80%. MS (m/z, %): 410 (M, 100). ^{1}H NMR (500 MHZ, $CDCl_3$): $\delta = 6.97$–7.40 (4H, m, 4CH), 7.45–7.89 (15H, m, $3C_6H_5$) ppm.^{13}C NMR (125.8 MHZ, $CDCl_3$): $\delta = 119.12$, 120.83, 121.24, 125.19, 134.49, 153.38, 171.75 (7C benzothiazole), 129.11 ($^2J_{PC} = 12$ Hz), 128.52 (d, $^1J_{PC} = 100$ Hz), 132.83 (d, $^4J_{PC} = 3$ Hz), 133.68 (d, $^3J_{PC} = 10$ Hz). ^{31}P NMR ($CDCl_3$): δ 15.19 (Ph_3P=N) ppm.

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