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A Facile Synthesis of Stable Phosphorus Ylides Containing Chlorine and Sulfur Derived from 6-Chloro-2benzoxazolethiol and 2-Chlorophenothiazine

Malek Taher Maghsoodlou^a, Nourollah Hazeri

^a, Sayyed Mostafa Habibi Khorasani^a, Hadi

Mahmoudi Moghaddam $^{\rm a}$, Mahmoud Nassiri $^{\rm a}$ & Jaber Salehzadeh $^{\rm a}$

^a Department of Chemistry, The University of Sistan and Baluchestan, Zahedan, Iran Published online: 22 Jun 2009.

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A Facile Synthesis of Stable Phosphorus Ylides Containing Chlorine and Sulfur Derived from 6-Chloro-2-benzoxazolethiol and 2-Chloro-phenothiazine

Malek Taher Maghsoodlou, Nourollah Hazeri, Sayyed Mostafa Habibi Khorasani, Hadi Mahmoudi Moghaddam, Mahmoud Nassiri, and Jaber Salehzadeh

Department of Chemistry, The University of Sistan and Baluchestan, Zahedan, Iran

Stable crystalline phosphorus ylides containing chlorine and sulfur were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylene-dicarboxylates in the presence of 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine. These stable ylides exist in solution as a mixture of two geometrical isomers. This is caused by the conjugation of the ylide moiety with the adjacent carbonyl group, which results in a restricted rotation around the respective carbon-carbon bond.

Keywords Acetylenic ester; geometrical isomers; NH-acids; stable phosphorus ylides; triphenylphosphine

INTRODUCTION

The synthesis of phosphorus ylides is important in organic chemistry because of the application of these compounds in the synthesis of organic products,¹⁻¹⁴ especially in the synthesis of naturally occurring products with biological and pharmacological activity.^{15–19} Phosphorus ylides are usually prepared by deprotonation of phosphonium salts, which can be obtained by the reaction of triphenylphosphine with an alkyl halide.¹⁻³ In recent years, a three-component method has been developed^{20–30} for the synthesis of organophosphorus compounds using a novel approach that employs vinylphosphonium salts. Here we

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Address correspondence to Malek Taher Maghsoodlou, Department of Chemistry, The University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran. E-mail: mt_maghsoodlou@yahoo.com

describe an efficient synthetic route to stable phosphorus ylides derived from 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine. The benzoxazole and phenothiazine moieties as well as their derivatives are widely used in making medicines.^{31,32} Thus, the reaction of triphenylphosphine **1** and dialkyl acetylenedicaboxylates **2** in the presence of compounds **3** leads to the corresponding stable heterocyclic phosphorus ylides **4** in excellent yields (see Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The reaction of 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine with dialkyl-acetylenedicarboxylates **2** in the presence of triphenylphosphine **1** proceeded in ethyl acetate as solvent at room temperature and was completed within a few hours. The ¹H and ¹³C NMR spectrum of the crude product clearly indicated the formation of the stable phosphorus ylides **4**. No product other than **4** could be detected by NMR spectroscopy. The structures of compounds **4a–e** were determined from the IR, ¹H, ¹³C, and ³¹P NMR spectra. The ¹H, ¹³C, and ³¹P NMR spectra of ylides **4a–e** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group resulting in a hindered rotation around the C-C bond connecting these two groups. Interconversion of the geometrical isomers (*E*)-**4** and (*Z*)-**4** is slow on the NMR time scale at ambient temperature (see Scheme 2). Selected ¹H, ¹³C, and ³¹P NMR chemical shifts and coupling constants for the major (M) and the minor (m) geometrical isomers of compounds **4a–e** are shown in Table I.



SCHEME 2

As can be seen, only one geometrical isomer was observed for the di*tert*-butyl derivatives of **4**, presumably, because of the bulky *tert*-butyl groups.

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,¹⁻³ it is reasonable to assume that the formation of the phosphorus ylides **4** is initiated by the addition of triphenylphosphine to the corresponding acetylenic esters. Protonation of the resulting 1:1 adduct by the acid Z-H followed by addition of the conjugated base $Z^$ yields the phosphoranes **4** (see Scheme 3).

$$\mathbf{1} + \mathbf{2} + \mathbf{3} \longrightarrow \begin{bmatrix} \mathsf{Ph}_3^{+} \\ \mathsf{RO}_2 \mathsf{C}' \end{bmatrix} = \mathsf{C} + \mathbf{z} = \mathsf{A}$$

SCHEME 3

The ¹H NMR spectrum of **4a** showed four sharp lines at $\delta = 3.21$, 3.80, 3.81, and 3.83 ppm arising from the methoxy protons. The signal for methine protons appeared as doublet at $\delta = 5.78$ ppm (³ $J_{\rm PH} =$

TABLE I Selected ¹H, ¹³C, and ³¹P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for 2-H, OR, CO₂R, C-2, and C-3 in the Major (M) and Minor (m) Isomers of Compounds 4a–e

| | Isomer | $\text{H-2}(^3J_{\rm PH})$ | OR | $\rm CO_2R$ | C-2 $(^2J_{\rm PC})$ | $\text{C-3}~(^1J_{\text{PC}})$ | ³¹ P |
|-----------|--------------|----------------------------|------|-------------|----------------------|--------------------------------|-----------------|
| 4a | М | 5.78 (17.3) | 3.21 | 3.80 | 62.8 (17.4) | 40.5 (124.0) | 23.9 |
| 4a | m | 5.72(17.0) | 3.81 | 3.83 | 63.3(14.1) | 41.9 (131.9) | 25.0 |
| 4b | \mathbf{M} | 5.74(17.8) | 3.78 | 4.25 | 62.9 (17.5) | 40.2 (123.6) | 23.9 |
| 4b | m | 5.57 (19.8) | 3.82 | 4.34 | 63.2 (5.9) | 40.7 (132.2) | 25.4 |
| 4c | \mathbf{M} | 5.56 (18.5) | 1.00 | 1.57 | 63.5 (17.9) | 39.6 (123.8) | 23.5 |
| 4d | \mathbf{M} | 4.21 (14.6) | 3.81 | 3.96 | 65.4 (14.7) | 41.4 (124.2) | 24.5 |
| 4d | m | 4.14 (16.1) | 3.93 | 3.98 | 64.8 (14.6) | 41.6 (135.5) | 23.5 |
| 4e | \mathbf{M} | 4.19^{a} | 3.44 | 4.28 | 65.0 (16.9) | 40.3 (123.6) | 24.8 |
| 4e | m | 4.24^{a} | 3.80 | 4.44 | 65.6 (14.9) | 41.3 (135.2) | 23.5 |
| | | | | | | | |

^aBroad signal.

17.3 Hz) and 5.72 ppm (${}^{3}J_{PH} = 17.0$ Hz) for the *E* and *Z* isomers, respectively. The 13 C NMR spectrum of **4a** displayed 26 distinct resonances in good agreement with the presence of a mixture of the two conformational isomers.

The ¹H and ¹³C NMR spectra of compounds **4b**–**e** are similar to those of **4a**, except for the signals resulting from the ester group, which are characteristic for the respective substituent R. The structural assignments made for compounds **4a–e** on the basis of the ¹H and ¹³C NMR spectra were supported also by the IR spectra. The carbonyl region of the spectra exhibits absorption bands for each compound. Of special interest is the ester absorption of these compounds at 1731–1612 cm⁻¹. Conjugation with the ylide moiety accounts for the shift of the carbonyl absorption bands to lower wave numbers.

In summary, we have prepared novel phosphorus ylides using a onepot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 6-chloro-2-benzoxazolethiol or 2-chlorophenothiazine. The present method carries the advantage that not only is the reaction performed under neutral conditions, but the substances also can be mixed without any activation or modifications. The 6-chloro-2-benzoxazolethiol and 2-chloro-phenothiazine containing phosphorus ylides **4a–e** may be considered as potentially useful synthetic intermediates. The procedure described here might be employed as a general method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. The ¹H, ¹³C, and ³¹P NMR spectra were obtained with a Bruker DRX-300 Avance instrument in $CDCl_3$ as solvent at 300.1, 75.4, and 121.5 MHz, respectively. The mass spectra were measured with a GCMS-QP 5050A mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenlphosphine, 6-chloro-2-benzoxazolethiol, and 2-chloro-phenothiazine were purchased from Fluka, and were used without further purification.

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and 6-chloro-2-benzoxazolethiol (1 mmol) or 2-chlorophenothiazine (1 mmol) in 10 mL of dry ethyl acetate, a solution of the corresponding acetylenedicarboxylate (1 mmol) in 4 mL of dry ethyl acetate was added dropwise over a period of 10 min. After approximately 6 h of stirring at room temperature, the product was filtered and washed with cold diethyl ether (3×5 mL).

Dimethyl-2-(6-chloro-2-benzoxazolethiol-*N*-yl)-3-(triphenyl-phosphanylidene)-butanedioate (*4a*)

Colorless crystals; mp: 162–164°C; yield: 0.54 g (92%). IR (KBr) (ν_{max} , cm⁻¹): 1728, 1617 (C=O). MS (m/z, %): 471 (M-2CO2Me, 31), 408 (M-C₇H₃ClNOS, 22), 262 (PPh₃, 100), 183 (PPh₂, 94), 108 (PPh, 43), 77 (Ph, 16). Anal. Calcd. for C₃₁H₂₅ClNO₅PS (590.0): C, 63.10; H, 4.27; N, 2.37%. Found: C, 63.33; H, 4.48; N, 2.29%.

Major Isomer (72%): ¹H NMR (CDCl₃): $\delta = 3.21$ (s, 3H, CH₃), 3.80 (s, 3H, CH₃), 5.78 (d, ³J_{PH} = 17.3 Hz, 1H, P=C-CH), 7.28–7.86 (m, 18H arom-H). ¹³C NMR (CDCl₃): $\delta = 40.5$ (d, ¹J_{PC} = 124.0 Hz, P=C), 49.6 (CH₃), 52.3 (CH₃), 62.8 (d, ²J_{PC} = 17.4 Hz, P=C-CH), 110.2, 114.2, 124.9, 125.6 (d, ¹J_{PC} = 92.0 Hz, C-*i*), 129.2 (d, ³J_{PC} = 12.7 Hz, C-*m*), 129.8, 132.0, 132.6 (C-*p*), 133.4 (d, ²J_{PC} = 9.7 Hz, C-*o*), 147.2, 169.9 (d, ³J_{PC} = 11.4 Hz, C=O ester), 170.0 (d, ²J_{PC} = 11.3 Hz, P-C=C), 180.0 (C=S). ³¹P NMR (CDCl₃): $\delta = 23.9$.

Minor Isomer (28%): ¹H NMR (CDCl₃): δ = 3.81, (s, 3H, CH₃), 3.83 (s, 3H, CH₃), 5.72 (d, ³J_{PH} = 17.0 Hz, 1H, P=C-CH), 6.88–7.86 (m, 18H, arom-H). ¹³C NMR (CDCl₃): δ = 40.9 (d, ¹J_{PC} = 131.9 Hz, P=C), 53.0 (CH₃), 53.6 (CH₃), 63.3 (d, ²J_{PC} = 14.1 Hz, P=C-CH), 110.5, 113.3, 124.5 124.9 (d, ¹J_{PC} = 92.0 Hz, C-*i*), 125.5, 129.2 (d, ³J_{PC} = 12.7 Hz, C-*m*), 130.0, 132.2, 132.6 (C-*p*), 133.5 (d, ²J_{PC} = 8.6 Hz, C-*o*), 147.4, 169.6 (d, ³J_{PC} = 13.9 Hz, C=O), 170.4 (d, ²J_{PC} = 12.9 Hz, P-C=C), 180.3 (C=S). ³¹P NMR (CDCl₃): δ = 25.0.

Diethyl-2-(6-chloro-2-benzoxazolethiol-*N*-yl)-3-(triphenyl-phosphanylidene)-butanedioate (*4b*)

White solid; mp: 149–151°C; yield: 0.56 g (90%). IR (KBr) (ν_{max} , cm⁻¹): 1731, 1620 (C=O). MS (m/z, %): 433 (M-PPh₂, 21), 282 (M-PPh₂ and CO₂Et, 38), 262 (PPh₃, 100), 183 (PPh₂, 83), 108 (PPh, 44), 77 (Ph, 9). Anal. Calcd. for C₃₃H₂₉ClNO₅PS (618.1): C, 64.13; H, 4.73; N, 2.27%. Found: C, 64.27; H, 4.79; N, 2.11%.

Major Isomer (78%): ¹H NMR (CDCl₃): $\delta = 0.49$ (t, ³ $J_{HH} = 7.1$ Hz, 3H, CH₃), 1.29 (t, ³ $J_{HH} = 7.1$ Hz, 3H, CH₂), 3.76–3.80 (m, ABX₃ system, CH₂), 4.16–4.34 (m, ABX₃ system, CH₂), 5.74 (d, ³ $J_{PH} = 17.8$ Hz, 1H, P=C-*CH*), 7.27–7.90 (m, 18H, arom-*H*). ¹³C NMR (CDCl₃): $\delta = 14.0$

(CH₃), 14.2 (CH₃), 40.2 (d, ${}^{1}J_{PC} = 123.6$ Hz, P=C), 58.4 (CH₂), 61.8 (CH₂), 62.9 (d, ${}^{2}J_{PC} = 17.5$ Hz, P=C-*C*H), 110.2, 114.3, 124.8, 125.8 (d, ${}^{1}J_{PC} = 92.0$ Hz, C-*i*), 129.1 (d, ${}^{3}J_{PC} = 12.2$ Hz, C-*m*), 129.9, 132.0, 132.5 (d, ${}^{4}J_{PC} = 2.3$ Hz, C-*p*), 133.5 (d, ${}^{2}J_{PC} = 9.7$ Hz, C-*o*), 147.2, 169.2 (d, ${}^{3}J_{PC} = 13.2$ Hz, C=O), 169.5 (d, ${}^{2}J_{PC} = 12.4$ Hz, P-C=*C*), 180.1 (C=S).³¹P NMR (CDCl₃): $\delta = 23.9$.

Minor Isomer (22%): ¹H NMR (CDCl₃): $\delta = 1.21$ (t, ³ $J_{HH} = 7.1$ Hz, 3H, CH₃), 1.34 (t, ³ $J_{HH} = 7.1$ Hz, CH₃), 3.75–3.82 (m, ABX₃ system, CH₂), 4.30–4.40 (m, ABX₃ system, CH₂), 5.57 (d, ³ $J_{PH} = 19.8$ Hz, 1H, P=C-CH), 6.85–7.90 (m, 18H, arom-H). ¹³C NMR (CDCl₃): $\delta = 14.1$ (CH₃), 14.8 (CH₃), 40.7 (d, ¹ $J_{PC} = 132.2$ Hz, P=C), 61.3 (CH₂), 61.7 (CH₂), 63.2 (d, ² $J_{PC} = 5.9$ Hz, P=C-CH), 110.5, 113.4, 124.3, 125.2 (d, ¹ $J_{PC} = 92.4$ Hz, C-i), 128.5 (d, ³ $J_{PC} = 12.2$ Hz, C-m), 130.1, 132.1, 132.5 (d, ⁴ $J_{PC} = 2.3$ Hz, C-p), 133.5 (d, ² $J_{PC} = 9.7$ Hz, C-o), 147.4, 169.5 (d, ³ $J_{PC} = 13.6$ Hz, C=O), 170.0 (d, ² $J_{PC} = 17.8$ Hz, C=O), 180.4 (C=S).³¹P NMR (CDCl₃): $\delta = 25.4$.

Di-*tert*-buthyl-2-(6-chloro-2-benzoxazolethiol-*N*-yl)-3-(tri-phenylphosphanylidene)-butanedioate (*4c*)

White solid; mp: 161–163°C; yield: 0.63 g (94%). IR (KBr) (ν_{max} , cm⁻¹): 1725, 1613 (C=O). MS (m/z, %): 572 (M-CO₂CMe₃, 32), 377 (M-C₇H₃ClNOS and 2 CMe₃, 42), 288 (M-PPh₂ and 2 CO₂CMe₃, 25), 262 (PPh₃, 100), 183 (PPh₂, 63), 108 (PPh, 33), 57 (CMe₃, 57). Anal. Calcd. for C₃₇H₃₇ClNO₅PS (674.2): C, 65.92; H, 5.53; N, 2.08%. Found: C, 66.07; H, 5.72; N, 2.03%.

¹H NMR (CDCl₃): $\delta = 1.00$ (s, 9H, CH₃), 1.57 (s, 9H, CH₃), 5.56 (d, ³J_{PH} = 18.5 Hz, 1H, P=C-*CH*), 7.24–8.40 (m, 18H, arom-*H*). ¹³C NMR (CDCl₃): $\delta = 28.1$ (CH₃), 28.3 (CH₃), 39.6 (d, ¹J_{PC} = 123.8 Hz, P=C), 63.5 (d, ²J_{PC} = 17.9 Hz, P=C-*CH*), 78.0 (*C*Me₃), 81.7 (*C*Me₃), 110.0, 114.3, 124.7, 126.2 (d, ¹J_{PC} = 91.7 Hz, C-*i*), 128.9 (d, ³J_{PC} = 12.2 Hz, C_{-m}), 130.0, 132.0, 132.4 (d, ⁴J_{PC} = 2.2 Hz, C-*p*), 133.5 (d, ²J_{PC} = 9.7 Hz, C-*o*), 147.2, 167.7 (d, ³J_{PC} = 13.1 Hz, C=O), 169.0 (d, ²J_{PC} = 11.8 Hz, P-C= *C*), 180.2 (C=S). ³¹P NMR (CDCl₃): $\delta = 23.5$.

Dimethyl-2-(2-chloro-phenothiazine-*N*-yl)-3-(triphenyl-phosphanylidene)-butanedioate (4d)

Yellow powder; mp: 134–136°C; yield: 0.61 g (95%). IR (KBr) (ν_{max} , cm⁻¹): 1735, 1629 (C=O). MS (m/z, %): 519 (M-2CO₂Me, 25), 345 (M-PPh₃ and OCH₃, 23), 262 (PPh₃, 100), 183 (PPh₂, 97), 108 (PPh, 43),

77 (Ph, 23). Anal. Calcd. for C₃₆H₂₉ClNO₄PS (638.1): C, 67.76; H, 4.58; N, 2.20%. Found: C, 67.80; H, 4.65; N, 2.18%.

Major Isomer (54%): ¹H NMR (CDCl₃): δ = 3.81 (s, 3H, CH₃), 3.96 (s, 3H, CH₃), 4.21 (d, ³J_{PH} = 14.6 Hz, 1H, P=C-*CH*), 6.65–7.72 (m, 22H, arom-*H*). ¹³C NMR (CDCl₃): δ = 41.4 (d, ¹J_{PC} = 124.2 Hz, P= *C*), 49.1 (CH₃), 52.8 (CH₃), 65.4 (d, ²J_{PC} = 14.7 Hz, P=C-*CH*), 113.3, 114.6, 115.1, 120.1, 122.2, 124.0, 126.4 (d, ¹J_{PC} = 92.0 Hz, C-*i*), 126.1, 126.4, 126.9, 128.5 (d, ³J_{PC} = 12.3 Hz, C-*m*), 131.8 (d, ⁴J_{PC} = 2.7 Hz, C-*p*), 132.0, 132.1, 132.61, 133.4 (d, ²J_{PC} = 9.7 Hz, C-*o*), 169.0 (d, ³J_{PC} = 13.2 Hz, C=O), 173.6 (d, ²J_{PC} = 17.6 Hz, P-C=*C*).³¹P NMR (CDCl₃): δ = 24.5.

Minor Isomer (46%): ¹H NMR (CDCl₃): δ = 3.93 (s, 3H, CH₃), 3.98 (s, 3H, CH₃), 4.14 (d, ³J_{PH} = 16.1 Hz, 1H, P=C-*CH*), 6.65-7.72 (m, 22H, arom-*H*). ¹³C NMR (CDCl₃): δ = 41.6 (d, ¹J_{PC} = 135.5 Hz, P=*C*), 52.6 (CH₃), 52.9 (CH₃), 64.8 (d, ²J_{PC} = 14.6 Hz, P=C-*CH*), 113.3, 114.6, 115.1, 120.1, 122.2, 124.0, 125.2 (d, ¹J_{PC} = 91.8 Hz, C-*i*), 126.2, 126.5, 127.0, 128.5 (d, ³J_{PC} = 12.2 Hz, C-*m*), 131.8 (d⁴J_{PC} = 2.7 Hz, C-*p*), 132.1, 132.2, 132.7, 133.5 (d, ²J_{PC} = 9.8 Hz, C-*o*), 168.9 (d, ³J_{PC} = 13.5 Hz, C=O), 173.8 (d, ²J_{PC} = 16.8 Hz, C=O). ³¹P NMR (CDCl₃): δ = 23.5.

Diethyl-2-(2-chloro-phenothiazine-*N*-yl)-3-(triphenyl-phosphanylidene)-butanedioate (4e)

White powder; mp: 153–155°C; yield: 0.61 g (91%). IR (KBr) (ν_{max} , cm⁻¹): 1722, 1612 (C=O). MS (m/z, %):MS (m/z, %): 520 (M-2CO₂Et, 26), 440 (M-C₁₂H₇ClNS, 19), 359 (M-PPh₃ and OEt, 31), 262 (PPh₃, 100), 183 (PPh₂, 97), 108 (PPh, 48), 77 (Ph, 17). Anal. Calcd. for C₃₈H₃₃ClNO₄PS (666.2): C, 68.51; H, 4.99; N, 2.10%. Found: C, 68.64; H, 5.13; N, 2.06%.

Major Isomer (60%): ¹H NMR (CDCl₃): $\delta = 0.43$ (broad, 3H, CH₃), 1.32 (broad, 3H, CH₃), 3.44 (broad, 2H, CH₂), 4.19 (broad, 1H, P=C-*CH*), 4.28 (broad, 2H, CH₂), 6.66–7.96 (m, 22H, arom-*H*). ¹³C NMR (CDCl₃): $\delta = 14.1$ (CH₃), 14.3 (CH₃), 40.3 (d, ¹*J*_{PC} = 123.6 Hz, P=*C*), 57.7 (CH₂), 61.3 (CH₂), 65.0 (d, ²*J*_{PC} = 16.9 Hz, P=C-*CH*), 113.5, 114.7, 115.2, 121.5, 121.6, 122.4, 125.6, 126.0, 126.3, 126.8 (d, ¹*J*_{PC} = 92.4 Hz, C-*i*), 128.4 (d, ³*J*_{PC} = 11.7 Hz, C-*m*), 131.7 (d, ⁴*J*_{PC} = 2.7 Hz, C-*p*), 132.0, 132.1, 132.6, 133.5 (d, ²*J*_{PC} = 9.7 Hz, C-*o*), 168.2 (d, ³*J*_{PC} = 13.3 Hz, P-C=*C*), 172.9 (d, ²*J*_{PC} = 12.4 Hz, C=O).³¹P NMR (CDCl₃): $\delta = 24.8$.

Minor Isomer (40%): ¹H NMR (CDCl₃): $\delta = 1.34$ (broad, 6H, CH₃), 3.80 (broad, 2H, CH₂), 4.24 (broad, 1H, P=C-*CH*), 4.44 (broad, 2H, CH₂), 6.66–7.96 (m, 22H, arom-*H*).¹³C NMR (CDCl₃): $\delta = 13.9$ (CH₃),

14.0 (CH₃), 41.3 (d, ${}^{1}J_{PC} = 135.2$ Hz, P=C), 60.9 (CH₂), 61.3 (CH₂), 65.6 (d, ${}^{2}J_{PC} = 14.9$ Hz, P=C-*CH*), 113.4, 114.5, 115.3, 121.4, 121.7, 122.4, 125.5, 126.2, 126.4, 126.6 (d, ${}^{1}J_{PC} = 92.3$ Hz, C-*i*), 128.4 (d, ${}^{3}J_{PC} = 12.5$ Hz, C-*m*), 131.7 (d, ${}^{4}J_{PC} = 2.7$ Hz, C-*p*), 132.0, 132.1, 132.7, 133.5 (d, ${}^{2}J_{PC} = 9.7$ Hz, C-*o*), 168.7 (d, ${}^{3}J_{PC} = 12.6$ Hz, C=O), 173.4 (d, ${}^{2}J_{PC} = 13.1$ Hz, P-C= C). ³¹P NMR (CDCl₃): $\delta = 23.5$.

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