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Synthesis of 1-Aryl-1,2,3,4,5,6-hexahydrophosphinine 1-Oxides

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ABSTRACT

Possibilities for the synthesis of 1-(2,4,6-triisopropylphenyl-)1,2,3,4,5,6-hexahydrophosphinine oxide (**2**) have been explored. The trivial method based on the hydrogenation of the corresponding dihydrophosphinine

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oxides (**8a–e**) was suitable only for the preparation of hexahydrophosphinine oxides containing a trimethylphenyl or methylphenyl group on the phosphorus atom (**9a–c**). The triisopropylphenyl product (**2**) was synthesized by the stepwise reduction of the double bonds of starting material **1**. Hence, the ring contraction side reaction, observed during the catalytic hydrogenation, could be eliminated. The unusual reactivity was studied by quantum chemical calculations.

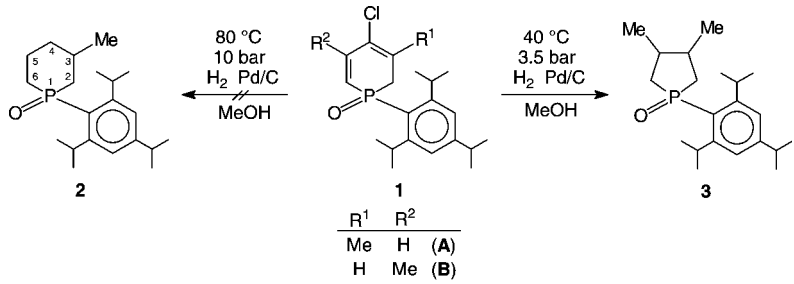
Key Words: Dihydrophosphinine oxides; Reduction; Ring contraction hexahydrophosphinine oxides; Theoretical calculations.

Organophosphorus compounds with sterically demanding substituents on the phosphorus atom are of interest, because the stability and the reactivity of the parent molecule are affected. Yoshifuji was successful in stabilizing low-coordinated species by the introduction of the 2,4,6-trialkylphenyl substituent.[1] Quin and Keglevich et al. could planarize the P-pyramid around the phosphorus atom of phospholes by attaching a trialkylphenyl group to the heteroatom.[2–4] As a consequence of this, the phospholes became aromatic. Phosphabicyclo[2.2.2]octenes with bulky substituents on the phosphorus atom were used to study the mechanism of their fragmentation-related phosphorylations.[5,6] Three of us discovered that P-trialkylphenyl cyclic phosphine oxides entered into a novel reaction with acetylenic dicarboxylic esters to afford stabilized phosphonium ylides.[7–9] The elaboration of this project requires additional model compounds with an aryl group on the phosphorus atom.

In this article, the synthesis of a few 2,4,6-trialkylphenyl- and methylphenyl-1,2,3,4,5,6-hexahydrophosphinine oxides is described.

The practical synthesis of 1-substituted 1,2,3,4,5,6-hexahydrophosphinine oxides involves the hydrogenation of 1,2-dihydroposphinine oxides,[10] or that of 3-phosphabicyclo[3.1.0]hexane 3-oxides[11] under appropriate conditions. We found, however, that the reduction of the mixture of the double-bond isomers (**A** and **B**) of 1-triisopropylphenyl-1,2-dihydrophosphinine oxide (**1**)[12] with catalytically activated hydrogen furnished a 52–29–19% mixture of three isomers of 3,4-dimethyl-2,3,4,5-tetrahydro-1H-phosphole oxide **3** instead of the 3-methyl-hexahydrophosphinine oxide (**2**) required (Scheme 1).[13] This surprising ring contraction is unique in the sphere of reductive transformations. Another aryl-dihydrophosphinine oxide, the di-*tert*-butyltolyl derivative, underwent the expected ring saturation smoothly on hydrogenation.[13]

We decided to investigate how the conditions of the catalytic hydrogenation affect the outcome of the reduction of **1**. Assuming that the hydrochloric acid formed during the reduction may catalyze the ring transformation, the



Scheme 1.

hydrogenation of **1** was carried out in the presence of a base, such as 3 equivalents of triethylamine or sodium hydroxide. Otherwise, the usual conditions of temperature of (80°C) and pressure (10 bar) were applied. We found, however, that the presence of base in the reaction mixture had practically no effect on the outcome. A similar result was obtained by running the reduction at 60°C and 8 bar; the isomers of dimethyl-tetrahydro-1H-phosphole oxide (**3**) were formed in 95% yield, and only traces of the expected product **2** could be detected.

The preferred outcome in the hydrogenation of triisopropylphenyl-dihydrophosphinine oxide **1** was studied by quantum chemical calculations. First, the energy content and the geometry of the different isomers of the possible products (**2** and **3**) were calculated by the PM3 semiempirical method implemented in MOPAC93.[14] The fully optimized geometries obtained were used as the initial structures in HF/6-31G*//HF/6-31G* calculations applying Gaussian98.[15] On the basis of the calculations, no significant differences were found between the energy contents of the 6- and the 5-membered ring products (**2** and **3**, respectively). To simplify the situation, average values are given for the different isomers. According to the PM3 method, the difference in the heat of formation ($\Delta\Delta H_f$) was -0.99 kcal/mol, whereas using the HF/6-31G* approach, the difference in the scaled (0.89 as scaling factor) zero point vibrational energy (ZPVE) corrected energy ($\Delta\Delta E^0$) was $+0.7$ kcal/mol. Placing a phenyl group instead of the triisopropylphenyl substituent on the phosphorus atom of P-heterocycles **3** and **2**, the differences were -2.5 kcal/mol ($\Delta\Delta H_f$, PM3) and -3.3 kcal/mol ($\Delta\Delta E^0$, HF/6-31G*). It can be seen that according to the calculations, the P-aryl substituent has no significant effect on the energy content. Hence, the reasons for the special reactivity of dihydrophopshinie oxide **1** still remain speculative.

We next tried to synthesize hexahydrophosphinine oxide **2** by substitution at phosphorus. Phosphinic ester **4**[10] was converted by reaction with

phosphorus pentachloride into the corresponding phosphinic chloride, which then gave the phosphinous chloride **5** by deoxygenation using trichlorosilane. The reaction of **5** with arylmagnesium bromide, followed by oxidation of the phosphine so obtained by hydrogen peroxide, led to an 88–12% mixture of phosphinic ester **6** and phosphine oxide **2**, both as mixtures of diastereomers (Scheme 2).

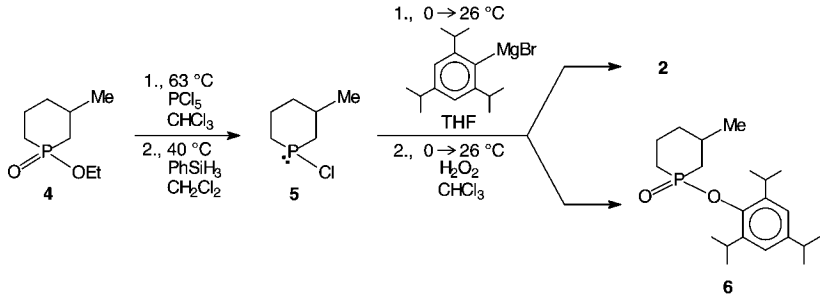
The O-insertion probably occurred during the Grignard reaction. We have also come across this in other cases,[16] and it is known from the literature.[17]

In the third approach, the unsaturated bonds of 1,2-dihydrophopshinine oxide **1A** were reduced in two steps. First, the electron-poor double bond was saturated through hydroboration by dimethylsulfide-borane, to yield tetrahydrophosphinine oxide **7** in 50% yield after column chromatography. Catalytic hydrogenation of **7** provided a 55–45% diastereomeric mixture of hexahydrophosphinine oxide **2** in 89% yield after purification (Scheme 3).

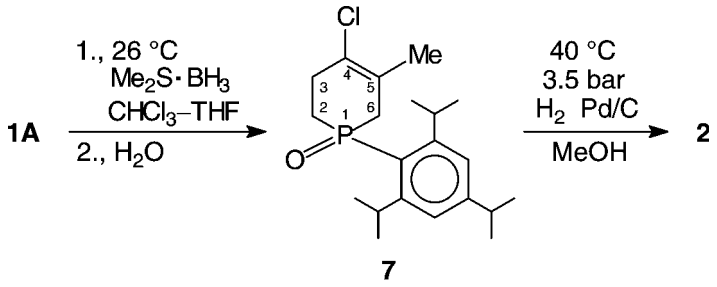
Intermediate **7** and product **2** were characterized by ^{31}P, ^{13}C, and ^{1}H NMR as well as by mass spectrometry.

Finally, three other aryl-dihydrophosphinine oxides (**8a–c**) were subjected to hydrogenation at 80°C and 10 bar. Both the trimethylphenyl-hexahydrophosphinine oxide (**9a**) and the methylphenyl derivatives (**9b** and **9c**) were obtained as about 71–29% mixtures of diastereomers and in good yields (ca. 70%) after column chromatography (Scheme 4). The hexahydrophosphinine oxides (**9a–c**) were characterized by ^{31}P, ^{13}C, and ^{1}H NMR as well as by mass spectrometry.

In summary, new 1-aryl-1,2,3,4,5,6-hexahydrophosphinine oxides were prepared. The basic procedure involves catalytic hydrogenation of the corresponding 1,2-dihydrophosphinine oxides. Due to a ring contraction side reaction, another route, the stepwise saturation of the double bonds of the starting dihydrophosphinine oxide, was necessary for the synthesis of the 2,4,6-triisopropylphenyl derivative.



Scheme 2.



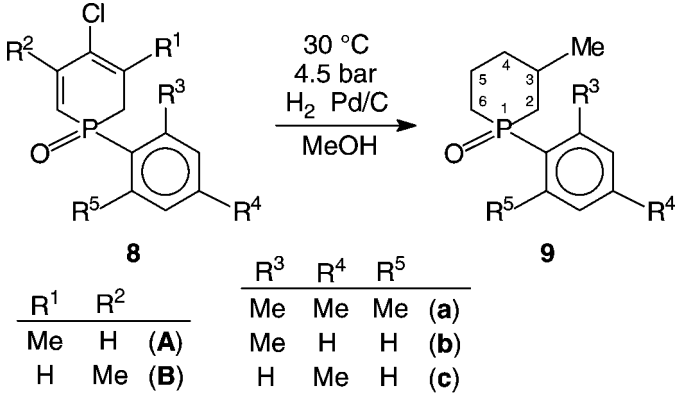
Scheme 3.

EXPERIMENTAL

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were obtained on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. The couplings are given in Hz. Mass spectrometry was performed on a ZAB-2SEQ instrument. The starting dihydrophosphinine oxides **1** and **8a** were prepared as described earlier.[12,17,18]

General Procedure for the Preparation of 1,2,3,4,5,6-Hexahydrophosphinine 1-Oxides (9a–c)

A solution of 0.79 mmol of the 75–25% isomeric mixture of 3- and 5-methyl-1,2-dihydrophosphinine 1-oxide (**8a–c**) in 30 mL of methanol and



R^1	R^2	
Me	H	(**A**)
H	Me	(**B**)

R^3	R^4	R^5	
Me	Me	Me	(**a**)
Me	H	H	(**b**)
H	Me	H	(**c**)

Scheme 4.

0.2 g of 10% Pd/C was measured in an autoclave equipped with a magnetic stirrer. The hydrogenation was carried out at 80°C and 10 bar for 14 hr. The suspension was filtered and the solvent was evaporated. Purification of the crude product by column chromatography (silica gel, 3% methanol in chloroform) afforded product (**9a–c**).

2,4,6-Trimethylphenyl-3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-Oxides (9a)

Yield: 68%, as a 75–25% mixture of **9a$_1$** and **9a$_2$** isomers; HRMS $(M+H)^+_{found} = 251.1524$; $C_{13}H_{19}OP$ requires 251.1565.

9a$_1$

^{31}P NMR ($CDCl_3$) δ 39.5; ^{13}C NMR ($CDCl_3$) δ 21.0 (p-CH_3), 21.5 ($^1J = 4.6$, C_5), 23.6 ($^1J = 12.9$, C_3–CH_3), 23.7 ($^1J = 3.8$, o-CH_3), 30.7 ($^1J = 3.6$, C_3), 31.8 ($^1J = 63.7$, C_6), 34.5 ($^1J = 3.5$, C_4), 39.9 ($^1J = 61.7$, C_2), 126.8 ($^1J = 93.3$, $C_{1'}$), 131.2 ($^1J = 10.7$, $C_{3'}$), 140.9 ($C_{4'}$), 141.7 ($^1J = 9.7$, $C_{2'}$); ^{1}H NMR ($CDCl_3$) δ 1.06 (dd, $^1J = 6.5$, 3H, C_3–Me), 2.27 (s, 3H, $C_{4'}$–Me), 2.63 (s, 6H, $C_{2'}$–Me), 6.88 (s, 2H, ArH).

9a$_2$

^{31}P NMR ($CDCl_3$) δ 39.3; ^{13}C NMR ($CDCl_3$) δ 21.1 (p-CH_3), 21.5 ($^1J = 4.6$, C_5), 23.7 ($^1J = 3.8$, o-CH_3), 25.0 ($^1J = 14.8$, C_3–CH_3), 29.1 ($^1J = 4.8$, C_3), 29.6 ($^1J = 64.0$, C_6), 35.5 ($^1J = 5.3$, C_4), 38.9 ($^1J = 62.7$, C_2), 126.9 ($^1J = 93.3$, $C_{1'}$), 131.4 ($^1J = 11.0$, $C_{3'}$), 141.2 ($C_{4'}$), 141.8 ($^1J = 10.4$, $C_{2'}$).

2-Methylphenyl-3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-Oxides (9b)

Yield: 72%, as a 75–25% mixture of **9b$_1$** and **9b$_2$** isomers; HRMS $(M+H)^+_{found} = 223.1221$; $C_{13}H_{19}OP$ requires 223.1252.

9b$_1$

^{31}P NMR ($CDCl_3$) δ 36.8; ^{13}C NMR ($CDCl_3$) δ 21.1 ($^1J = 4.2$, o–CH_3), 22.5 ($^1J = 4.0$, C_5), 24.0 ($^1J = 14.9$, C_3–CH_3), 27.7 ($^1J = 64.8$, C_6), 31.2 ($^1J = 4.0$, C_3), 34.4 ($^1J = 4.8$, C_4), 36.5 ($^1J = 61.4$, C_2), 125.2 ($^1J = 11.6$,

$C_{5'}$)*, 129.3 ($^1J = 92.6$, $C_{1'}$), 130.2 ($^1J = 11.2$, $C_{6'}$),* 131.3 ($^1J = 2.3$, $C_{4'}$), 132.0 ($^1J = 9.8$, $C_{3'}$)*, 141.8 ($^1J = 7.5$, $C_{2'}$), *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.07 (dd, 3H, C_3–Me), 2.72 (s, 3H, $C_{2'}$–Me), 7.24–7.53 (m, 4H, ArH).

9b$_2$

^{31}P NMR ($CDCl_3$) δ 35.2; ^{13}C NMR ($CDCl_3$) δ 20.6 ($^1J = 5.6$, C_5), 21.1 ($^1J = 4.2$, o–CH_3), 24.5 ($^1J = 14.9$, C_3–CH_3), 28.7 ($^1J = 62.3$, C_6), 33.2 ($^1J = 9.4$, C_3), 35.2 ($^1J = 4.8$, C_4), 35.8 ($^1J = 64.5$, C_2), 129.4 ($^1J = 11.5$, $C_{5'}$)*, 130.0 ($^1J = 10.9$, $C_{6'}$)*, 131.3 ($^1J = 2.3$, $C_{4'}$), 132.0 ($^1J = 9.8$, $C_{3'}$),* 141.5 ($^1J = 7.9$, $C_{2'}$), *tentative assignment.

4-Methylphenyl-3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-Oxides (9c)

Yield: 74%, as a 64–36% mixture of **9c$_1$** and **9c$_2$** isomers; HRMS $(M + H)^+_{found} = 223.1232$; $C_{13}H_{19}OP$ requires 223.1252.

9c$_1$

^{31}P NMR ($CDCl_3$) δ 34.8; ^{13}C NMR ($CDCl_3$) δ 20.8 (p–CH_3), 21.6 ($^1J = 4.0$, C_5), 23.3 ($^1J = 14.6$, C_3–CH_3), 26.2 ($^1J = 65.4$, C_6), 30.3 ($^1J = 3.6$, C_3), 33.8 ($^1J = 5.0$, C_4), 35.1 ($^1J = 63.4$, C_2), 128.3 ($^1J = 95.8$, $C_{1'}$), 128.9 ($^1J = 11.1$, $C_{2'}$)*, 129.1 ($^1J = 9.5$, $C_{3'}$)*, 141.3 ($^1J = 2.6$, $C_{4'}$), *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.08 (dd, 3H, C_3–Me), 2.42 (s, 3H, $C_{4'}$–Me), 7.28–7.70 (m, 4H, ArH).

9c$_2$

^{31}P NMR ($CDCl_3$) δ 33.5; ^{13}C NMR ($CDCl_3$); δ 20.3 ($^1J = 5.6$, C_5), 20.8 (p–CH_3), 24.1 ($^1J = 15.0$, C_3–CH_3), 26.8 ($^1J = 66.4$, C_6), 27.9 ($^1J = 4.6$, C_3), 33.8 ($^1J = 5.0$, C_4), 36.0 ($^1J = 64.9$, C_2), 128.6 ($^1J = 11.5$, $C_{2'}$)*, 129.4 ($^1J = 9.6$, $C_{3'}$)*, 141.3 ($^1J = 2.6$, $C_{4'}$), *tentative assignment.

Hydrogenation of the double bond isomers (**A** and **B**) of triisopropylphenyl-1,2-dihydrophosphinine oxide (**1**) under similar conditions led to a 29–52–19% mixture of dimethyl-2,3,4,5-tetrahydro-1H-phosphole 1-oxide **3**.

Attempted Conversion of 1-Ethoxy-hexahydrophosphinine 1-Oxide 4 to 1-Triisopropylphenyl-hexahydrophosphinine 1-Oxide (2)

To 0.89 g (5.0 mmol) of the diastereomers of ethoxy-hexahydrophosphinine 1-oxide (**4**) in 20 mL of dry chloroform, 1.1 g (5.3 mmol) of phosphorus pentachloride was added. The mixture was stirred at room temperature and then at the boiling point for 5 hr. The volatile components were removed in vacuo to provide the corresponding phosphonic chloride in quantitative yield.

To 0.84 g (~5.0 mmol) of phosphonic chloride (from the previous reaction) in 20 mL of dry dichloromethane, 0.25 mL (2.0 mmol) phenylsilane was added in nitrogen atmosphere. The contents of the flask were stirred at the boiling point for 5.5 hr under nitrogen. The reaction mixture was concentrated in vacuo to give 0.84 g (~100%) phosphinic chloride **5**.

To 0.74 g (~5.0 mmol) of phosphinic chloride (**5**) in 15 mL of dry tetrahydrofuran was added 5.5 mmol of arylmagnesium bromide [prepared from 0.13 g (5.5 mmol) of magnesium and 1.55 g (5.5 mmol) of 2,4,6-triisopropyl-1-bromobenzene in 15 mL of tetrahydrofuran] dropwise at 0°C, and the mixture was then stirred at room temperature for 14 hr. The solvent was evaporated in vacuo and the residue was taken up in a mixture of 15 ml of chloroform and 5 mL of water containing 3 drops of hydrochloric acid. The organic phase was separated and dried (Na_2SO_4). Evaporation of the solvent led to 2.1 g (64%) of crude arylphosphine.

2.1 g (6.6 mmol) of arylphosphine in 50 mL chloroform was treated with 1.5 mL (~13.2 mmol) of 30% hydrogen peroxide at 0°C. The cooling bath was removed and the mixture was stirred at 26°C for 2 hr. Excess of the peroxide was removed by extraction with 3 × 10 mL of water. The chloroform phase was dried (Na_2SO_4), and the solvent was evaporated to afford a mixture (2.0 g) of arylphosphine oxide **2** (125, ^{31}P NMR [$CDCl_3$) δ 32.9 (63%) and 39.3 (37%)] and arylphosphinate **6** (88%).

Repeated column chromatography (3% methanol in chloroform, silica gel) furnished 1.7 g (88%) of **6** in a pure form. ^{31}P NMR ($CDCl_3$) δ 53.7 (53%) and 54.2 (47%); HRMS $(M + H)^+_{found} = 351.2421$, $C_{21}H_{36}O_2P$ requires 351.2453.

The Two-Step Conversion of 1-Triisopropylphenyl-1,2-dihydrophosphinine 1-Oxide (1A) to Hexahydrophosphinine 1-Oxide (2)

A. 4-Chloro-5-methyl-1-(2,4,6-triisopropylphenyl) 1,2,3,6-tetrahydrophosphinine 1-oxide (**7**)

To a solution of 0.5 g (1.4 mmol) of 1-triisopropylphenyl-dihydrophosphinine 1-oxide (**1A**) in 30 mL of CH_2Cl_2 was added 1.1 mL (2.2 mmol)

2 M borane-dimethyl sulfide in THF. The mixture was stirred at 24°C for 15 min and then at 40°C for 24 hr. After completion of the reaction, 1.4 mL of H_2O was added, and the contents of the flask were stirred for 15 min. The mixture was filtered and the organic phase separated and dried (Na_2SO_4). The crude product obtained after evaporating the solvent was purified by column chromatography (silica gel, 3% MeOH in $CHCl_3$) to give 0.25 g (36%) **7**; ^{31}P NMR ($CDCl_3$) δ 34.1; ^{13}C NMR ($CDCl_3$) δ_C 23.2 ($^1J = 9.7$, C_5–CH_3), 23.9 ($C_{2'}$–$CH(CH_3)_2$),[a] 25.3 ($C_{4'}$–$CH(CH_3)_2$)*, 25.4 ($C_{6'}$–$CH(CH_3)_2$)*, 29.4 ($^1J = 65.8$, C_6), 30.3 ($^1J = 3.9$, *orto*-$CH(CH_3)_2$), 30.6 ($^1J = 6.4$, C_3), 34.4 (*para*-$CH(CH_3)_2$), 38.9 ($^1J = 64.3$, C_2), 123.1 ($^1J = 11.1$, $C_{3'}$), 124.6 ($^1J = 5.9$, C_5), 127.3 ($^1J = 11.9$, C_4), 152.5 ($C_{4'}$), 153.9 ($^1J = 11.1$, $C_{2'}$), *tentative assignment; ^{1}H NMR ($CDCl_3$) δ 1.21–1.34 (m, 18H, $CH(CH_3)_2$), 1.94 (s, 3H, C_5–Me), 7.15 (s, 2H, ArH); FAB; $(M + H)^+_{found}$ 367.1904, $C_{21}H_{33}ClOP$ requires 367.1958 for the ^{35}Cl isotope.

B. 1-(2,4,6-triisopropylphenyl-)1,2,3,4,5,6-hexahydrophosphinine 1-oxide (**2**)

7 was hydrogenated, as described for the **8** → **9** transformation. Column chromatography of the crude product afforded 0.08 g (89%) of **2** as a 55–45 % mixture of $\mathbf{2_1}$ and $\mathbf{2_2}$ diastereomers. HR-FAB; $(M + H)^+_{found}$ 335.2472, $C_{21}H_{36}OP$ requires 335.2504; ^{1}H NMR ($CDCl_3$) δ 1.16–1.31 (m, 18H, $CH(CH_3)_2$), 1.91 (s, 3H, C_3–Me), 7.10 (s, 2H, ArH).

Isomer $\mathbf{2_1}$

^{31}P NMR ($CDCl_3$) δ 38.4; ^{13}C NMR ($CDCl_3$) δ 20.2 ($^1J = 4.7$, C_5), 22.9 ($^1J = 9.9$, C_3–CH_3), 23.8 ($C_{2'}$–$CH(CH_3)_2$)*, 25.1 ($C_{4'}$–$CH(CH_3)_2$)*, 25.3 ($C_{6'}$–$CH(CH_3)_2$)*, 30.2 ($^1J = 4.5$, C_3), 30.8 ($^1J = 4.3$, *orto*-$CH(CH_3)_2$), 32.5 ($^1J = 64.1$, C_6), 33.4 ($^1J = 6.3$, C_4), 34.2 (*para*-$CH(CH_3)_2$), 40.1 ($^1J = 62.1$, C_2), 121.1 ($^1J = 96.1$, $C_{1'}$), 122.9 ($^1J = 10.6$, $C_{3'}$ and $C_{5'}$), 151.9 ($^1J = 2.6$, $C_{4'}$), 153.6 ($^1J = 10.6$, $C_{2'}$ and $C_{6'}$), *tentative assignment.

Isomer $\mathbf{2_2}$

^{31}P NMR ($CDCl_3$) δ 37.3; ^{13}C NMR ($CDCl_3$) δ 18.9 ($^1J = 5.1$, C_5), 23.8 ($C_{2'}$–$CH(CH_3)_2$),* 25.1 ($C_{4'}$–$CH(CH_3)_2$),* 25.2 ($C_{6'}$–$CH(CH_3)_2$),* 27.1 ($^1J = 15.6$, C_3–CH_3), 28.7 ($^1J = 68.1$, C_6), 30.1 ($^1J = 4.5$, C_3), 30.8 ($^1J = 4.3$, *orto*-$CH(CH_3)_2$), 32.3 ($^1J = 9.7$, C_4), 34.2 (*para*-$CH(CH_3)_2$), 40.1 ($^1J = 62.1$, C_2), 123.0 ($^1J = 10.9$, $C_{3'}$ and $C_{5'}$), 125.1 ($^1J = 92.2$, $C_{1'}$), 151.9 ($^1J = 2.6$, $C_{4'}$), 154.3 ($^1J = 10.9$, $C_{2'}$ and $C_{6'}$), *tentative assignment.

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