Convenient and Convergent Syntheses of Long-Chain α,ω-Dibromides and Diphosphines of the Formula X(CH_2)_nX (n = 18–32)

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Abstract: The known tetrahydropyranyl ethers Br(CH_2)_yOPTH (y = 6, 9, 11), which are easily prepared from commercial bromoalcohols, are sequentially treated with Mg, Li_2CuCl_4, and X(CH_2)_zX (z/X = 6/Br, 7/Br, 8/Br, 10/Br, 10/I) to give the diethers THPO(CH_2)_yOPTH in 68–90% yields (n = 2y + z = 18, 19, 20, 22, 24, 28, 32). Subsequent reactions with Ph_2P and 2,4,4,6-tetramethylcyclohexa-2,5-dieneone give the title compounds Br(CH_2)_nBr in 91–75% yields. Reactions with commercial K^+–PPh_2 give the diphosphines Ph_2P(CH_2)_nPPh_2 in 95–74% yields.

Key words: THP ethers, Grignard reagents, cross-coupling, bromination, phosphines

Long-chain α,ω-difunctional compounds of the formula X(CH_2)_nX have played an important historical role in organic chemistry. They served as building blocks for some of the earliest syntheses of large carbocyclic rings,1 as well as rotaxanes and catenanes.2 They have also figured in the development of nanochemistry over the last decade, and the frequent need for ‘oversized’ or ‘high axial ratio’ molecular components,6 such species are of renewed relevance.

In connection with several ongoing projects, we required a range of α,ω-diphosphines of the formula Ar_2P(CH_2)_nPAr_2.7 There are of course many such species known, but with what might be termed ‘medium’ values of n (e.g. n = 6–12, 16 for Ar = Ph).8,9 In addition to such compounds, we required diphosphines with much higher values of n. Alkyl diarylmorpholinosphines are often prepared from alkyl halides and diarylmorpholino anions –PAr_2. The latter can be conveniently generated by several procedures. Accordingly, we surveyed the existing literature syntheses of α,ω-dibromides Br(CH_2)_nBr, with n ranging from 18 to 30.10–20

To our surprise, we found various limitations with regard to the efficiency of chain-lengthening, the number of steps and convenience. For example, Hünig’s classic method for the synthesis of long-chain α,ω-dicarboxylic acids21 can be combined with a subsequent reduction to give α,ω-diols HO(CH_2)_nOH as illustrated in Scheme 1. However, this requires (1) a shorter-chain α,ω-dicarboxylic acid dichloride and the morpholine-derived enamine of cyclohexanone; (2) four separate steps, including two harsh reductions; and (3) is limited to twelve-carbon chain extensions of the diacid dichloride. Also, under some conditions the complete bromination of α,ω-diols HO(CH_2)_nOH is complicated by phase separation problems [e.g. diminished aqueous solubility of the less polar initial product Br(CH_2)_nOH]. Forcing sealed-tube conditions can be necessary (47% aqueous HBr, 140–160 °C).19b

In this paper, we describe an efficient and general route to such dibromides that is based upon commercially available shorter-chain α,ω-bromoalcohols Br(CH_2)_nOH and α,ω-dihalides X(CH_2)_nX (X = Br, I). The sequence exploits Grignard cross-coupling methodology originally developed by Kochi22 and extended by others.23 To confirm the overall utility of the method, the dibromides are subsequently converted to the α,ω-diphosphines Ph_2P(CH_2)_nPPh_2. These have been used as bidentate ligands in various diplatinum complexes, including some that adopt novel double-helical conformations of the general type I (Figure 1).7,24

Figure 1 Structure of double helical conformation I

The α,ω-bromoalcohols Br(CH_2)_nOH were first converted to their known tetrahydropyranyl ethers Br(CH_2)_yOPTH (y = 6, 9, 11) under standard conditions (dihydropyran, POCl_3, THF).25 As shown in Scheme 2, the corresponding Grignard reagents were generated, and treated with a catalytic amount of the copper salt Li_2CuCl_4.23 Then 0.28–0.39 equivalents of a commercial α,ω-dibromide or diiodide, X(CH_2)_nX (z = 6, 7, 8, 10) was added. Work-ups gave the expected cross-coupling products, the α,ω-bis(tetrahydropyranyl) ethers THPO(CH_2)_nOPTH (n = 2y + z = 18, 19, 20, 22, 24, 28, 32), as white powders in 68–40% unoptimized yields based upon the limiting dihalide reactant. Although only one dihalide is specified for each synthesis in the experimental section, dibromides and diiodides could be used interchangeably.
Since the products were mixtures of diastereomers and not of special interest, most were characterized only by $^1$H NMR and IR spectroscopy, as summarized in the experimental section. However, the highest representative ($n = 32$), which was obtained in analytically pure form in 59% yield, was completely characterized. This sequence has previously been used by Schill to prepare $\alpha,\alpha$-diethers THPO(CH$_2$)$_n$OHP with $n = 34$ and 35. Although these were not elaborated further, related unsymmetrical species were. Lower homologs are also known ($n = 8, 10, 12, 16$), but all examples in Scheme 2 are new.

Tetrahydropyranyl ethers are commonly deprotected to alcohols, but they have been directly converted to the corresponding bromides at room temperature using Ph$_3$P and 2,4,4,6-tetrabromocyclohexa-2,5-diene. As shown in Scheme 2, reactions of THPO(CH$_2$)$_n$OHP under these conditions gave the target $\alpha,\alpha$-dibromides Br(CH$_2$)$_n$Br in 91–75% yields. All are known compounds, as referenced in the experimental section, and were characterized by IR and NMR ($^1$H, $^{13}$C) spectroscopy. The highest representative ($n = 32$) was obtained as an analytically pure wax in 75% yield.

In accord with the original goal of this study, the dibromides were treated with >2.0 equivalents of the potassium diphenylphosphido salt K$^+$-PPh$_2$, which is commercially available as a THF solution. Work-up gave the target $\alpha,\alpha$-diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$ in 95–74% yields. Alternatively, the easily-generated lithium salt Li$^+$-PPh$_2$ could also be employed. These new compounds were characterized by IR and NMR ($^1$H, $^{13}$C, $^{31}$P) spectroscopy, and mass spectrometry, as summarized in the experimental section. Microanalyses were obtained for representative cases.
Finally, syntheses of five analogous diphosphines with shorter methylene chains were executed (n = 8, 10, 11, 12, 14). All of these are known compounds, although some characterization data are lacking and in the last case only a patent report is available. Unlike the examples in Scheme 2, these involve dibromides that are either commercially available or can be accessed from inexpensive commercial diols. However, the data are included here to avoid literature fragmentation.

We note in passing that there are conflicting claims in the literature regarding the assignment of $^{13}$C NMR signals in Ar$_2$P(C$_6$H$_4$R)$_2$H$_2$ systems.9,28 Pulse sequences described in the experimental section unambiguously show that the $C_6$, $C_9$, and $C_7$ signals fall into the following chemical shift and coupling constant ranges (n = 8–28): δ = 27.6–28.1 ppm ($^3J_{CP}$ = 10.2–11.1 Hz), 25.4–26.0 ppm ($^2J_{CP}$ = 15.7–16.2 Hz), and 31.1–31.2 ppm ($^1J_{CP}$ = 12.6–13.2 Hz). Thus, in accord with observations with other organo-phosphorus compounds, the magnitudes of the $J_{CP}$ values do not correlate to the distance of the carbon from phosphorus.

The convenience and convergent nature of the methodology described above for the synthesis of α,ω-dibromides Br(CH$_2$)$_n$Br scarcely needs to be emphasized. Unlike some older syntheses to such compounds or the corresponding diols, generality is not limited by ‘gaps’ in commercially available starting materials. As of this writing, α,ω-bromoalcohols Br(CH$_2$)$_y$OH with y = 3, 6, 7, 8, 9, 10, 11, and 12 can be purchased. The most expensive cost ca. 200/5 g and the least expensive ca. 85 €/50 g. Practical large-scale syntheses have also been developed.29 Similarly, shorter-chain starting α,ω-dibromides Br(CH$_2$)$_z$Br with z = 8, 9, 10, 11, and 12 can be purchased. The most expensive cost ca. 62 €/13 g and the least expensive ca. 106 €/500 g.

Accordingly, modular syntheses of virtually any target α,ω-dibromide Br(CH$_2$)$_z$Br can be designed, up to a limit of n = 36 (2 y + z), based upon the commercial building blocks in the preceding paragraph. Furthermore, the dibromide products can be subjected to additional cycles of chain lengthening, substituting for X(CH$_2$)$_y$X in Scheme 2. In other efforts, we have extended the above syntheses by the use of substituted diarylphosphido anions $M^+ – P(C_6H_4R)_2$.24c However, it should be emphasized in closing that this work has only packaged established reactions in new ways. The power of this type of approach to α,ω-difunctional compounds was recognized by Schill earlier,23 but not applied towards these exact ends. Additional uses of the dibromides and diphosphines described herein will be reported in future publications.7,24

Instrumentation was identical with that given in recent full papers25–30 and additional details can be found elsewhere.24 The alcohol Br(CH$_2$)$_y$OH used to prepare Br(CH$_2$)$_y$OTP25 was obtained from Aldrich, the Li$_2$CuCl$_4$ solutions were freshly generated from LiCl (0.1696 g, 4.00 mmol), CuCl$_2$ (0.2689 g, 2.00 mmol), and THF (10 mL),26 and 2,4,4,6-tetramethylcyclohexa-2,5-diene was synthesized by a literature method.31 THF was distilled from Na/benzophenone, and CH$_2$Cl$_2$ was distilled from CaH$_2$. Other solvents and the following reagents were used as received: α-ω-X(CH$_2$)$_z$X (Avocado and Aldrich), PPh$_3$ (ABCR), and K$^+$ – PPh$_2$ (Aldrich, 0.5 M in THF).

**THPO(CH$_2$)$_y$OTP: Typical Procedure**

A Schlenk flask was charged with Mg (0.192 g, 7.90 mmol), and a dropping funnel containing a solution of Br(CH$_2$)$_y$OTP (1.230 g, 4.003 mmol)23 in THF (50 mL) was attached. The THF solution was slowly added with stirring. The mixture was stirred for 1 h at 50 °C and cooled in a ~20 °C bath. Then freshly prepared Li$_2$CuCl$_4$ (1.0 mL, 0.2 M in THF) and a solution of I(CH$_2$)$_z$I (0.520 g, 1.32 mmol) in THF (5 mL) were added with stirring. The cold bath was removed. After 14 h, sat. aq NH$_4$OAc (20 mL) was added. The emulsion was stirred for 0.5 h, and the organic phase was separated. The aqueous phase was extracted with Et$_2$O (3 × 50 mL). The combined organic phases were washed with H$_2$O (2 × 10 mL) and dried (Na$_2$SO$_4$). The solvent was removed by oil pump vacuum, and the residue crystallized from EtOH to give THPO(CH$_2$)$_y$OTP as a white powder (0.393 g, 50%).

IR (powder film): 2918 (s), 2819 (s), 1034 cm$^{-1}$ (s).

$^1$H NMR (CDCl$_3$): δ = 4.58 (t, $^3J_{HH}$ = 5.0 Hz, 2 H, OCH), 3.85 (m, 2 H, CH$_2$), 3.70 (m, 2 H), 3.50 (m, 2 H), 3.35 (m, 2 H), 1.80–1.30 (m, 64 H).

**THPO(CH$_2$)$_y$OTP**

This synthesis was conducted analogously using Br(CH$_2$)$_y$OTP (3.161 g, 11.92 mmol),25 Mg (0.385 g, 15.8 mmol), Li$_2$CuCl$_4$ (1.0 mL, 0.2 M in THF), and Br(CH$_2$)$_z$Br (0.994 g, 4.074 mmol); yield: 1.072 g (58%).

IR (powder film): 2919 (s), 2819 (s), 1034 cm$^{-1}$ (s).

$^1$H NMR (CDCl$_3$): δ = 4.60 (t, $^3J_{HH}$ = 5.0 Hz, 2 H, OCH), 3.84 (m, 2 H, CH$_2$), 3.74 (m, 2 H), 3.50 (m, 2 H), 3.34 (m, 2 H), 1.80–1.30 (m, 44 H).

**THPO(CH$_2$)$_y$OTP**

This synthesis was conducted analogously using Br(CH$_2$)$_y$OTP (2.782 g, 10.49 mmol),25 Mg (0.389 g, 16.0 mmol), Li$_2$CuCl$_4$ (1.0 mL, 0.2 M in THF), and Br(CH$_2$)$_z$Br (1.032 g, 4.000 mmol); yield: 0.931 g (50%).

IR (powder film): 2918 (s), 2819 (s), 1034 cm$^{-1}$ (s).

$^1$H NMR (CDCl$_3$): δ = 4.58 (t, $^3J_{HH}$ = 5.0 Hz, 2 H, OCH), 3.84 (m, 2 H, CH$_2$), 3.71 (m, 2 H), 3.52 (m, 2 H), 3.37 (m, 2 H), 1.80–1.30 (m, 46 H).

**THPO(CH$_2$)$_y$OTP**

This synthesis was conducted analogously using Br(CH$_2$)$_y$OTP (3.004 g, 11.33 mmol),25 Mg (0.440 g, 18.1 mmol), Li$_2$CuCl$_4$ (1.0 mL, 0.2 M in THF), and I(CH$_2$)$_z$I (1.628 g, 4.469 mmol); yield: 1.465 g (68%).

IR (powder film): 2919 (s), 2818 (s), 1034 cm$^{-1}$ (s).

$^1$H NMR (CDCl$_3$): δ = 4.58 (t, $^3J_{HH}$ = 5.0 Hz, 2 H, OCH), 3.84 (m, 2 H, CH$_2$), 3.70 (m, 2 H), 3.52 (m, 2 H), 3.35 (m, 2 H), 1.80–1.30 (m, 48 H).

**THPO(CH$_2$)$_y$OTP**

This synthesis was conducted analogously using Br(CH$_2$)$_y$OTP (3.326 g, 12.55 mmol),25 Mg (0.394 g, 16.2 mmol), Li$_2$CuCl$_4$ (1.0 mL, 0.2 M in THF), and Br(CH$_2$)$_z$Br (1.200 g, 4.000 mmol); yield: 0.914 g (45%).

IR (powder film): 2918 (s), 2819 (s), 1035 cm$^{-1}$ (s).
This synthesis was conducted analogously using Br(CH$_2$)$_2$OTHP (5.085 g, 16.55 mmol), Mg (0.443 g, 18.2 mmol), Li$_2$CuCl$_4$ (1.2 ml, 0.2 M in THF), and Br(CH$_2$)$_2$Br (1.113 g, 4.562 mmol); yield: 0.983 g (40%).

IR (powder film): 2919 (s), 2853 (s), 1472 (s), 718 cm$^{-1}$ (m).

This synthesis was conducted analogously using THPO(CH$_2$)$_{18}$OTHP (0.511 g, 1.00 mmol); yield: 0.400 g (85%); white powder.

IR (powder film): 2915 (s), 2852 (s), 1470 (s), 718 cm$^{-1}$ (m).

1H NMR (CDCl$_3$): δ = 3.37 (t, $J_{HH} = 6.9$ Hz, 4 H, CH$_2$Br), 1.83 (m, 4 H, CH$_2$CH$_2$Br), 1.34–1.20 (m, 28 H, CH$_2$).

13C{$_1$H} NMR (CDCl$_3$): δ = 34.1 (s, CH$_2$Br), 32.8 (s, CH$_2$CH$_2$Br), 29.7 (s, CH$_2$), 29.6 (s, multiple intensity, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 28.8 (s, CH$_2$), 28.2 (s, CH$_2$).

Br(CH$_2$)$_3$Br$_{16}$ This synthesis was conducted analogously using THPO(CH$_2$)$_3$OTHP (0.539 g, 1.00 mmol); yield: 0.446 g (90%); white powder.

IR (powder film): 2919 (s), 2853 (s), 1471 (s), 718 cm$^{-1}$ (m).

1H NMR (CDCl$_3$): δ = 3.37 (t, $J_{HH} = 6.9$ Hz, 4 H, CH$_2$Br), 1.83 (m, 4 H, CH$_2$CH$_2$Br), 1.34–1.20 (m, 28 H, CH$_2$).

13C{$_1$H} NMR (CDCl$_3$): δ = 34.1 (s, CH$_2$Br), 32.8 (s, CH$_2$CH$_2$Br), 29.7 (s, CH$_2$), 29.6 (s, multiple intensity, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 28.8 (s, CH$_2$), 28.2 (s, CH$_2$).

Br(CH$_2$)$_4$Br$_{11}$ This synthesis was conducted analogously using THPO(CH$_2$)$_4$OTHP (0.469 g, 1.00 mmol); yield: 0.321 g (75%); white powder.

IR (powder film): 2918 (s), 2852 (s), 1471 (s), 718 cm$^{-1}$ (m).

1H NMR (CDCl$_3$): δ = 3.37 (t, $J_{HH} = 6.9$ Hz, 4 H, CH$_2$Br), 1.83 (m, 4 H, CH$_2$CH$_2$Br), 1.40 (m, 4 H, CH$_2$CH$_2$CH$_2$Br), 1.34–1.20 (m, 26 H, CH$_2$).

13C{$_1$H} NMR (CDCl$_3$): δ = 34.1 (s, CH$_2$Br), 32.8 (s, CH$_2$CH$_2$Br), 29.7 (s, CH$_2$), 29.6 (s, multiple intensity, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 28.8 (s, CH$_2$), 28.2 (s, CH$_2$).

Br(CH$_2$)$_5$Br$_{12,13}$ This synthesis was conducted analogously using THPO(CH$_2$)$_5$OTHP (0.483 g, 1.00 mmol); yield: 0.364 g (83%); white powder.

IR (powder film): 2915 (s), 2852 (s), 1472 (s), 719 cm$^{-1}$ (m).

1H NMR (CDCl$_3$): δ = 3.37 (t, $J_{HH} = 6.9$ Hz, 4 H, CH$_2$Br), 1.83 (m, 4 H, CH$_2$CH$_2$Br), 1.39 (m, 4 H, CH$_2$CH$_2$CH$_2$Br), 1.34–1.20 (m, 28 H, CH$_2$).

13C{$_1$H} NMR (CDCl$_3$): δ = 34.1 (s, CH$_2$Br), 32.8 (s, CH$_2$CH$_2$Br), 29.7 (s, CH$_2$), 29.6 (s, multiple intensity, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 28.8 (s, CH$_2$), 28.2 (s, CH$_2$).

Br(CH$_2$)$_6$Br$_{14}$ This synthesis was conducted analogously using THPO(CH$_2$)$_6$OTHP (0.511 g, 1.00 mmol); yield: 0.400 g (85%); white powder.

IR (powder film): 2919 (s), 2853 (s), 1472 (s), 718 cm$^{-1}$ (m).

1H NMR (CDCl$_3$): δ = 3.37 (t, $J_{HH} = 6.9$ Hz, 4 H, CH$_2$Br), 1.83 (m, 4 H, CH$_2$CH$_2$Br), 1.40 (m, 4 H, CH$_2$CH$_2$CH$_2$Br), 1.34–1.20 (m, 32 H, CH$_2$).

13C{$_1$H} NMR (CDCl$_3$): δ = 34.1 (s, CH$_2$Br), 32.8 (s, CH$_2$CH$_2$Br), 29.7 (s, CH$_2$), 29.6 (s, multiple intensity, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 28.8 (s, CH$_2$), 28.2 (s, CH$_2$).

Br(CH$_2$)$_7$Br$_{15,16}$ This synthesis was conducted analogously using THPO(CH$_2$)$_7$OTHP (0.539 g, 1.00 mmol); yield: 0.446 g (90%); white powder.

IR (powder film): 2919 (s), 2853 (s), 1471 (s), 719 cm$^{-1}$ (m).

1H NMR (CDCl$_3$): δ = 3.37 (t, $J_{HH} = 6.9$ Hz, 4 H, CH$_2$Br), 1.83 (m, 4 H, CH$_2$CH$_2$Br), 1.40 (m, 4 H, CH$_2$CH$_2$CH$_2$Br), 1.34–1.20 (m, 36 H, CH$_2$).

13C{$_1$H} NMR (CDCl$_3$): δ = 34.1 (s, CH$_2$Br), 32.8 (s, CH$_2$CH$_2$Br), 29.7 (s, CH$_2$), 29.6 (s, multiple intensity, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 28.8 (s, CH$_2$), 28.2 (s, CH$_2$).

Br(CH$_2$)$_8$Br$_{17}$ This synthesis was conducted analogously using THPO(CH$_2$)$_8$OTHP (0.539 g, 1.00 mmol); yield: 0.446 g (90%); white wax, mp 69–70 °C.

IR (powder film): 2917 (s), 2853 cm$^{-1}$ (s).

1H NMR (CDCl$_3$): δ = 3.38 (t, $J_{HH} = 6.9$ Hz, 4 H, CH$_2$Br), 1.83 (m, 4 H, CH$_2$CH$_2$Br), 1.42 (m, 4 H, CH$_2$CH$_2$CH$_2$Br), 1.23 (m, 52 H, CH$_2$).

13C{$_1$H} NMR (CDCl$_3$): δ = 34.0 (s, CH$_2$Br), 32.8 (s, CH$_2$CH$_2$Br), 29.7 (s, multiple intensity, CH$_2$), 29.6 (s, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 28.8 (s, CH$_2$), 28.2 (s, CH$_2$).

MS: $m/z$ = 529 ([M – Br]$^+$, 30) and progressively more intensive fragments corresponding to the loss of CH$_2$.

Anal. Calcd for C$_{60}$H$_{122}$O$^*$: C, 77.12; H, 12.30.
**Ph₂P(CH₂)₂PPh₂** Typical Procedure

A Schlenk flask was charged with Br(CH₂)₂Br (0.825 g, 2.00 mmol) and THF (10 mL). Then K⁺PPPh₂ (0.80 mL, 0.5 M in THF, 4.00 mmol) was added via syringe with stirring until a light yellow color remained. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with CH₂Cl₂ (2 x 10 mL). The extracts were filtered through a 3 cm silica gel pad, which was rinsed with CH₂Cl₂. The solvent was removed by oil pump vacuum to give Ph₂P(CH₂)₂PPPh₂ as a white solid (1.101 g, 88%); mp 66–128.3 °C.

**Elemental Analysis**

Calculated for C₃₀H₅₆Br₂: C, 63.15; H, 10.60. Found: C, 63.32; H, 10.87.

**Ph₂P(CH₂)₂PPh₂**

This synthesis was conducted analogously using Br(CH₂)₂Br (0.937 g, 2.00 mmol); yield: 1.180 g (87%); white solid; mp 60–62 °C.

**IR (powder film):** 3073 (w), 2926 (m), 2853 (m), 1640 (w), 1482 (w), 1463 (w), 1436 (m), 911 (m), 737 (s), 695 cm⁻¹ (s).

**¹³C{¹H} NMR (CDCl₃):** δ = 7.43–7.38 (m, 8 H atom, o to P), 7.33–7.28 (m, 12 H atom, m/p to P), 2.03 (t, J_H/H = 7.6 Hz, 4 H, PCH₂), 1.46–1.34 (m, 8 H, PCH₂CH₂CH₂), 1.29–1.18 (m, 24 H, CH₂).

**¹³C{¹H} NMR (CDCl₃):** δ = 139.1 (d, J_Cp = 13.1 Hz, C arom, o to P), 132.7 (d, J_Cp = 18.4 Hz, CH₂CH₂CH₂ to P), 128.4 (s, CH₃CH₂ to P), 128.3 (d, J_Cp = 6.6 Hz, CH₃CH₂ to P), 31.2 (d, J_Cp = 13.2 Hz, PCH₂CH₂CH₂), 29.7 (s, CH₂), 29.6 (s, CH₂), 29.5 (s, CH₃), 29.3 (s, CH₂), 29.2 (s, CH₂), 28.0 (d, J_Cp = 15.9 Hz, PCH₂CH₂CH₂), 26.0 (d, J_Cp = 15.9 Hz, PCH₂CH₂CH₂).

**¹³P{¹H} NMR (CDCl₃):** δ = 15.4 (s).

**MS:** m/z = 683 ([M + 2 O]⁺, 100), 667 ([M + O]⁺, 50), 651 ([M⁺, 80]).

This synthesis was conducted analogously using Br(CH₂)₂Br (0.937 g, 2.00 mmol); yield: 1.180 g (87%); white solid; mp 60–62 °C.

**IR (powder film):** 3073 (w), 3019 (w), 2918 (s), 2849 (s), 1590 (w), 1471 (m), 1436 (m), 737 (s), 695 cm⁻¹ (s).

**¹³C{¹H} NMR (CDCl₃):** δ = 7.43–7.38 (m, 8 H atom, o to P), 7.33–7.28 (m, 12 H atom, m/p to P), 2.03 (t, J_H/H = 7.6 Hz, 4 H, PCH₂), 1.46–1.34 (m, 8 H, PCH₂CH₂CH₂), 1.29–1.18 (m, 32 H, CH₂).

**¹³C{¹H} NMR (CDCl₃):** δ = 139.1 (d, J_Cp = 13.1 Hz, C arom, o to P), 132.6 (d, J_Cp = 18.4 Hz, CH₂CH₂CH₂ to P), 128.4 (s, CH₃CH₂ to P), 128.3 (d, J_Cp = 6.6 Hz, CH₂CH₂CH₂ to P), 31.2 (d, J_Cp = 13.2 Hz, PCH₂CH₂CH₂), 29.7 (s, CH₂), 29.6 (s, CH₂), 29.5 (s, CH₃), 29.4 (s, CH₂), 29.3 (s, CH₂), 29.2 (s, CH₂), 28.0 (d, J_Cp = 11.0 Hz, PCH₂CH₂CH₂), 25.9 (d, J_Cp = 15.9 Hz, PCH₂CH₂CH₂).

**¹³P{¹H} NMR (CDCl₃):** δ = 15.4 (s).

**MS:** m/z = 711 ([M + 2 O]⁺, 100), 695 ([M + O]⁺, 50), 679 ([M⁺, 80]).

This synthesis was conducted analogously using Br(CH₂)₂Br (0.993 g, 2.00 mmol); yield: 1.20 g (85%); white solid; mp 58–60 °C.

**IR (powder film):** 3073 (w), 3019 (w), 2918 (s), 2849 (s), 1590 (w), 1471 (m), 1436 (m), 737 (s), 695 cm⁻¹ (s).

**¹³C{¹H} NMR (CDCl₃):** δ = 7.43–7.38 (m, 8 H atom, o to P), 7.33–7.28 (m, 12 H atom, m/p to P), 2.04 (t, J_H/H = 7.6 Hz, 4 H, PCH₂), 1.46–1.34 (m, 8 H, PCH₂CH₂CH₂), 1.29–1.18 (m, 36 H, CH₂).

**¹³C{¹H} NMR (CDCl₃):** δ = 139.1 (d, J_Cp = 13.1 Hz, C arom, o to P), 132.7 (d, J_Cp = 18.4 Hz, CH₂CH₂CH₂ to P), 128.4 (s, CH₃CH₂ to P), 128.3 (d, J_Cp = 6.6 Hz, CH₂CH₂CH₂ to P), 31.2 (d, J_Cp = 13.2 Hz, PCH₂CH₂CH₂), 29.7 (s, CH₂), 29.6 (s, CH₂), 29.5 (s, CH₃), 29.4 (s, CH₂), 29.3 (s, CH₂), 29.0 (s, CH₂), 27.8 (d, J_Cp = 11.0 Hz, PCH₂CH₂CH₂), 25.8 (d, J_Cp = 15.9 Hz, PCH₂CH₂CH₂).

**¹³P{¹H} NMR (CDCl₃):** δ = –15.1 (s).

**MS:** m/z = 740 ([M + 2 O]⁺, 15), 724 ([M + O]⁺, 20), 707 ([M⁺, 40]).

**Ph₂P(CH₂)₃PPh₂**

This synthesis was conducted analogously using Br(CH₂)₂Br (1.105 g, 2.00 mmol); yield: 1.312 g (86%); white solid; mp 59–62 °C.

**IR (powder film):** 3073 (w), 3019 (w), 2918 (s), 2849 (s), 1590 (w), 1471 (m), 1436 (m), 737 (s), 695 cm⁻¹ (s).

**¹³C{¹H} NMR (CDCl₃):** δ = 7.43–7.38 (m, 8 H atom, o to P), 7.33–7.28 (m, 12 H atom, m/p to P), 2.03 (t, J_H/H = 7.6 Hz, 4 H, PCH₂), 1.45–1.35 (m, 8 H, PCH₂CH₂CH₂CH₂), 1.29–1.18 (m, 28 H, CH₂).

**¹³C{¹H} NMR (CDCl₃):** δ = 138.8 (d, J_Cp = 13.1 Hz, C arom, o to P), 132.6 (d, J_Cp = 18.4 Hz, CH₂CH₂CH₂CH₂ to P), 128.4 (s, CH₃CH₂ to P), 128.3 (d, J_Cp = 6.6 Hz, CH₂CH₂CH₂CH₂ to P), 31.2 (d, J_Cp = 13.2 Hz, PCH₂CH₂CH₂CH₂), 29.7 (br s, CH₂), 29.6 (s, CH₂), 29.5 (s, CH₃), 29.3 (s, CH₂), 29.2 (s, CH₂), 28.1 (d, J_Cp = 11.0 Hz, PCH₂CH₂CH₂CH₂), 26.0 (d, J_Cp = 15.9 Hz, PCH₂CH₂CH₂CH₂).

**¹³P{¹H} NMR (CDCl₃):** δ = 15.3 (s).

**MS:** m/z = 951 ([M + 2 O]⁺, 100), 933 ([M + O]⁺, 50), 911 ([M⁺, 80]).

**Ph₂P(CH₂)₃PPh₂**

This synthesis was conducted analogously using Br(CH₂)₂Br (0.937 g, 2.00 mmol); yield: 1.180 g (87%); white solid; mp 60–62 °C.
This synthesis was conducted analogously using Br(CH₂)₂Br (0.290 g, 0.476 mmol); yield: 0.371 g (95%); white solid; mp 66 °C.  
IR (powder film): 2922 (s), 2849 (s), 1436 (s), 737 (s), 695 cm⁻¹ (s).

³¹P{¹H} NMR (CDCl₃): δ = –15.1 (s).

MS: m/z = 795 ([M + 2 O]⁺, 75), 779 ([M + O]⁺, 50), 763 (M⁺, 100). ³²P

PPh₃(CH₂)₁₂PPh₃

This synthesis was conducted analogously using Br(CH₂)₂Br (0.656 g, 2.00 mmol); yield: 0.937 g (87%); white solid; mp 66–69 °C.

IR (powder film): 3069 (w), 2918 (m), 2849 (m), 1482 (w), 1467 (w), 1432 (m), 1100 (w), 1069 (w), 1023 (w), 1000 (w), 737 (s), 718 (m), 695 cm⁻¹ (s).

¹H NMR (CDCl₃): δ = 7.44–7.36 (m, 8 H arom, o to P), 7.32–7.28 (m, 12 H arom, m/p to P), 2.00 (t, JHH = 7.8 Hz, 4 H, PCH₂), 1.45–1.32 (m, 8 H, PCH₂CH₂CH₂), 1.21 (m, 4 H, CH₂).

¹³C{¹H} NMR (CDCl₃): δ = 138.9 (d, JCP = 13.2 Hz, C arom, i to P), 132.7 (d, JCP = 18.3 Hz, CH₃ o to P), 128.4 (s, CH₃ p to P), 128.3 (d, JCP = 6.6 Hz, CH₃ m to P), 31.1 (d, JCP = 13.2 Hz, PCH₂CH₂), 29.7 (s, multiple intensity, CH₂), 29.5 (s, multiple intensity, CH₂), 29.3 (s, multiple intensity, CH₂), 29.0 (s, multiple intensity, CH₂), 28.0 (d, JCP = 11.0 Hz, PCH₂CH₂), 25.9 (d, JCP = 16.1 Hz, PCH₂CH₂).

³¹P{¹H} NMR (CDCl₃): δ = –15.6 (s).

MS: m/z = 818 (M⁺, 20), 711 ([M – PPh₃]⁺, 100), and fragments with lower mass corresponding to the loss of CH₂₃. ³³P

Ph₂P(CH₂)₈PPh₂

This synthesis was conducted analogously using Br(CH₂)₂Br (1.088 g, 4.000 mmol); yield: 1.624 g (84%); white solid; mp 103–105 °C.

IR (powder film): 3069 (w), 2918 (m), 2849 (w), 1482 (w), 1459 (w), 1432 (m), 1305 (w), 1096 (w), 1027 (w), 1000 (w), 961 (w), 911 (w), 822 (w), 737 (s), 695 cm⁻¹ (vs).

¹H NMR (CDCl₃): δ = 7.74–7.26 (m, 20 H, C₆H₅), 2.02 (t, JHH = 7.6 Hz, 4 H, PCH₂), 1.38 (m, 8 H, PCH₂CH₂CH₂), 1.3–1.2 (m, 52 H, CH₃).

¹³C{¹H} NMR (CDCl₃): δ = 137.6 (d, JCP = 11 Hz, C arom, i to P), 132.7 (d, JCP = 17 Hz, CH₃ o to P), 128.7 (s, CH₃ p to P), 128.4 (d, JCP = 7 Hz, CH₃ m to P), 31.1 (d, JCP = 13 Hz, PCH₂CH₂), 29.7 (s, multiple intensity, CH₂), 29.6 (s, multiple intensity, CH₂), 29.2 (s, multiple intensity, CH₂), 27.8 (d, JCP = 7 Hz, PCH₂CH₂), 25.7 (d, JCP = 14 Hz, PCH₂CH₂).

³¹P{¹H} NMR (CDCl₃): δ = –15.4 (s).

MS: m/z = 524 (M⁺, 50), 447 ([M – Ph⁺]², 22), 370 ([M – 2Ph⁺]², 43), 339 ([M – PPh₂⁺]², 81), and fragments with lower mass corresponding to the loss of CH₂₃ (185 (PPh₂⁺)², 55, 108 (PPh⁺)², 62).

Anal. Calculated for C₃₄H₄₀P₂: C, 79.97; H, 7.84. ³⁴P

Ph₃P(CH₂)₈PPh₃

This synthesis was conducted analogously using Br(CH₂)₂Br (0.656 g, 2.00 mmol); yield: 0.937 g (87%); white solid; mp 66–69 °C.

IR (powder film): 3069 (w), 2918 (m), 2849 (m), 1482 (w), 1467 (w), 1432 (m), 1100 (w), 1069 (w), 1023 (w), 1000 (w), 737 (s), 718 (m), 695 cm⁻¹ (s).

¹H NMR (CDCl₃): δ = 7.43–7.37 (m, 8 H arom, o to P), 7.33–7.29 (m, 12 H arom, m/p to P), 2.02 (t, JHH = 7.6 Hz, 4 H, PCH₂), 1.44–1.32 (m, 8 H, PCH₂CH₂CH₂), 1.26–1.15 (m, 12 H, CH₃).

¹³C{¹H} NMR (CDCl₃): δ = 138.8 (d, JCP = 12.0 Hz, C arom, i to P), 132.6 (d, JCP = 18.5 Hz, CH₃ o to P), 128.5 (s, CH₃ p to P), 128.3 (d, JCP = 6.9 Hz, CH₃ m to P), 31.2 (d, JCP = 13.0 Hz, PCH₂CH₂), 29.6 (s, CH₂), 29.5 (s, CH₂), 29.2 (s, CH₂), 28.0 (d, JCP = 10.2 Hz, PCH₂CH₂), 25.4 (d, JCP = 15.7 Hz, PCH₂CH₂).

³¹P{¹H} NMR (CDCl₃): δ = –15.3 (s).

MS: m/z = 538 (M⁺, 66), 461 ([M – Ph⁺]², 23), 353 ([M – PPh₂⁺]², 100), and fragments with lower mass corresponding to the loss of CH₂₃ (185 (PPh₂⁺)², 66, 108 (PPh⁺)², 93).

Ph₂P(CH₂)₈PPh₂

This synthesis was conducted analogously using Br(CH₂)₂Br (0.712 g, 2.00 mmol); yield: 0.995 g (88%); white solid; mp 86–88 °C.

IR (powder film): 3073 (w), 2926 (m), 2853 (m), 1640 (w), 1482 (w), 1463 (w), 1436 (m), 911 (m), 737 (s), 695 cm⁻¹ (s).

¹H NMR (CDCl₃): δ = 7.44–7.37 (m, 8 H arom, o to P), 7.33–7.27 (m, 12 H arom, m/p to P), 2.02 (t, JHH = 7.6 Hz, 4 H, PCH₂), 1.49–1.32 (m, 8 H, PCH₂CH₂CH₂), 1.30–1.13 (m, 16 H, CH₃).

¹³C{¹H} NMR (CDCl₃): δ = 139.1 (d, JCP = 13.2 Hz, C arom, i to P), 132.7 (d, JCP = 18.1 Hz, CH₃ o to P), 128.4 (s, CH₃ p to P), 128.3 (d, JCP = 6.6 Hz, CH₃ m to P), 31.2 (d, JCP = 12.6 Hz, PCH₂CH₂), 29.4 (s, CH₂), 29.2 (s, CH₂), 28.0 (d, JCP = 11.0 Hz, PCH₂CH₂), 25.9 (d, JCP = 15.9 Hz, PCH₂CH₂).

³¹P{¹H} NMR (CDCl₃): δ = –15.4 (s).

MS: m/z = 566 (M⁺, 33), 489 ([M – Ph⁺]², 14), 381 ([M – PPh₂⁺]², 100), and fragments with lower mass corresponding to the loss of CH₂₃ (185 (PPh₂⁺)², 42, 108 (PPh⁺)², 40).

Anal. Calculated for C₃₅H₃₈P₂: C, 80.53; H, 8.54. Found: C, 80.44; H, 8.65.
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References

(32) m/z for most intense peak of isotope envelope (relative intensity, %): (a) El (b) (+)-FAB, 3-NBA/CH 3 Cl 2.
(33) The PCH 2 CH 2 CH 2 linkages of the free phosphines exhibit a characteristic pattern of 13 C signals. A 1H-13 C COSY experiment with Ph 2 P(CH 2 ) 14 PPh 2 was used to make definitive assignments of the corresponding 1H signals, and a 1D-NOE experiment (DPFGSE-NOE) confirmed the PCH 2 signal (close contact to the ortho protons of the phenyl ring). A 1H-13 C COSY experiment in turn gave a definitive assignment of the PCH 2 -13 C signal and a selective 1D-NOE experiment (DPFGSE-NOE) confirmed the PCH 2 signal (close contact to the ortho protons of the phenyl ring).