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The difference in reactivity of (−)-mono and dimenthyl vs. diethyl alkylphosphonates in the α-lithiation reaction: Carbanionic synthesis of unknown (−)-dimenthyl 1-iodoalkylphosphonates and their first use in the radical iodine atom transfer addition (I-ATRA) and cyclisation (I-ATRC) reactions

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Abstract

Unknown (−)-dimenthyl and ethyl (−)-menthyl 1-iodoethylphosphonates were synthesized via 1-lithio derivatives in 85–87% yields. Starting (−)-dimenthyl alkylphosphonates (R = Me, Et, *i*-Pr) were obtained in the Michaelis–Becker reaction (75–81% yields) and/or in the methylation reaction of the corresponding 1-lithio-alkylphosphonates (78–92% yields). An interesting concentration and time correlations, never observed for diethyl alkylphosphonates, were found for the metalation of bulky (−)-menthyl alkylphosphonates with *n*-BuLi and general reaction conditions for the carbanion generation were elaborated. The first example of the I-ATRA reaction of (−)-dimenthyl 1-iodoethylphosphonate with 1-hexene (AIBN) gave four diastereomers (1.6:1:1:0.4), separated into two pairs. The I-ATRC reaction was not effective due to a steric hindrance around the reactive center. The X-ray analysis of (−)-dimenthyl methylphosphonate confirmed a considerable steric hindrance in higher (−)-dimenthyl alkylphosphonate esters in comparison to their diethyl analogs.

Keywords: Metalation; Ethyl (−)-menthyl phosphonate; (−)-Dimenthyl phosphonate; Steric hindrance; Asymmetric amplification; Radical reaction

1. Introduction

The comprehensive database search shows attempts of applications of (−)-dimenthyl and (−)-monomenthyl phosphonate esters in various stereocontrolled reactions, as for instance in a multiple asymmetric induction (vide infra). One of reasons of this interest is an easy availability of (−)-menthol which constitutes a cheap reagent in syntheses of (−)-dimenthyl and (−)-trimenthyl phosphites, starting materials for the discussed phosphonates.

Thus, (−)-dimenthyl alkylphosphonates were synthesized from (−)-menthol and the corresponding phosphonic dichlorides [1]. (−)-Tetramenthyl benzene-1,2-bisphosphonate was prepared from the corresponding aromatic phosphoryl chloride and potassium menthoxide in the presence of 18-crown-6 and further used as an effective sensitizer for the geometrical (*Z*)/(*E*) photoisomerisation of cyclooctene [2]. (−)-Dimenthyl phosphite was cyclized with 1,6-dienes under free radical conditions (AIBN) to give the cyclic product in 58% yields [3]. It was also employed in the

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condensation with carbon disulfide in the synthesis of (−)-dimenthyl phosphoryldithioformate and used in spin trapping [4], electrochemical and cyclic voltammetric reduction [5]. (−)-Dimenthyl phosphite as well as its sodium and ethylzinc salts were added by Kolodyazhnyi [6,7] to chiral C=N and C=C compounds as an example of efficient multistereoselectivity. The addition of (−)-trimenthyl phosphite to nitrostyrene led to formation of optically active β-nitroalkylphosphonates [7], while addition to C=N bond gave (−)-dimenthyl α-aminoalkylphosphonates [8]. The condensation with aldehydes [8] afforded (−)-dimenthyl α-hydroxyalkylphosphonates and with phenacylchloride gave (−)-dimenthyl α-ketophophonates [8].

Further application of (−)-dimenthyl phosphite was demonstrated in addition to aldehydes under conditions of the Pudovik and the Kabachnik–Fields reactions [9,10]. In particular, its condensation with trioxane (cyclic polymer of formaldehyde) followed by allylation of the resulted product, gave (−)-dimenthyl allyloxymethylphosphonate which underwent a sigmatropic [2,3] – Wittig rearrangement in 92% d.e [11]. Sulfur [12,13] and nitrogen [14] versions of this rearrangement were also carried out. Double and triple asymmetric induction was demonstrated in the phosphaaldol addition of (−)-dimenthyl phosphite to 2,3-isopropylidene (*R*)-glyceraldehyde [15]. Wiemer et al. described a rearrangement of (−)-dimenthyl vinylphosphate to the corresponding (−)-dimenthyl β-ketophosphonate [16]. The one-pot Pummerer reaction of thiolane-*S*-oxide with (−)-trimenthyl phosphite allowed an efficient synthesis of (−)-dimenthyl 2-tetrahydrothienylphosphonate in 99% yield [17]. This compounds may be also obtained in the intramolecular radical addition [12,13] of α-sulfanyl radical to homoallylphosphonate. The free radical addition of (−)-dimenthyl thiophosphite to 1-octene and 2-methyl-2-propenyl phenyl ether (Et_3B/O_2) followed by oxidation of the P=S to the P=O bond, resulted in formation of the corresponding (−)-dimenthyl phosphonates in 85% and 47% yields respectively [18].

(−)-Monomenthyl phosphonates were obtained in a very efficient tetrazol catalyzed synthesis from phosphonic dichlorides [19]. Both (−) and (+)-menthyl phosphonic monochlorides were used to activate *Candida rugosa* lipase by binding with Ser 209 [20]. (−)-Menthyl 1-bromophosphonoamidate was utilized in the menthoxide induced rearrangement to produce the corresponding (−)-menthyl methyl 1-aminomethylphosphonate [21,22]. Methyl phenylphosphonic acid was esterified with (−)-menthol in 81% yield using (benzotriazolyloxy)phosphonium hexafluorophosphates [23]. (−)-Menthyl arylphosphonic acid were also esterified with diazomethane [24]. Both (−)-menthyl and (+)-neomenthyl phenylphosphonic acids may be obtained from the corresponding phosphinates via the P–H → P–OH oxidation [25]. The addition of ethyl (−)-menthyl trimethylsilyloxy phosphite (P^{III}) generated in situ from the corresponding P^{IV} derivative to α-haloacrylates and acrylonitriles provided a general route to the corresponding ethyl (−)-menthyl vinylphosphonates [26]. The nucleophilic substitution at phosphoryl group in (−)-menthyl *S*-methyl(methyl or phenyl)phosphonothioates by methoxide ion afforded the corresponding (−)-menthyl methyl [27] or (−)-menthyl phenylphosphonothioates [28]. Diethyl [29] and diphenyl [30] phosphonates were used in the transesterification reaction with the (−)-menthoxide ion to give (−)-monomenthyl phosphonates. Mass fragmentation of (−)-menthyl arylphosphonates was also investigated [31].

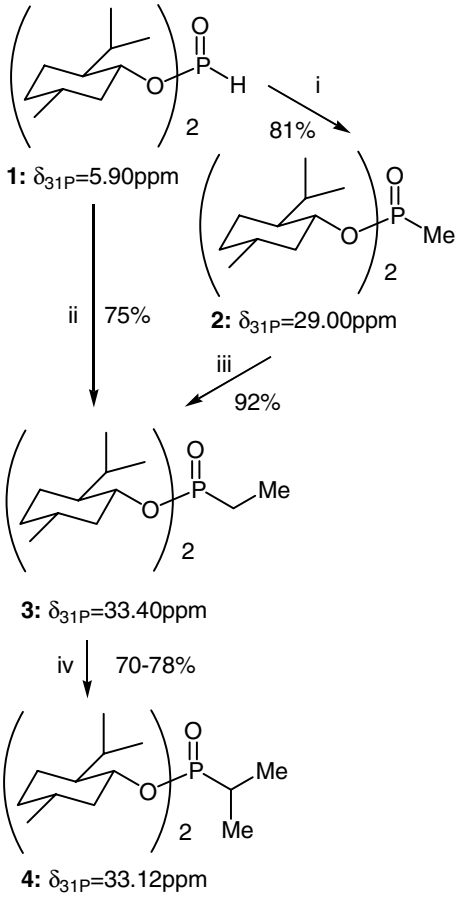
The aim of our research was synthesis of unknown (−)-dimenthyl 1-iodoalkylphosphonates and comparison of their reactivity with diethyl analogs both in carbanion and radical asymmetric reactions.

2. Results and discussion

2.1. Synthesis and metalation of (−)-dimenthyl phosphites and alkylphosphonates

Our first experiences with functionalization of unknown (−)-(mono and di)menthyl alkylphosphonates showed that their α-lithiation was much more difficult than α-lithiation of diethyl analogs which were commonly used phosphonate reagents in the laboratory practice. Therefore, this class of compounds required elaboration of new reaction conditions. For this reason, we synthesized phosphonates with primary, secondary and tertiary α-P alkyl groups. Thus, (−)-dimenthyl methylphosphonate **2** was synthesized in 81% yield from the corresponding sodium salt of (−)-dimenthyl phosphite **1** [30] and methyl iodide in the Michaelis–Becker reaction. The metalation of the phosphite **1** with NaH in THF proceeded effectively at 50 °C in contrast to diethyl phosphite which was deprotonated at room temperature (Scheme 1). (−)-Dimenthyl ethylphosphonate was obtained in a similar way from ethyl iodide in 75% yield or via methylation of **2-Li**. The isopropylphosphonate **4** was synthesized from **3** via methylation of **3-Li** in 70–78% yield. Of these three phosphonates, only methylphosphonate **2** was a solid and allowed a deeper insight in an arrangement of bulky dimenthyl groups around the α-phosphonate carbon atom in crystal.

The crystal structure of **2** contained two crystallographically independent molecules (A and B) in the asymmetry unit (Fig. 1).The packing of molecules **2** in the unit cell is shown in Fig. 2. The PCO3 tetrahedron in both molecules was deformed. The valency angles in this tetrahedron ranged from 102.9(1) to 115.1(1) and from 102.8(1)° to 114.9(1)° in molecules A and B, respectively.The dihedral angles between mean planes of the two cyclohexane rings were 42.2(1)° and 43.1(1)° in the molecule A and B, respectively. The only significant differences between orientation of the two menthyl substituents with respect to the phosphorus tetrahedron were observed (Torsion angles in molecules A and B, respectively, C1–P1–O1–C11: −50.4(2) and −47.9(2), O2–P1–O1–C11: 60.2(2) and 62.8(2), O3–P1–O1–C11: −176.0(2) and −173.7(2), C1–P1–O2–C21: −144.4(2) and −147.6(2), O1–P1–O2–C21: 101.5(2) and



Scheme 1. (i) NaH, THF/50 °C/1 h; MeI/25 °C/24 h; (ii) as in i, only MeI was replaced by EtI; (iii) *n*-BuLi/−78 °C, MeI/−30 °C; (iv) *n*-BuLi (2 eq.); MeI/−78 °C.

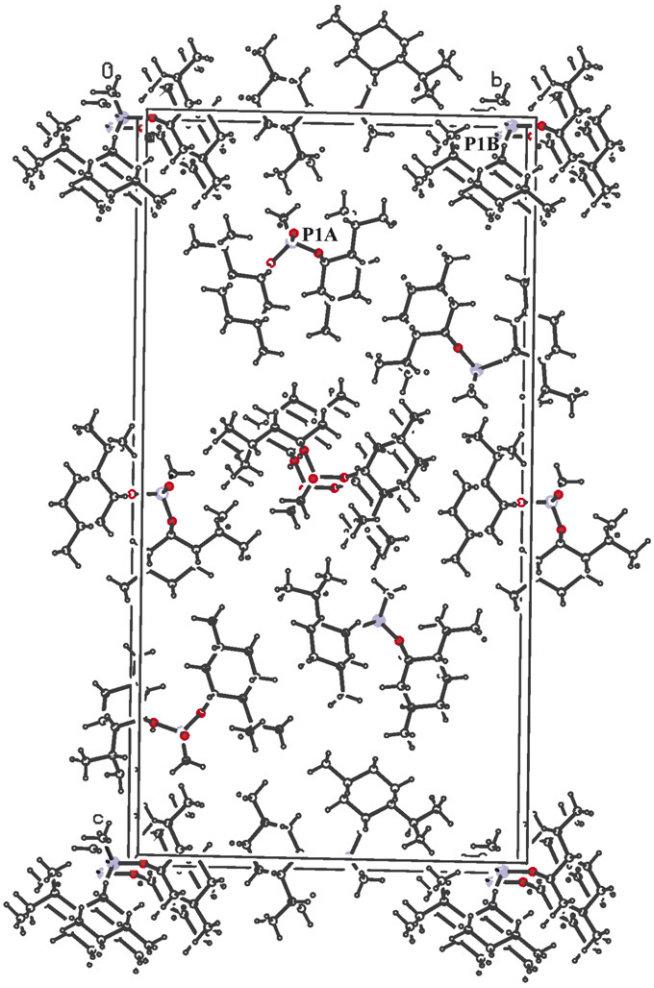


Fig. 2. The packing of the molecules in the unit cell.

97.7(2), O3–P1–O2–C21: −19.1(2) and −22.6(2), P1–O1–C11–C12: 140.8(2) and 140.7(2), P1–O1–C11–C16: −97.6(2) and −98.0(3), P1–O2–C21–C22: 121.2(2) and 124.0(2), P1–O2–C21–C26: −117.1(2) and −114.4(2). These data applied to the models of **3** and **4**, indeed, suggested an increasing steric hindrance caused by bulky menthoxy groups around the α-phosphonate carbon atoms of more substituted (−)-dimenthyl alkylphosphonates.

As we have already mentioned, the carbanionic pathway to (−)-dimenthyl alkylphosphonates **3** and **4** required metalation of the corresponding **2** and **3** with *n*-BuLi followed by alkylation with methyl iodide. This simple reaction showed that the reactivity of (−)-dimenthyl alkylphosphonates was significantly lower than their ethyl

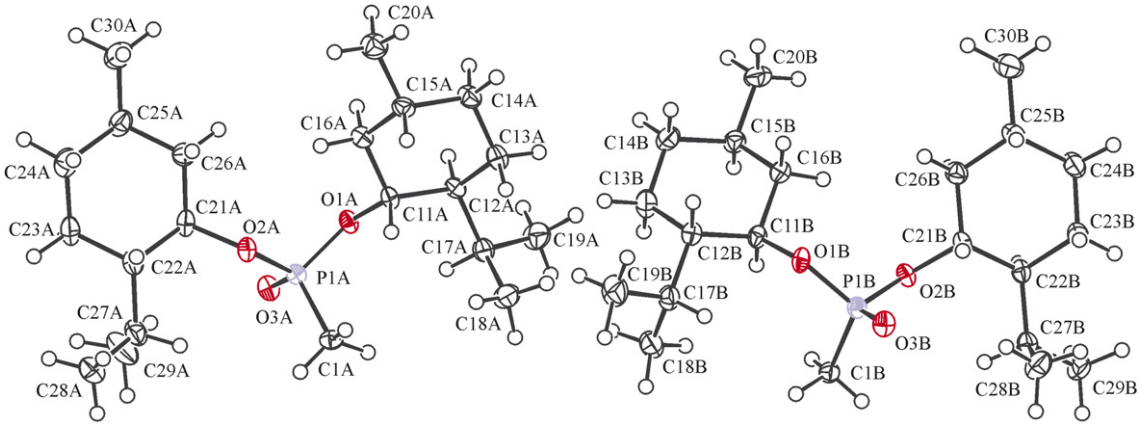


Fig. 1. The structure of two independent molecules of (−)-dimenthyl methylphosphonate **2** showing 50% probability displacement ellipsoids.

analogs which were common organophosphorus reagents in synthesis and decreased in the following order: P–Me > P–Et > P–*i*-Pr. Although ^{31}P NMR investigations at low temperatures revealed that lithiation of both (−)-dimenthyl **2** and diethyl methylphosphonates occurred almost immediately at −78 °C upon addition of stoichiometric amount of *n*-BuLi and methylation of the resulting **Li**-anions with methyl iodide was fast and effective, the same reaction sequence (deprotonation and methylation) carried out with **3** at −78 °C gave only the starting material. However, if twofold excess of *n*-BuLi was used and the lithiation time was increased to 20 min. (at $c = 0.005$–0.014 mol/L of **3** in THF depending on reaction scale), the corresponding phosphonate **4** was obtained in 70–78% yield (Scheme 1, Table 1). Shorter reaction times (3 min) required application of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) that facilitated a generation of **3-Li**. In this case, the best yield of **4** (70%) was achieved when *n*-BuLi/TMEDA/MeI in a 2/2/1 ratio was employed. Collignon et al. [11] confirmed that deprotonation of (−)-dimenthyl phosphonates required an excess of *n*-BuLi. They use even 5 equiv. of *n*-BuLi in order to deprotonate (−)-dimenthyl allyloxymethylphosphonate in the [2,3]-sigmatropic Wittig rearrangement. Interestingly, the use of bulky lithium diisopropylamide (LDA) instead of *n*-BuLi was ineffective even with an excess of this base and prolonged reaction time (Table 1).

The large steric hindrance caused by the dimenthyl groups handicaps a free approach of the bulky, oligomeric structure of *n*-BuLi to α hydrogen atoms of the phosphonate. This oligomeric structure exists mainly as a mixture of a tetramer and a dimer, obtained from the irreversible cleavage of the corresponding hexamer [32,33]. Because (a) the dimer is more reactive than the tetramer and they equilibrate and (b) no evidence was obtained for small monomeric *n*-BuLi in THF solution, one can conclude that **2** can be deprotonated by both tetrameric and dimeric forms of *n*-BuLi but the more hindered **3** is deprotonated mostly by the dimeric form. This also explains a necessity to use in our experiments an excess of *n*-BuLi, prolonged reaction time and TMEDA for shortening of the reaction time (TMEDA decreases the state of aggregation of *n*-BuLi and increases the dimer concentration).

We have also found that a partial deprotonation of **3** was also possible with 1.1 equiv. of *n*-BuLi within 15 min, when around 10 times higher concentration of the substrate in THF was employed than before. This interesting correlation is shown in Fig. 3. At this concentration (103 mg of **3**/5 mL of THF), it was also revealed that **3-Li** was not very much stable in a function of time (after 5/15/25 min., ratios **3/4** = 1/3, 1/1.5, 1/0.66 and 5/16/30% of the anion decay products were found, respectively).

Table 1
Reaction conditions for deprotonation and methylation of **3**

Temperature/time (°C)/(min)	*n*-BuLi/	*n*-BuLi/MeI	*n*-BuLi/TMEDA/MeI
3 → ***4*** *(%)*			
−78/ 3	1/1 [0]	1/1 [0]	1/1/1 [48]
	2/1 [0]	1/1 [0]	1.5/1.5/1.5
	2/1 [0]	1/1 [0]	[56]
			2/2/1 [70]
−78/10	1/1 [0]	1/1 [0]	
−78/20	2/1 [0]	2/1 [78]	

2.2. Synthesis and α-lithiation of (−)-menthyl 1-iodoalkylphosphonates

The synthesis of the title compounds was accomplished applying the modified Savignac's approach [34] in which one of the α-P acidic hydrogen atoms was temporarily replaced by the –$SiMe_3$ group and released in the final step of the synthesis. In the original work, Savignac et al. [34] synthesized diethyl 1-iodoalkylphosphonates using LDA as a base for the α-P deprotonation stage and observed that *n*-BuLi was completely ineffective. Opposite to these observations, we have found that (−)-dimenthyl alkylphosphonates required at least 1.5 equiv. of *n*-BuLi and the sterically more requiring LDA did not work in this case (Table 1). The synthesis proceeded via the intermediate 1-silylated 1-iodoethylphosphonate (**5**), which in contrast to the diethyl series, turned out to be a stable compound, isolable by chromatography on silica gel (Scheme 2).

Analysis of crude reaction mixtures with ^{31}P NMR showed that silylation/iodination step of the sterically hindered (−)-dimenthyl phosphonate carbanions occurred in a stereocontrolled manner (**5**: 1/1.44–1/2.60). During the silicagel chromatography it was possible to enrich the product in one of diastereomers shifting the obtained ratio even to 1:5 (full resolution was not possible). However, the desilylation/protonation step gave **6** in a ratio 1:1. The resistance of **5** to the desilylation with sodium ethanolate was higher than in the case of diethyl 1-iodo-1-trimethylsilylalkylphosphonates. For instance after the 15 min.

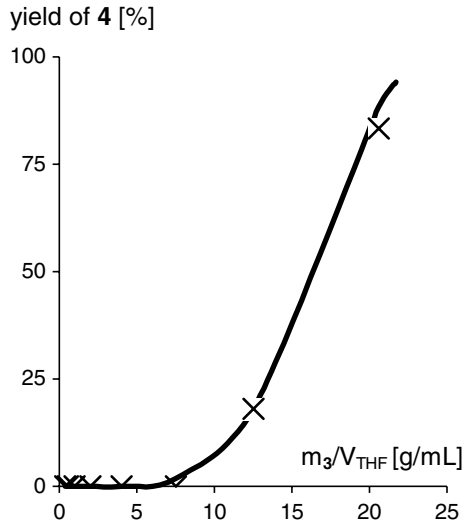
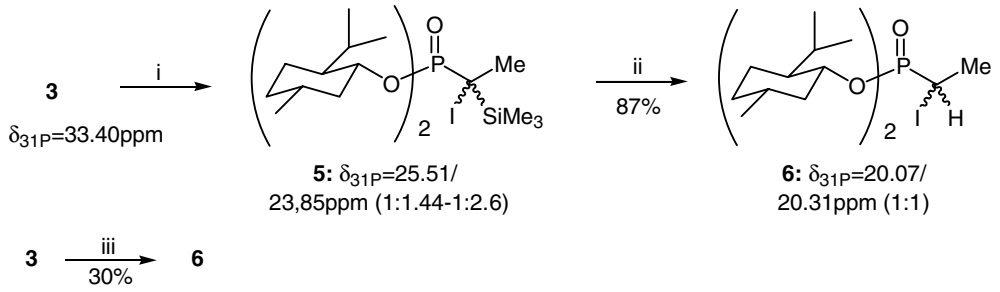


Fig. 3. Plot of dependence between concentration of **3** in THF and yield of **4**.



Scheme 2. (i) 1, *n*-BuLi; 2, Me_3SiCl; 3, I_2/THF, −78 °C. (ii) EtONa, EtOH/25 °C. (iii) 1, *n*-BuLi; 2, I_2; 3, aq. NH_4Cl (sat.)/THF, −78 °C.

treatment of **5** with EtONa, only the substrate was present in the ^{31}P NMR spectrum. Longer 2 h reaction gave a mixture of **5** in a ratio 2.6:1 and **6** in a ratio 1:1 (four ^{31}P NMR signals, (Scheme 2).

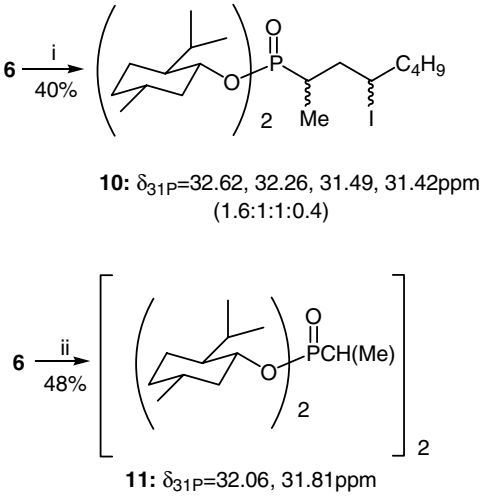
It is also worthy to note that a direct α-iodination of **3-Li** with elemental iodine I_2 gave **6** in 30% yield (Scheme 2, iii route). Some time ago, we reported 15% yield of the corresponding diethyl 1-iodoethylphosphonate, after optimization, in the α-iodination reaction of diethyl 1-lithioethylphosphonate with I_2 [35].

Unsymmetrical ethyl (−)-menthyl 1-iodoethylphosphonate (**9**) was obtained according to our modified Savignac's procedure (see Section 3) in 85% yield as a mixture of four nonseparable diastereomers ($\delta_{31P} = 21.65$, 21.77, 21.89 and 22.02) in a 1:1.2:1.6:1.3 ratio. The starting ethyl (−)-menthyl ethylphosphonate (**8**) was synthesized from diethyl ethylphosphonate **7** in 94% yield as a mixture of two nonseparable diastereomers ($\delta_{31P} = 32.75$, 32.98) in a 1.8:1 ratio based on a procedure of Naso et al. [29] for synthesis of ethyl (−)-menthyl 1-sulfinylmethylphosphonates (Scheme 3). The I-ATRA reaction with 1-hexene in the presence of AIBN gave a nonseparable complex mixture of products.

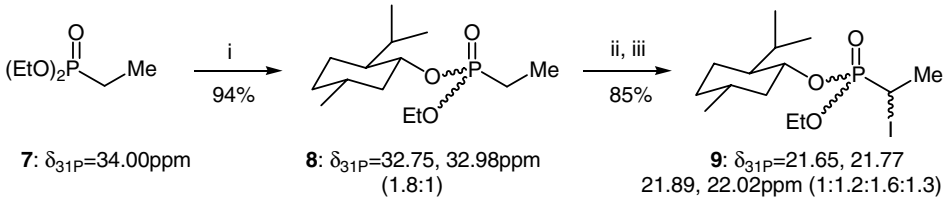
2.3. The radical iodine atom transfer addition reaction (I-ATRA) using (−)-dimenthyl 1-iodoethylphosphonate (6)

The title reaction was carried out in boiling 1-hexene in the presence of 1 equiv. of AIBN. Although **6** was used as a mixture of 1:1 diastereomers, however, upon the reaction with AIBN, the racemic pyramidal center should become flat in the corresponding alkyl radical and the transfer of chirality should be controlled by menthyl groups only. The reaction was monitored with ^{31}P NMR showing after 8 h a group of signals in a range of 34–31 ppm. The reaction was continued with additional equivalent of AIBN after 16 h. After 24 h, the substrate **6** disappeared almost completely (10% left) and in the ^{31}P NMR spectrum remained four signals at $\delta_{31P} = 32.62$, 32.26, 31.49 and 31.42 ppm in a ratio of 1.6:1:1:0.4 due to four diastereomers of (−)-dimenthyl 3-iodo-1-methyl-*n*-heptylphosphonate (Scheme 4).

Using column chromatography over silica gel, these four products were separated onto two pairs of diastereomers: 32.62/32.26 ppm (1.6:1, the first pair) and 31.49/31.42 (2.5:1, the second pair) in overall 40% yield. It should be mentioned that general reaction conditions, elaborated in our lab [36–38] for the I-ATRA reaction of diethyl 1-iodoalkylphosphonates (10 equiv. of alkene, 0.5–1 equiv. of AIBN, boiling benzene, 7 h) were not effective in the case (−)-dimenthyl analogs. After 7 h, the ^{31}P NMR spectrum showed only a signal of the substrate **6**. Similar results were



Scheme 4. i: 1-Hexene (solvent)/AIBN/reflux. (ii) 1-Hexene/Et_3B-O_2/toluene/−78 °C.



Scheme 3. (i) (−)-MentOK, THF/0 °C ↗ 25 °C, 24 h. (ii) 1, *n*-BuLi; 2, Me_3SiCl; 3, I_2/THF, −78 °C. (iii) EtONa, EtOH/25 °C.

obtained when benzene was replaced by other solvents like chloroform or 1,2-dichloroethane.

Replacement of AIBN for the Et_3B/O_2 initiating system which, for a better diastereoselectivity, allowed decreasing the reaction temperature to −78 °C, brought unexpectedly a formation of (−)-tetramenthyl ethylenebisphosphonate **11** instead of **10** (Scheme 4). Most probably, in the reaction of ethyl radicals (derived from autooxidation of Et_3B) with **6**, a bigger concentration of easily dimerizing (−)-dimenthoxyphosphoryloeth-1-yl radicals was achieved than in the reversible reaction of isobutyronitrile radicals with **6**. This is the first example of the total domination of the termination over the propagation step in the I-ATRA process involving phosphonate substrates. For a comparison in the reaction of diethyl iodomethylphosphonate with 1-hexene, the analogous termination product, i.e. tetraethyl ethylenebisphosphonate was formed only in 0–2% yields [37].

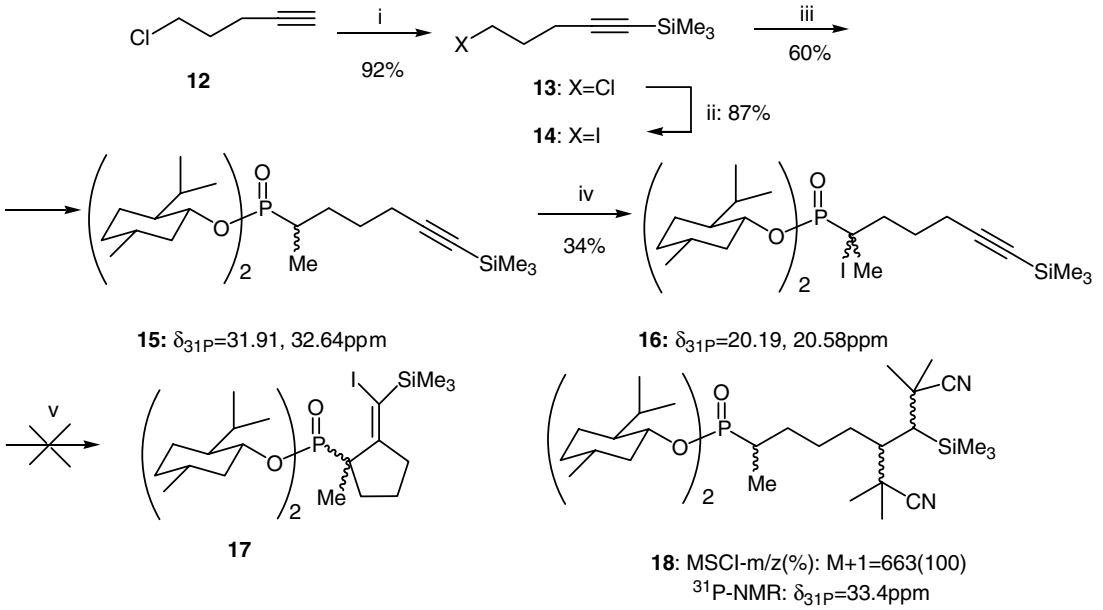
2.4. The radical iodine atom transfer cyclisation reaction (I-ATRC)

The starting material **16** for this reaction was synthesized from a commercially available 5-chloro-1-pentyne (**12**), which at the outset was converted to 5-chloro-1-trimethylsilyl-1-pentyne (**13**) [39] in 92% yield (Scheme 5).

The Finkelstein reaction of the latter produced the iodide **14** in 87% yield which was next condensed with **3-Li** to give the phosphonate **15** in 60% yield. α-Iodination of **15-Li** to give **16** did not require the Savignac's procedure and was carried out directly with I_2. Deprotonation of **15** to **15-Li** required again 2 equiv. of *n*-BuLi at −78 °C (20 min). The I-ATRC reaction did not bring the required **17** even after 72 h reflux in benzene with 3 equiv. of AIBN. Instead the complex mixture of products was formed ($\delta_{31P} = 19.8$–33.4 ppm) from which only **18** (~3% yield) could be detected with MS-CI and ^{31}P NMR after column chromatography over silicagel. It is interesting to mention that the reaction with 1 equiv. of AIBN under standard reaction conditions for the intramolecular reaction [38] (7 h), brought in the ^{31}P NMR spectrum signals of mainly unreacted substrate (>90%) accompanying by two signals at $\delta_{31P} = 33.4$ due to **18** and $\delta_{31P} = 27.3$ ppm which might be attributed to the expected **17** in 4% and 7.5% yields, respectively. The former signal at $\delta_{31P} = 33.4$ ppm remained at the level of 4–14% during the reaction and the latter was gradually increasing from 12% (after 30 h and addition of the second eq. of AIBN) to 27% (after 50 h and addition of the third eq. of AIBN). After next 10 h, it remained unchanged and it finally almost disappeared in the complex mixture after total 72 h. The formation of **18** was a result of: (1) the deiodination reaction with isobutyronitrile radical followed by the reduction of the resulting α-P phosphonate radical; and (2) addition of two equivalents of isobutyronitrile radical to the triple bond combined with a double reduction of the intermediate radicals.

The source of reducing agent was isobutyronitrile radical decomposing to methacrylonitrile and hydrogen [38]. Such an outcome of the I-ATRC reaction of **16** might be explained as a consequence of a greater steric hindrance at the phosphonate reactive center in comparison to **6** (dimenthoxy groups, additional α-P substituent and 1,1-disubstitution in alkyne) as well as a general lower reactivity of alkynes in comparison to alkens in radical reactions (higher LUMO and lower HOMO levels for alkynes and both SOMO–LUMO and SOMO–HOMO interactions more difficult).

In a conclusion, both (−)-dimenthyl phosphite and (−)-dimenthyl alkylphosphonates revealed a lower reactivity



Scheme 5. (i) 1, *n*-BuLi/THF/−78 °C, 2 h; 2, Me_3SiCl/−78 °C ↗ 25 °C, 2 h. (ii) NaI/acetone, reflux, 24 h. (iii) 3-Li/THF/−78 °C ↗ 25 °C, 2 h. (iv) 1, *n*-BuLi/THF, −78 °C, 20 min; 2, I_2/−78 °C ↗ 25 °C, 1 h. (v) AIBN/benzene/reflux.

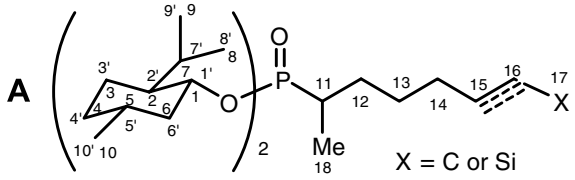
in carbanionic and radical reactions in comparison to their diethyl analogs. This effect was confirmed in metalation reactions of (−)-dimenthyl phosphite and (−)-menthyl alkylphosphonates with the aggregated dimeric and/or tetrameric *n*-BuLi and bulky LDA as well as in the first radical I-ATRA and I-ATRC reactions of the unknown (−)-dimenthyl 1-iodoalkylphosphonates. The X-ray data of **2** applied to molecular models of more substituted (−)-dimentyl alkylphosphonates confirmed a possibility of their lower reactivity. Concentration and time correlations versus amounts of the lithiating agent allowed elaboration of synthetic protocols for the effective deprotonation of this particular group of phosphonates. These protocols reflect a subtle interplay between generation, stability and reactivity of the resulting carbanions.

3. Experimental

3.1. General

The ^{1}H NMR (200 and 500 MHz) and ^{13}C NMR (50 and 125 MHz) spectra were recorded using a Bruker AC-200 and a Bruker DRX-500 spectrometers . The IR spectra were recorded using an ATI Mattson Infinity FTIR 60 spectrometer. The mass spectra of pure compounds were obtained using a Finnigan Mat 95 spectrometer. Column chromatography was done using Merck silica gel (F_{254} 60, 70–230 and 270–400 mesh). Organic solvents were purified by standard procedures. All optically active menthyl derivatives were prepared from 1*R*,2*S*,5*R*-(−)-menthol.

Numbering of atoms in compounds **1**–**16** is presented in skeletal fragments **A** and **B**.



3.2. Crystallographic data

Crystal data for (−)-dimenthyl methylphosphonate: $C_{21}H_{41}O_3P$, orthorhombic, space group $P2_12_12_1$, $a = 5.549(3)$, $b = 20.646(4)$, $c = 39.660(9)$ Å, $V = 4544$ (3) Å^3, $M_r = 372.51$, $Z = 8$, $d_{calc} = 1.089$ g/cm^3, $\mu = 0.14$ mm^{-1}, $T = 100(2)$ K, $F(000)$ 1648. *Data collection*: colourless plate $0.50 \times 0.20 \times 0.10$ mm from *n*-hexane, Kuma KM4-CCD diffractometer. Measured reflections 30011 (θ_{max} 28.5°), 10605 independent (R_{int} 0.097). *Structure solution*: direct method, anisotropic refinement on F^2 (SHELXL 97) [39] for all non H atoms, hydrogen atoms attached to C atoms were included using a riding model. The structure was refined over 7241 reflections with $I > 2\sigma(I)$ (466 refined parameters with 15.5 reflections on parameter). The correct absolute structure was proved by Flack parameter [40] $x = 0.04(9)$. For all data the final wR_2 was 0.1205, $R_1 = 0.0629$, $S = 1.041$, max. $\Delta\rho = 0.290$ e Å^{-3}. Extinction correction (SHELXL 97), extinction coefficient was 0.0023(4).

3.3. Synthetic part

3.3.1. (−)-Dimenthyl phosphite (*1*)

To a mechanically stirred solution of (−)-menthol (109.2 g, 0.7 mol) and triethylamine (106.4 g, 146.5 mL, 1.05 mol) in dry toluene (1000 mL), phosphorus trichloride (48.3 g, 30.7 mL, 0.35 mol) dissolved in toluene (350 mL) was added dropwise at −30 °C within 30–45 min. Then the reaction mixture was slowly warmed to room temperature and stirred for 2 h at this temperature. The ^{31}P NMR spectrum showed a signal at $\delta_{31P} = 147.46$ ppm assigned to (−)-dimenthyl chlorophosphite as the main reaction product. The hydrolysis of the chlorophosphite to (−)-dimenthyl phosphite (**1**) was accomplished by addition of water (80–100 ml). Then the reaction mixture was vigorously stirred for 2 h and the control ^{31}P NMR spectrum showed a signal at $\delta_{31P} = 5.9$ ppm attributed to the phosphite **1** ($\delta_{31P} = 3.6$ ppm in $CDCl_3$ was reported in the literature [11]. Next the toluene layer was separated, dried ($MgSO_4$), filtered and evaporated. The residue required a removal of the unreacted (−)-menthol (19.1 g) using a short path distillation under vacuum (0.05 Torr/ ∼ 40 °C, the temperature of the oil bath <145 °C) to give the crude (−)-dimenthyl phosphite (**1**) (91.6 g, 74% yield) having a satisfactory purity for further reactions (^{1}H NMR spectrum was free of menthol signals). Analytically pure phosphite **1** was obtained after high vacuum distillation (145–150 °C/ 0.02 Torr, the temperature of the oil bath must not exceed 200 °C otherwise the phosphite decomposes).

Yield: 47–51% (59.5–64 g starting from 0.35 mol of PCl_3), n_D^{20} 1.4714; $[\alpha]_D^{20}$ −96.6 ($c = 2.0$, acetone).

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.79$ (d, 3H, $^{3}J_{H-H} = 6.91$ Hz $C^{10'}H_3$), 0.80 (d, 3H, $^{3}J_{H-H} = 6.88$ Hz $C^{10}H_3$), 0.83–0.86 (m, 2H, $C^{4}H$, $C^{4'}H$), 0.89 (2 × d, 12H, $^{3}J_{H-H} = 6.75$ Hz, $^{3}J_{H-H} = 6.74$ Hz, $C^{8}H_3$, $C^{8'}H_3C^{9}H_3$, $C^{9'}H_3$), 0.96–1.13 (m, 4H, $C^{3}H$, $C^{3'}H$, $C^{6}H$, $C^{6'}H$), 1.15–1.18 (m, 2H, $C^{5}H$, $C^{5'}H$), 1.26–1.35 (m, 2H, $C^{2}H$, $C^{2'}H$), 1.64, 1.67 (2 × s-br, 4H, $C^{3}H$, $C^{3'}H$, $C^{4}H$, $C^{4'}H$), 2.10–2.18 (2 × m, 2H, $C^{7}H$, $C^{7'}H$), 2.20–2.24 (m, 2H, $C^{6}H$, $C^{6'}H$), 4.10–4.20 (m, 2H, $C^{1}H$, $C^{1'}H$), 6.89 (d, 1H, $^{1}J_{H-P} = 686.94$ Hz, P(O)–H).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.96$, 16.07 (2 × s, $C^{9}H_3$, $C^{9'}H_3$), 21.09 (s, $C^{8}H_3$, $C^{8'}H_3$), 22.12 (2 × s, $C^{10}H_3$, $C^{10'}H_3$), 23.13, 23.19 (2 × s, $C^{3}H_2$, $C^{3'}H_2$), 25.91, 26.21 (2 × s, $C^{7}H$, $C^{7'}H$), 31.58, 31.68 (2 × s, $C^{5}H$, $C^{5'}H$), 34.23 (s, $C^{4}H_2$, $C^{4'}H_2$), 43.24, 43.86 (2 × s, $C^{6}H_2$, $C^{6'}H_2$), 48.69

($2\times$d, $^{3}J_{C-P} = 5.81$ Hz, C^{2}H, $C^{2'}$H), 77.27 ($2\times$d, $^{2}J_{C-P} = 6.12$ Hz, C^{1}H, $C^{1'}$H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 5.90$ ppm.

IR (film): 2928, 2870, 2421, 1456, 1257, 1013, 963.

MS [CI (isobutane)]: m/z (%) = 359 (M^++1, 100).

HRMS [CI (isobutane)]: m/z calcd. for $C_{20}H_{40}O_3P$ 359.2719; found: 359.2731.

3.3.2. (−)-Dimenthyl methylphosphonate (2)

To a stirred solution of (−)-dimenthyl phosphite **1** (31.99 g, 0.092 mol) in dry THF (300 mL), sodium hydride (4.46 g, 0.2 mol; 50% dispersion in oil) was added in one portion at room temperature under argon atmosphere. The resulting solution was refluxed for approximately 1 h until sodium hydride dissolved completely (the vigorous evolution of hydrogen occurred at 50 °C). After cooling to room temperature, methyl iodide (15.67 g, 6.87 mL, 0.11 mol) was added dropwise and the resulting solution was stirred overnight under argon atmosphere. After evaporation of the solvent, the residue was partitioned between chloroform (200 mL) and water (150 mL). The chloroform solution was washed again with water (100 mL) then dried over $MgSO_4$, filtered and evaporated to give a residue which was distilled (b.p. = 140 °C/0.03 Torr) to give 27.7 g (81% reproducible yield) of **2** as a liquid (n_D^{23} 1.4705), which solidified in the fridge (m.p. = 33–38 °C); $[\alpha]_D^{20}$ −95.2 ($c = 2.0$, acetone).

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.80$, 0.81 ($2\times$d, 6H, $^{3}J_{H-H} = 6{,}92$ Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.86–0.90 (m, 2H, $C^{4}H$, $C^{4'}H$), 0.93 (d, 12H, $^{3}J_{H-H} = 6{,}76$ Hz, $C^{8}H_3$, $C^{8'}H_3$, $C^{9}H_3$, $C^{9'}H_3$), 0.98–1.05 (m, 2H, $C^{3}H$, $C^{3'}H$), 1.10–1.20 (m, 2H, $C^{6}H$, $C^{6'}H$), 1.25–1.35 (m, 2H, $C^{2}H$, $C^{2'}H$), 1.40–1-44 (m, 2H, $C^{5}H$, $C^{5'}H$), 1.48 (d, 3H, $^{2}J_{H-P} = 17.35$ Hz, $C^{11}H_3$), 1.64, 1.66 ($2\times$s-br, 4H, , $C^{3}H$, $C^{3'}H$, $C^{4}H$, $C^{4'}H$), 2.00–2.18 (2m, 2H, $C^{7}H$, $C^{7'}H$), 2.20–2.28 (m, 2H, $C^{6}H$, $C^{6'}H$), 4.10–4.20 (m, 2H, $C^{1}H$, $C^{1'}H$).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.09$ (d, $^{1}J_{P-C} = 145.95$ Hz, $C^{11}H_3$), 15.60, 15.78 ($2\times$s, $C^{9}H_3$, $C^{9'}H_3$), 20.93 (s, $C^{8}H_3$, $C^{8'}H_3$), 21.81, 21.85 ($2\times$s, $C^{10}H_3$, $C^{10'}H_3$), 22.69, 22.78 ($2\times$s, $C^{3}H_2$, $C^{3'}H_2$), 25.31, 25.57 ($2\times$s, $C^{7}H$, $C^{7'}H$), 31.37, 31.44 ($2\times$s, $C^{5}H$, $C^{5'}H$), 34.01 (s, $C^{4}H_2$, $C^{4'}H_2$), 42.99, 43.55 ($2\times$s, $C^{6}H_2$, $C^{6'}H_2$), 48.46 ($2\times$d, $^{3}J_{C-P} = 6.84$ Hz, C^{2}H, $C^{2'}$H), 76.78 ($2\times$d, $^{2}J_{C-P} = 7.57$ Hz, C^{1}H, $C^{1'}$H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 29.00$ ppm.

IR (film): 2954, 2927, 2869, 1456, 1370, 1307, 1248, 1029, 1009, 987, 943.

MS [CI (isobutane)]: m/z (%) 373 (M^++1, 100), 235 (M^++1-menthene, 52), 97 (M^++1-2× menthene, 30).

HRMS [CI (isobutane)]: m/z calcd. for $C_{21}H_{42}O_3P$: 373.2862; found: 373.2871.

Anal. Calc. for $C_{21}H_{41}O_3P$ (372.53); C, 67.71; H, 11.09; P, 8.31. Found: C, 67.64; H, 11.28; P, 8.40%.

3.3.3. (−)-Dimenthyl ethylphosphonate 3 (from 1)

To a stirred solution of (−)-dimenthyl phosphite **1** (1 g, 2.8 mmol) in dry THF (60 mL), sodium hydride (140 mg, 5.6 mmol; 50% dispersion in oil) was added at room temperature under argon atmosphere. Then the resulting mixture was stirred for 1 h at 50 °C and ethyl iodide (467 mg, 240 μL, 3 mmol) was added after cooling the mixture to room temperature. After 24 h, aqueous solution of NH_4Cl was added, the solvent was evaporated and the residue was partitioned between chloroform and water. The chloroform layer was dried with anhydrous $MgSO_4$, filtered and evaporated to give the crude product which was purified using column chromatography (eluent: petroleum ether/acetone in a gradient).

Yield: 75%; light yellow oil; $[\alpha]_D^{20}$ −94.8 ($c = 2.0$, acetone).

3.3.4. (−)-Dimenthyl ethylphosphonate 3 (from 2)

To a stirred solution of (−)-dimenthyl methylphosphonate **2** (1 g, 2.7 mmol) in dry THF (100 mL), *n*-BuLi (1.8 mL, 2.7 mmol, 1.6 M solution in *n*-hexane) was added under argon atmosphere at −78 °C. The dry ice/acetone bath was removed and when temperature reached 30 °C, methyl iodide was added (383 mg, 168 μL, 2.7 mmol). Then the reaction mixture was allowed to warm to room temperature and left for 1hr at this temperature. Then aqueous solution of NH_4Cl was added, solvents were evaporated and the residue was partitioned between water and chloroform. The chloroform layer was dried with anhydrous $MgSO_4$, filtered and evaporated to give the crude product which was purified with column chromatography (eluent: petroleum ether/acetone in a gradient).

Yield: 92%; light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.77$ (d, 6H, $^{3}J_{H-H} = 6.97$ Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.79–0.85 (m, 2H, $C^{4}H$, $C^{4'}H$), 0.87 (d, 12H, $^{3}J_{H-H} = 6.86$ Hz, $C^{8}H_3$, $C^{8'}H_3$, $C^{9}H_3$, $C^{9'}H_3$), 0.92–1.01 (m, 2H, $C^{3}H$, $C^{3'}H$), 1.05–1.10 (m, 2H, $C^{6}H$, $C^{6'}H$), 1.12 ($2\times$t, 3H, $^{3}J_{H-H} = 7.60$ Hz, $^{3}J_{H-P} = 19.66$ Hz, $C^{18}H_3$), 1.21–1.30 (m, 2H, $C^{2}H$, $C^{2'}H$), 1.37–1.45 (m, 2H, $C^{5}H$, $C^{5'}H$), 1.60, 1.63 ($2\times$s-br, 4H, $C^{3}H$, $C^{3'}H$, $C^{4}H$, $C^{4'}H$), 1.67 ($2\times$q, 2H, $^{3}J_{H-H} = 7.75$ Hz, $^{2}J_{H-P} = 25.74$ Hz, $C^{11}H_2$), 2.05–2.18 ($2\times$m, 2H, $C^{7}H$, $C^{7'}H$), 2.20–2.27 (m, 2H, $C^{6}H$, $C^{6'}H$), 4.08–4.18 (m, 2H, $C^{1}H$, $C^{1'}H$).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 6.98$ (d, $^{2}J_{P-C} = 7.27$ Hz, $C^{18}H_3$), 15.56, 15.78 ($2\times$s, $C^{9}H_3$, $C^{9'}H_3$), 20.66 (d, $^{1}J_{P-C} = 144.35$ Hz, $C^{11}H_2$), 21.01 (s, $C^{8}H_3$, $C^{8'}H_3$), 21.89, 21.92 ($2\times$s, $C^{10}H_3$, $C^{10'}H_3$), 22.69, 22.75 ($2\times$s, $C^{3}H_2$, $C^{3'}H_2$), 25.25, 25.45 ($2\times$s, $C^{7}H$, $C^{7'}H$), 31.40, 31.48 ($2\times$s, $C^{5}H$, $C^{5'}H$), 34.07 (s, $C^{4}H_2$, $C^{4'}H_2$), 43.07, 43.70 ($2\times$s, $C^{6}H_2$, $C^{6'}H_2$), 48.56, 48.59 ($2\times$d, $^{3}J_{C-P} = 6.19$ Hz, C^{2}H, $C^{2'}$H), 76.57, 76.63 ($2\times$d, $^{2}J_{C-P} = 7.08$ Hz, C^{1}H, $C^{1'}$H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 33.40$ ppm.

IR (film): 2953, 2926, 2868, 1456, 1239, 1034, 1008, 989, 965.

MS [CI (isobutane)]: m/z (%) 387 (M^++1, 100), 249 (M^++1-menthene, 48), 125 (M^++1-2 × menthene, 55).

HRMS [CI (isobutane)]: m/z calcd. for $C_{22}H_{44}O_3P$: 387.3000; found: 387.3028.

*3.3.5. (−)-Dimenthyl isopropylphosphonate (**4**)*

3.3.5.1. Procedure A (with TMEDA). To a stirred solution of (−)-dimenthyl ethylphosphonate **3** (1 g, 2 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA; 0.6 g, 0.8 mL, 5.2 mmol) in dry THF (180 mL), *n*-BuLi (3.2 mL, 5.2 mmol, 1.6 M solution in *n*-hexane) was added at −78 °C under argon atmosphere. After 3 min methyl iodide (0.37 g, 0.16 mL, 2.6 mmol) was added and the resulting mixture was allowed to warm to room temperature. Stirring was continued for additional 1 h at this temperature and aqueous solution of NH_4Cl was added, solvents were evaporated and the residue was extracted with chloroform. The organic layer was dried over anhydrous $MgSO_4$, then filtered and evaporated to give a crude product which was purified with column chromatography over silica gel (eluent:petroleum ether/acetone in a gradient).

Yield: 70%.

3.3.5.2. Procedure B (without TMEDA). To a stirred solution of **3** (1 g, 2.6 mmol) in dry THF (180 mL), *n*-BuLi (3.2 mL, 5.2 mmol, 1.6 M solution in *n*-hexane) was added at −78 °C under argon atmosphere. After 20 min methyl iodide (0.37 g, 0.16 mL, 2.6 mmol) was added and the product was workuped as in Section 3.3.5.1.

Yield: 78%, yellow oil.

$[\alpha]_D^{20}$ −100.90 ($c = 2.0$, acetone).

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.75$ (d, 6H, $^3J_{H-H} =$ 6.98 Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.77–0.82 (m, 2H, C^4H, $C^{4'}H$), 0.87 (d, 12H, $^3J_{H-H} = 6.86$ Hz, C^8H_3, $C^{8'}H_3$, C^9H_3, $C^{9'}H_3$), 0.92–0.97 (m, 2H, C^3H, $C^{3'}H$), 1.03–1.07 (m, 2H, C^6H, $C^{6'}H$), 1.11 (4 × d, 6H, $^3J_{H-H} = 7.18$ Hz, $^3J_{H-P} =$ 18.23 Hz, $C^{12}H_3$, $C^{18}H_3$), 1.20–1.30 (m, 2H, C^2H, $C^{2'}H$), 1.34–1.42 (m, 2H, C^5H, $C^{5'}H$), 1.59, 1.61 (2 × s-br, 4H, C^3H, $C^{3'}H$, C^4H, $C^{4'}H$), 1.76–1.87 (2 × m, 1H, $J^2_{H-P} =$ 25.56 Hz, $C^{11}H$), 1.99–2.16 (m, 2H, C^6H, $C^{6'}H$), 2.18–2.25 (m, 2H, C^7H, $C^{7'}H$), 4.05–4.15 (m, 2H, C^1H, $C^{1'}H$).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.45$, 15.75 (2 × s, C^9H_3, $C^{9'}H_3$), 16.45, 16.50 (d, $^2J_{P-C} = 5.99$ Hz, $C^{12}H_3$, $C^{18}H_3$), 21.01 (s, C^8H_3, $C^{8'}H_3$), 21.89, 21.92 (2 × s, $C^{10}H_3$, $C^{10'}H_3$), 22.61 (s, C^3H_2, $C^{3'}H_2$), 25.12, 25.24 (2 × s, C^7H, $C^{7'}H$), 27.36 (d, $^1J_{P-C} = 144.34$ Hz, $C^{11}H$), 31.38, 31.44 (2 × s, C^5H, $C^{5'}H$), 34.05 (s, C^4H_2, $C^{4'}H_2$), 43.07, 43.77 (2 × s, C^6H_2, $C^{6'}H_2$), 48.61, 48.67 (2 × d, $^3J_{C-P} = 7.59$ Hz, C^2H, $C^{2'}H$), 76.36, 76.51 (2 × d, $^2J_{C-P} =$ 7.67 Hz, C^1H, $C^{1'}H$).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 33.92$ ppm.

IR (film): 2955, 2928, 2870, 1456, 1229, 1025, 1008, 986, 965, 890.

MS [CI (isobutane)]: *m*/*z* (%) 401 (M^++1, 100), 263 (M^++1-menthene, 64), 125 (M^++1-2 × menthene, 76).

HRMS [CI (isobutane)]: *m*/*z* calcd. for $C_{23}H_{46}O_3P$: 401.3167; found: 401.3184.

*3.3.6. (−)-Dimenthyl 1-iodoethylphosphonate (**6**)*

3.3.6.1. Procedure A (by a direct iodination). To a stirred solution of (−)-dimenthyl ethylphosphonate **3** (1 g, 2.6 mmol) in dry THF (180 mL), *n*-BuLi (2.4 mL, 3.9 mmol, 1.6 M solution in *n*-hexane) was added at −78 °C under argon atmosphere. After 20 min a solution of iodine (60 mg, 5.2 mmol) in THF (10 mL) was added and the resulting mixture was allowed to warm to room temperature. Stirring was continued for 1 h at this temperature and aqueous solution of NH_4Cl was added. Solvents were evaporated and the residue was extracted with chloroform. The organic layer was washed with water and 10% aqueous solution of $Na_2S_2O_3$, dried over anhydrous $MgSO_4$, filtered and evaporated to give the crude product **6** which was purified with column chromatography over silica gel (eluent: petroleum ether/acetone in a gradient).

Yield: 30%.

3.3.7. Procedure B (a modification of the Savignac's protocol [34])

To a stirred solution of (−)-dimenthyl ethylphosphonate **3** (1 g, 2.6 mmol) in dry THF (180 mL), the following reagents were added in the given order at −78 °C, under argon atmosphere and in 20 min intervals: *n*-BuLi (2.4 mL, 3.9 mmol, 1.6 M solution in *n*-hexane), Me_3SiCl (330 μL, 28 mg, 2.6 mmol), *n*-BuLi (2.4 mL, 3.9 mmol), iodine (60 mg, 5.2 mmol). The resulting mixture was allowed to warm to room temperature and a solution of EtONa in EtOH (60 mg, 2.6 mmol of Na in 2 mL of EtOH) was added. Stirring was continued for a few hours at this temperature to completion (^{31}P NMR) and aqueous solution of NH_4Cl was added. Solvents were evaporated and the residue was extracted with chloroform. The chloroform layer was washed with water and 10% aqueous solution of $Na_2S_2O_3$ and water, dried over anhydrous $MgSO_4$, filtered and evaporated to give the crude product **6** which was purified with column chromatography over silica gel (eluent: petroleum ether/acetone in a gradient).

Yield: 87%, yellow oil.

$[\alpha]_D^{20}$ −75.35 ($c = 2.3$, acetone).

^{1}H NMR (500 MHz $CDCl_3$): $\delta = 0.80$ (d, 6H, $^3J_{H-H} =$ 6.90 Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.90 (d, 12H, $^3J_{H-H} = 6.40$ Hz, C^8H_3, $C^{8'}H_3$, C^9H_3, $C^{9'}H_3$), 0.93–0.98 (m, 2H, C^4H, $C^{4'}H$), 1.00–1.08 (m, 2H, C^3H, $C^{3'}H$), 1.12–1.28 (m, 4H, C^6H, $C^{6'}H$, C^2H, $C^{2'}H$), 1.30–1.40 (m, 2H, C^5H, $C^{5'}H$), 1.65, 1.68 (2 × s-br, 4H, C^3H, $C^{3'}H$, C^4H, $C^{4'}H$), 1.99 (2 × d, 3H, $^3J_{H-H} = 7.41$ Hz, $^3J_{H-P} = 16.70$ Hz, $C^{18}H_3$), 2.15–2.25 (2 × m, 2H, C^7H, $C^{7'}H$), 2.28–2.35 (m, 2H, C^6H, $C^{6'}H$), 3.75–3.85 (2 × q, 1H, $^3J_{H-H} = 7.44$ $^2J_{H-P} =$ 24.10 Hz, $C^{11}H$), 4.18–4.28 (m, 2H, C^1H, $C^{1'}H$).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 8.63$, 9.30 (2 × d, $^1J_{P-C} = 156.01$ Hz, $C^{11}H$), 15.69, 15.76, 15.80, 15.88 (4 × s, C^9H_3, $C^{9'}H_3$), 21.07 (s, C^8H_3, $C^{8'}H_3$), 21.96 (s, $C^{10}H_3$, $C^{10'}H_3$), 22.31, 22.35 (2 × d, $^2J_{P-C} = 5.97$ Hz, $C^{18}H_3$), 22.65, 22.68, 22.70, 22.73 (4 × s, C^3H_2, $C^{3'}H_2$), 25.22, 25.25, 25.30, 25.39 (4 × s, C^7H, $C^{7'}H$), 31.50, 31.58 (2 × s, C^5H, $C^{5'}H$), 33.90, 34.02 (2 × s, C^4H_2, $C^{4'}H_2$), 42.76, 42.99, 43.50, 43.67 (4 × s, C^6H_2, $C^{6'}H_2$), 48.51, 48.58, 48.64, 48.73 (2 × d, $^3J_{C-P} = 7.39$ Hz, C^2H, $C^{2'}H$), 78.27, 78.40, 78.77, 79.03 (2 × d, $^2J_{C-P} = 7.69$ Hz, C^1H, $C^{1'}H$).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 21.59$, 21.96 ppm.

IR (film): 2952, 2926, 1456, 1372, 1232, 1029, 1011, 991, 912.

MS [CI (isobutane)]: *m/z* (%) 513 (M^++1, 100).

HRMS [CI (isobutane)]: *m/z* calcd. for $C_{22}H_{43}O_3PI$: 513.1975; found: 513.1994.

3.3.8. Ethyl (−)-menthyl ethylphosphonate (**8**)

To a stirred solution of menthol (1 g, 6.4 mmol) in dry THF (50 mL), *n*-BuLi (4.0 mL, 6.4 mmol, 1.6 M solution in *n*-hexane) was added at 0 °C under argon atmosphere. After 10 min a solution of diethyl ethylphosphonate 7 (0.53 g, 3.2 mmol) in THF (20 mL) was added. The resulting mixture was warmed to room temperature and left overnight. Then aqueous solution of NH_4Cl was added, solvents were evaporated and the residue was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated to give the crude product **8** which was purified with column chromatography over silica gel (eluent: petroleum ether/ acetone in a gradient).

Yield: 94%, yellow oil.

$[\alpha]_D^{20}$ −48.73 ($c = 2.3$, acetone).

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.80$ (d, 3H, $^3J_{H-H} = 6.92$ Hz, $C^{10}H_3$), 0.85–0.95 (m, 2H, C^4H, C^3H, and d, 6H, $^3J_{H-H} = 6.80$ Hz, C^8H_3, C^9H_3), 1.05–1.10 (m, 1H, C^6H), 1.12 (t, 3H, $^3J_{H-H} = 7.60$ Hz, $^3J_{H-P} = 19.66$ Hz, $C^{12}H_3$), 1.21–1.28 (m, 1H, C^2H), 1.30 (t, 3H, $^3J_{H-H} = 7.1$ Hz, $C^{14}H_3CH_2OP$); 1.37–1.45 (m, 1H, C^5H), 1.60, 1.63 (2 × s-br, 2H, C^3H, C^4H), 1.67 (2 × q, 2H, $^3J_{H-H} = 7.75$ Hz $^2J_{H-P} = 25.74$ Hz, $C^{11}H_2$), 2.05–2.27 (m, 2H, C^6H, C^7H), 3.95–4.30 (m, 3H, $CH_3C^{13}H_2OP$ C^1H).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 6.71$ (d, $^2J_{P-C} = 6.99$ Hz, $C^{12}H_3$), 15.57 (s, C^9H_3), 16.41 (d, $^3J_{C-P} = 6.01$ Hz, $C^{14}H_3CH_2OP$) 19.98 (d, $^1J_{P-C} = 143.57$ Hz, $C^{11}H_2$), 20.92 (s, C^8H_3), 21.87 (s, $C^{10}H_3$), 22.73 (s, C^3H_2), 25.37 (s, C^7H), 31.40 (s, C^5H), 34.02 (s, C^4H_2), 43.40 (s, C^6H_2), 48.46 (d, $^3J_{C-P} = 6.24$ Hz, C^2H), 61.32 (d, $^2J_{C-P} = 6.38$ Hz, $CH_3C^{13}H_2OP$); 76.71 (d, $^2J_{C-P} = 7.41$ Hz, C^1H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 32.75$, 32.98 ppm (1.8:1).

IR (film): 2955, 2928, 2870, 1457, 1251, 1226, 1055, 1008, 994, 791.

MS [CI (isobutane)]: *m/z* (%) 277 (M^++1, 30); 139 (menthene, 100).

HRMS [CI (isobutane)]: *m/z* calcd. for $C_{14}H_{30}O_3P$: 277.1925; found: 277.1932.

3.3.9. Ethyl (−)-menthyl 1-iodoethylphosphonate (**9**)

This compound was obtained in the same way as **6** (Procedure B).

Yield: 85%, yellow oil.

$[\alpha]_D^{20}$ −38.75 ($c = 2.5$, acetone).

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.80$ (d, 3H, $^3J_{H-H} = 6.89$ Hz, $C^{10}H_3$), 0.91 (d, 6H, $^3J_{H-H} = 6.77$ Hz, C^8H_3, C^9H_3), 0.93–1.08 (m, 2H, C^4H, C^3H), 1.12–1.28 (m, 2H, C^6H, C^2H), 1.30–1.50 (m, 1H, C^5H, 3H, $^3J_{H-H} = 7.05$ Hz, $C^{14}H_3CH_2OP$); 1.63, 1.68 (2 × s-br, 2H, C^3H, C^4H), 2.00 (2 × d, 3H, $^3J_{H-H} = 7.45$ Hz, $^3J_{H-P} = 16.94$ Hz, $C^{12}H_3$), 2.10–2.35 (m, 2H, C^7H, C^6H), 3.75–3.93 (m, 1H, $C^{11}H$), 4.05–4.35 (m, 3H, $CH_3C^{13}H_2OP$, C^1H,).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 6.22$, 6.77, 9.34, 9.88 (4 × d, $^1J_{P-C} = 156.96$ Hz, $C^{11}H$), 15.54, (4 × s, C^9H_3), 16.35 (d, $^3J_{C-P} = 5.98$ Hz, $C^{14}H_3CH_2OP$); 20.07 (s, C^8H_3), 20.87 (s, $C^{10}H_3$), 21.87 (d, $^2J_{P-C} = 4.07$ Hz, $C^{12}H_3$), 22.69 (s, C^3H_2), 25.36 (s, C^7H), 31.41 (s, C^5H), 33.90, (s, C^4H_2), 43.07 (2 × s, C^6H_2), 48.42 (d, $^3J_{C-P} = 6.37$ Hz, C^2H), 64.03 (d, $^2J_{C-P} = 6.58$ Hz, $CH_3C^{13}H_2OP$); 78.27, (d, $^2J_{C-P} = 7.96$ Hz, C^1H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 21.65$, 21.77, 21.89, 22.02 ppm (1.00:1.15:1.60:1.30).

IR (film): 2955, 2927, 2869, 1454, 1241, 1047, 1010, 993, 966.

MS [CI (isobutane)]: *m/z* (%) 403 (M^++1, 45), 264 (M^++1-menthene, 100).

HRMS [CI (isobutane)]: *m/z* calcd. for $C_{14}H_{29}O_3PI$: 403.0906; found: 403.0899.

3.3.10. (−)-Dimenthyl 3-iodo-1-methyl-n-heptylphosphonate (**10**)

A stirred solution of (−)-dimenthyl 1-iodoethylphosphonate **6** (1 g, 1.95 mmol) and AIBN (320 mg, 1.95 mmol) in 1-hexene (50 mL) was refluxed for 24 h under argon atmosphere. After 16 h a new portion of AIBN (320 mg, 1.95 mmol) was added. After complexion of the reaction, the excess of 1-hexene was evaporated and the product containing four diastereomers in a 1.6:1:1:0.4 ratio was separated into two pairs using column chromatography over silica gel (eluent: petroleum ether/ acetone in a gradient).

Yield: 40%, yellow oils.

First pair of diastereomers:

$[\alpha]_D^{20}$ −55.35 ($c = 1.5$, acetone).

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.82$ (d, 6H, $^3J_{H-H} = 6.67$ Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.82–0.87 (m, 2H, C^4H, $C^{4'}H$), 0.87 (d, 12H, $^3J_{H-H} = 6.27$ Hz, C^8H_3, $C^{8'}H_3$, C^9H_3, $C^{9'}H_3$), 0.92–0.97 (m, 5H, C^3H, $C^{3'}H$, $C^{17}H_3$), 1.03–1.10 (m, 2H, C^6H, $C^{6'}H$), 1.17 (2 × d, 3H, $^3J_{H-H} = 7.23$ Hz, $^3J_{H-P} = 18.49$ Hz, $C^{18}H_3$), 1.20–1.30 (m, 2H, C^2H, $C^{2'}H$), 1.35–1.45 (m, 4H, C^5H, $C^{5'}H$, $C^{16}H_2$), 1.50–1.54 (m, 2H, $C^{14}H_2$), 1.59, 1.62 (2 × s-br, 4H, C^3H, $C^{3'}H$, C^4H, $C^{4'}H$), 1.65–1.75 (m, 2H, $C^{15}H_2$); 1.90–1.96 (m, 1H, $C^{11}H$), 2.05–2.15 (m, 4H, C^6H, $C^{6'}H$,$C^{12}H_2$), 2.20–2.31 (2 × m, 2H, C^7H, $C^{7'}H$), 4.05–4.15 (m, 2H, C^1H, $C^{1'}H$), 4.35–4.45 (m, 1H, $C^{13}H$-I).

^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 13.38$, 13.42 (2 × d, $^2J_{P-C} = 5.52$ Hz, $C^{18}H_3$), 13.91, 13.94 (2 × s, $C^{17}H_3$), 15.50, 15.55, 15.76, 15.81 (4 × s, C^9H_3, $C^{9'}H_3$), 21.10 (s, C^8H_3, $C^{8'}H_3$), 21.96 (s, $C^{10}H_3$,$C^{10'}H_3$), 22.35 (s, $C^{16}H_2$), 22.45, 22.55 22.65, 22.68 (4 × s, C^3H_2, $C^{3'}H_2$), 25.14, 25.18, 25.27, 25.32 (4 × s, C^7H, $C^{7'}H$), 29.71, 29.86 (2 × s, $C^{15}H_2$), 31.44, 31.50 (2 × s, C^5H, $C^{5'}H$), 32.45 (d, $^1J_{C-P} = 141.35$ Hz, $C^{11}H$), 33.96, 34.10 (2 × s, C^4H_2, $C^{4'}H_2$), 36.18

(d, $^3J_{C-P} = 18.54$ Hz, C^{13}H-I), 40.93, 41.05 (2 × s, $C^{12}H_2$, $C^{14}H_2$); 43.10, 43.24, 43.82, 43.93 (4 × s, C^6H_2, $C^{6'}H_2$), 48.66, 48.68, 48.71, 48.75 (2 × d, $^3J_{C-P} = 6.10$ Hz, C^2H, $C^{2'}$H), 76.38, 76.44, 76.56, 76.62 (2 × d, $^2J_{C-P} = 7.79$ Hz, C^1H, $C^{1'}$H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 31.42$, 31.49 ppm.

IR (film): 2956, 2928, 2869, 1456, 1260, 1146, 1006, 1023, 978, 965, 802.

MS [CI (isobutane)]: *m/z* (%) 597 (M^++1, 100), 469 (M^++1-HI, 28); 459 (M^++1-menthene, 14), 331 (M^++1-HI-menthene, 16), 321 (M^++1−2× menthene, 7), 193 (M^++1-HI−2× menthene, 16).

HRMS [CI (isobutane)]: *m/z* calcd. for $C_{28}H_{55}O_3PI$: 597.2916; found: 597.2933.

Second pair of diastereomers:

$[\alpha]_D^{20}$ −52.17 (*c* = 1.5, acetone).

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.81$ (d, 6H, $^3J_{H-H} = 6.94$ Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.81–0.86 (m, 2H, C^4H, $C^{4'}H$), 0.91 (d, 12H, $^3J_{H-H} = 6.31$ Hz, C^8H_3, $C^{8'}H_3$,C^9H_3, $C^{9'}H_3$), 0.92–0.98 (m, 5H, C^3H, $C^{3'}H$, $C^{17}H_3$), 1.05–1.13 (m, 2H, C^6H, $C^{6'}H$), 1.17 (2 × d, 3H, $^3J_{H-H} = 7.23$ Hz, $^3J_{H-P} = 17.56$ Hz, $C^{18}H_3$), 1.24–1.30 (m, 2H, C^2H, $C^{2'}H$), 1.32–1.37 (m, 4H, C^5H, $C^{5'}H$, $C^{16}H_2$), 1.40–1.46 (m, 2H, $C^{14}H_2$), 1.66, 1.66 (2 × s-br, 4H, C^3H, $C^{3'}H$, C^4H, $C^{4'}H$), 1.72–1.82 (m, 2H, $C^{15}H_2$); 1.85–1.96 (m, 1H, $C^{11}H$), 2.10–2.20 (m, 4H, C^6H, $C^{6'}H$, $C_{12}H_2$), 2.23–2.33 (2 × m, 2H, C^7H, $C^{7'}H$), 4.15–4.25 (m, 2H, C^1H, $C^{1'}H$), 4.51–4.57 (m, 1H, $C^{13}H$-I).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.43$, 13.55 (2 × d, $^2J_{P-C} = 5.35$ Hz, $C^{18}H_3$), 14.01, 14.14 (2 × s, $C^{17}H_3$), 15.43, 15.52, 15.64, 15.75 (4 × s, C^9H_3, $C^{9'}H_3$), 21.17 (s-br, C^8H_3, $C^{8'}H_3$), 22.06 (s, $C^{10}H_3$,$C^{10'}H_3$), 22.98 (s, $C^{16}H_2$), 23.15, 23.23 23.39, 23.45 (4 × s, C^3H_2, $C^{3'}H_2$), 25.13, 25.19, 25.28, 25.34 (4 × s, C^7H, $C^{7'}$H), 29.86, 29.94 (2 × s, $C^{15}H_2$), 31.44, 31.52 (2 × s, C^5H, $C^{5'}$H), 32.48 (d, $^1J_{C-P} = 141.35$ Hz, C^{11}H), 33.82, 34.01 (2 × s, C^4H_2, $C^{4'}H_2$), 36.12 (d, $^3J_{C-P} = 17.99$ Hz, C^{13}H-I), 40.90, 41.02 (2 × s, $C^{12}H_2$, $C^{14}H_2$); 43.10, 43.21, 43.78, 43.91 (4 × s, C^6H_2, $C^{6'}H_2$), 47.63, 47.68, 47.72, 47.77 (2 × d, $^3J_{C-P} = 6.25$ Hz, C^2H, $C^{2'}$H), 76.32, 76.36, 76.48, 76.52 (2 × d, $^2J_{C-P} = 7.92$ Hz, C^1H, $C^{1'}$H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 32.26$, 32.62 ppm.

IR (film): 2958, 2929, 2863, 1456, 1263, 1039, 1003, 965, 804.

MS [CI (isobutane)]: *m/z* (%) 597 (M^++1, 100), 469 (M^++1-HI, 28); 459 (M^++1-menthene, 14), 331 (M^++1-HI-menthene, 16), 321 (M^++1−2× menthene, 7), 193 (M^++1-HI−2× menthene, 16).

HRMS [CI (isobutane)]: *m/z* calcd. for $C_{28}H_{55}O_3PI$: 597.2916; found: 597.2929.

*3.3.11. (−)-Tetramenthyl 1,1′-dimethylethylene-bisphosphonate (**11**)*

To a stirred solution of (−)-dimenthyl 1-iodoethylphosphonate **6** (1 g, 1.95 mmol) and 1-hexene (1.64 g, 2.44 mL, 19.5 mmol) in toluene, Et_3B (1.95 mL, 1.95 mmol, 1 M solution in *n*-hexane) was added at −78 °C and the solution was stirred at this temperature for 2 h. Then the temperature was raised to 25 °C and the solvent was evaporated. The crude product was purified four times using column chromatography (CC) over silica gel (eluent: petroleum ether/acetone in a gradient), however the final material still contained ca. 10% of impurities based on ^{1}H NMR (although it was pure based on ^{31}P NMR).

Yield: ca. 48% after first CC, oil.

^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 0.80$ (d, 12H, $^3J_{H-H} = 6.90$ Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.90 (d, 24H, $^3J_{H-H} = 6.73$ Hz, C^8H_3, $C^{8'}H_3$, C^9H_3, $C^{9'}H_3$), 0.92–0.97 (m, 8H, C^4H, $C^{4'}H$, C^3H, $C^{3'}H$), 1.03–1.10 (m, 8H, C^6H, $C^{6'}H$), 1.17 (2 × m, 6H, $C^{18}H_3$), 1.20–1.30 (m, 4H, C^2H, $C^{2'}H$), 1.35–1.45 (m, 4H, C^5H, $C^{5'}H$), 1.59, 1.62 (2 × s-br, 8H, C^4H, $C^{4'}H$, C^3H, $C^{3'}H$), 1.90–1.96 (m, 2H, $C^{11}H$), 2.05–2.20 (2 × m, 4H, C^7H, $C^{7'}H$), 4.05–4.35 (2×m, 4H, C^1H, $C^{1'}H$).

^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 15.66$, 15.86 (2 × s, C^9H_3, $C^{9'}H_3$), 15.91, 15.97 (2 × s, $C^{18}H_3$), 21.05, 21.07 (2 × s, C^8H_3, $C^{8'}H_3$), 21.91, 21.95 (2 × s, $C^{10}H_3$,$C^{10'}H_3$), 22.89, 23.05 (2 × s, C^3H_2, $C^{3'}H_2$), 25.34, 25.54 (2 × s, C^7H, $C^{7'}$H), 27.23, 27.29 (2 × s,C^{11}H), 30.60, 31.50 (2 × s, C^5H, $C^{5'}$H), 34.00, 34.17 (2 × s, C^4H_2, $C^{4'}H_2$), 43.21, 43.42 (2 × s, C^6H_2, $C^{6'}H_2$), 48.57, 48.70 (2 × s, C^2H, $C^{2'}$H), 76.36, 76.60 (2 × s, C^1H, $C^{1'}$H).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 31.81$, 32.06 ppm.

IR (film): 2924, 1456, 1378, 1224, 987, 888, 730.

MS [CI (isobutane)]: *m/z* (%) 771 (M^++1, 26), 385(100), 247(56), 111(63).

5-Chloro-1-trimethylsilylpent-1-yne (**13**) and 5-Iodo-1-trimethylsilylpent-1-yne (**14**) were obtained based on the procedure by Koft et al. [41] in 92% and 87% yields, respectively.

*3.3.12. (−)-Dimenthyl 1-methyl-6-trimethylsilyl-n-hex-5-ynylphophonate (**15**)*

To a stirred solution of (−)-dimenthyl ethylphosphonate **3** (1 g, 2.6 mmol) in dry THF (180 mL), *n*-BuLi (2.2 mL, 5.2 mmol, 2.4 M solution in *n*-hexane) was added at −78 °C under argon atmosphere. After 20 min the iodide **14** (60 mg, 2.8 mmol) was added. The reaction mixture was warmed to room temperature and left for 2 h at this temperature. Then aqueous solution of NH_4Cl was added and solvents were evaporated. The residue was extracted with chloroform and the organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated to give the crude product which was purified with column chromatography over silica gel (eluent: petroleum ether/ acetone in a gradient).

Yield: 60%, yellow oil.

$[\alpha]_D^{20}$ −46.84 (*c* = 2.4, acetone).

^{1}H NMR (500 MHz $CDCl_3$): $\delta = 0.14$ (s, 9H, $Si(CH_3)_3$), 0.80 (d, 6H, $^3J_{H-H} = 6.87$ Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.90 (d, 12H, $^3J_{H-H} = 6.73$ Hz, C^8H_3, $C^{8'}H_3$, C^9H_3, $C^{9'}H_3$), 0.93–0.98 (m, 4H, C^4H, $C^{4'}H$, C^3H, $C^{3'}H$), 1.02–1.09 (m, 2H, C^6H, $C^{6'}H$), 1.12–1.20 (m, 2H, $C^{13}H_2$) 1.23–1.35 (m, 4H, C^2H, $C^{2'}H$, C^5H, $C^{5'}H$), 1.64, 1.67 (2 × s-br, 4H, C^3H, $C^{3'}H$,

C^4H, $C^{4'}H$), 1.70–1.80 (2 × m, 1H, $^2J_{H-P} = 23.15$ Hz, $C^{11}H$), 1.83–1.89 (m, 2H, $C^{12}H_2$), 2.20 (2 × d, 3 H, $^3J_{H-H} = 6.72$ Hz, $^3J_{H-P} = 16.12$ Hz, $C^{18}H_3$), 2.22–2.31 (2 × m, 2H, C^7H, $C^{7'}H$), 2.30–2.37 (m, 2H, $C^{14}H_2$) 2.40–2.48 (m, 2H, C^6H, $C^{6'}H$), 4.12–4.20 (m, 2H, C^1H, $C^{1'}H$).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.17$ (s, Si(CH_3)$_3$), 13.42, 13.57, 15.54, 15.61 (4 × s, C^9H_3, $C^{9'}H_3$, C^8H_3, $C^{8'}H_3$), 15.85, 15.92 (s, $C^{10}H_3$, $C^{10'}H_3$), 21.15, 22.00 (2 × s, $C^{13}H_2$, $C^{14}H_2$), 22.59, 22.70 (2 × s, C^3H_2, $C^{3'}H_2$), 25.21, 25.34 (2 × s, C^7H, $C^{7'}H$), 26.85, 26.97 (2 × s, $C^{12}H_3$), 29.68, 29.75 (2 × s, $C^{18}H_3$), 31.48, 31.55 (2 × s, C^5H, $C^{5'}H$), 33.03 (d, $^2J_{P-C} = 142.35$, $C^{11}H$), 34.13 (s, C^4H_2, $C^{4'}H_2$), 43.15, 43.24 (2 × s, C^6H_2, $C^{6'}H_2$), 48.73 (s, C^2H, $C^{2'}H$), 78.15, 78.22, 78.36, 79.42 (4 × s, C^1H, $C^{1'}H$), 82.31 (s, C^{15}), 107.13 (s, C^{16}).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 31.91$, 32.64 ppm.

IR (film): 2955, 2927, 2869, 2174, 1456, 1370, 1223, 1026, 986, 978, 842, 755.

MS [CI (isobutane)]: *m/z* (%) 525 (M^++1, 100), 387 (M^++1-menthene, 36), 249 (M^++1−2× menthene, 46).

HRMS [CI (isobutane)]: *m/z* calcd. for $C_{30}H_{58}O_3PSi$: 525.3898; found: 525.3892.

*3.3.13. (−)-Dimenthyl 1-iodo-1-methyl-6-trimethylsilyl-n-hex-5-ynylphosphate (**16**)*

To a stirred solution of the phosphonate **15** (100 mg, 0.19 mmol) in dry THF (50 mL), *n*-BuLi (0.16 mL, 0.38 mmol, 2.4 M solution in *n*-hexane) was added at −78 °C under argon atmosphere. After 20 min iodine (96 mg, 0.38 mmol) was added and the resulting mixture was warmed to room temperature. After additional 1 h, an aqueous solution of NH_4Cl was added. Solvents were evaporated and the residue was extracted with chloroform. The chloroform layer was washed with water and 10% aqueous solution of $Na_2S_2O_3$, dried over anhydrous $MgSO_4$, filtered and evaporated to give the crude product which was purified with column chromatography over silica gel (eluent: petroleum ether/acetone in a gradient).

Yield: 34%, yellow oil.

$[\alpha]_D^{20}$ − 40.65 ($c = 2.3$, acetone).

^{1}H NMR (500 MHz $CDCl_3$): $\delta = 0.15$ (s, 9H, Si(CH_3)$_3$), 0.83 (d, 6H, $^3J_{H-H} = 6.96$ Hz, $C^{10}H_3$, $C^{10'}H_3$), 0.87 (d, 12H, $^3J_{H-H} = 6.68$ Hz, C^8H_3, $C^{8'}H_3$, C^9H_3, $C^{9'}H_3$), 0.90–1.08 (m, 6H, C^4H, $C^{4'}H$, C^3H, $C^{3'}H$, C^6H, $C^{6'}H$), 1.12–1.20 (m, 2H, $C^{13}H_2$) 1.26–1.39 (m, 4H, C^2H, $C^{2'}H$, C^5H, $C^{5'}H$), 1.63, 1.66 (2 × s-br, 4H, C^3H, $C^{3'}H$, C^4H, $C^{4'}H$), 1.73–1.82 (m, 2H, $C^{12}H_2$), 2.03 (2 × d, 3H, $^3J_{H-H} = 6.41$ Hz, $^3J_{H-P} = 15.48$ Hz, $C^{18}H_3$), 2.15–2.25 (2 × m, 2H, C^7H, $C^{7'}H$), 2.29–2.45 (m, 4H, $C^{14}H_2$, C^6H, $C^{6'}H$), 4.20–4.30 (m, 2H, C^1H, $C^{1'}H$).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.54$ (s, Si(CH_3)$_3$), 12.63, 13.30 (2 × s. C^{11}), 14.32, 14.49, (2 × s, C^9H_3, $C^{9'}H_3$), 16.38, 16.44 (2 × s, C^8H_3, $C^{8'}H_3$), 16.64 (s, $C^{10}H_3$,$C^{10'}H_3$), 20.01, 20.05 (2 × s, $C^{14}H_2$) 21.57, 21.60 (2 × s, $C^{13}H_2$), 23.05, 23.17 (2 × s, C^3H_2, $C^{3'}H_2$), 25.43, 25.63 (2 × s, C^7H, $C^{7'}H$), 27.38, 27.45 (2 × s, $C^{12}H_3$), 29.72, 29.78 (2 × s, $C^{18}H_3$), 31.88, 31.92 (2 × s, C^5H, $C^{5'}H$), 33.08 33.16 (2 × s, C^4H_2, $C^{4'}H_2$), 44.14, 44.18 (2 × s, C^6H_2, $C^{6'}H_2$), 49.49, 49.55 (2 × s, C^2H, $C^{2'}H$), 78.60, 78.67, 78.86, 79.93 (4 × s, C^1H, $C^{1'}H$), 85.31 (s, C^{15}), 106.95 (s, C^{16}).

^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 20.19$, 20.58 ppm.

IR (film): 2957, 2929, 2869, 2174, 1456, 1243, 1375, 1225, 1026, 978, 965, 842.

MS [CI (isobutane)]: *m/z* (%) 651 (M^++1, 100), 523 (M^++1-HI, 62); 513 (M^++1-menthene, 38), 385 (M^++1-HI-menthene, 32), 375 (M^++1−2× menthene, 46), 247 (M^+ +1- HI – 2 × menthene, 33).

HRMS [CI (isobutane)]: *m/z* calcd. for $C_{30}H_{57}O_3PISi$: 651.2862; found: 651.2859.

4. Supplementary material

CCDC 296401 contains contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.ac.uk.

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