Pentaphosphaferrocene-mediated synthesis of asymmetric organo-phosphines starting from white phosphorus

Stephan Reichl1, Eric Mädl1, Felix Riedlberger1, Martin Piesch1, Gábor Balázs1, Michael Seidl1 & Manfred Scheer1✉

The synthesis of phosphines is based on white phosphorus, which is usually converted to PCl₃, to be afterwards substituted step by step in a non-atomic efficient manner. Herein, we describe an alternative efficient transition metal-mediated process to form asymmetrically substituted phosphines directly from white phosphorus (P₄). Thereby, P₄ is converted to [Cp*Fe(η⁵-P₅)] (1) (Cp* = η⁵-C₅(CH₃)₅) in which one of the phosphorus atoms is selectively functionalized to the 1,1-diorgano-substituted complex [Cp*Fe(η⁴-P₃R′R″)] (3). In a subsequent step, the phosphine PR′R″ (R′ ≠ R″) is released by reacting it with a nucleophile R‴M (M = alkali metal) as racemates. The starting material 1 can be regenerated with P₄ and can be reused in multiple reaction cycles without isolation of the intermediates, and only the phosphine is distilled off.
he interest in organophosphorus compounds in life science, material science, and especially in ligand design for catalysis is an omnipresent topic\textsuperscript{2,5}. Besides the use of phosphines as ligands\textsuperscript{1–6}, the resulting complexes are widely used as catalysts in all areas of organic and organometallic chemistry\textsuperscript{7}. One of the most prominent examples of a catalyst containing phosphines represents the Wilkinson’s catalyst [RhCl(PPh\textsubscript{3})\textsubscript{3}]\textsuperscript{1}, which catalyses, e.g., the hydrogenation of olefins. Over the last decades, a plethora of organophosphorus compounds was synthesised and investigated\textsuperscript{8–13}. Although organophosphorus chemistry is a well-established area, the synthesis of asymmetrically substituted organophosphorus compounds is a crucial and challenging topic\textsuperscript{14,15}. Its importance in catalysis was awarded, e.g. with the Nobel prize\textsuperscript{16}. The classical way to synthesise phosphines is via hydrophosphination\textsuperscript{17},18. Interestingly, acidic aqueous media\textsuperscript{18}. Note that, aryl phosphines cannot be synthesised and investigated\textsuperscript{9}.

The major drawback to all of these processes is that they do not lead to the formation of asymmetrically substituted phosphines, which are crucial for catalysis. In this report, we present a conceptually innovative strategy for a controlled and directed synthesis of symmetrically and asymmetrically substituted phosphines starting from P\textsubscript{4} and carbon-centred nucleophiles and electrophiles by using [Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{5}}-P\textsubscript{5})]\textsuperscript{(3)} (Cp\textsuperscript{″} = \textsuperscript{η\textsuperscript{5}}-C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) as a P-atom carrier.

**Results**

**Synthesis and structural characterization of the mono-substituted complexes 2c–e.** In our previous works, we were able to show that [Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{5}}-P\textsubscript{5})]\textsuperscript{(3)} readily reacts with main-group nucleophiles such as Me\textsubscript{3}SiCH\textsubscript{2}− or Me\textsubscript{3}N− via the formation of a P−C/P−N bond\textsuperscript{18}, leading to the complexes [Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{4}}-P\textsubscript{4}′R′)]; R′ = CH\textsubscript{2}SiMe\textsubscript{3} (2a), NM\textsubscript{e}\textsubscript{2} (2b)). However, we found now that the nucleophile used can be freely varied, and basically any alkali metal organyl can be used (Fig. 2). The reaction of [Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{4}}-P\textsubscript{4})]\textsuperscript{(3)} with MeLi, tBuLi and PhLi, respectively, at −80 °C leads to an immediate colour change from green to brown. After workup, the complexes [Li(dime)\textsubscript{3}][Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{4}}-P\textsubscript{4}Me)] (2c), [Li(12c4)\textsubscript{2}][Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{4}}-P\textsubscript{4}′Bu)] (2d), [Li(12c4)(thf)][Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{4}}-P\textsubscript{4}P\textsubscript{3}Ph)] (2e) can be isolated in crystalline yields of 84%, 86% and 75%, respectively.

The single-crystal X-ray structure analysis of 2 shows anionic complexes with a folded P\textsubscript{3}R′-ligand in an envelope conformation (Fig. 3, Supplementary Figs. 40–43). The four coordinating phosphorus atoms of the P\textsubscript{3}R′ ligand build a nearly square planar P\textsubscript{4} unit which coordinates symmetrically to the Cp\textsuperscript{″}Fe fragment. The P1 atom to which the organic group is attached (P1−C1 bond length of 1.849(2) Å (2c), 1.898(3) Å (2d) and 1.841(3) Å (2e)) deviates from this plane. All P2−P5 bond lengths (1.993(12)−2.1575(10) Å) are in the range between a single and a double bond\textsuperscript{29,30}.

**Reactivity of 2 towards electrophiles.** The presence of the negative charge renders the compounds 2 nucleophilic, which is why they can be quenched with electrophiles such as alkyl or aryl halides. Thus, the compounds 2 were treated with alkyl halides R\textsuperscript{″}X (R\textsuperscript{″} = Me, iPr; R = Br, I) as common carbon-centred electrophiles. Indeed, the neutral organo-substituted polyphosphorus complexes [Cp\textsuperscript{″}Fe(\textsuperscript{η\textsuperscript{4}}-P\textsubscript{4}P\textsubscript{3}R\textsubscript{′}R\textsubscript{″})] (3; Fig. 2) were obtained in almost quantitative yields according to \textsuperscript{31}P NMR spectroscopy. The isolated compounds 2 and 3 were characterized by NMR spectroscopy (Supplementary Figs. 1–9; 17–26), mass
Due to the large diversity of organo-phosphine derivatives, a large number of precursors for quite rare asymmetrically substituted nucleophiles are available. Of particular interest are the compounds that possess a phosphonium ion-like character (Fig. 4). Functionalized phosphorus atoms P1 carry two organic substituents and possess a phosphonium ion-like character (Fig. 4). The functionalized phosphorus atoms P1 carry two organic substituents and possess a phosphonium ion-like character (Fig. 4). The functionalized phosphorus atoms P1 carry two organic substituents and possess a phosphonium ion-like character (Fig. 4). The functionalized phosphorus atoms P1 carry two organic substituents and possess a phosphonium ion-like character (Fig. 4). The functionalized phosphorus atoms P1 carry two organic substituents and possess a phosphonium ion-like character (Fig. 4).

Fig. 2 Synthesis of asymmetric phosphines 4, via successive nucleophilic, electrophilic, nucleophilic attack. Synthesis of the anionic precursor complexes 2 by nucleophilic attack; electrophilic quenching of 2 (synthesis of 3); asymmetric phosphine abstraction by nucleophiles (synthesis of 4, 5); regeneration of 1 by thermolysis with P₄ in addition to synthesis of 1 by thermolysis with P₄ alternative synthesis of 3 by nucleophilic quenching of 1'.

spectrometry, elemental analysis, and single-crystal XRD (Fig. 3). Supplementary Figs. 40–50). The latter shows that, in 3, the folded η₋₄-P₃ unit remains intact and the introduced electrophile is attached to the phosphorus atom, which bears the first organo-substituent (former nucleophiles; R′, Fig. 3), leading to a 1,1-substitution pattern with a P1–C2 bond length (1.785(5)–1.922(11) Å) corresponding to single bonds. The functionalized phosphorus atoms P1 carry two organic substituents and possess a phosphonium ion-like character (Fig. 4). Of particular interest are the compounds 3a,b and 3f since they represent precursors for quite rare asymmetrically substituted organo-phosphine derivatives. Due to the large diversity of organo-substituents (P1) and the anion [Cp*Fe(η₋₄-P₃)]⁻ (Supplementary Fig. 55). This strategy can be extended for the synthesis of a series of asymmetric phosphines, with PR'R"R‴ (4a-c) (a: R′ = Ph, R" = Ph, R‴ = Bn; b: R′ = 1-Bu, R" = Ph, R‴ = Bn; c: R′ = Ph, R" = Ph, R‴ = Bn) being isolated as air-sensitive viscous liquids in 82% (4a), 55% (4b), 80% (4c) yields, respectively. The identity of the phosphine was proven by NMR spectroscopy and, after oxidation with sulfur to the corresponding phosphine sulfides (Supplementary Figs. 10–16; 27–32; 34–39), also by single-crystal X-ray diffraction analysis (Fig. 3). Furthermore, by changing the nucleophile to MeLi and 1-BuLi, the corresponding phosphines PMe₃ and PMe₃-Bu can be obtained in the reaction with 3c (Supplementary Figs. 56, 57). The latter is less selective, PMe₃, however, can be synthesized via this route in 84% yield (according to NMR).

To identify potential intermediates in the reaction of 3 with nucleophiles, the reaction of 3c with MeLi at −80 °C in THF-d₈ was monitored by 3[P-H] NMR spectroscopy at this temperature. The 31P NMR spectrum clearly shows the full conversion of 3 to 4, and quantitative formation of 5 (Supplementary Fig. 61).

Synthesis of (a)symmetric phosphines—reactivity of 3 towards nucleophiles. The electrostatic potential surface of compound 3c (B3LYP/def2-TZVPP level of theory; Fig. 4) shows a rather localized positive potential on the phosphorus atom bearing the organo-sulphur substituent (P1). Therefore, the attack of a nucleophile is expected to occur at the position P1. Indeed, the reaction of 3d with benzyl potassium lead to the formation of the asymmetrically substituted phosphine PMe₃PrBn (4a) in 82% yield (Supplementary Fig. 61) and the anion [Cp*Fe(η₋₄-P₃)]⁻ (Supplementary Fig. 55). This strategy can be extended for the synthesis of a series of asymmetric phosphines, with PR'R"R‴ (4a-c) (a: R′ = Me, R" = Ph, R‴ = Bn; b: R′ = 1-Bu, R" = Me, R‴ = Bn; c: R′ = Ph, R" = Ph, R‴ = Bn) being isolated as air-sensitive viscous liquids in 82% (4a), 55% (4b), 80% (4c) yields, respectively. The identity of the phosphine was proven by NMR spectroscopy and, after oxidation with sulfur to the corresponding phosphine sulfides (Supplementary Figs. 10–16; 27–32; 34–39), also by single-crystal X-ray diffraction analysis (Fig. 3). Furthermore, by changing the nucleophile to MeLi and 1-BuLi, the corresponding phosphines PMe₃ and PMe₃-Bu can be obtained in the reaction with 3c (Supplementary Figs. 56, 57). The latter is less selective, PMe₃, however, can be synthesized via this route in 84% yield (according to NMR).

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The other product of the reaction of 3 with nucleophiles, the reaction of 3c with MeLi at −80 °C in THF-d₈ was monitored by 31P NMR spectroscopy at this temperature. The 31P NMR spectrum clearly shows the full conversion of 3 to 4, and quantitative formation of 5 (Supplementary Fig. 61). This very fast reactions agree with the results of the DFT calculations which show a very low activation barrier for this process (Figs. 5B, S71).
31P{1H} NMR spectrum of 5, a singlet is observed at 118.9 ppm (Supplementary Fig. 39). The lithium derivative of 5 can be detected in all reactions of 3b-e with organolithium reagents but decomposes partly over time in solution.

Formation of phosphines and regeneration of the carrier platform [Cp*Fe(η5-P5)] (1) in a ‘semi-catalytic’ cyclic process.

The phosphines generated in the reaction of 3 with nuclophiles can be easily isolated either by extraction with n-hexane (5 is not soluble in n-hexane) or, in the case of volatile phosphines, by condensation. That is why we were interested in designing a closed-cycle-process for the generation of phosphines in which 1 represents the platform for the phosphorus atom transfer. To close the circle, 5 was reacted with one equivalent of P4 with 1 being formed in almost quantitative yield, among KP5, which partly decomposes to polyphosphides36 (Supplementary Fig. 65). After workup, 1 can be isolated in 81% crystalline yield (Fig.6). If required, KP5 can be transformed into the corresponding pentaphosphaferrocene by reacting with [Cp*FeBr]237 to increase the atom efficiency of this process. Moreover, it is possible to perform a larger scale synthesis of the phosphines in a one-pot reaction to easily reuse 1 and to avoid the workup of the reaction solution. In a one-pot reaction, compound 1 was dissolved in 2,5,8,11,14-pentaoxapentadecane (tetraglyme) and stoichiometric amounts of MeLi and MeI were successively added at r.t. with 5 min stirring in between (Fig.6, steps I and II). Subsequently, the solution was cooled to −30 °C and one equivalent of KBnz in tetraglyme was added (Fig. 6, step III). The cooling bath was removed, the formed phosphine PMe 2Bnz was distilled off under reduced pressure (1 × 10−3 mbar, 55 °C) and was obtained in 87% yield (Fig. 6, step III, Supplementary Fig. 67). To the remaining solution, one equivalent of white phosphorus was added and heated under reflux for 1 h at 275 °C (IV). The 31P{1H} NMR spectrum (Supplementary Fig. 63) shows the almost quantitative regeneration of 1. The same protocol was repeated two more times on the same reaction solution (see Supplementary Fig. 64). The phosphine PMe2Bnz was isolated in 82–67% yield (overall isolated yield 79%, see Supplementary Fig. 67, Supplementary Table 40). After these three cycles, 1 can be isolated from the reaction solution in 69% yield (Supplementary Fig. 66), indicating that this process could be carried on for many more cycles.

In summary, the polyphosphorus compound [Cp*Fe(η5-P5)] (1) can be used as a recyclable platform for the targeted synthesis of symmetric or asymmetric phosphines, via a sequence of nucleophilic-electrophilic-nucleophilic reactions, directly from white phosphorus, avoiding the use of intermediate products.
Fig. 6 ‘Semi-catalytic’ cycle for the synthesis of asymmetric phosphines. One-pot reaction of [Cp*Fe(η⁵-P₅)] (I) with MeLi (I, R' = Me), quenching with Mel (II, R' = Me), reaction with KBNz (III, R'' = Bnz) and subsequent thermolysis with white phosphorus (IV).

such as PCl₃ or PH₃. With this modular system, asymmetric phosphines are obtained in high yields in significant preparative scales and I can be regenerated and reused in a ‘semi-catalytic’ cyclic process, which can be run for several cycles in a one-pot reaction. The presented results pave the way for a selective and easy synthetic route to asymmetric and (in future work potential) chiral phosphines based on white phosphorus. This conceptual innovative approach avoids radicals and is not limited to aryl or alkyl substituents, but phosphines with a variety of different substitution patterns are now accessible in high yields by a very simple approach.

Methods

General methods. All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME), 2,5,8,11-tetraoxadodecane (triglyme) and 2,5,8,11,14-pentaoxapentadecane (tetraglyme) were dried and deoxygenated by distillation under argon atmosphere from sodium (DME) or calcium hydride. All other solvents were dried using a MB SPS-800 device of the company MBRAUN and stored over molecular sieve. NMR spectra were recorded on a Bruker Avance III 400/600 MHz NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for 1H and 85% H₃PO₄ for 3¹P as external standard. Signal multiplicities are described using common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad).

Synthetic protocols

Synthesis of [Cp*Fe(η⁴-P₅)] (I)⁴. The complex [Cp*Fe(CO)]₂ (10.0 g, 20.0 mmol) and white phosphorus (7 g, 56.5 mmol) are dissolved in 1,3-diisopropylbenzene (500 ml) and heated to reflux for 5 h. The solvent was removed in vacuo. The residue was dissolved in dichloromethane, silica was added and the solvent was removed under reduced pressure. The preabsorbed reaction mixture was purified via column chromatography (SiO₂, hexane, 10 × 3 cm). Using n-hexane, compound I (12.3 g, 35.6 mmol, 89%) can be eluted as a dark green fraction. Complex 1 can be obtained after 1 day from a concentrated solution stored at –30 °C as green needles.

Synthesis of [Li(dme)₂][Cp*Fe(η⁴-P₅)] (I)². A solution of I (0.4 g, 1.16 mmol, 1 eq) in DME (30 ml) was added to potassium (0.136 g, 3.47 mmol, 3 eq). The solution was stirred at ambient temperature for 4 h. The solution was filtered; the product was extracted from an insoluble residue with DME (70 ml). The volume of the combined solution was reduced to ca. 30 ml and Et₂O (30 ml) was added. The suspension was stirred overnight and the product was collected on a frit, washed with Et₂O (30 ml) and dried in vacuum to give I' (0.74 g, 0.95 mmol) as dark brown-green powder.

Synthesis of [Li(thf)₂][Cp*Fe(η⁴-P₅)NMe₂] (2a)³. To a solution of I (176 mg, 0.31 mmol) in 5 ml THF a solution of LiNMe₂ (26 mg, 0.51 mmol) was added at
Synthesis of [Li(dme)][Cp*Fe(η^5-PMe2)η^5-PPh3] (2b). To a solution of 1.380 g (0.4 mmol, 1 eq) of 1 in DME at 90 °C, a 1.6 molar solution of MeI (0.4 mmol, 0.27 mL, 1 eq) in DME (diethyl ether) was added and stirred at room temperature. After 4 days, a brown solution and a dark green solid were isolated after 2 days at 0 °C.

Synthesis of [Li(dme)][Cp*Fe(η^5-PMe2)η^5-PPh3] (2b). To a solution of [(trimethylsilyl)methyl][lium][68 mg, 0.72 mmol] in Et2O (3 mL) at 35 °C was added a solution of 1 (250 mg, 0.72 mmol) in Et2O (15 mL). Immediate colour change was observed. The solution was cooled down to −10 °C and 12-crown-4 was added (for coupling constants, see Supplementary Table 5). LIFDI-MS (toluene): 448.03 (100%, [M]+); analysis (calcld., found for C42H29Fe3P3S): C (40.20, 39.64), H (6.52, 6.48).

Synthesis of [Li(dme)][Cp*Fe(η^5-PMe2)η^5-PMe2] (3b). Compound 2b (1.33 mmol, 686.8 mg, 1 eq) was dissolved in 100 mL THF. A 1.2 molar solution of Mel in Et2O (1.33 mmol, 1 eq) was added under strong stirring at room temperature and the solution was stirred overnight. The formation of a white precipitate was observed on the glass wall. The solvent was removed. 3b extracted with

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The colour of the solution turned immediately from green to brown. The reaction mixture was stirred over 2 h, and then the solvent was concentrated to 3 mL and finally to dryness. After 4 days, brown square-shaped crystals of 2a (150 mg, 0.25 mmol, 50%) were formed.

Synthesis of [Li(dme)][Cp*Fe(η^5-PMe2)η^5-PMe2] (3b). Compound 2b (1.33 mmol, 686.8 mg, 1 eq) was dissolved in 100 mL THF. A 1.2 molar solution of Mel in Et2O (1.33 mmol, 1 eq) was added under strong stirring at room temperature and the solution was stirred overnight. The formation of a white precipitate was observed on the glass wall. The solvent was removed, 3b extracted with
solution of Mel (0.4 mmol, 0.36 mL, 1 eq.) in EtO was added. The solution was stirred for 18 h, the solvent removed under reduced pressure, the remaining brown residue extracted with 3 x 5 mL of n-hexane and filtered over diastereomeric earth. The volume was reduced in vacuo and the solution stored at −30 °C. Compound 3f was isolated after 3 days as dark green plates. Yield: 132.0 mg (0.30 mmol, 75%). 1H NMR (CD5-D5, 293 K): δ ppm = 7.00 (m, 5H, -CH2-Ch), 6.77 (m, 3H, CH-C5H5), 1.95 (dt, 3H, Jp-C17 = 17.1 Hz, -Ph), 0.94 (3Jp-C18 = 13.0 Hz, -(CH5)3), 0.64 (s, 15H, C5(CH3)3), 26.8 Hz, -(CH)-((CH3)2); 4b′ (CD5-D5, 293 K): δ ppm = 7.12 (m, 3H, -CH2-C6H5), 2.87 (s, 3Jp-C18 = 15.3 Hz, -CH-(CH3)2); 4c (CD5-D5, 293 K): δ ppm = 7.00 (m, 5H, -CH2-Ch), 6.77 (m, 3H, CH-C5H5), 1.95 (dt, 3H, Jp-C17 = 17.1 Hz, -Ph), 0.94 (3Jp-C18 = 13.0 Hz, -(CH5)3), 0.64 (s, 15H, C5(CH3)3), 26.8 Hz, -(CH)-((CH3)2); 4d (CD5-D5, 293 K): δ ppm = 7.12 (m, 3H, -CH2-C6H5), 2.87 (s, 3Jp-C18 = 15.3 Hz, -CH-(CH3)2); 4e′ (CD5-D5, 293 K): δ ppm = 7.00 (m, 5H, -CH2-Ch), 6.77 (m, 3H, CH-C5H5), 1.95 (dt, 3H, Jp-C17 = 17.1 Hz, -Ph), 0.94 (3Jp-C18 = 13.0 Hz, -(CH5)3), 0.64 (s, 15H, C5(CH3)3), 26.8 Hz, -(CH)-((CH3)2); 4f′ (CD5-D5, 293 K): δ ppm = 7.83 (d, 3H, Jp-C17 = 17.1 Hz, -Ph), 2.87 (s, 3Jp-C18 = 15.3 Hz, -CH-(CH3)2); 4g′ (CD5-D5, 293 K): δ ppm = 8.86 (m), 4′ (CD5-D5, 293 K): δ ppm = 8.86 (m).

Synthesis of PR′R′R″ (4a′-c). Compound 3d (0.1 mmol, 40 mg, 1 eq) 3e (0.02 mmol, 18.6 mg, 1 eq) 3f (0.01 mmol, 13.1 mg, 1 eq) was dissolved in DCE and cooled to −50 °C. To the brown green solution, a 50 °C cold solution of KBN (0.2 mmol, 279.5 mg, 1 eq) in 50 mL tetraglyme was added. The reaction mixture was stirred overnight and allowed to reach room temperature. The solvent was slowly removed under reduced pressure (note: in order to avoid the loss of the desired phosphine by removal of the solvent, lower boiling solvents like THF can be used for the reaction). The oily residue was extracted with n-pentane (5 x 5 mL) and decanted off from the remaining solid (compound 5, see below). The solvent was removed in vacuo to afford a compound (R = Me, R′ = Ifr, R″ = Br); R = Br, R′ = Br, R″ = Me, R′ = Br, R″ = Me (3%) can be isolated as a viscous liquid. Yield: 4a′: 14.8 mg (0.082 mmol, 82%); 4b′: 21.5 mg (0.11 mmol, 55%); 4c′: 17.1 mg (0.080 mmol, 88%).

1H NMR (CD5-D5, 293 K): δ ppm = 7.05 (m, 5H, -CH2-Ch), 6.81 (m, 3H, CH-C5H5), 1.97 (dt, 3H, Jp-C17 = 17.1 Hz, -Ph), 0.92 (3Jp-C18 = 13.0 Hz, -(CH5)3), 0.65 (s, 15H, C5(CH3)3), 26.8 Hz, -(CH)-((CH3)2); 4b′ (CD5-D5, 293 K): δ ppm = 7.77 (d, 3H, Jp-C17 = 17.1 Hz, -Ph), 2.70 (s, 3Jp-C18 = 15.3 Hz, -CH-(CH3)2); 4c′ (CD5-D5, 293 K): δ ppm = 7.00 (m, 5H, -CH2-Ch), 6.77 (m, 3H, CH-C5H5), 1.95 (dt, 3H, Jp-C17 = 17.1 Hz, -Ph), 0.94 (3Jp-C18 = 13.0 Hz, -(CH5)3), 0.64 (s, 15H, C5(CH3)3), 26.8 Hz, -(CH)-((CH3)2); 4d′ (CD5-D5, 293 K): δ ppm = 7.12 (m, 3H, -CH2-C6H5), 2.87 (s, 3Jp-C18 = 15.3 Hz, -CH-(CH3)2); 4e′ (CD5-D5, 293 K): δ ppm = 8.86 (m), 4′ (CD5-D5, 293 K): δ ppm = 8.86 (m).
