Keywords: alkoxides · chromium · epoxides · oxidations · radicals

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[7] **3** · CH_2Cl_2**:** $C_{20}H_{27}Cl_2CrO_3 \cdot CH_2Cl_2$, $M_r = 523.26$, monoclinic, space group $C2/c$, $Z = 8$, $a = 22.574(5)$, $b = 10.534(2)$, $c = 20.629(4)$ Å, $\beta = 117.06(3)$, $V = 4368.5(15)$ Å^3, $4.1 < 2\theta < 52.1^\circ$, ω scan, $T = 200$ K, $\rho_{calcd} = 1.591$ g cm^{-3}, 34592 measured reflections, 4300 independent, and 3534 observed reflections with $I > 2\sigma(I)$, Lp-correction ($\mu = 1.035$ mm^{-1}), 264 refined parameters with $R = 0.032$, residual electron density: max/min: 0.404/ − 0.309 e Å^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, the structure was solved by direct methods (SHELXS-97), and refined versus F^2 (SHELXL-97) with anisotropic temperature factors for all non-hydrogen atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115684. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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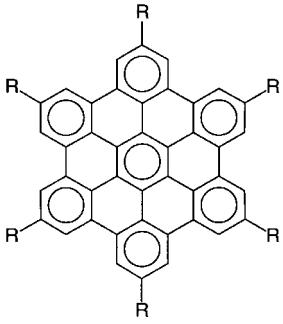
Highly Ordered Columnar Structures from Hexa-*peri*-hexabenzocoronenes—Synthesis, X-ray Diffraction, and Solid-State Heteronuclear Multiple-Quantum NMR Investigations**

Andreas Fechtenkötter, Kay Saalwächter, Martha A. Harbison, Klaus Müllen,* and Hans Wolfgang Spiess*

The generation of new functional materials requires both intelligent design and the high-yield synthesis of tailor-made building blocks, as well as methods that enable the highly selective characterization of their organization into supermolecular structures.[1] Interdisciplinary studies involving advanced physical charaterization methods, closely coupled with the synthetic work, is the key to success. Herein, we present an example of such an endeavor through the development of new columnar structures.



1 (R = H)
1a (R = *n*-$C_{12}H_{25}$)

Hexa-*peri*-hexabenzocoronene (HBC, **1**) with long chain alkyl substituents, such as $C_{12}H_{25}$ (HBC-C_{12} **1a**) or $C_{14}H_{29}$, is of considerable interest on account of the unusually large liquid crystalline (LC) phase widths and favorable physical, electronic, and optoelectronic properties that are obtained. An example of such a property is their very high one-dimensional charge carrier mobility.[2] In addition, HBC-C_{12} has the ability to form adsorbate layers on graphite, which have been investigated by scanning tunneling microscopy (STM).[3] These substituted HBCs form columnar liquid crystals,[4] in which the aromatic cores undergo rapid axial rotation on the μs time scale, although the order parameter of the discs, $S = 0.84$, is found to be considerably lower than in other columnar discotics.[5] Since high mobility and low order limit the charge carrier mobility, we set out to synthesize a less mobile mesogen, which at the same time should improve the hexagonal columnar ordering. With this in mind, phenyl rings were inserted between the planar HBC discs and the pendent alkyl chains. In this communication we report the synthesis of hexa(*para-n*-dodecylphenyl)-substituted HBC (HBC-PhC_{12},

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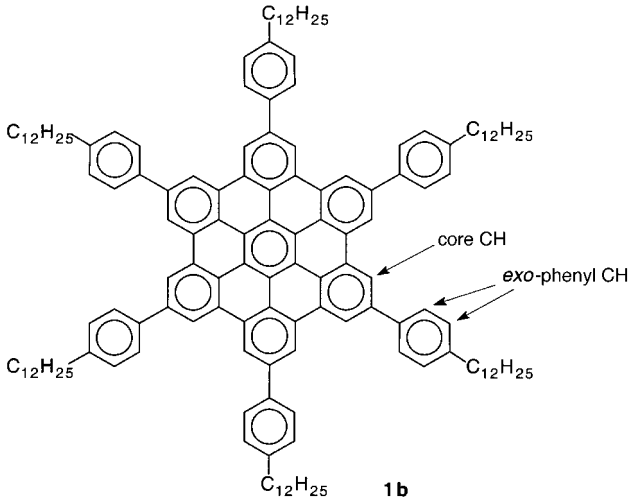


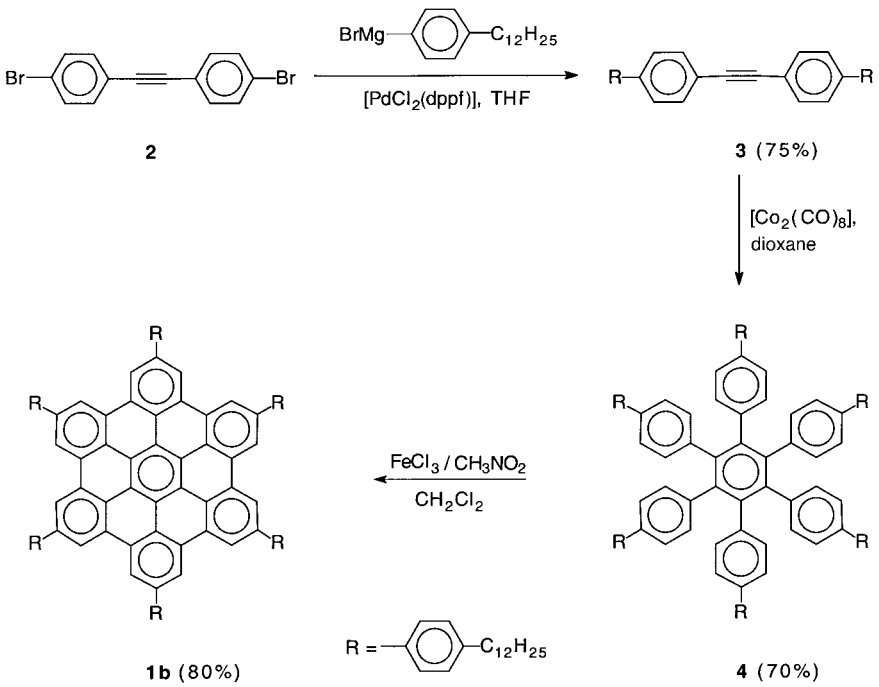
1b

1b), and probe its order and mobility by X-ray diffraction and solid-state NMR spectroscopy.

The synthesis of HBC-PhC_{12} is outlined in Scheme 1. First, in a Kumada-type Grignard reaction catalyzed with $[PdCl_2(dppf)]$[6] (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene), 4,4′-dibromotolane (**2**) reacts with 4-*n*-dodecylphenylmagnesium bromide to give di(4-*n*-dodecylbiphenyl)acetylene (**3**) in 75% yield. Cyclotrimerization of **3**, catalyzed by $[Co_2(CO)_8]$, in dioxane then afforded hexa(4-*n*-dodecylbiphenyl)benzene (**4**) in 70% yield after workup. The key step for the synthesis of HBCs is the oxidative cyclodehydrogenation.[7] Here, **4** was dissolved in CH_2Cl_2 and flushed with argon for several minutes, before adding a solution of $FeCl_3$ in CH_3NO_2. Precipitation with MeOH and work-up finally afforded HBC-PhC_{12} (**1b**) in 80% yield. The synthesis of **1a** has been published recently.[7]

Both HBC-PhC_{12} (**1b**) and HBC-C_{12} (**1a**) form thermotropic mesophases. The differential scanning calorimetry (DSC) results showed that the transition from the room-temperature phase occurs at 80 °C for HBC-PhC_{12}, while that for HBC-C_{12} occurs at 107 °C, and in addition, the temperature range over which the phase transition occurs is broader in HBC-PhC_{12}. Furthermore, HBC-PhC_{12} exhibits a much higher solubility in common organic solvents than any other reported HBC derivative, for example, HBC-PhC_{12} has a solubility greater than 10 g L^{-1} in THF while that for HBC-C_{12} is less than 1 g L^{-1}. The X-ray diffraction patterns for both **1a** and **1b** demonstrated that the high-temperature LC mesophases exist as ordered columnar hexagonal (Col_{ho}) superstructures. For a perfect hexagonal lattice reflections at small angles with relative spacings of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ are expected, where the intensities depend on the perfection of the lattice and the order parameter. As shown in Figure 1, only the first three peaks (100), (110), and (200) are observed for HBC-C_{12}, while for HBC-PhC_{12} the fourth peak (210) is apparent above the noise level, which indicates an improved long-range packing of the columns into a hexagonal arrangement. In addition, the packing of the cores within the columns is improved, as indicated by the sharp (001) reflection at $2\theta \approx 25.6°$. This reflection corresponds to an intermolecular distance of 0.350 nm between the aromatic cores, which should be compared to a spacing of about 0.355 nm in the LC phase of HBC-C_{12}, where the (001) reflexion is significantly broader.[5]

Structure and dynamics on a molecular level can be probed in detail by advanced solid-state NMR spectroscopy.[8] The rapid rotation of the disc-shaped molecules about the



Scheme 1. Synthesis of hexaphenyl-substituted HBC (HBC-PhC_{12}).

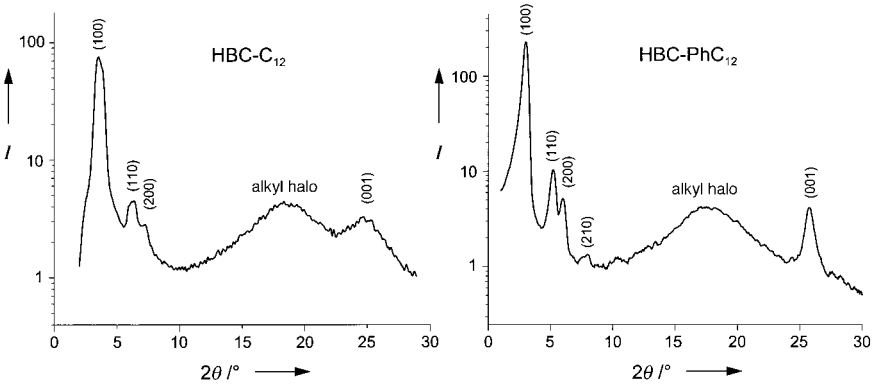


Figure 1. X-ray diffraction patterns of the Col_{ho} mesophases of HBC-PhC_{12} and HBC-C_{12} obtained with $Cu_{K\alpha}$ radiation. The intensities (arbitrary units) are plotted on a logarithmic scale.

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columnar axis in the high-temperature LC phase has been confirmed by ^{2}H NMR measurements,[5] and more recently by ^{1}H double-quantum (DQ) magic-angle spinning (MAS) NMR spectroscopy.[7] This rotation leads to an averaging of the respective interaction tensors, namely, the quadrupolar coupling tensor in the case of ^{2}H NMR, and the homonuclear dipolar coupling tensor in the case of ^{1}H DQ MAS NMR spectroscopy. Thus, fast motional processes can by quantified by measuring the reduction of the coupling constants. If the symmetry axes of the tensors (the CH bond vector and the H-H internuclear vector of the two core CH protons) lie in a plane perpendicular to the rotational axis, the coupling constants are reduced by a factor of 0.5. With the two methods employed, reduction factors of 0.40 and 0.42 have been observed, which corresponds to order parameters[4] for the discs of 0.80 and 0.84, respectively, and is indicative of additional out-of-plane or librational motions.

The application of both methods mentioned above is limited. ^{2}H NMR spectroscopy requires specifically isotopically labeled samples, which represents a considerable synthetic challenge, while ^{1}H DQ MAS NMR spectroscopy is unsuitable in the case of HBC-PhC_{12} (**1b**), since the core CH and the *exo*-phenyl CH proton resonances can not be differentiated. Both limitations are overcome by a recently developed heteronuclear multiple-quantum correlation method. REPT-HMQC (*Re*coupled *P*olarization-*T*ransfer *H*eteronuclear *M*ultiple-*Q*uantum *C*orrelation)[8] is a two-dimensional correlation experiment for solids under very fast MAS, which exploits the concept of "separated local field" spectroscopy.[9] An advantage of this technique is the enhanced site resolution that is made available by the observation of ^{13}C rather than ^{1}H resonances. As in ^{1}H solid-state DQ MAS spectra, the signal in the MQ dimension can be distributed over several orders of spinning side bands, with intensities depending on the dipolar coupling and the spinning frequency.[10] These side-band intensities can then be used to quantitatively evaluate the heteronuclear dipolar coupling of site-resolved ^{13}C atoms to their neighboring protons. The sensitivity of the technique to dipolar couplings of different magnitudes can be chosen by simply changing the so-called recoupling time τ_{rcpl}, which corresponds to the number of rotor periods (τ_R) used to excite the MQ modes.

By measuring the dipolar coupling within a CH moiety, one can use such 2D experiments to obtain site-resolved dynamical information in complex molecules without the need for isotopic labeling. It should be emphasized that the REPT-HMQC method is applicable to samples naturally abundant in ^{13}C, and only requires small amounts of sample (typically 10–15 mg). Both the heteronuclear dipolar and quadrupolar coupling tensor of a C-^{1}H and a C-^{2}H group, respectively, exhibit the same symmetry; hence the results from the experiments described here can be seen as being analogous to those obtained by ^{2}H NMR spectroscopy, the latter being a well-established method for the investigation of liquid crystals.[4]

In Figure 2 the MQ spinning side-band patterns corresponding to the core CH signals of HBC-C_{12} and HBC-PhC_{12} are displayed for different temperatures and different recoupling times. In the latter case, as shown in the ^{13}C CP MAS

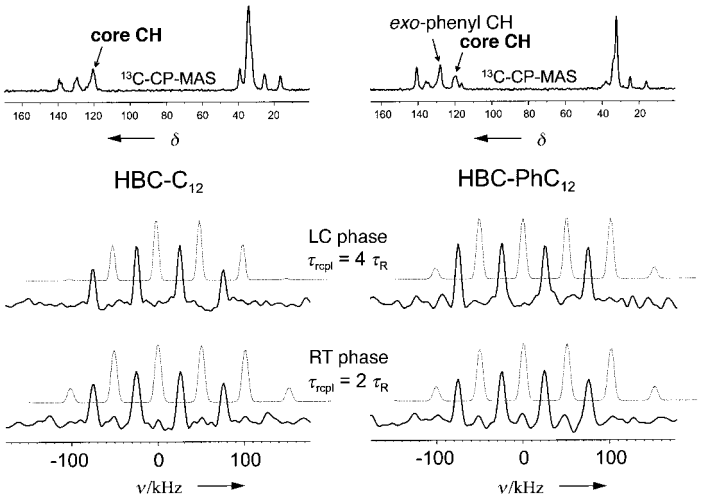

Figure 2. Solid-state ^{1}H-^{13}C heteronuclear multiple-quantum spinning side-band patterns, obtained at a spinning frequency of 25 kHz, using the REPT-HMQC pulse sequence. The patterns are the sum projections over the core ^{13}CH signal in the 2D spectra of HBC-C_{12} and HBC-PhC_{12}. The spectra for the room temperature and high temperature LC phases were recorded at 35 °C and 120 °C, respectively. The dotted traces represent simulated spectra, obtained by taking into account the best-fit dipolar coupling constants for the CH groups. The recoupling time τ_{rcpl} is given in rotor periods τ_R. The top diagrams are ^{13}C-CP-MAS spectra taken at a spinning speed of 15 kHz, with the signal positions of the aromatic CH signals identified.

spectra, the *exo*-phenyl CH signals are resolved from the core CH signals. The side-band pattern for very fast MAS[11, 12] is that of an isolated spin pair, namely being composed of odd-order side bands only, with the observed intensity distribution depending on the product of the recoupling time and the dipolar coupling constant.[8, 10] The shown side-band patterns for the room-temperature and high-temperature LC phases of both materials are similar, but the recoupling times are $2\tau_R$ and $4\tau_R$ for the RT and LC phases, respectively. This means that the dipolar couplings are reduced by approximately 50 %. A closer inspection reveals that the side-band pattern for the LC phase of HBC-C_{12} exhibits less intense third-order side bands, which indicates a weaker coupling than in HBC-PhC_{12}.

The dipolar coupling constants were evaluated quantitatively by numerically fitting the side-band patterns to the analytical solution for the case of a heteronuclear spin pair; such best-fit spectra are shown as dotted lines in Figure 2. The average dipolar coupling constant for a rigid, aromatic CH group—as found in the RT phase of both materials—was determined from various independent measurements to be 20.9 ± 0.5 kHz, which corresponds to an internuclear distance of 113 ± 1 pm, while the motionally reduced coupling constants for the LC phases were determined to be 8.2 ± 0.9 and 9.7 ± 0.9 kHz for HBC-C_{12} and HBC-PhC_{12}, respectively. Thus, reduction factors of 0.39 ± 0.04 and 0.46 ± 0.04 were calculated for the motional processes in the two materials, which corresponds to order parameters of 0.78 ± 0.09 and 0.93 ± 0.09. The value for HBC-C_{12} thus agrees with the earlier findings within the limits of experimental error.[5, 7] In contrast, the order parameter for the discs in HBC-PhC_{12} has increased by 15 %, which means that the rotational motion is better defined and that additional out-of-plane motions are

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suppressed more effectively. It should be emphasized that the *increase* in the order parameter is better defined than its absolute value, the latter being subject to systematic deviations.

It may further be noted that the MQ measurements were carried out at 120 °C, such that the motional processes in both HBC samples are assured to be fast on the NMR time scale, namely at least in the μs range. In this respect, the decrease of line widths in the ^{1}H MAS spectra upon heating the sample made it become clear that the degree of motional averaging for HBC-PhC_{12}, despite its lower calorimetric phase transition temperature of 80 °C, still increases up to about 110 °C. One should keep in mind that these thermally activated motions, though fast on an NMR time scale, are not expected to interfere with the dynamics of the hopping process of charge transport, which takes place on a time scale of less than 1 ns.

These NMR investigations strongly support the conclusion of the existence of high intracolumnar order as drawn from the X-ray data, and thus we can state that order phenomena in the LC phase of HBC-PhC_{12} not only extend to longer ranges—as detected by scattering experiments—but also manifest themselves in a well-defined packing of the rotating discs on a molecular level. We also note that preliminary results concerning motional processes in the side chains at different temperatures indicate an initially surprising *higher* mobility in HBC-PhC_{12} relative to HBC-C_{12}, which indicates that a higher order of the HBC cores does not necessarily lead to an overall reduction of mobility in the system. Since the charge-carrier transport properties in such systems are limited by the degree of long-range order within the columns, the possibility of the system undergoing molecular reorientations as a result of this motional freedom, thus allowing for self-healing, is highly desirable.

In summary, the design, synthesis, and mesophase characterization of a hexaphenyl-substituted HBC has indicated that symmetric substitution can inhibit out-of-plane mesogen mobility without interrupting the columnar hexagonal superstructure. Both MQ NMR results and X-ray diffraction patterns indicate higher inter- and intracolumnar ordering in the mesophase. The possibility of studying the motional processes of the mesogens in a site-resolved way using technologically advanced heteronuclear multiple-quantum NMR methods, without the synthetic difficulties of isotopic labeling, has greatly enhanced our ability to understand the mesogenic properties of these fascinating materials.

Experimental Section

3: A 1M solution of 4-*n*-dodecylphenylmagnesium bromide(18 mL) was added dropwise to a solution of **2** (1 g, 3 mmol) in dry THF (100 mL) in a 250-mL Schlenk flask. [$PdCl_2$(dppf)] catalyst (200 mg) was added to this solution. The resulting mixture was stirred under reflux in an inert atmophere for 20 h. While cooling the mixture to room temperature, a white solid precipitated. The solid was then filtered and washed several times with petrol ether and methanol to yield **3** (1.5 g, 75 %). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): $\delta = 7.58$ (s, 8H; CH), 7.51 (d, ^3J(H,H) = 7 Hz, 4H; CH), 7.24 (d, ^3J(H,H) = 7 Hz, 4H; CH), 2.65 (m, 4H; α-CH_2), 1.67 (m, 4H; β-CH_2), 1.25 – 1.45 (m, 36H; CH_2), 0.91 (t, ^3J(H,H) = 6 Hz, 6H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 143.10$, 141.40, 138.0, 132.50, 129.30, 127.23, 127.17, 122.60, 90.70, 36.00, 32.30, 31.50, 30.04, 30.03, 30.00, 29.96, 29.87, 29.76, 29.67, 23.00, 14.36; MS (FD, 8 kV): *m*/*z* (%): 666.9 (100) [M^+] (calcd for $C_{50}H_{66}$: 666.5)

4: A suspension of **3** (1 g, 1.5 mmol) in dioxane (50 mL) was degassed several times in a 100-mL round bottom flask equipped with a reflux condensor. [$Co_2(CO)_8$] (78 mg, 0.23 mmol) was then added and the resulting mixture was refluxed for 3 h. The solvent was evaporated under vacuum, and the residue purified by column chromatography on silica gel with petrol ether/CH_2Cl_2 (8/2) to yield **4** (0.7 g, 70 %) as an off-white solid. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): $\delta = 7.31$ (d, ^3J(H,H) = 8 Hz, 12H; CH), 7.1 (d, ^3J(H,H) = 8 Hz, 12H; CH), 7.06 (d, ^3J(H,H) = 8 Hz, 12H; CH), 6.88 (d, ^3J(H,H) = 8 Hz, 12H; CH), 2.51 (m, 12H; α-CH_2), 1.52 (m, 12H; β-CH_2), 1.30 – 1.15 (m, 108H; CH_2), 0.83 (t, ^3J(H,H) = 6 Hz, 18H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): $\delta = 142.05$, 140.37, 139.94, 138.10, 137.26, 132.27, 128.91, 126.83, 125.18, 35.82, 32.21, 31.76, 29.98 (2 × CH_2), 29.94, 29.90, 29.82, 29.70, 29.65, 23.02, 14.52; MS (FD, 8 kV): *m*/*z* (%): 2002.1 (100) [M^+] (calcd for $C_{150}H_{196}$: 2001.2).

1b: A 250-mL two-necked round bottom flask was charged with **4** (0.53 g 0.27 mmol) and CH_2Cl_2 (70 mL). A constant stream of argon was bubbled into the solution through a glass capillary. A solution of $FeCl_3$ (0.8 g, 5 mmol) in CH_3NO_2 was then added dropwise with a syringe. After 30 min the mixture was quenched with MeOH and the precipitate was filtered off. The resulting yellow solid was recrystallized from hot THF and dried under vacuum to yield **1b** (0.42 g, 80 %). ^{1}H NMR (500 MHz, *p*-$C_6D_4Cl_2$, 85 °C): $\delta = 8.57$ (s, 12H; CH), 7.92 (d, ^3J(H,H) = 6.5 Hz, 12H; CH), 7.58 (d, ^3J(H,H) = 6.5 Hz, 12H; CH), 3.18 (m, 12H; α-CH_2), 2.25 (m, 12H; β-CH_2), 1.95 (m, 12H; γ-CH_2), 1.88 (m, 12H; δ-CH_2), 1.8 – 1.45 (m, 84H; CH_2), 1.13 (m, 18H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 85 °C): $\delta = 141.87$, 140.65, 136.73, 129.83, 129.35, 128.93, 122.63, 120.31, 118.32, 37.37, 33.25, 33.22, 31.40, 31.34, 31.27, 31.21, 31.08, 30.90, 30.7, 23.91, 15.12; MS (MALDI-TOF): *m*/*z* (%): 1989.1 (100) [M^+] (calcd for $C_{150}H_{186}$: 1989.1).

NMR spectroscopy: All NMR experiments were carried out on a Bruker DSX 300 spectrometer equipped with a commercial Bruker 2.5 mm double-resonance MAS probe and operating at 300.23 MHz for ^{1}H and 75.49 MHz for ^{13}C. The 90° pulse lenghts were 2 μs on both channels, and proton dipolar decoupling with a B_1 frequency of 125 kHz. CP contact times were 2 ms, and the repeating time amounted to 1 s. Details concerning the REPT-HMQC pulse sequence can be obtained from reference [8].

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