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Synthesis and Structures of a Series of Bulky "Rind-Br" Based on a Rigid Fused-Ring *s*-Hydrindacene Skeleton

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A series of octa-R-substituted bromo-*s*-hydrindacenes, "Rind-Br," have been synthesized by a sequence of the Lewis acid catalyzed intramolecular Friedel–Crafts reaction, bromination and vice versa. Their structural features and physical properties depend on the eight R-substituents at the four benzylic positions on the *s*-hydrindacenyl skeleton. The molecular structures of the Rind-Br have been confirmed by X-ray crystallography, indicating the unique structural diversities of the bulky Rind groups.

The development of substituents or ligands that play supporting roles in both the fundamental and applied chemistries, has been the subject of intense interest for many years. Since the discovery of the stable silene ($R_2Si{=}CR_2$),[1] disilene ($R_2Si{=}SiR_2$),[2] and diphosphene ($RP{=}PR$)[3] were reported in 1981 by introducing a concept of steric protection with bulky substituents, a variety of unsaturated compounds of the heavier main group elements have successfully been isolated by many leading scientists using their own, newly developed bulky ligands.[4–12] For example, in organosilicon chemistry, many unsaturated compounds, such as silaaromatics (silabenzene),[13–22] trisilaallene ($R_2Si{=}Si{=}SiR_2$),[23–27] and disilyne ($RSi{\equiv}SiR$),[28–34] have been synthesized by taking advantage of the steric protection by the appropriate bulky groups.[35]

The bulky protecting groups so far developed can be categorized into three types, i.e., aryl,[2,3,13–19,21,22,34] alkyl,[1,23–27] and silyl[20,28–33] groups. Among them, the bulky aryl groups have been the most widely used in this chemistry. The bulky aryl groups can also be further categorized into two types, i.e., 2,4,6-trialkylphenyl groups and 2,6-diarylphenyl groups. Some of their characteristic features are summarized as follows.

Typical 2,4,6-trialkylphenyl groups include the 2,4,6-trimethylphenyl (Mes),[2] 2,4,6-tri(isopropyl)phenyl (Tip), 2,4,6-tri(*tert*-butyl)phenyl (Mes*),[3] 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt), and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt)[13–19,21,22,34] groups. The steric bulkiness of these aryl groups increases with an increase in the size of the *ortho* alkyl substituents in the following order: methyl (Mes) < isopropyl (Tip) < *tert*-butyl (Mes*); the Tbt and Bbt groups seem to be bulkier. Among the 2,6-diarylphenyl groups, the 2,6-bis(2,6-dialkylphenyl)phenyl groups have proven to be widely useful to stabilize a reactive low-coordinated atom center.[36–48] What is the most significant difference between these two series? The difference resides in the ease of the rotation around the C–C bond between the core-benzene ring carbon and the substituent carbon atom. Thus, in the 2,4,6-trialkylphenyl series, *free-rotation* about the C–C bond is possible in principle (Figure 1, **A**), while in the 2,6-diarylphenyl cases, especially in the 2,6-bis(2,6-dialkylphenyl)phenyl groups, the *hindered-rotation* about the C–C bond is caused by the *ortho*-substituted biphenyl unit (Figure 1, **B**). The free-rotation in the former case might cause interference in the space necessary for the particular substituent at the C1 position on the core phenyl group. The hindered-rotation in the latter case partially guarantees the space for the substituent, thus increasing the overall protecting ability which includes the lowered probability of intramolecular quenching reactions.

We envisioned that the *freeze-rotation* in certain rigid fused-ring aromatic systems would perfectly guarantee the space for the substituent (Figure 1, **C**). One example was previously

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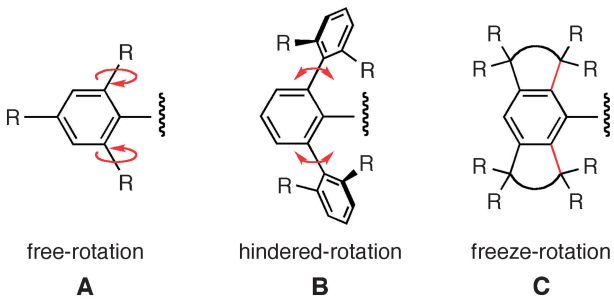
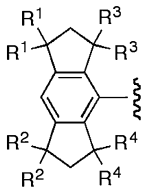


Figure 1. Three types of bulky aryl groups: 2,4,6-trialkylphenyl groups (**A**), 2,6-bis(2,6-dialkylphenyl)phenyl groups (**B**), and octa-R-substituted fused-ring aryl groups (**C**).



Mind: $R^1 = R^2 = R^3 = R^4 = Me$
Eind: $R^1 = R^2 = R^3 = R^4 = Et$
EMind: $R^1 = R^2 = Et$, $R^3 = R^4 = Me$
MEind: $R^1 = R^2 = Me$, $R^3 = R^4 = Et$
xMEind: $R^1 = R^4 = Me$, $R^2 = R^3 = Et$
PEind: $R^1 = R^2 = n$-Pr, $R^3 = R^4 = Et$
EPind: $R^1 = R^2 = Et$, $R^3 = R^4 = n$-Pr
BEind: $R^1 = R^2 = n$-Bu, $R^3 = R^4 = Et$
EBind: $R^1 = R^2 = Et$, $R^3 = R^4 = n$-Bu
P^5Eind: $R^1 = R^2 =$ pentyl, $R^3 = R^4 = Et$
EP^{5}ind: $R^1 = R^2 = Et$, $R^3 = R^4 =$ pentyl
HEind: $R^1 = R^2 =$ hexyl, $R^3 = R^4 = Et$
EHind: $R^1 = R^2 = Et$, $R^3 = R^4 =$ hexyl
MPind: $R^1 = R^2 = Me$, $R^3 = R^4 = n$-Pr
M^{s}Hind: $R^1 = R^2 = Me$, $R^3 = R^4 = -(CH_2)_5-$
MPhind: $R^1 = R^2 = Me$, $R^3 = R^4 = Ph$
M^{s}Fluind: $R^1 = R^2 = Me$, $R^3 = R^4 =$ 1,1'-biphenyl-2,2'-diyl

Chart 1.

reported by Yoshifuji et al.; thus the 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthryl group, involving two six-membered-ring fused phenyl groups, was used to stabilize a diphosphene derivative.[49] However, this fused ring group is rather hard to prepare; the corresponding anthracene derivative is obtained as a by-product during preparation of the tri-*tert*-butylbenzene. We have focused on the development of the five-membered-ring fused 1,1,3,3,5,5,7,7-octa-R-substituted *s*-hydrindacenyl groups, called the "Rind" groups as shown in Chart 1. The readily available Rind groups have several advantages over the existing bulky groups, as represented by the versatility and size-controllability by introduction of various R-substituents at the four benzylic positions in the rigid *s*-hydrindacenyl skeleton. As anticipated, we have already found that the Rind groups can stabilize some reactive species of boron, silicon, phosphorous, copper, etc.[50–59]

This report describes the synthesis and X-ray molecular structures of a series of bulky aryl bromide "Rind-Br" based on a rigid fused-ring *s*-hydrindacenyl skeleton.

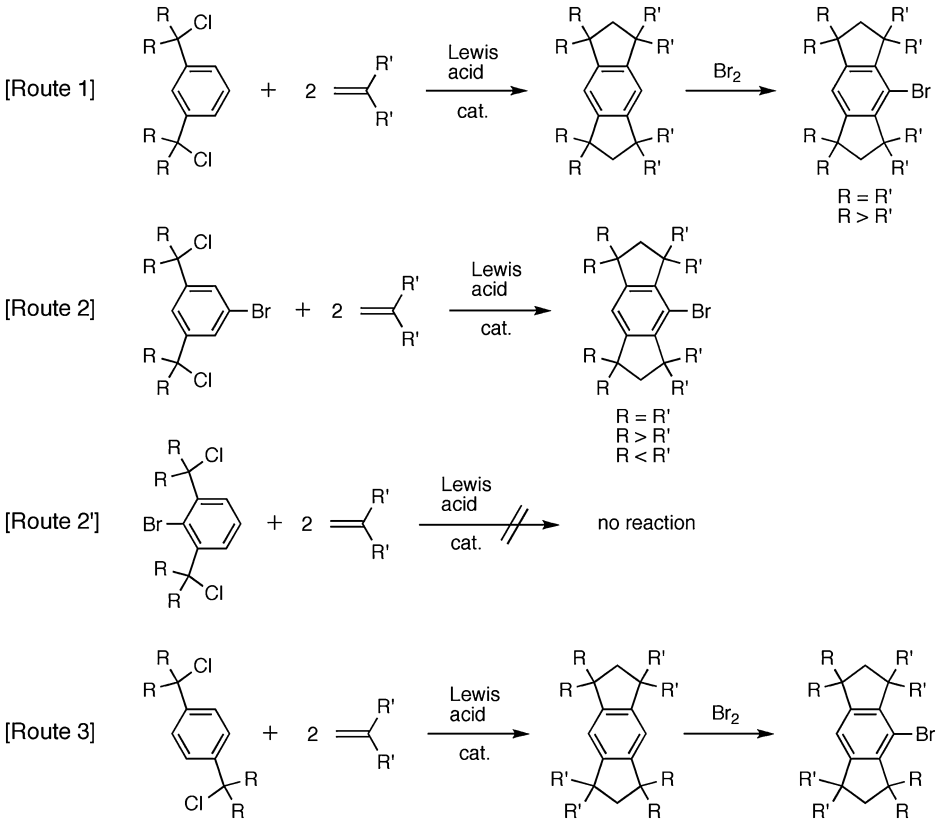
Results and Discussion

Abbreviation of Rind Groups. As shown in Chart 1, we have developed a series of octa-R-substituted *s*-hydrindacenyl groups, called the "Rind" groups.[60] The following abbreviations were used. (1) When the *s*-hydrindacenyl groups have the same eight substituents on the benzylic positions (R^1, R^2, R^3, and R^4), we abbreviated them as "Rind" groups, where R denotes the initial of the substituents as follows: M (methyl), E (ethyl), P (propyl), B (butyl), P^5 (pentyl), H (hexyl), H^7 (heptyl), O (octyl), and Ph (phenyl). For example, the octamethyl-*s*-hydrindacenyl group ($R^1 = R^2 = R^3 = R^4 = Me$) was abbreviated as the Mind group. (2) When the peripheral substituents (R^1 and R^2) are different from the proximate substituents (R^3 and R^4), we abbreviated them as "RR′ind" groups, where R and R′ denote the peripheral and proximate substituents, respectively. For example, an EMind group has the peripheral ethyl substituents and the proximate methyl substituents ($R^1 = R^2 = Et$, $R^3 = R^4 = Me$). (3) When the *s*-hydrindacenyl groups assume a cross-type arrangement of the substituents, we put an "x" ahead of RR′ind as "xRR′ind" groups, where the R substituents are smaller than the R′ substituents. For example, an xMEind group has the substituent arrangement of $R^1 = R^4 = Me$, $R^2 = R^3 = Et$. (4) When the *s*-hydrindacenyl groups have a spiro-type connection at the benzylic positions, we put a superscript "s" on R as "^{s}R," where R denotes the spiro rings. For example, an M^{s}Fluind group has two fluorene rings at the proximate benzylic positions in a spiro fashion.

In this paper, monobromo and *para*-dibromo Rind derivatives are expediently represented as "Rind-Br" and "Br-Rind-Br," respectively.

Summary of the Synthetic Routes and Characteristic Features of a Series of Rind-Br. A series of Rind-Br prepared in this study were categorized into three regioisomers, for which we developed three synthetic routes, as summarized in Scheme 1. All of them involve a sequence of intramolecular double Friedel–Crafts cyclization reactions, bromination and vice versa. In Route 1, a four-R-substituted *meta*-bisbenzylic chloride was cyclized with a 1,1-dialkylethene $CH_2{=}CR'_2$ followed by bromination. Since the bromination preferentially proceeds on the less hindered side, this route can be used only for the cases $R = R'$ and $R > R'$. Route 2, involving the bromination–cyclization sequence, can be used even for the case of $R < R'$. Thus, a *meta*-brominated precursor is subjected to the Friedel–Crafts cyclization to selectively form the desired product. This method is particularly effective for the case of $R = Me$; the cyclization reaction becomes sluggish with longer R groups ($R \geq Et$). Route 2′, starting from an *ortho*-brominated precursor, would also be envisioned as an alternative route. However, we found no reaction occurring despite many trials, thus the precursor being recovered unchanged. The reason may be ascribed to the fact that the formation of the benzylic cation is significantly retarded by the *ortho* halogen atom, as reported by H. C. Brown more than 50 years ago.[61] Route 3 is for the cross-type Rind-Br, starting from a *para*-bisbenzylic chloride.

Some significant features of the bulky Rind groups are listed below and shown in Figure 2. (1) The Rind groups are easily prepared in quantity by the intramolecular Friedel–Crafts reaction of olefins with readily available starting materials. (2) A variety of R-substituents can be introduced at the benzylic positions of the *s*-hydrindacenyl skeleton. (3) The steric bulkiness of the Rind groups can be controlled by the proximate substituents (R^3 and R^4). (4) The physical properties of the Rind groups, such as solubility or crystallinity, may be mainly attributed to the peripheral substituents (R^1 and R^2).



Scheme 1. Synthetic routes to Rind-Br.

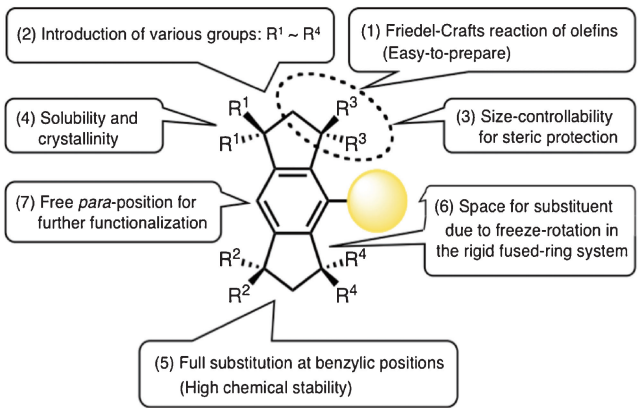


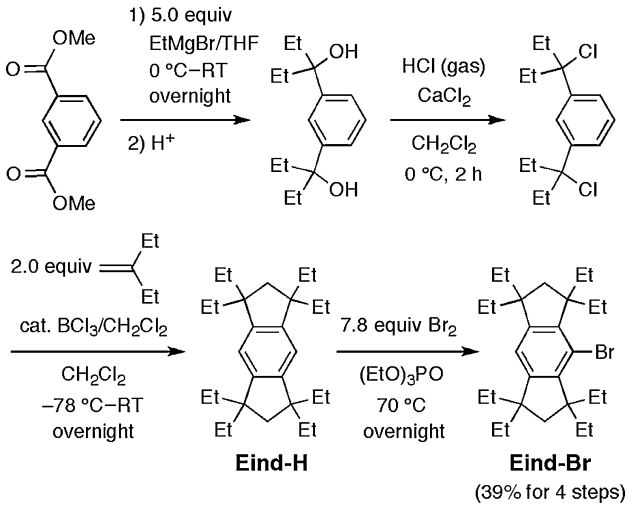
Figure 2. Features of Rind groups.

(5) The Rind groups have a high chemical stability due to the full substitution at all benzylic positions. (6) The Rind groups consisting of the rigid fused-ring framework provide a space fitted for an appropriately designed substituent between the two substituted benzylic moieties (vide infra); this space is only slightly restricted by the benzylic substituents because of the freeze-rotation fixed in the five-membered fused rings. (7) As another unique feature, the Rind groups have the unsubstituted *para*-position open for further functionalization, which would provide potentially useful *para*-phenylene types of difunctional compounds.[62–65]

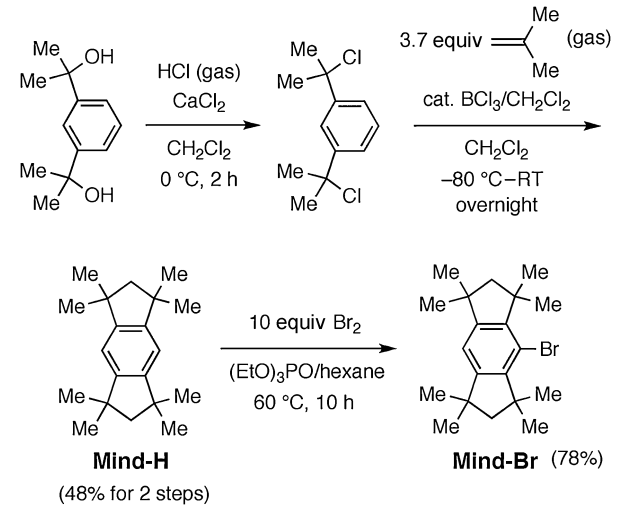
While the two *para*-dibromo derivatives, Br-Rind-Br, are described in this paper, the difunctional chemistry will be reported in detail as a future study.

Preparation of Rind-Br, Eind-Br, and Mind-Br as the Standard Symmetric Models. In 1981, Chang and Kennedy reported the formation of octamethyl-*s*-hydrindacene, Mind-H ($R^1 = R^2 = R^3 = R^4 = Me$), as an undesirable side product but in rather high yields during the cationic polymerization of isobutene with 1,4-bis(1-chloro-1-methylethyl)benzene (*para*-cumyl chloride).[66] Before that, Mind-H could be obtained by alkylation of 1,1,3,3-tetramethylindane with 2,4-dimethyl-2,4-pentanediol in the presence of $AlCl_3$.[67] Although the Kennedy's acid-catalyzed intramolecular Friedel–Crafts reaction should be useful for the construction of the *s*-hydrindacene skeleton, further experimental studies had not been explored. After a quarter of century, we started to prepare a series of Rind groups as new bulky protecting groups based on Kennedy's method.

Scheme 2 summarizes the synthetic route of Eind-Br as the most versatile.[50] 1,3-Bis(1-chloro-1-ethylpropyl)benzene, obtained from commercially available dimethyl isophthalate in two steps by textbook methods, was allowed to react with 2 equiv of 2-ethyl-1-butene in the presence of a catalytic amount of BCl_3. The intramolecular double Friedel–Crafts reaction smoothly proceeded at room temperature to produce octaethyl-*s*-hydrindacene, Eind-H. Subsequent bromination could be achieved under a rather forced condition, thus with an excess amount of Br_2 (ca. 8 to 10 equiv (molar ratio)) in $(EtO)_3PO$ as the essential solvent[68,69] at about 70 °C overnight. The desired Eind-Br was obtained after recrystallization from hexane/*i*-PrOH in 4 steps with a 39% overall yield. We can now obtain more than 50 g of colorless crystals of Eind-Br at a time by a convenient large-scale synthesis.



Scheme 2. Synthesis of Eind-Br.



Scheme 3. Synthesis of Mind-Br.

Three points deserve comment. (1) For the Lewis acid catalyzed Friedel–Crafts cyclization, we soon found that the amount of BCl_3 can be reduced to ca. 0.2 to 0.03 equiv, in contrast to Kennedy's original work in which an excess amount of BCl_3 was used.[66] (2) We also examined the use other Lewis acid catalysts such as $AlCl_3$, $AlBr_3$, and $FeCl_3$, for the preparation of Eind-H, but the cyclization reaction did not cleanly proceed. The employment of the BF_3 etherate catalyst also resulted in a lower yield. Thus, BCl_3 is considered as the most effective catalyst for this Friedel–Crafts reaction at this moment. (3) For the bromination reaction, the use of a large excess amount of Br_2 (more than 40 equiv) led to the clean formation of the *para*-dibromo-*s*-hydrindacene derivative, Br-Eind-Br. This compound can also be isolated as colorless crystals.

As shown in Scheme 3, a less bulky aryl bromide Mind-Br[62,70] was also prepared similar to Eind-Br starting from the commercially available 1,3-bis(1-hydroxy-1-methylethyl)benzene. In the Friedel–Crafts reaction, the use of a moderately excess amount of isobutene gas (ca. 4 equiv) was effective for the formation of Mind-H. A larger excess amount of isobutene gave rise to an increase in the polymer products as reported by Kennedy,[66] which made it difficult to isolate Mind-H. For the bromination reaction, a mixed solvent of $(EtO)_3PO$/hexane was applied because of the poor solubility of Mind-H in $(EtO)_3PO$. In this case, a prolonged reaction time caused further bromination of Mind-Br to give the dibromo compound, Br-Mind-Br. Thus, the careful monitoring for the appropriate reaction time (ca. 10 h) was essential to obtain the pure Mind-Br in a good yield.

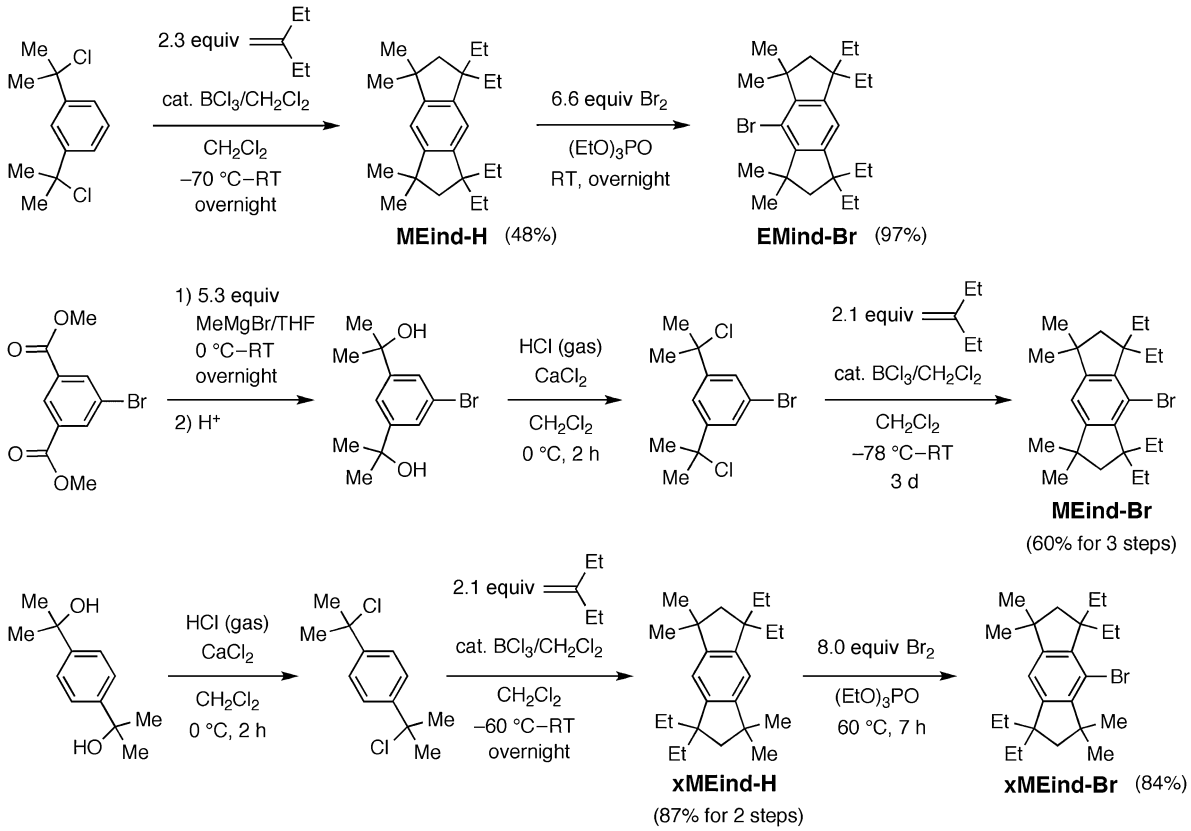
EMind-Br, MEind-Br, and xMEind-Br as Regioisomer Models. The selective synthetic routes for the three possible regioisomers containing methyl/ethyl mixed side chains are summarized in Scheme 4. The two regioisomers, EMind-Br and MEind-Br, were selectively prepared by the cyclization–bromination and bromination–cyclization sequence, respectively. Thus, the Friedel–Crafts reaction of 1,3-bis(1-chloro-1-methylethyl)benzene with 2-ethyl-1-butene gave MEind-H in 48% yield. The subsequent bromination of MEind-H with Br_2 at room temperature selectively took place on the methyl side to give EMind-Br in 97% yield. This fact clearly indicated that the methyl side is less bulky than the ethyl side.

The MEind-Br regioisomer with the bromine atom on the more hindered side was prepared starting from dimethyl 5-bromoisophthalate, which is commercially available or can be obtained via the bromination of dimethyl isophthalate with *N*-bromosuccinimide (NBS) in H_2SO_4.[71] 1-Bromo-3,5-bis(1-chloro-1-methylethyl)benzene was prepared in two steps by textbook methods. Although a prolonged reaction time (3 days) was required for the subsequent Friedel–Crafts reaction at room temperature, MEind-Br was successfully isolated as colorless crystals in 60% yield.

The cross-type xMEind-Br was also prepared starting from the commercially available 1,4-bis(1-hydroxy-1-methylethyl)-benzene. A similar Friedel–Crafts cyclization reaction of 1,4-bis(1-chloro-1-methylethyl)benzene with 2-ethyl-1-butene produced xMEind-H in 87% yield, followed by bromination to cleanly give xMEind-Br in 84% yield.

Based on the regioselectivity of the bromination, the steric bulkiness of the Rind groups, if qualitative, increases with the increasing size of the proximate substituents (R^3 and R^4) in the following order: Mind, EMind ($R^3 = R^4 = Me$) < xMEind ($R^3 = Et$, $R^4 = Me$) < MEind, Eind ($R^3 = R^4 = Et$).

PEind-Br, BEind-Br, P^{5}Eind-Br, and HEind-Br with a Series of Peripheral Alkyl Chains. For improving the solubility, a series of Rind groups having longer alkyl chains, i.e., propyl, butyl, pentyl, and hexyl, as the peripheral substituents were prepared, as shown in Scheme 5. For the introduction of the longer alkyl chains in the first step by the Grignard reaction, diethyl ether (Et_2O) was found to be better than THF to prevent the concomitant dehydration at the side chains. The Friedel–Crafts reactions with 2-ethyl-1-butene in the presence of 0.5 to 0.25 equiv of BCl_3, followed by bromination afforded a mixture of regioisomers, REind-Br and ERind-Br, in ca. 4:1 ratios. Thus, the ethyl side is somewhat less bulky than the longer alkyl side. To improve the selectivity of REind-Br, we examined various bromination conditions. For example, the bromination of EP^{5}ind-H and EHind-H with gentle warming to about 35 °C using a large excess amount of Br_2 (ca. 20 equiv) led to a somewhat better selectivity to generate P^{5}Eind-Br and HEind-Br, but the formation of minor



Scheme 4. Synthesis of EMind-Br, MEind-Br, and xMEind-Br.

products, EP[5]ind-Br and EHind-Br, could not be suppressed even under these conditions. However, the major products, PEind-Br, BEind-Br, P[5]Eind-Br, and HEind-Br, could be isolated as colorless crystals by recrystallization from hexane or hexane/EtOH in 10–21% overall yields for the 4 steps. The minor isomers, ERind-Br, could not be isolated in pure form. Among the major products, the molecular structure of HEind-Br has been determined by X-ray crystallography (vide infra). While a higher solubility arises from the longer alkyl chains, the crystallinity might be based on the rigid fused-ring *s*-hydrindacene framework.

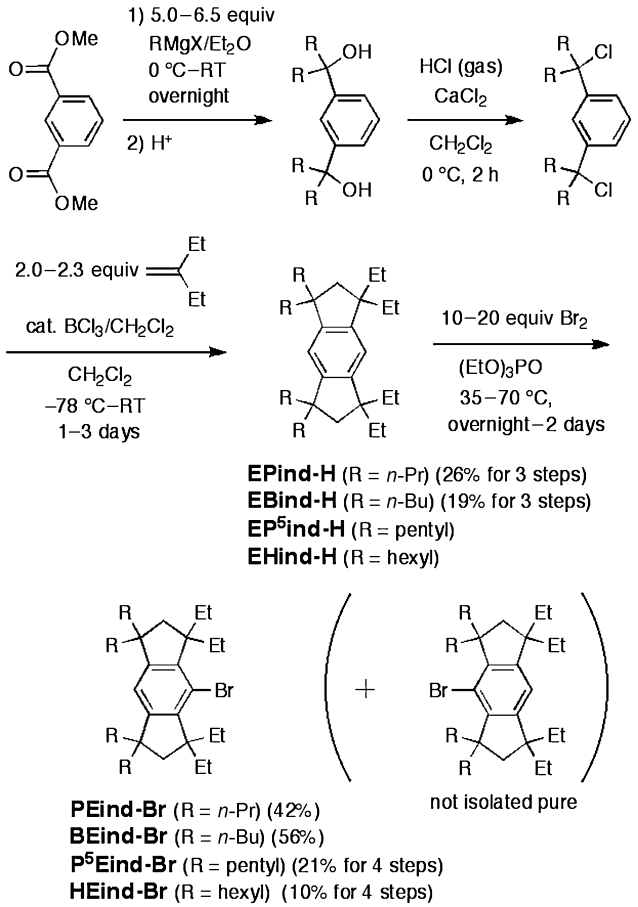
As expected, these four REind-Br have higher solubilities in the common organic solvents with the alkyl chain extension. For example, the solubility in hexane increases in the following order: Eind-Br ($0.03\,g\,mL^{-1}$) < PEind-Br ($0.10\,g\,mL^{-1}$) ≈ BEind-Br ($0.10\,g\,mL^{-1}$) < P[5]Eind-Br ($0.22\,g\,mL^{-1}$) < HEind-Br ($0.28\,g\,mL^{-1}$) ≈ MEind-Br ($0.27\,g\,mL^{-1}$): the last is an exception due to unknown factors.

MPind-Br, M[s]Hind-Br, MPhind-Br, and M[s]Fluind-Br with a Variety of Proximate Substituents. The steric effects of the Rind groups are mainly dependent on the identity of the proximate R-substituents. We have synthesized two pairs of MRind-Br, consisting of two open-chain substituents and their closed-ring spiro-type analog; one pair is MPind-Br and M[s]Hind-Br, and the other is MPhind-Br and M[s]Fluind-Br. All compounds were prepared by the bromination–cyclization sequence starting from 1-bromo-3,5-bis(1-chloro-1-methylethyl)benzene, as shown in Scheme 6. The former two were obtained without difficulty using 2-propyl-1-pentene and methylenecyclohexane, respectively. It may be noted that 2-propyl-1-pentene was prepared by the nickel-catalyzed cross-coupling reaction between 1,1-dichloroethene and *n*-PrMgCl.[72,73] The spiro M[s]Hind-Br has a lower solubility in the common solvents relative to MPind-Br, due to the higher rigidity of the spiro-ring system (vide infra).

The Friedel–Crafts reaction with 1,1-diphenylethene competed with its self-dimerization to give an indane derivative as a side product, but the MPhind-Br was isolated as colorless crystals in 26% yield after removal of the by-product by Kugelrohr distillation followed by recrystallization from acetone/hexane. The spiro compound, M[s]Fluind-Br, in which the *s*-hydrindacene skeleton is connected to the two fluorene rings through the two quaternary carbon atoms at the benzylic positions, was obtained by the Friedel–Crafts reaction using dibenzofulvene in 76% yield, without the competing self-dimerization of the latter.

Molecular Structures of Rind-Br. The molecular structures of a series of bromo-*s*-hydrindacenes, Eind-Br, HEind-Br, MPind-Br, M[s]Hind-Br, MPhind-Br, and M[s]Fluind-Br,[52] have been determined by X-ray crystallography, as shown in Figure 3. These molecules display unique structural diversities based on the rigid fused-ring *s*-hydrindacenyl skeleton and the side groups, as can be seen from the space-filling models. Their crystallographic and structural features are as follows.

Eind-Br: This molecule has a C_2 symmetry in the crystal with the twofold axis through the Br–C bond. The eight ethyl groups are alternatively arranged in two different orientations, i.e., the up and side directions.



Scheme 5. Synthesis of REind-Br.

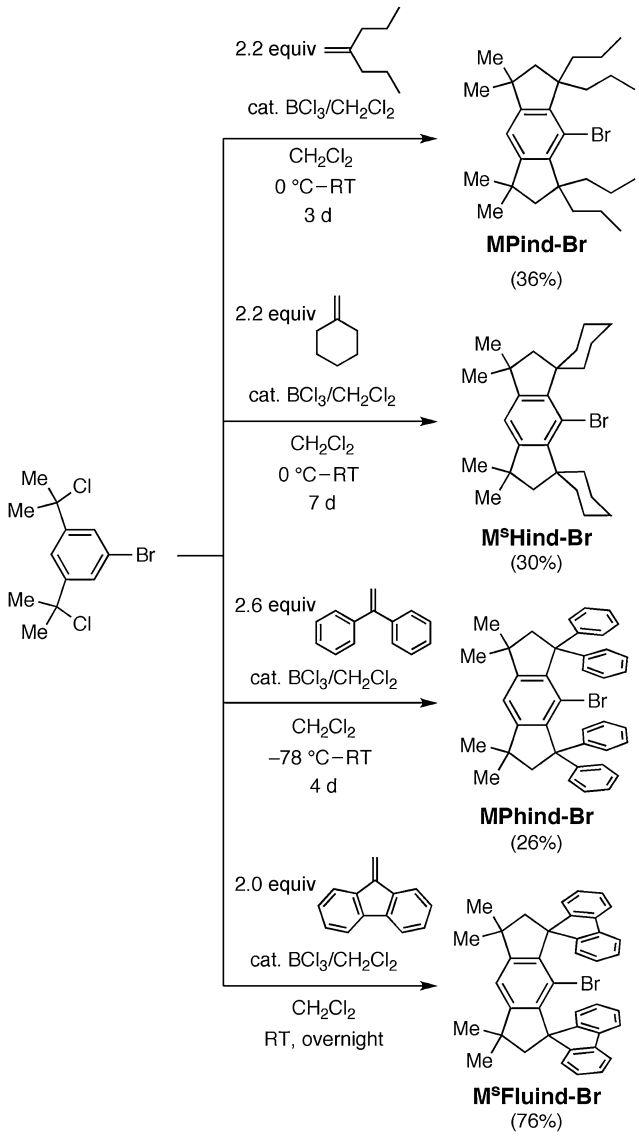
HEind-Br: The four peripheral hexyl groups tend to align perpendicular to the *s*-hydrindacene plane in the crystal. The distance between the terminal carbon atoms of the two hexyl substituents on the same benzylic position is about 13 Å.

MPind-Br: An alignment of the proximate propyl groups is found in the crystal. The distance between the terminal carbon atoms of the two propyl substituents on the same benzylic position is about 7.5 Å. The packing diagram of the MPind-Br indicates the existence of intermolecular C–H$\cdots\pi$ interactions between the central benzene ring and the terminal C–H bonds of the propyl chains (not shown in text).

M^{s}Hind-Br: The two cyclohexane rings adopt the chair conformation with staying separated from the bromine atom. Thus, the molecular structure is much different from that of the MPind-Br mentioned above.

MPhind-Br: The four phenyl groups are oriented not in the C_2 symmetric, but in nearly the C_s symmetric structure with a mirror plane perpendicular to the central benzene ring in the crystal. The distances between the bromine atom and the closest *ipso*-carbon atoms of the phenyl groups are 3.230 and 3.263 Å.

M^{s}Fluind-Br: The bromine atom is sandwiched between the two fluorene planes connected to the *s*-hydrindacene skeleton. The atomic distances between the bromine atom and the closest aromatic carbon atoms in the five-membered rings of the fluorenyl groups are 3.305–3.549 Å, somewhat longer than those in the MPhind-Br.



Scheme 6. Synthesis of MRind-Br.

As shown in the top and front views of the space-filling models of Rind-Br, the steric environment around the bromine atom in the crystals seems to be much different from each other. However, it is still difficult to estimate the precise steric bulkiness of the Rind groups on the basis of the X-ray molecular structures, because dynamic steric factors must be taken into account in any reactions of the Rind-substituted species in solution. In this regard, we have obtained clear-cut results to demonstrate that the steric bulkiness of MPhind $\approx$ M^{s}Fluind is much greater than EMind $\approx$ Eind in organocopper(I) chemistry.[52] Thus, while the EMind and Eind groups on copper lead to the selective formation of dimers of organobromocuprate and diorganocuprate, the MPhind and M^{s}Fluind groups exclusively afforded the corresponding monomers.

Conclusion

We have developed a series of fused-ring octa-R-substituted *s*-hydrindacenyl bromides. All the Rind-Br can be transformed into the reactive bulky aryllithium "Rind-Li" as the key

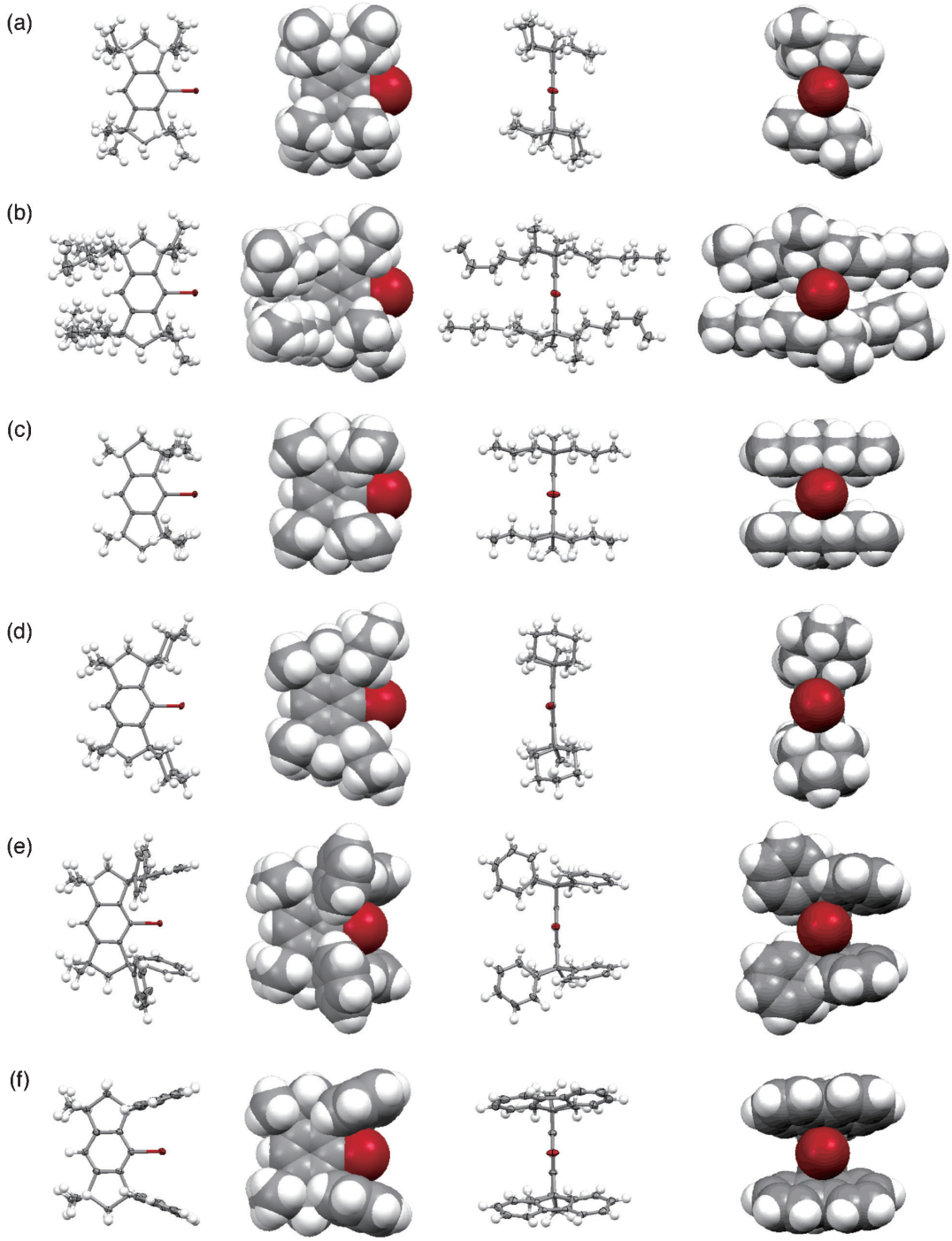


Figure 3. Molecular structures of (a) Eind-Br, (b) HEind-Br, (c) MPind-Br, (d) M^{s}Hind-Br, (e) MPhind-Br, and (f) M^{s}Fluind-Br: top views (left), front views (center), and space filling models (right).

reagents for introduction into a variety of main group elements and transition metals. Thus, a series of Rind groups have already been found to act as unique protecting groups not only in the main group chemistry of groups 13–17, but also in organo-transition metal chemistry.[50–59] Further structural elaboration would be envisaged for future and wider applications, as represented by the introduction of chirality and functional groups as the side groups and/or on the vacant *para*-position. Such studies are now under investigation.

Experimental

General Procedure. All experiments of the air- and moisture-sensitive compounds were performed under an inert atmosphere of argon or nitrogen. Anhydrous THF, Et_2O, dichloromethane, hexane, and toluene were dried by passage through columns of activated alumina and a supported copper catalyst supplied by Hansen & Co., Ltd. All other chemicals and gases were used as received. Dibenzofulvene[74] and dimethyl

5-bromoisophthalate[71] were prepared by the modified literature procedures. Thin layer chromatography (TLC) was performed on plates coated with 0.25 nm thick Silica Gel 60 F-254 (Merck Ltd.). Column chromatography was performed using neutral Silica Gel 60 N (Kanto Chemical Co., Ltd.), Kieselgel 60 (70–230 mesh) (Merck), or neutral silica gel PSQ 100B (Fuji Silysia Chemical). Gas chromatography mainly for the monitoring of the bromination reaction of Rind-H was performed by a SHIMADZU GC-8A with SHIMADZU column packing (Silicone SE-30 5% or OV-17%). The nuclear magnetic resonance (NMR) measurements were carried out by a JEOL ECS-400 spectrometer (399.8 MHz for ^{1}H and 100.5 MHz for ^{13}C) or JEOL EX-270 spectrometer (270.0 MHz for ^{1}H and 67.9 MHz for ^{13}C). Chemical shifts (δ) are listed by definition as dimensionless numbers and relative to ^{1}H (residual) or ^{13}C NMR chemical shifts of the solvent (residual C_6D_5H in C_6D_6, $^1H(\delta) = 7.15$ and $^{13}C(\delta) = 128.0$; residual $CHCl_3$ in $CDCl_3$, $^1H(\delta) = 7.24$ and $^{13}C(\delta) = 77.0$). The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). The elemental analyses (C and H) and mass spectroscopy were performed at the Advanced Technology Support Division of RIKEN Advanced Science Institute or Micro Analysis Division and Mass Spectrum Division of Institute for Chemical Research, Kyoto University. Melting points (mp) were determined by a Yazawa BY-2 instrument or a Stanford Research Systems MPA100 OptiMelt instrument.

The solubility measurement experimental procedure is as follows. A suspension of REind-Br in hexane was ultrasonically treated for 3 min. After the suspension was stored for 10 min, a portion of the upper clear saturated solution (100 μL) was transferred to a weighed flask. The solvent was evaporated and the remaining solid REind-Br was dried under vacuum for 2 h and weighed again.

Preparation of Eind-Br (4-Bromo-1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacene). A large-scale synthesis of Eind-Br was carried out on the basis of the previously reported procedures[50] with some modifications.

(1) 1,3-Bis(1-ethyl-1-hydroxypropyl)benzene: To a solution of ethylmagnesium bromide (1.65 mol) in THF (600 mL) was dropwise added a solution of dimethyl isophthalate (64.0 g, 0.33 mol) in THF (150 mL) at 0 °C over a 2-h period. After stirring overnight at room temperature, the reaction mixture was quenched with 3 M HCl aq. (600 mL) at 0 °C. After the organic layer was separated, the aqueous layer was extracted with Et_2O (200 mL). The combined organic layer was successively washed with water, $NaHCO_3$ aq., and brine and dried over Na_2SO_4. After evaporation of the solvent, *i*-PrOH (100 mL) was added to the residue. The volatiles were then removed under reduced pressure to give the crude 1,3-bis(1-ethyl-1-hydroxypropyl)benzene as a light yellow solid (81.5 g, 0.33 mol, 99% yield if pure). The crude product was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.73 (t, $J = 7.5$ Hz, 12H, CH_3), 1.76–1.91 (m, 8H, CH_2), 7.20–7.35 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$): δ 8.1, 35.3, 77.7, 122.7, 123.5, 127.8, 145.3.

(2) 1,3-Bis(1-chloro-1-ethylpropyl)benzene: To a solution of 1,3-bis(1-ethyl-1-hydroxypropyl)benzene (81.5 g, 0.33 mol if pure) in CH_2Cl_2 (500 mL) was added $CaCl_2$ powder (ca. 100 g), and then HCl gas was introduced into the mixture for 2 h at 0 °C. After the reaction was completed (checked by ^{1}H NMR spectra), N_2 gas was bubbled for 1 h to remove the remaining HCl gas, and the reaction mixture was filtered through a plug of Celite®. The filtrate was concentrated on a rotary evaporator to reduce the volume to ca. 200 mL. The CH_2Cl_2 solution of the crude product was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, $J = 7.5$ Hz, 12H, CH_3), 2.16 (q, $J = 7.5$ Hz, 8H, CH_2), 7.27–7.38 (m, 3H, ArH), 7.54–7.55 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$): δ 9.4, 37.7, 81.0, 125.2, 125.4, 127.8, 142.6.

(3) Eind-H (1,1,3,3,5,5,7,7-Octaethyl-*s*-hydrindacene): To the CH_2Cl_2 solution of 1,3-bis(1-chloro-1-ethylpropyl)benzene (ca. 200 mL, 0.33 mol if pure) and 2-ethyl-1-butene (55.5 g, 0.66 mol) was dropwise added BCl_3 (1.0 M solution in CH_2Cl_2, 115 mL, 115 mmol) at 0 °C over a 1 h period. After stirring overnight at room temperature, the reaction mixture was quenched with 1 M NaOH aq. (500 mL) at 0 °C. After the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (200 mL). The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After evaporation of the solvent, the residual solid was dissolved in hexane and filtered through a short silica gel column. The solvent was removed from the filtrate under reduced pressure to give the crude Eind-H as a colorless solid (94.2 g, 0.25 mol, 75% yield if pure). The crude product was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.79 (t, $J = 7.5$ Hz, 24H, CH_3), 1.48–1.69 (m, 16H, CH_2), 1.77 (s, 4H, CH_2), 6.63 (s, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.3, 33.2, 45.4, 48.9, 118.8, 147.6.

(4) Eind-Br: To a solution of Eind-H (94.2 g, 0.25 mol if pure) in triethyl phosphate (600 mL) was added bromine (100 mL, 312 g, 1.95 mol). The reaction mixture, protected from light and moisture, was stirred overnight at 70 °C. After completion of the reaction (checked by GC analysis), the residual bromine was quenched with Na_2SO_3 aq. The resulting yellow suspension was filtered and washed with water to give the crude product as a light yellow solid. This solid was dissolved in hexane and filtered through a short silica gel column. After the solvent was removed from the filtrate, the residue was recrystallized from hexane (200 mL) and *i*-PrOH (100 mL) to give Eind-Br as colorless crystals (59.2 g, 0.13 mol, 39% yield for 4 steps): mp 157.3–158.2 °C. ^{1}H NMR ($CDCl_3$): δ 0.77 (t, $J = 7.3$ Hz, 12H, CH_3), 0.81 (t, $J = 7.3$ Hz, 12H, CH_3), 1.49–1.57 (m, 4H, CH_2), 1.58–1.66 (m, 4H, CH_2), 1.77–1.86 (m, 4H, CH_2), 1.83 (s, 4H, CH_2), 1.92–2.01 (m, 4H, CH_2), 6.59 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.1, 9.3, 31.1, 32.9, 43.1, 47.9, 53.2, 118.2, 118.6, 144.9, 151.9. Anal. Calcd for $C_{28}H_{45}Br$: C, 72.86; H, 9.83%. Found: C, 72.82; H, 9.80%.

The ^{1}H and ^{13}C NMR spectra of Eind-Br are shown in Figure 4.

Preparation of Br-Eind-Br (4,8-Dibromo-1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacene). To a solution of Eind-H (20.2 g, 52.8 mmol) in triethyl phosphate (380 mL) was added bromine (150 mL, 468 g, 2.93 mol). The reaction mixture, protected from light and moisture, was stirred for 4 days at 70 °C. After completion of the reaction (checked by GC analysis), the residual bromine was quenched with Na_2SO_3 aq. The resulting

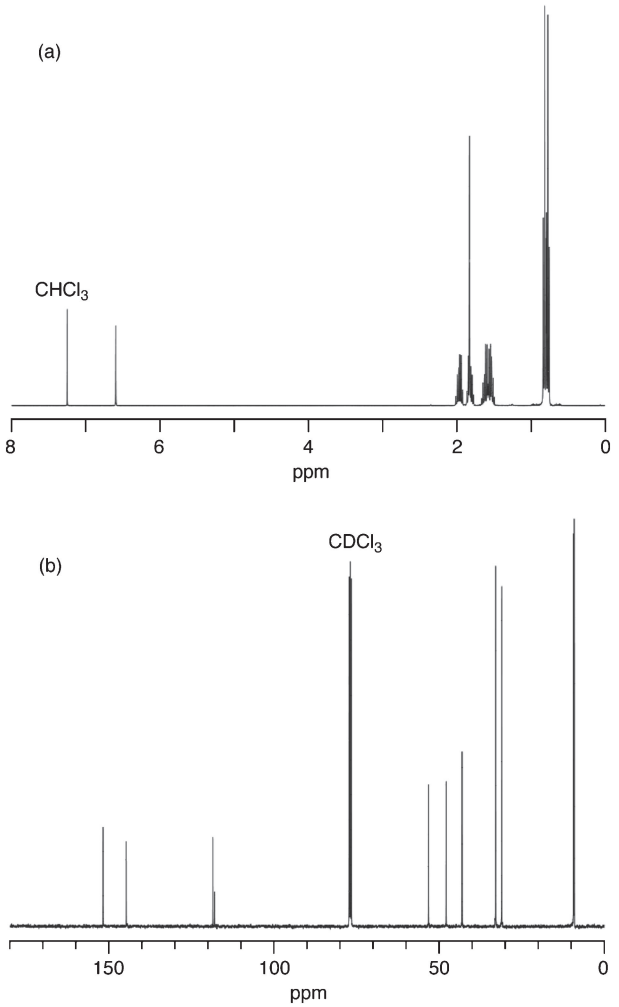


Figure 4. (a) ^{1}H and (b) ^{13}C NMR spectra of Eind-Br ($CDCl_3$, 298 K).

yellow suspension was filtered and the residue was washed with water and ethanol, and dried to give Br-Eind-Br as colorless crystals (15.5 g, 28.7 mmol, 54% yield): mp 209–211 °C. ^{1}H NMR ($CDCl_3$): δ 0.82 (t, $J = 7.3$ Hz, 24H, CH_3), 1.80–1.95 (m, 16H, CH_2), 1.89 (s, 4H, CH_2); ^{13}C NMR ($CDCl_3$): δ 9.2, 30.7, 40.5, 52.2, 118.9, 149.2. Anal. Calcd for $C_{28}H_{44}Br_2$: C, 62.23; H, 8.21%. Found: C, 62.24; H, 8.23%.

Preparation of Mind-Br (4-Bromo-1,1,3,3,5,5,7,7-octamethyl-*s*-hydrindacene).[62] **(1) 1,3-Bis(1-chloro-1-methylethyl)benzene:** 1,3-Bis(1-hydroxy-1-methylethyl)benzene (40.0 g, 206 mmol) was treated with HCl gas in the presence of $CaCl_2$ powder (ca. 40 g) in CH_2Cl_2 (400 mL) to give 1,3-bis(1-chloro-1-methylethyl)benzene as a light yellow oil (44.2 g, 190 mmol, 93% yield), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 12H, CH_3), 7.33 (t, $J = 7.8$ Hz, 1H, ArH), 7.49 (dd, $J = 1.8$ Hz, $J = 7.8$ Hz, 2H, ArH), 7.83 (t, $J = 7.8$ Hz, 1H, ArH).

(2) Mind-H (1,1,3,3,5,5,7,7-Octamethyl-*s*-hydrindacene): To a solution of 1,3-bis(1-chloro-1-methylethyl)benzene (44.5 g, 190 mmol if pure) in CH_2Cl_2 (300 mL) was introduced isobutene gas (ca. 40 g, ca. 0.71 mol) at −80 °C over a 2-h period. To the mixture was then added BCl_3 (1.0 M solution in CH_2Cl_2, 40 mL, 40 mmol) at −80 °C. The resulting mixture was warmed to 0 °C, then stirred overnight. After a similar work-up procedure to Eind-H, the crude Mind-H was filtered through a short silica gel column. The solvent was removed from the filtrate under reduced pressure to give Mind-H as a colorless solid (26.7 g, 98.7 mmol, 48% yield for 2 steps): mp 85 °C (sublimation), 210 °C (Ref. 66). ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 24H, CH_3), 1.89 (s, 4H, CH_2), 6.80 (s, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 31.7, 42.1, 57.2, 115.9, 149.9. Anal. Calcd for $C_{20}H_{30}$: C, 88.82; H, 11.18%. Found: C, 88.79; H, 11.23%.

(3) Mind-Br (4-Bromo-1,1,3,3,5,5,7,7-octamethyl-*s*-hydrindacene): To a heated solution of Mind-H (7.00 g, 25.9 mmol) in triethyl phosphate (120 mL) and hexane (120 mL) at 60 °C was added bromine (13.3 mL, 259 mmol). The reaction mixture, protected from light and moisture, was stirred for 10 h at 60 °C. After completion of the reaction (checked by GC analysis), the residual bromine was quenched with Na_2SO_3 aq. The resulting light yellow solid was collected by filtration and washed with ethanol to give Mind-Br as a colorless solid (first crop, 5.02 g. 14.3 mmol, 55% yield). To the filtrate was added toluene, the organic layer was separated, washed with H_2O and brine, dried over $MgSO_4$, and filtered. After evaporation of the solvent from the filtrate, the residual solid was washed with ethanol to give Mind-Br as a colorless solid (second crop, 2.15 g. 6.15 mmol, 23% yield): mp 130 °C (sublimation), 225–225.5 °C (Ref. 70). ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 12H, CH_3), 1.51 (s, 12H, CH_3), 1.93 (s, 4H, CH_2), 6.77 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 29.2, 31.6, 41.2, 45.6, 59.0, 115.8, 146.4, 150.1, 153.7. HRMS (EI) Calcd for $C_{20}H_{29}{}^{79}Br$: 348.1453. Found: 348.1461. Anal. Calcd for $C_{20}H_{29}Br$: C, 68.76; H, 8.37%. Found: C, 68.71; H, 8.42%.

Preparation of Br-Mind-Br (4,8-Dibromo-1,1,3,3,5,5,7,7-octamethyl-*s*-hydrindacene). To a solution of Mind-H (2.70 g, 10.0 mmol) in triethyl phosphate (80 mL) and hexane (80 mL) at 60 °C was added bromine (31 mL, 96.1 g, 0.60 mol). The reaction mixture, protected from light and moisture, was stirred for 8 h at 70 °C. After completion of the reaction (checked by ^{1}H NMR), the residual bromine was quenched with Na_2SO_3 aq. The resulting yellow suspension was filtered and the residue was washed with water and ethanol to give Br-Mind-Br as off-white crystals (3.66 g, 8.53 mmol, 85% yield): mp 178 °C (sublimation). ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 24H, CH_3), 1.96 (s, 4H, CH_2); ^{13}C NMR ($CDCl_3$): δ 29.1, 44.6, 61.2, 117.4, 150.1. Anal. Calcd for $C_{20}H_{28}Br_2$: C, 56.09; H, 6.59%. Found: C, 56.03; H, 6.51%.

Preparation of EMind-Br (4-Bromo-1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacene.[75] **(1) MEind-H (1,1,7,7-Tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacene):** This compound was prepared similar to Eind-H starting from 1,3-bis(1-chloro-1-methylethyl)benzene (37.5 g, 0.16 mol), 2-ethyl-1-butene (31.0 g, 0.37 mol), and BCl_3 (1.0 M solution in CH_2Cl_2, 10 mL, 10 mmol) in CH_2Cl_2 (200 mL), and was isolated as a colorless solid by Kugelrohr distillation (135–150 °C/0.1 mmHg) (25.6 g, 78.4 mmol, 48% yield): mp 63–65 °C. ^{1}H NMR ($CDCl_3$): δ 0.76 (t, $J = 7.4$ Hz, 12H, CH_3), 1.26 (s, 12H, CH_3), 1.56–1.61 (m, 8H, CH_2), 1.83 (s, 4H, CH_2), 6.59 (s, 1H, ArH), 6.75 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.2, 32.2, 33.1, 41.7, 49.5, 51.3, 115.9, 118.5, 146.4, 151.0. HRMS (EI) Calcd for $C_{24}H_{38}$: 326.2974. Found: 326.2958.

(2) EMind-Br: A reaction of MEind-H (14.3 g, 43.8 mmol) with bromine (15 mL, 0.29 mol) in triethyl phosphate (150 mL) at room temperature overnight gave EMind-Br. After the reaction mixture was quenched with Na_2SO_3 aq., the resulting yellow suspension was filtered and washed with water and EtOH, and dried in vacuo to afford EMind-Br as colorless crystals (17.2 g, 42.4 mmol, 97% yield): mp 112–113 °C. ^{1}H NMR ($CDCl_3$): δ 0.74 (t, $J = 7.6$ Hz, 12H, CH_3), 1.49 (s, 12H, CH_3), 1.53–1.58 (m, 8H, CH_2), 1.86 (s, 4H, CH_2), 6.54 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.0, 29.4, 33.1, 45.3, 48.6, 52.8, 116.9, 118.4, 147.4, 150.2. HRMS (EI) Calcd for $C_{24}H_{37}{}^{79}Br$: 404.2079. Found: 404.2068. Anal. Calcd for $C_{24}H_{37}Br$: C, 71.09; H, 9.20%. Found: C, 71.47; H, 9.11%.

Preparation of MEind-Br (4-Bromo-3,3,5,5-tetraethyl-1,1,7,7-tetramethyl-*s*-hydrindacene).[75] **(1) 1-Bromo-3,5-bis(1-hydroxy-1-methylethyl)benzene:** This compound was prepared similar to 1,3-bis(1-ethyl-1-hydroxypropyl)benzene starting from dimethyl 5-bromoisophthalate[71] (7.00 g, 25.6 mmol) and methylmagnesium bromide (3.0 M solution in Et_2O, 45 mL, 135 mmol) in THF (150 mL). The resulting light yellow solid was washed with hexane and CH_2Cl_2 to give the crude 1-bromo-3,5-bis(1-hydroxy-1-methylethyl)benzene as a colorless solid (5.54 g, 20.3 mmol, 79% if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 12H, CH_3), 7.48 (d, $J = 1.6$ Hz, 2H, ArH), 7.53 (t, $J = 1.6$ Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 31.7, 72.4, 119.2, 122.3, 126.1, 151.3.

(2) 1-Bromo-3,5-bis(1-chloro-1-methylethyl)benzene: The crude 1-bromo-3,5-bis(1-hydroxy-1-methylethyl)benzene (4.09 g, 15.0 mmol if pure) was treated with HCl gas in the presence of $CaCl_2$ powder (ca. 10 g) in CH_2Cl_2 (150 mL) to give 1-bromo-3,5-bis(1-chloro-1-methylethyl)benzene as a colorless solid (4.63 g, 15.0 mmol, 100% yield if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 1.96 (s, 12H, CH_3), 7.60 (d, $J = 1.8$ Hz, 2H, ArH), 7.72 (t, $J = 1.8$ Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 34.2, 68.5, 121.7, 122.1, 127.9, 148.3.

(3) MEind-Br: This compound was prepared from 1-bromo-3,5-bis(1-chloro-1-methylethyl)benzene (4.63 g, 15.0 mmol if pure), 2-ethyl-1-butene (2.70 g, 32.1 mmol), BCl_3 (1.0 M solution in CH_2Cl_2, 15 mL, 15 mmol), and CH_2Cl_2 (80 mL), and was isolated as colorless crystals by recrystallization from CH_2Cl_2/MeOH (3.65 g, 9.00 mmol, 60% yield for 3 steps): mp 86–89 °C. ^{1}H NMR ($CDCl_3$): δ 0.72 (t, $J = 7.6$ Hz, 12H, CH_3), 1.24 (s, 12H, CH_3), 1.58–1.68 (m, 4H, CH_2), 1.87 (s, 4H, CH_2), 2.03–2.13 (m, 4H, CH_2), 6.67 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.5, 31.4, 32.1, 40.8, 50.0, 54.1, 115.8, 117.6, 143.1, 155.2. HRMS (EI) Calcd for $C_{24}H_{37}{}^{79}Br$: 404.2079. Found: 404.2074. Anal. Calcd for $C_{24}H_{37}Br$: C, 71.09; H, 9.20%. Found: C, 70.64; H, 9.17%.

Preparation of xMEind-H (1,1,5,5-Tetraethyl-3,3,7,7-tetramethyl-*s*-hydrindacene).[75] **(1) 1,4-Bis(1-chloro-1-methylethyl)benzene:**[66] 1,4-Bis(1-hydroxy-1-methylethyl)benzene (19.4 g, 100 mmol) was treated with HCl gas in the presence of $CaCl_2$ powder (ca. 35 g) in CH_2Cl_2 (300 mL) to give 1,3-bis(1-chloro-1-methylethyl)benzene as a yellow solid (22.8 g, 98.7 mmol, 99% yield), which was used for the next reaction without further purification.

(2) xMEind-H (1,1,5,5-Tetraethyl-3,3,7,7-tetramethyl-*s*-hydrindacene): This compound was prepared similar to Eind-H starting from 1,4-bis(1-chloro-1-methylethyl)benzene (22.8 g, 98.7 mmol if pure), 2-ethyl-1-butene (17.2 g, 205 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 16 mL, 16 mmol) in CH_2Cl_2 (160 mL), and was isolated as colorless crystals (28.4 g, 86.9 mmol, 87% yield for 2 steps): mp 65–67 °C. ^{1}H NMR ($CDCl_3$): δ 0.78 (t, $J = 7.3$ Hz, 12H, CH_3), 1.26 (s, 12H, CH_3), 1.49–1.69 (m, 8H, CH_2), 1.84 (s, 4H, CH_2), 6.69 (s, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.2, 32.1, 32.9, 41.9, 49.5, 51.5, 117.2, 147.1, 150.4. HRMS (EI) Calcd for $C_{24}H_{38}$: 326.2974. Found: 326.2982.

(3) xMEind-Br: The reaction of xMEind-H (5.00 g, 15.3 mmol) with bromine (6.3 mL, 123 mmol) in triethyl phosphate (130 mL) at 60 °C for 7 h gave xMEind-Br as colorless crystals (5.20 g, 12.8 mmol, 84% yield): mp 96–97 °C. ^{1}H NMR ($CDCl_3$): δ 0.73 (t, $J = 8.0$ Hz, 6H, CH_3), 0.75 (t, $J = 8.0$ Hz, 6H, CH_3), 1.23 (s, 6H, CH_3), 1.48 (s, 6H, CH_3), 1.48–1.62 (m, 4H, CH_2), 1.60–1.71 (m, 2H, CH_2), 1.87 (s, 4H, CH_2), 2.00–2.07 (m, 2H, CH_2), 6.61 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.1, 9.5, 29.4, 31.3, 32.0, 33.1, 40.8, 45.2, 48.6, 49.7, 53.1, 54.1, 117.1, 117.2, 143.6, 147.1, 150.9, 154.5. HRMS (EI) Calcd for $C_{24}H_{37}{}^{79}Br$: 404.2079. Found: 404.2068. Anal. Calcd for $C_{24}H_{37}Br$: C, 71.09; H, 9.20%. Found: C, 70.69; H, 9.30%.

Preparation of PEind-Br (4-Bromo-3,3,5,5-tetraethyl-1,1,7,7-tetrapropyl-*s*-hydrindacene).[75] **(1) 1,3-Bis(1-hydroxy-1-propylbutyl)benzene:** The reaction of dimethyl isophthalate (7.77 g, 40.0 mmol) with propylmagnesium chloride (2.0 M solution in Et_2O, 100 mL, 200 mmol) in THF (100 mL) gave 1,3-bis(1-hydroxy-1-propylbutyl)benzene as a light yellow oil (11.3 g, 36.9 mmol, 92% if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.81 (t, $J = 7.2$ Hz, 12H, CH_3), 0.96–1.10 (m, 4H, CH_2), 1.18–1.34 (m, 4H, CH_2), 1.68–1.84 (m, 8H, CH_2), 1.78 (s, 2H, OH), 7.16–7.22 (m, 2H, ArH), 7.22–7.28 (m, 1H, ArH), 7.32–7.36 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.4, 16.7, 45.3, 77.2, 122.1, 123.1, 127.6, 146.1.

(2) 1,3-Bis(1-chloro-1-propylbutyl)benzene: The crude 1,3-bis(1-hydroxy-1-propylbutyl)benzene (11.3 g, 36.9 mmol if pure) was treated with HCl gas in the presence of $CaCl_2$ powder (ca. 15 g) in CH_2Cl_2 (100 mL) to give 1,3-bis(1-chloro-1-propylbutyl)benzene as a brown oil (12.7 g, 36.9 mol, 100% yield if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $J = 7.2$ Hz, 12H, CH_3), 1.12–1.24 (m, 4H, CH_2), 1.30–1.50 (m, 4H, CH_2), 2.04–2.12 (m, 8H, CH_2), 7.20–7.40 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.0, 17.9, 47.2, 79.4, 124.7, 125.1, 127.7, 143.3.

(3) EPind-H (1,1,7,7-Tetraethyl-3,3,5,5-tetrapropyl-*s*-hydrindacene): This compound was prepared similar to Eind-H starting from 1,3-bis(1-chloro-1-propylbutyl)benzene (12.7 g, 36.9 mmol if pure), 2-ethyl-1-butene (7.00 g, 82.6 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 40 mL, 40 mmol) in CH_2Cl_2 (80 mL), and was isolated as colorless crystals (4.21 g, 9.58 mmol, 26% yield for 3 steps): mp 125–128 °C. ^{1}H NMR ($CDCl_3$): δ 0.79 (t, $J = 7.3$ Hz, 12H, CH_3), 0.85 (t, $J = 7.3$ Hz, 12H, CH_3), 1.08–1.21 (m, 4H, CH_2), 1.22–1.35 (m, 4H, CH_2), 1.41–1.67 (m, 16H, CH_2), 1.78 (s, 4H, CH_2), 6.61 (s, 1H, ArH), 6.64 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.2, 15.0, 18.1, 33.1,

44.1, 46.4, 48.6, 49.0, 118.6, 118.9, 147.4, 148.4. HRMS (EI) Calcd for $C_{32}H_{54}$: 438.4226. Found: 438.4234.

(4) PEind-Br: The reaction of EPind-H (4.13 g, 9.42 mmol) and bromine (5.0 mL, 100 mmol) in triethyl phosphate (80 mL) at 60 °C overnight gave a mixture of regioisomers, PEind-Br and EPind-Br, in ca. 4:1 ratio as estimated by ^{1}H NMR spectrum. The major product, PEind-Br, was isolated as colorless crystals by repeated recrystallization from hexane (2.04 g, 3.94 mmol, 42% yield): mp 130–131 °C. ^{1}H NMR ($CDCl_3$): δ 0.77 (t, $J = 7.3$ Hz, 12H, CH_3), 0.86 (t, $J = 7.3$ Hz, 12H, CH_3), 1.11–1.37 (m, 8H, CH_2), 1.40–1.48 (m, 4H, CH_2), 1.53–1.61 (m, 4H, CH_2), 1.76–1.85 (m, 4H, CH_2), 1.84 (s, 4H, CH_2), 1.91–2.00 (m, 4H, CH_2), 6.61 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.4, 14.9, 18.0, 31.0, 43.8, 44.1, 47.7, 53.4, 118.1, 118.4, 144.6, 152.5. HRMS (EI) Calcd for $C_{32}H_{53}{}^{79}Br$: 516.3331. Found: 516.3325. Anal. Calcd for $C_{32}H_{53}Br$: C, 74.25; H, 10.32%. Found: C, 74.07; H, 10.44%.

Preparation of BEind-Br (4-Bromo-1,1,7,7-tetrabutyl-3,3,5,5-tetaethyl-*s*-hydrindacene). (1) 1,3-Bis(1-butyl-1-hydroxypentyl)benzene: The reaction of dimethyl isophthalate (15.0 g, 77.2 mmol) with butylmagnesium bromide (503 mmol in Et_2O) in Et_2O (250 mL) gave 1,3-bis(1-butyl-1-hydroxypentyl)benzene as a light yellow oil (27.3 g, 75.3 mmol, 98% if pure), which was used for the next reaction without further purification.

(2) 1,3-Bis(1-butyl-1-chloropentyl)benzene: The crude 1,3-bis(1-butyl-1-hydroxypentyl)benzene (14.8 g, 40.8 mmol if pure) was treated with HCl gas in the presence of $CaCl_2$ powder (7.0 g) in CH_2Cl_2 (100 mL) to give 1,3-bis(1-butyl-1-chloropentyl)benzene as a light yellow oil (16.3 g, 40.8 mmol, 100% yield if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.84 (t, $J = 7.5$ Hz, 12H, CH_3), 1.04–1.42 (m, 16H, CH_2), 1.96–2.08 (m, 8H, CH_2), 7.26–7.38 (m, 3H, ArH), 7.50–7.53 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.2, 23.0, 27.1, 45.0, 79.8, 124.7, 125.3, 128.4, 143.2.

(3) EBind-H (1,1,7,7-Tetrabutyl-3,3,5,5-tetraethyl-*s*-hydrindacene): This compound was prepared similar to Eind-H starting from 1,3-bis(1-butyl-1-chloropentyl)benzene (16.3 g, 40.8 mmol if pure), 2-ethyl-1-butene (6.89 g, 81.9 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 41 mL, 41 mmol) in CH_2Cl_2 (60 mL), and was isolated as colorless crystals by column chromatography (silica gel, hexane as eluent, $R_f = 0.75$) and recrystallization from hexane (3.85 g, 7.78 mmol, 19% yield for 3 steps): mp 66.5–67.3 °C. ^{1}H NMR ($CDCl_3$): δ 0.80, 0.86 (t × 2, $J = 7.5$ Hz, 24H, overlapped, CH_3), 1.08–1.31 (m, 16H, CH_2), 1.43–1.70 (m, 16H, CH_2), 1.79 (s, 4H, CH_2), 6.62 (s, 1H, ArH), 6.65 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.5, 14.4, 23.8, 27.3, 33.2, 41.4, 46.7, 48.5, 49.1, 118.86, 118.94, 147.5, 148.3. HRMS (EI) Cacld for $C_{36}H_{62}$: 494.4852. Found: 494.4857.

(4) BEind-Br: The reaction of EBind-H (3.50 g, 7.07 mmol) with bromine (3.8 mL, 73.8 mmol) in triethyl phosphate (50 mL) at 70 °C overnight gave a mixture of regioisomers, BEind-Br and EBind-Br, in ca. 4:1 ratio as estimated by ^{1}H NMR spectrum. The major product BEind-Br was isolated as colorless crystals by recrystallization from hexane (2.29 g, 3.99 mmol, 56% yield): mp 91.7–92.2 °C. ^{1}H NMR ($CDCl_3$): δ 0.77 (t, $J = 7.5$ Hz, 12H, CH_3), 0.87 (t, $J = 7.5$ Hz, 12H, CH_3), 1.12–1.27 (m, 16H, CH_2), 1.41–1.61 (m, 8H, CH_2), 1.76–2.00 (m, 12H, CH_2), 6.61 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.9, 14.6, 24.1, 27.7, 31.7, 41.7, 44.5, 48.1, 53.9, 100.9, 118.9, 145.3, 153.0. HRMS (EI) Cacld for $C_{36}H_{61}{}^{79}Br$: 572.3957. Found: 572.3979. Anal. Calcd for $C_{36}H_{61}Br$: C, 75.36; H, 10.72%. Found: C, 75.27; H, 10.89%.

Preparation of P^{5}Eind-Br (4-Bromo-3,3,5,5-tetraethyl-1,1,7,7-tetrapentyl-*s*-hydrindacene). (1) 1,3-Bis(1-hydroxy-1-pentylhexyl)benzene: The reaction of dimethyl isophthalate (50.0 g, 258 mmol) with pentylmagnesium bromide (1.29 mol in Et_2O (800 mL)) in Et_2O (400 mL) gave 1,3-bis(1-hydroxy-1-pentylhexyl)benzene as a light yellow gum (108 g, 258 mmol, 100% if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.81 (t, $J = 6.8$ Hz, 12H, CH_3), 0.96–1.05 (m, 4H, CH_2), 1.14–1.31 (m, 20H, CH_2), 1.68 (s, 2H, OH), 1.71–1.86 (m, 8H, CH_2), 7.21–7.29 (m, 3H, ArH), 7.31–7.33 (m, 1H, ArH).

(2) 1,3-Bis(1-chloro-1-pentylhexyl)benzene: The crude 1,3-bis(1-hydroxy-1-pentylhexyl)benzene (108 g, 258 mmol if pure) was treated with HCl gas in the presence of $CaCl_2$ powder (ca. 170 g) in CH_2Cl_2 (1.2 L) to give 1,3-bis(1-chloro-1-pentylhexyl)benzene as a brown oil (106 g, 0.23 mol, 90% yield if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.83 (t, $J = 6.4$ Hz, 12H, CH_3), 1.10–1.29 (m, 24H, CH_2), 2.06–2.19 (m, 8H, CH_2), 7.25–7.33 (m, 1H, ArH), 7.36–7.40 (m, 2H, ArH), 7.51 (s, 1H, ArH).

(3) EP^{5}ind-H (1,1,7,7-Tetraethyl-3,3,5,5-tetrapentyl-*s*-hydrindacene): This compound was prepared similar to Eind-H starting from 1,3-bis(1-chloro-1-pentylhexyl)benzene (106 g, 232 mmol if pure), 2-ethyl-1-butene (44.8 g, 533 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 116 mL, 116 mmol) in CH_2Cl_2 (600 mL), and was isolated as a light yellow oil (100 g, 181 mmol, 78% yield if pure). The crude product was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.80 (t, $J = 7.3$ Hz, 12H, CH_3), 0.85 (t, $J = 6.9$ Hz, 12H, CH_3), 1.14–1.32 (m, 24H, CH_2), 1.44–1.68 (m, 16H, CH_2), 1.79 (s, 4H, CH_2), 6.62 (s, 1H, ArH), 6.65 (s, 1H, ArH).

(4) P^{5}Eind-Br: The reaction of P^{5}Eind-H (100 g, 0.18 mol if pure) with bromine (186 mL, 3.63 mol) in triethyl phosphate (500 mL) at 35 °C for 2 days gave a mixture of regioisomers, P^{5}Eind-Br and EP^{5}ind-Br, in ca. 4:1 ratio as estimated by ^{1}H NMR spectrum. The major product, P^{5}Eind-Br, was isolated as colorless crystals by recrystallization from hexane/EtOH (33.5 g, 53.2 mmol, 21% yield for 4 steps): mp 88 °C. ^{1}H NMR ($CDCl_3$): δ 0.77 (t, $J = 7.3$ Hz, 12H, CH_3), 0.86 (t, $J = 6.9$ Hz, 12H, CH_3), 1.13–1.32 (m, 24H, CH_2), 1.43–1.50 (m, 4H, CH_2), 1.54–1.61 (m, 4H, CH_2), 1.77–1.87 (m, 8H, CH_2), 1.92–2.01 (m, 4H, CH_2), 6.61 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.5, 14.2, 22.8, 24.6, 31.2, 32.9, 41.4, 44.3, 47.7, 53.5, 118.2, 118.6, 144.8, 152.6. HRMS (EI) Calcd for $C_{40}H_{69}{}^{79}Br$: 628.4583. Found: 628.4560. Anal. Calcd for $C_{40}H_{69}Br$: C, 76.27; H, 11.04%. Found: C, 76.25; H, 11.12%.

Preparation of HEind-Br (4-Bromo-3,3,5,5-tetraethyl-1,1,7,7-tetrahexyl-*s*-hydrindacene). (1) 1,3-Bis(1-hydroxy-1-hexylheptyl)benzene: The reaction of dimethyl isophthalate (30.0 g, 155 mmol) with hexylmagnesium bromide (0.77 mol in Et_2O (500 mL)) in Et_2O (400 mL) to give 1,3-bis(1-hydroxy-1-hexylheptyl)benzene as a yellow gum (34.8 g, 73.3 mmol, 48% if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.83 (t, $J =$

6.9 Hz, 12H, CH_3), 0.96–1.05 (m, 4H, CH_2), 1.14–1.31 (m, 28H, CH_2), 1.69 (s, 2H, OH), 1.72–1.86 (m, 8H, CH_2), 7.21–7.29 (m, 3H, ArH), 7.31–7.33 (m, 1H, ArH).

(2) 1,3-Bis(1-chloro-1-hexylheptyl)benzene: The crude 1,3-bis(1-hydroxy-1-hexylheptyl)benzene (34.8 g, 73.3 mmol if pure) was treated with HCl gas in the presence of $CaCl_2$ powder (ca. 50 g) in CH_2Cl_2 (500 mL) to give 1,3-bis(1-chloro-1-hexylheptyl)benzene was obtained as a brown oil (35.0 g, 68.4 mmol, 93% yield if pure), which was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.84 (t, $J = 6.9$ Hz, 12H, CH_3), 1.10–1.42 (m, 32H, CH_2), 2.08–2.15 (m, 8H, CH_2), 7.23–7.31 (m, 1H, ArH), 7.36–7.40 (m, 2H, ArH), 7.51 (s, 1H, ArH).

(3) EHind-H (1,1,7,7-Tetraethyl-3,3,5,5-tetrahexyl-*s*-hydrindacene): This compound was prepared similar to Eind-H starting from 1,3-bis(1-chloro-1-hexylheptyl)benzene (35.0 g, 68.4 mmol if pure), 2-ethyl-1-butene (13.2 g, 157 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 34 mL, 34 mmol) in CH_2Cl_2 (300 mL), and was isolated as a light yellow oil (32.3 g, 53.2 mmol, 78% yield if pure). The crude product was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.80 (t, $J = 7.4$ Hz, 12H, CH_3), 0.87 (t, $J = 6.9$ Hz, 12H, CH_3), 1.11–1.32 (m, 32H, CH_2), 1.42–1.69 (m, 16H, CH_2), 1.79 (s, 4H, CH_2), 6.63 (s, 1H, ArH), 6.65 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.4, 14.3, 22.9, 25.0, 30.4, 32.1, 33.2, 41.7, 46.7, 48.6, 49.1, 118.9, 119.0, 147.6, 148.4.

(4) HEind-Br: The reaction of EHind-H (32.3 g, 53.2 mmol if pure) with bromine (54.5 mL, 1.06 mol) in triethyl phosphate (300 mL) at 35 °C for 2 days gave a mixture of regioisomers, HEind-Br and EHind-Br, in ca. 4:1 ratio as estimated by ^{1}H NMR spectrum. The major product HEind-Br was isolated as colorless crystals by recrystallization from hexane/EtOH (10.5 g, 15.3 mmol, 10% yield for 4 steps): mp 87 °C. ^{1}H NMR ($CDCl_3$): δ 0.77 (t, $J = 7.3$ Hz, 12H, CH_3), 0.87 (t, $J = 6.9$ Hz, 12H, CH_3), 1.13–1.31 (m, 32H, CH_2), 1.43–1.50 (m, 4H, CH_2), 1.54–1.61 (m, 4H, CH_2), 1.77–1.86 (m, 8H, CH_2), 1.92–2.01 (m, 4H, CH_2), 6.60 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 9.5, 14.2, 22.9, 24.9, 30.4, 31.2, 32.1, 41.5, 44.4, 47.7, 53.5, 118.2, 118.7, 144.8, 152.6. HRMS (EI) Calcd for $C_{44}H_{77}{}^{79}Br$: 684.5209. Found: 684.5199. Anal. Calcd for $C_{44}H_{77}Br$: C, 77.04; H, 11.31%. Found: C, 77.14; H, 11.46%.

Preparation of 2-Propyl-1-pentene. To a suspension of 1,1-dichloroethene (25.0 g, 0.26 mol) and [$NiCl_2$(dppp)][72,73] (700 mg, 1.29 mmol) in Et_2O (100 mL) was dropwise added to a solution of propylmagnesium chloride (2.0 M solution in Et_2O, 270 mL, 0.54 mol) at 0 °C. After the mixture was vigorously stirred for 1 day at room temperature, the resulting suspension was quenched with a dilute HCl aq. After the organic layer was separated, the aqueous layer was extracted with Et_2O. The combined organic layer was washed with water and brine, and dried over Na_2SO_4. The mixture was distilled at atmospheric pressure to give 2-propyl-1-pentene as a colorless oil (bp 117 °C) (9.30 g, 82.9 mmol, 32% yield): ^{1}H NMR ($CDCl_3$): δ 0.88 (t, $J = 7.4$ Hz, 6H, CH_3), 1.38–1.47 (m, 4H, CH_2), 1.96 (t, $J = 7.8$ Hz, 4H, CH_2), 4.68 (s, 2H, C=CH_2); ^{13}C NMR ($CDCl_3$): δ 13.8, 20.9, 38.2, 108.6, 149.8.

Preparation of MPind-Br (4-Bromo-1,1,7,7-tetramethyl-3,3,5,5-tetrapropyl-*s*-hydrindacene). This compound was prepared from 1-bromo-3,5-bis(1-chloro-1-methylethyl)benzene (21.5 g, 69.3 mmol), 2-propyl-1-pentene (17.1 g, 153 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 10 mL, 10 mmol) in CH_2Cl_2 (80 mL), and was isolated as colorless crystals by recrystallization from acetone (11.6 g, 25.1 mmol, 36% yield): mp 86–88 °C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, $J = 7.3$ Hz, 12H, CH_3), 0.95–1.31 (m, 20H, CH_2 and CH_3), 1.52–1.60 (m, 4H, CH_2), 1.89 (s, 4H, CH_2), 1.95–2.02 (m, 4H, CH_2), 6.62 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 15.0, 18.5, 32.2, 41.0, 42.0, 51.2, 53.4, 115.8, 117.7, 143.9, 154.8. HRMS (EI) Calcd for $C_{28}H_{45}{}^{79}Br$: 460.2705. Found: 460.2686. Anal. Calcd for $C_{28}H_{45}Br$: C, 72.86; H, 9.83%. Found: C, 72.81; H, 9.98%.

Preparation of M^{s}Hind-Br (Dispiro[cyclohexane-1,3′-(4′-bromo-1′,1′,7′,7′-tetramethyl-*s*-hydrindacene)-5′,1″-cyclohexane]). This compound was prepared from 1-bromo-3,5-bis(1-chloro-1-methylethyl)benzene (26.2 g, 85 mmol), methylenecyclohexane (17.9 g, 0.19 mol), and BCl_3 (1.0 M solution in CH_2Cl_2, 15 mL, 15 mmol) in CH_2Cl_2 (500 mL), and was isolated as colorless crystals by recrystallization from acetone (10.9 g, 25 mmol, 30% yield): mp 230 °C (sublimation). ^{1}H NMR ($CDCl_3$): δ 1.20–1.69 (m, 28H, CH_2 and CH_3), 1.99 (s, 4H, CH_2), 2.70–2.77 (m, 4H, CH_2), 6.77 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 23.4, 25.7, 32.4, 35.0, 41.7, 50.7, 52.5, 116.2, 117.4, 146.1, 154.3. HRMS (EI) Calcd for $C_{26}H_{37}{}^{79}Br$: 428.2079. Found: 428.2063. Anal. Calcd for $C_{26}H_{37}Br$: C, 72.71; H, 8.68%. Found: C, 72.42; H, 8.75%.

Preparation of MPhind-Br (4-Bromo-1,1,7,7-tetramethyl-3,3,5,5-tetraphenyl-*s*-hydrindacene).[75] This compound was prepared from 1-bromo-3,5-bis(1-chloro-1-methylethyl)-benzene (4.00 g, 13.0 mmol), 1,1-diphenylethene (6.18 g, 34.3 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 13 mL, 13 mmol) in CH_2Cl_2 (100 mL). During the course of the Friedel–Crafts reaction, the self-dimerization of 1,1-diphenylethene also took place to give 1-methyl-1,3,3-triphenylindane as a side product. After the removal of 1-methyl-1,3,3-triphenylindane by Kugelrohr distillation (100–130 °C/0.1 mmHg), MPhind-Br was isolated as colorless crystals by recrystallization from acetone/hexane (2.05 g, 3.43 mmol, 26% yield): mp 270 °C (sublimation). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 12H, CH_3), 2.91 (s, 4H, CH_2), 7.07 (s, 1H, ArH), 7.12–7.24 (m, 20H, ArH); ^{13}C NMR ($CDCl_3$): δ 29.9, 42.8, 62.8, 64.6, 115.5, 124.0, 125.7, 127.4, 129.6, 146.0, 146.2, 155.7. HRMS (EI) Calcd for $C_{40}H_{37}{}^{79}Br$: 596.2079. Found: 596.2075. Anal. Calcd for $C_{40}H_{37}Br$: C, 80.39; H, 6.24%. Found: C, 80.26; H, 6.24%.

Preparation of M^{s}Fluind-Br (Dispiro[fluorene-9,3′-(4′-bromo-1′,1′,7′,7′-tetramethyl-*s*-hydrindacene)-5′,9″-fluorene]).[52] This compound was prepared from 1-bromo-3,5-bis(1-chloro-1-methylethyl)benzene (3.10 g, 10.0 mmol), dibenzofulvene[74] (3.61 g, 20.3 mmol), and BCl_3 (1.0 M solution in CH_2Cl_2, 10 mL, 10 mmol) in CH_2Cl_2 (200 mL), and was isolated as a light yellow crystalline powder by recrystallization from CH_2Cl_2/MeOH (4.52 g, 7.61 mmol, 76% yield): mp 274 °C (sublimation). ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 12H, Me), 2.46 (s, 4H, CH_2), 7.03–7.05 (m, 4H, ArH), 7.08–7.13 (m, 4H, ArH), 7.15–7.20 (m, 4H, ArH), 7.16 (s, 1H, ArH), 7.49–7.52 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$): δ 32.6, 43.3, 56.4, 63.7, 115.4, 118.0, 119.3, 123.6, 126.6, 127.3, 140.7, 143.0, 153.0, 156.9. Anal. Calcd for $C_{40}H_{33}Br$: C, 80.94; H, 5.60%. Found: C, 80.87; H, 5.98%.

Table 1. Crystal Data

	Eind-Br	EHind-Br	MPind-Br	M^{s}Hind-Br	MPhind-Br·Et_2O
Formula	$C_{28}H_{45}Br$	$C_{44}H_{77}Br$	$C_{28}H_{45}Br$	$C_{26}H_{37}Br$	$C_{40}H_{37}Br$·0.5($C_4H_{10}O$)
FW	461.55	685.97	461.55	429.48	634.67
T/K	90	100	100	100	100
λ/Å	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Color	colorless	colorless	colorless	colorless	colorless
Crystal size/mm^3	0.16 × 0.07 × 0.06	0.40 × 0.20 × 0.10	0.29 × 0.12 × 0.08	0.20 × 0.20 × 0.20	0.20 × 0.10 × 0.10
Crystal system	monoclinic	orthorhombic	triclinic	triclinic	triclinic
Space group	$C2/c$ (#15)	$Pbcn$ (#60)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a/Å	20.140(4)	20.262(4)	8.4274(13)	6.3529(12)	8.8274(17)
b/Å	8.6661(18)	8.9372(17)	11.8851(17)	8.5568(16)	13.267(2)
c/Å	15.204(3)	22.399(4)	14.588(2)	20.213(4)	15.267(3)
α/°	90	90	74.611(9)	83.182(6)	105.015(3)
β/°	111.377(3)	90	80.232(11)	85.701(6)	106.783(2)
γ/°	90	90	70.911(9)	79.568(5)	91.205(2)
V/Å	2471.1(9)	4056.1(13)	1325.8(3)	1071.4(4)	1644.4(5)
Z	4	4	2	2	2
D_X/Mg m^{-3}	1.241	1.123	1.156	1.331	1.272
μ/mm^{-1}	1.675	1.041	1.561	1.932	1.280
Measured reflections	32118	35782	16729	10088	22602
Unique reflections (R_{int})	3920 (0.050)	4651 (0.037)	7646 (0.043)	4865 (0.053)	8665 (0.033)
Reflections [$I > 2\sigma(I)$]	3456	4347	5137	4028	7041
Refined parameters	145	248	281	245	483
$R(F)$ [$I > 2\sigma(I)$]	0.0588	0.0800	0.0470	0.0441	0.0372
$wR(F^2)$ (all data)	0.1309	0.1651	0.1088	0.1042	0.0864
S	1.156	1.322	1.007	1.041	1.043
$(\Delta r)_{min,max}$/e Å^{-3}	−0.71, 0.98	−0.72, 0.52	−0.49, 0.66	−0.81, 1.42	−0.31, 0.70

X-ray Crystallography. The crystallographic data are summarized in Table 1. Single crystals suitable for X-ray diffraction were obtained from hexane for Eind-Br as colorless blocks, from EtOH for HEind-Br as colorless blocks, from acetone for MPind-Br and M^{s}Hind-Br as colorless blocks, and from $CDCl_3/Et_2O$ for MPhind-Br as colorless blocks. The crystals were immersed in Paraton-N oil on a nylon loop or MicroMount™ and mounted on a Rigaku AFC-8 diffractometer with a Saturn70 CCD detector (for Eind-Br and MPind-Br), or a Rigaku AFC-10 diffractomter with a Saturn724+ CCD detector (for MPhind-Br, M^{s}Hind-Br, and HEind-Br) using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The integration and scaling of the diffraction data were carried out using the program CrystalClear.[76] Lorentz-polarization and absorption corrections were also performed. All structures were solved by direct methods (SIR92[77] for M^{s}Hind-Br and SIR2004[78] for others), and refined on F^2 by the full-matrix least-squares method (SHELXL-97[79]). The anisotropic atomic displacement parameters were applied to all non-hydrogen atoms. The hydrogen atoms were located on difference Fourier maps for Eind-Br, and placed on calculated positions for the others. The positions of the hydrogen atoms were refined by applying riding models.

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC-789716, -789717, -789718, -789719, -789720, and -780798 for Eind-Br, HEind-Br, MPind-Br, M^{s}Hind-Br, MPhind-Br, and M^{s}Fluind-Br, respectively. Copies of the 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, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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60 The abbreviation "Rind" means in English the thick outer skin of some types of fruit for protection of the inside fruity flesh such as orange. This is fully in accordance with our research concept.
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