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Numbers of Asymmetric and Pseudoasymmetric Centers in Enumeration of Achiral and Chiral Alkanes of Given Carbon Contents

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Abstract

Asymmetric and pseudoasymmetric centers in alkanes (as tree-dimensional trees of degree 4) have been specified by means of newly-defined criteria based on three kinds of attributes of *RS*-stereoisomers (chirality, *RS*-stereogenicity, and sclerality), where the classification into five *RS*-stereoisomeric types (Types I to V) according to S. Fujita, *J. Org. Chem.*, **69**, 3158–3165 (2004), S. Fujita, *MATCH Commun. Math. Comput. Chem.*, **54**, 39–52 (2005), and S. Fujita, *MATCH Commun. Math. Comput. Chem.*, **58**, 611–634 (2007) plays an important role. Among three types of *RS*-stereogenic promolecules (Types I, III, and V), the central atom of each alkane as a promolecule of Types I and III (chiral/*RS*-stereogenic) is regarded as an asymmetric center, while the central atom of each alkane as a promolecule of Types V (achiral/*RS*-stereogenic) is regarded as a pseudoasymmetric center. The data of alkyl ligands, which have been recursively calculated by a personal computer and stored as the coefficients of the term $x^k y^\ell z^m$ of generating functions involving carbon content (k), the number of asymmetric carbons (ℓ), as well as the number of pseudoasymmetric carbons (m), have been used to count centroidal and bicentroidal alkanes on the basis of a tetrahedral skeleton. Each itemized number has been obtained as the coefficient of the term $x^k y^\ell z^m$ appearing in a respective generating function, which has been derived by following Fujita's proligand method. The itemized values up to carbon content 30 have been listed in tabular forms, which are distinctively concerned with Type I, …, or Type V as well as with achiral stereoisomers and chiral stereoisomers.

1 Introduction

Enumeration of alkanes (or trees) has been one of long-pending problems which have attracted various approaches of chemists (e.g., Henze and Blair [1, 2]) as well as of mathematicians (e.g., Cayley [3, 4], Pólya [5, 6], Otter [7], and Robinson et al. [8]), as summarized in books [9–12] and reviews [13–16]. Although Robinson et al. [8] reported the enumeration of achiral and chiral alkanes by modifying Pólya's cycle indices (CIs), even their treatment did not fully take account of problems due to inner structures of ligands, e.g., pseudoasymmetry and *meso*-compounds.

We have recently developed the *proligand method*, which takes inner structures of ligands into explicit consideration [17–19]. The merit of Fujita's proligand method for enumerating three-dimensional (3D) objects (e.g., stereoisomers) was discussed in comparison with Pólya's theorem by using simple examples of *meso* and pseudoasymmetric compounds [20]. As an application of the proligand method, we have enumerated monosubstituted alkanes (or alkyl ligands, or mathematically speaking, planted 3D-trees or rooted 3D-trees at the same time) [21–23] so as to provide fundamental data for enumerating alkanes. Thereby, we have been able to investigate the enumeration of achiral and chiral alkanes (mathematically speaking, 3D-trees of degree 4) as further applications of Fujita's proligand method, which have been conducted:

1. by using the dichotomy of centroidal and bicentroidal alkanes [24],
2. by using another dichotomy of balanced alkanes and unbalanced alkanes, where dual recognition as uninuclear and binuclear promolecules is emphasized so as to get rid of abnormal categorization into achiral and chiral alkanes [25],
3. by using the dichotomy of balanced alkanes and unbalanced alkanes, where an alternative method of compensating the abnormal categorization into achiral and chiral alkanes is discussed along with an implementation with the Maple programming language [26],
4. by the combination of the two dichotomies [27], and
5. by combining Fujita's proligand method with Fujita's PCI (partial-cycle-index) method in order to obtain numbers of alkanes subdivided with respect to their point-group symmetries [28].

In these enumerations, we took asymmetric atoms and pseudoasymmetric ones into consideration, but without distinguishing them, because we had no reliable criterion for such distinction. It follows that the resulting values did not concerned with the numbers of asymmetric carbon atoms and those of pseudoasymmetric carbon atoms. For practical purposes of depicting compounds enumerated, it is desirable to enumerate achiral and chiral alkanes with given carbon numbers, where the numbers of asymmetric and pseudoasymmetric atoms were taken into explicit consideration.

As another project of ours, on the other hand, we have investigated the classification of promolecules by means of three kinds of attributes of *RS*-stereoisomers (chirality, *RS*-stereogenicity, and sclerality), where any promolecules have been concluded to belong to one of five *RS*-stereoisomeric types (Types I to V) [29, 30]. This approach has been applied to the enumeration of promolecules, the calculated number of which have been itemized into the five *RS*-stereoisomeric types (Types I to V) [31].

In the present paper, we first discuss rigorous distinction between asymmetric atoms and pseudoasymmetric ones after we briefly discuss conventional terminologies on them. Thus,

the five *RS*-stereoisomeric types based on chirality, *RS*-stereogenicity, and sclerality [29, 30] are applied to produce a criterion for such rigorous discrimination. According to the newly developed criterion, we next enumerate achiral and chiral alkanes with given carbon numbers by taking numbers of asymmetric and pseudoasymmetric centers into consideration.

2 Asymmetric and Pseudoasymmetric Centers

2.1 The Conventional Terminology

In his famous book [32, page 11], van't Hoff has claimed that the number of stereoisomers of the formula $C(R_1R_2R_3)C(R_4R_5)C(R_1R_2R_3)$ (**1**) was equal to three (a pair of enantiomers and an achiral compound) on the same line as there exist three stereoisomers (a pair of enantiomers and an achiral so-called *meso*-compound) for the formula $C(R_1R_2R_3)C(R_1R_2R_3)$ (**2**). If our speculation was right, he apparently recognized that the central carbon atom of **1** was not "asymmetric" and the number of asymmetric carbon atoms in **1** was equal to two (then $2^{(2/2-1)} \times (1+2^{2/2}) = 3$ according to eq. 2 of [32, page 12]), because the two terminals (i.e., $C(R_1R_2R_3)$) were seemingly equivalent. The erroneous conclusion of van't Hoff on **1** seemed to provide Fischer with some difficulties in his famous work on sugars [33–35]. After he had developed Fischer's projection as a new device for representing configuration [34], Fischer decided the configuration of pentoses through their relation to trihydroxyglutaric acids (as a special case of **1**), as found in his autobiography [35, page 134]. The case of **1** has been now recognized as a pseudoasymmetric case, where there exist four stereoisomers (a pair of enantiomers and two achiral compounds).

Interests on such pseudoasymmetric cases [36] have been revived in connection with the CIP (Cahn-Ingold-Prelog) system for *RS*-nomenclature [37], because the revised version of the CIP system [37] resulted in a significant change of the connotation of the term "pseudoasymmetry", as pointed out by Mislow [38]. According to the revised CIP system [37], tetrahedral atoms are recognized as stereogenic units (more specifically as chirality centers or asymmetric centers) or pseudoasymmetric stereogenic units (more specifically as pseudoasymmetric centers), where the algebraic sign (or corresponding descriptor) of a pseudoasymmetric unit is reflection-invariant in contrast to the algebraic sign of a chirality element (a stereogenic unit). As a result, two achiral compounds corresponding to $C(ABp\overline{p})$ ($A = R_4$, $B = R_5$, $p = R$-$C(R_1R_2R_3)$ and $\overline{p} = S$-$C(R_1R_2R_3)$, where A and B are achiral ligands) and four chiral compounds (two pairs of enantiomers) corresponding to $C(Ap\overline{p}q)$ or $C(Ap\overline{pq})$ ($A = R_4$, q = a chiral ligand, $p = R$-$C(R_1R_2R_3$ and $\overline{p} = S$-$C(R_1R_2R_3)$ have been claimed to be both pseudoasymmetric. Note that only the former compound ($C(ABp\overline{p})$) is in agreement of the original definition of pseudoasymmetry (cf. [36]). Although this change has given some convenience to the descriptive stereochemistry such as the *RS*-nomenclature, it causes essential difficulties from the viewpoints of geometry and combinatorial enumeration. From the geometrical point of view, the central carbon atom of the pseudoasymmetric case of $C(ABp\overline{p})$ is locally achiral (achirotopic according to [39, 40]), while the central carbon atom of the "pseudoasymmetric" case of $C(Ap\overline{p}q)$ (or $C(Ap\overline{pq})$) is locally chiral (chirotopic according to [39, 40]). The concept "reflection-invariant" implies that the non-existence of an enantiomeric pair for the former achiral case is equalized to the existence of an enantiomeric pair $C(Ap\overline{p}q)$ and $C(Ap\overline{pq})$) for the latter case. This point results in a drawback from the viewpoint of combinatorial enumeration such that the "pseudoasymmetric" case of $C(Ap\overline{p}q)$ or $C(Ap\overline{pq})$ gives the same number (4) of stereoisomers as the "asymmetric"

case of C(ABXp) or C(ABX$\overline{\text{p}}$) does, whereas the pseudoasymmetric case of C(ABp$\overline{\text{p}}$) gives 2 as the number of achiral compounds.

2.2 New Terminology Based on *RS*-Stereoisomeric Types

As clarified in the preceding subsection, a more rigorous standpoint is necessary to obtain a reliable criterion for distinguishing between asymmetric atoms and pseudoasymmetric ones. Recently, our analysis of the conventional concepts "chirality" and "stereogenicity" [41–44] has led to the formulation of more specifiable concepts, i.e., *chirality*, *RS-stereogenicity*, and *sclerality* [29, 45, 46]. We adopt these concepts to derive such a reliable criterion.

According to this formulation [29, 45, 46], a quadruplet of promolecules contained in a *stereoisogram* are called *RS-stereoisomers*, which are characterized by three relationships, i.e., *enantiomeric*, *RS-diastereomeric*, and *holantimeric*. These relationships correspond to the attributes of the quadruplet (and those of each *RS*-stereoisomer of the quadruplet at the same time), i.e., *chirality*, *RS-stereogenicity*, and *sclerality*. By combining the three attributes, the quadruplet of promolecules (*RS*-stereoisomers) is characterized as either one of five *RS*-stereoisomeric types, i.e., Type I (chiral/*RS*-stereogenic/ascleral), Type II (chiral/*RS*-astereogenic/-scleral), Type III (chiral/*RS*-stereogenic/scleral), Type IV (achiral/*RS*-astereogenic/ascleral), and Type V (achiral/*RS*-stereogenic/scleral). The existence of only five types has been proven on a more mathematical basis [47, 30]. Pseudoasymmetry [45] and prochirality [48] have been discussed by using stereoisograms.

By considering Types I–V, we are able to derive a reliable criterion for distinguishing between asymmetric atoms and pseudoasymmetric ones. Suppose that a quadruplet of entities (e.g., promolecules, planted promolecules, etc.) contained in a stereoisogram is characterized as being *RS*-stereogenic. Then, the center of each entity is characterized as follows:

Criterion 1 (Asymmetric and pseudoasymmetric centers)

1. If the quadruplet of entities contained in a stereoisogram is *RS*-stereogenic/-chiral (i.e., Type I or III), the center of each entity is referred to as being *asymmetric*.
2. If the quadruplet of entities contained in a stereoisogram is *RS*-stereogenic/-achiral (i.e., Type V), the center of each entity is referred to as being *pseudoasymmetric*.

This criterion means that an asymmetric center is capable of generating enantiomers along with *RS*-diastereomers because of the *RS*-stereogenic/chiral nature. In contrast, a pseudoasymmetric center is capable of generating *RS*-diastereomers, but incapable of generating enantiomers (i.e., achiral) because of the *RS*-stereogenic/achiral nature. This point has been already discussed by using several illustrative examples [45, 49]. It should be emphasized that *RS*-diastereomers of Type I are superposed upon enantiomers.

2.3 Centroidal Alkanes

2.3.1 Centroids as Asymmetric or Pseudoasymmetric Centers

In the present paper, we start from the dichotomy of centroidal/bicentroidal 3D-trees, which we once applied to the enumeration of alkanes as stereoisomers [24, 50]. We shall first show how to apply Criterion 1 to centroidal alkanes by using representative examples shown in Fig. 1 [51].

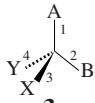
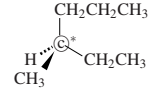
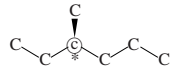
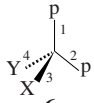
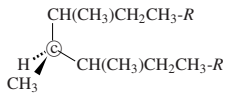
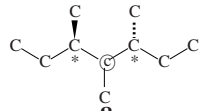
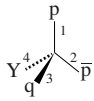
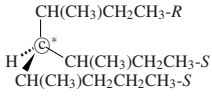
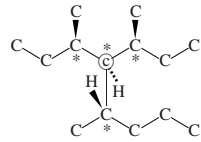
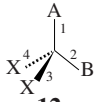
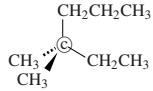
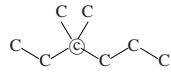
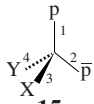
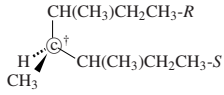
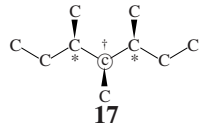
RS-stereoisomeric type	promolecular representation	centroidal representation	carbon-skeletal representation
Type I chiral/ *RS*-stereogenic/ ascleral	 **3**	 **4**	 **5**
Type II chiral/ *RS*-astereogenic/ scleral	 **6**	 **7**	 **8**
Type III chiral/ *RS*-stereogenic/ scleral	 **9**	 **10**	 **11**
Type IV achiral/ *RS*-astereogenic/ ascleral	 **12**	 **13**	 **14**
Type V achiral/ *RS*-stereogenic/ scleral	 **15**	 **16**	 **17**

Figure 1: Examples of five *RS*-stereoisomeric types for alkanes as 3D-trees. The letters A, B, X, and Y denote achiral proligands, while p/$\overline{\text{p}}$ and q/$\overline{\text{q}}$ represent pairs of enantiomeric proligands. The symbol ⓒ indicates the centroid of each alkane. Each centroid with an asterisk (*) is asymmetric under Criterion 1, while each centroid with a dagger (†) is pseudoasymmetric under Criterion 1.

In Fig. 1, an alkane to be examined is represented in three ways [51]. A promolecular representation (e.g., **3**) shows general features of the *RS*-stereoisomeric type of the alkane, where the letters A, B, X, and Y denote achiral proligands. On the other hand, a centroidal representation (e.g., **4**) emphasizes the centroid of the alkane (denoted by the symbol ⓒ) and relevant ligands. Finally, a carbon-skeletal representation (e.g., **5**) corresponds to a common structural formula having wedges and broken bold lines, without showing hydrogen atoms except being necessary to indicate configuration.

The promolecule of Type I (e.g., **3**) is chiral, *RS*-stereogenic, and ascleral so that a quadruplet of a Type-I stereoisogram consists of one pair of enantiomers (corresponding to the chiral nature), which can be alternatively regarded as one pair of *RS*-diastereomers (corresponding to *RS*-stereogenic). The superposition of the enantiomeric relationship onto the *RS*-diastereomeric one is ascribed to the ascleral nature of Type I. The application of Criterion 1 to 2-methylhexane (as an entity) shows that its centroid (ⓒ) is an asymmetric center, as indicated by the centroidal representation (**4**) and by the carbon-skeletal representation (**5**). The asymmetric nature is denoted by an asterisk (ⓒ*). It should be noted that the term *asymmetric* is linked with the *RS*-stereogenic nature but not directly with the chirality [52].

The promolecule of Type II (e.g., **6**) is chiral, *RS*-astereogenic, and scleral so that a quadruplet of a Type-II stereoisogram consists of one pair of enantiomers but exhibits *RS*-astereogenic nature. The application of Criterion 1 to (3*R*,5*R*)-3,4,5-trimethylheptane (as an entity) shows that its centroid (ⓒ) is not asymmetric nor pseudoasymmetric, as indicated by the centroidal representation (**7**) and by the carbon-skeletal representation (**8**). The centroidal carbon in **7** (or **8**) and the centroidal carbon in its enantiomer $\overline{\mathbf{7}}$ (or $\overline{\mathbf{8}}$) is in an enantiomeric relationship, so that each of the centroids is locally chiral. It follows that the centroid of being not asymmetric nor pseudoasymmetric is not linked with the chirality, but with the *RS*-astereogenic nature.

The promolecule of Type III (e.g., **9**) is chiral, *RS*-stereogenic, and scleral, so that a quadruplet of a Type-III stereoisogram consists of two pairs of enantiomers, which can be alternatively regarded as two pairs of *RS*-diastereomers. The application of Criterion 1 to (3*R*,4*r*,5*S*)-3,5-dimethyl-4-[(2*S*)-butan-2-yl]octane (as an entity) shows that its centroid (ⓒ*) is asymmetric, as indicated by the centroidal representation (**10**) and by the carbon-skeletal representation (**11**). It should be noted that the term *asymmetric* is linked with the *RS*-stereogenic nature but not with the chirality [52]. According to the CIP-nomenclature, on the other hand, the centroid (ⓒ*) is recognized to be reflection-invariant (i.e., "pseudoasymmetric" due to the revised CIP system) so that the descriptor 4*r* is adopted in the IUPAC name.

Because of the achiral, *RS*-astereogenic, and ascleral nature of Type IV (e.g., **12**), a quadruplet of a Type-IV stereoisogram consists of one promolecule of being self-enantiomeric and of being self-*RS*-diastereomeric. The application of Criterion 1 to 3,3-dimethylhexane (as an entity) shows that its centroid (ⓒ) is not asymmetric nor pseudoasymmetric, as indicated by the centroidal representation (**13**) and by the carbon-skeletal representation (**14**).

The promolecule of Type V (e.g., **15**) is achiral, *RS*-stereogenic, and scleral, so that a quadruplet of a Type-V stereoisogram consists of one pair of *RS*-diastereomers, which can be alternatively regarded as two self-enantiomeric pairs (i.e., two achiral promolecules). The application of Criterion 1 to (3*R*,4*r*,5*S*)-3,4,5-trimethylheptane (as an entity) shows that its centroid (ⓒ†) is pseudoasymmetric, as indicated by the centroidal representation (**16**) and by the carbon-skeletal representation (**17**).

2.3.2 Asymmetric or Pseudoasymmetric Centers Other Than Centroids

The next task is to determine by Criterion 1 whether each carbon center other than the centroid in an alkane is asymmetric, pseudoasymmetric, or not either. To do this task, it is important to select an appropriate entity to which we apply Criterion 1, where the selection should be well-defined so as to give a definite result.

Once a given alkane is determined to be centroidal, its centroid is uniquely fixed. Thereby, the alkane can be regarded as a directed graph (digraph) [9]. In other words, it can be regarded as a kind of rooted tree, in which its centroid is a root. In the present context, a new matter is that the centroidal alkane is regarded as a rooted *three-dimensional* (3D) tree [24]. This idea is applied to select entities for Criterion 1, as depicted in Fig. 2

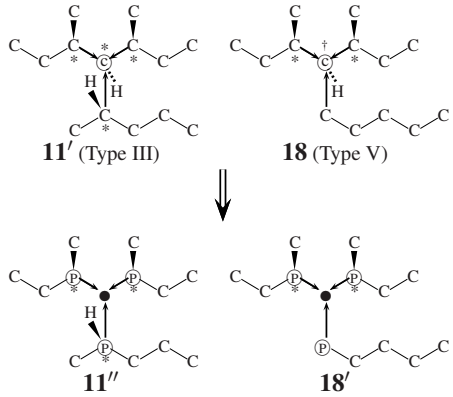


Figure 2: Selection of recursive alkyl ligands by means of directed-tree representations of centroidal alkanes. Each of the alkanes is divided into recursive alkyl ligands (as planted 3D-trees). The symbol Ⓟ indicates the principal node of each alkyl ligand, while the symbol ● indicates the root which is occupied commonly by the resulting alkyl ligands.

To discuss distinction between asymmetric centers and pseudoasymmetric ones, let us regard centroidal alkanes of Type III and V as directed 3D-trees, where incident bonds to each centroid are marked with arrows aiming at the centroid. Thereby, we obtain directed-tree representations of the centroidal alkanes, **11′** (Type III) and **18** (Type V), where the methyl ligand in **17** is replaced by a pentyl ligand in **18** for convenience of explanation. Then, suppose that each centroid is replaced by a root (●) and each neighboring node is regarded as a principal vertex (Ⓟ). As a result, we obtain such alkyl ligands as contained in **11″** or **18′**, where they share a single root. Each alkyl ligand in isolation can be regarded as a planted 3D-tree, so that it is categorized into any one of Types I to V (Fig. 3).

As found easily by Fig. 3, *RS*-stereoisomeric types for alkyl ligands (planted 3D-trees) are discussed in a parallel way to those for centroidal alkanes (Fig. 1), because principal nodes (Ⓟ) for Fig. 3 and centroids (Ⓒ) for Fig. 3 play a common role in determining Types I–V. This means that such alkyl ligands (planted 3D-trees) can be used as entities for Criterion 1, where their principal nodes are used as centers to be examined and their roots are regarded as null proligands (or hypothetical achiral proligands). According to Criterion 1, the principal node of

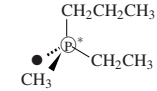
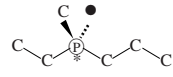
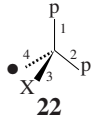
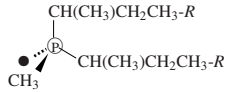
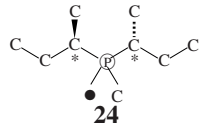
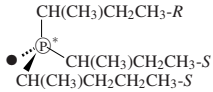
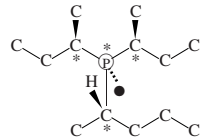
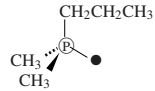
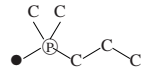
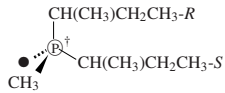
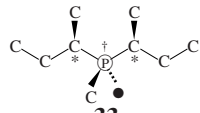
RS-stereoisomeric type	promolecular representation	planted-3D-tree representation	carbon-skeletal representation
Type I chiral/ *RS*-stereogenic/ ascleral	**19**	 **20**	 **21**
Type II chiral/ *RS*-astereogenic/ scleral	 **22**	 **23**	 **24**
Type III chiral/ *RS*-stereogenic/ scleral	**25**	 **26**	 **27**
Type IV achiral/ *RS*-astereogenic/ ascleral	**28**	 **29**	 **30**
Type V achiral/ *RS*-stereogenic/ scleral	**31**	 **32**	 **33**

Figure 3: Examples of five *RS*-stereoisomeric types for alkyl ligands as planted 3D-trees. The letters A, B, X, and Y denote achiral proligands, while p/$\overline{\text{p}}$ and q/$\overline{\text{q}}$ represent pairs of enantiomeric proligands. The symbol Ⓟ indicates the principal node of each alkyl ligand, while the symbol ● indicates the root. The bond between the principal node and the root is called a *stem*. Each principal node with an asterisk (*) is asymmetric under Criterion 1, while each principal node with a dagger (†) is pseudoasymmetric under Criterion 1.

a Type-I (or Type-III) alkyl ligand is determined to be asymmetric as marked by an asterisk (*); the principal node of a Type-V alkyl ligand is determined to be pseudoasymmetric as marked by a dagger (†); and the principal node of a Type-II (or Type-IV) is unmarked to be neither asymmetric nor pseudoasymmetric.

Each alkyl ligand is further considered to be a directed 3D-tree in a similar way to Fig. 2 so that the procedure for generating such a directed 3D-tree is found to be recursive, as reported in [21, 22, 23]. Hence, we call such an alkyl ligand a *recursive alkyl ligand* if necessary.

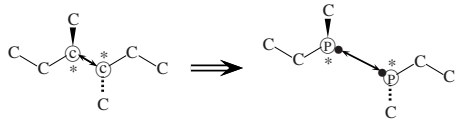
Criterion 2 (Selection of Entities for Criterion 1)

1. A centroidal alkane serves as an entity for Criterion 1, where its centroid plays as a center to be examined.
2. A recursive alkyl ligand serves as an entity for Criterion 1, where its principal node plays as a center to be examined.

2.4 Bicentroidal Alkanes

Bicentroidal alkanes have a bicentroid, each terminal of which accommodates a recursive alkyl ligand. Hence, it is sufficient that two recursive alkyl ligands selected from a bicentroidal alkane by Criterion 2 are examined by Criterion 1.

For example, a bicentroidal alkane of *meso*-type is represented by a directed-tree representation (**34**), as shown in Fig. 4. Each terminal is dually considered to be a principal vertex (Ⓟ) of one alkyl ligand and to be a root (●) of the other alkyl ligand. As a result, we obtain such alkyl ligands as contained in **35**. Each alkyl ligand in isolation can be regarded as a planted 3D-tree, so that it is categorized into any one of Types I to V (Fig. 3). Hence, each alkyl ligand in isolation can be regarded as a recursive alkyl ligand defined by Criterion 2 so as to be selected as an entity for Criterion 1, where its principal node (Ⓟ) is regarded as a center to be examined.



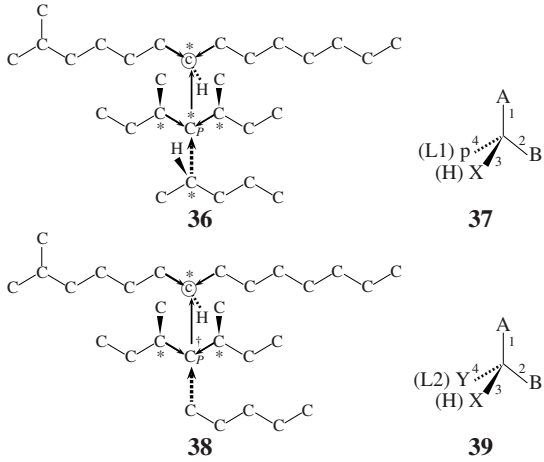
34 **35**

Figure 4: Selection of recursive alkyl ligands by means of directed-tree representations of a bicentroidal alkane. The alkane is divided into two recursive alkyl ligands (as planted 3D-trees) at the bicentroid. The symbol Ⓟ indicates the principal node of each alkyl ligand, while the symbol ● indicates the root which is occupied commonly by the resulting alkyl ligands.

2.5 The Present Methodology vs. the Conventional One

It is worthwhile to compare the present methodology with the conventional one by referring to examples which we encounter in the enumeration of alkanes as 3D-trees.

The centroid of a centroidal alkane of carbon content 29 (**36**) is determined to be asymmetric in terms of Criterion 1, because the corresponding promolecule (**37**) belongs to Type III



36 **37**

38 **39**

Figure 5: Examples of centroidal alkanes, where the determination of asymmetry or pseudoasymmetry (for the center C_P) by the present methodology is different from the determination by the revised CIP-system.

(chiral/*RS*-stereogenic/scleral). The proligands around the centroid of **36** (or **37**) are a heptyl ligand (Type IV: A, achiral), a 5-methylhexyl ligand (Type IV: B, achiral) and a 4-(butan-2-yl)-3,5-dimethyloctan-4-yl ligand (named L1, Type III: p, chiral) and a hydrogen (X, achiral) so as to be represented by C(ABXp) (i.e., Type III). The centroid marked by the symbol ⓒ in **36** is determined to be asymmetric (stereogenic) and to have *R*-configuration even when we rely on the revised CIP-system.

The centroid of another centroidal alkane of carbon content 29 (**38**) is determined to be asymmetric in terms of Criterion 1, because the corresponding promolecule (**39**) belongs to Type I (chiral/*RS*-stereogenic/ascleral). The proligands around the centroid of **38** (or **39**) are found to be a heptyl ligand (Type IV: A, achiral), a 5-methylhexyl ligand (Type IV: B, achiral) and a 4-(butan-2-yl)-3-methylnonan-4-yl ligand (named L2, Type V: Y, achiral) and a hydrogen (X, achiral) so as to be represented by C(ABXY) (i.e., Type I). The centroid marked by the symbol ⓒ is determined to be asymmetric (stereogenic) and to have *R*-configuration even when we rely on the revised CIP-system.

As long as we focus our attention on the centroids of **36** and **38**, they seem to behave similarly under the present methodology and under the revised CIP-system. However, their inner structures behave differently due to the change of viewpoints.

According to Criterion 2 applied to **36**, the heptyl ligand (Type IV), the 5-methylhexyl ligand (Type IV) and the 4-(butan-2-yl)-3,5-dimethyloctan-4-yl ligand (named L1, Type III) are selected as entities for Criterion 1. Because Ligand L1 in isolation belongs to Type III (corresponding to the proligand C(p$\overline{\text{p}}$q), cf. Fig. 3), the principal node represented by the symbol C_P is determined to be asymmetric, as marked by an asterisk. If we alternatively consider the principal node (C_P) to be the center of another tetrahedral molecule (the same compound as **36**) regardless of Criterion 2, the tetrahedral molecule belongs to Type III (corresponding to the

promolecule C(p$\overline{\text{p}}$qr), cf. Fig. 1). Hence, the principal node (C_P) as such a tentative center in **36** is also concluded to be asymmetric.

According to Criterion 2 applied to **38**, the heptyl ligand (Type IV), the 5-methylhexyl ligand (Type IV) and the 4-(butan-2-yl)-3-methylnonan-4-yl ligand (named L2, Type V) are selected as next entities for Criterion 1. Because Ligand L2 in isolation belongs to Type V (corresponding to the proligand C(Xp$\overline{\text{p}}$), cf. Fig. 3), the principal node represented by the symbol C_P is determined to be pseudoasymmetric, as marked by a dagger. If we consider the principal node (C_P) to be the tentative center of a tetrahedral molecule, the principal node (C_P) is changed to be asymmetric, because the tetrahedral molecule belongs to Type III (corresponding to the promolecule C(p$\overline{\text{p}}$qX): cf. Fig. 1).

According to the revised CIP-system, on the other hand, the configuration at the the node denoted by C_P in **36** is reflection-invariant so that the node (C_P) is determined to be pseudoasymmetric. On the same line, the configuration at the the node denoted by C_P in **38** is reflection-invariant so that the node (C_P) is determined to be pseudoasymmetric. It follows that the *S*-configurations at C_P in **36** and **38** are designated by a lowercase letter *s* according to the revised CIP-system. Thus, the viewpoint of the revised CIP-system, which takes no thought of centroids, is in sharp contrast with the present one, where Ligand L1 (p, chiral) around the centroid of **37** and Ligand L2 (Y, achiral) around the centroid of **39** are selected as entities to be examined in agreement with Criterion 2.

3 Enumeration

3.1 Enumeration of Alkyl Ligands

In order to take account of asymmetric and pseudoasymmetric centers, we shall enumerate planted promolecules of Type I and III (for asymmetric centers) and planted promolecules of Type V (for pseudoasymmetric centers). The obtained cycle indices with chirality fittingness (CI-CFs) are then converted into functional equations for counting alkyl ligands.

3.1.1 Cycle Indices with Chirality Fittingness

First, we consider the action of the $\mathbf{C}_{3v}$-point group

$$\mathbf{C}_{3v} \sim \{(1)(2)(3), (1\ 2\ 3), (1\ 3\ 2); \overline{(1)(2\ 3)}, \overline{(1\ 3)(2)}, \overline{(1\ 2)(3)}\}, \tag{1}$$

which is represented by its right coset representation $((\mathbf{C}_s\backslash)\mathbf{C}_{3v})$ according to the three substitution positions of a methyl skeleton. Note that each overbar indicates the alternation of ligand chirality. We have recently reported the enumeration of monosubstituted alkanes [21–23] after we developed *the proligand method* as a general methodology for enumerating stereoisomers [17–19]. Although the previous results have taken no account of Types I–V [21], a new view added to explain them in the present paper serves us with one of important parts to evaluate planted promolecules (alkyl ligands) of Types I–V distinctly.

We are able to use Theorem 3 of Ref. 19 and the derived eq. 3 of Ref. 21:

$$\text{CI-CF}^{(\text{I–V})}(\mathbf{C}_3; b_d) = \frac{1}{3}(b_1^3 + 2b_3) \tag{2}$$

to count steric isomers also in the present context without any modification, where the symbol b_d represents a sphericity index (SI) which characterizes a hemispheric d-cycle. Note that the

term *steric isomers* is used to denote Types I—V achiral planted promolecules and chiral planted promolecules, where two enantiomers of each pair are counted separately.

To count achiral planted promolecules of Types IV and V only, the elements corresponding to reflections in eq. 1 are used according to eq. 4 of Ref. 21, which has been derived from the first proposition of Theorem 4 of Ref. 19. Thereby we obtain the following CI-CF:

$$\text{CI-CF}^{(\text{IV/V})}(\mathbf{C}_{3v};a_d,c_d) = a_1c_2. \tag{3}$$

Note that the symbols a_d and c_d are used to represent sphericity indices (SIs) other than b_d, where the SI a_d characterizes a homospheric d-cycle and the SI c_d characterizes an enantiospheric d-cycle.

Let us next consider the action of the permutation group represented by

$$\mathbf{C}_{3\tilde{v}} \sim \{(1)(2)(3),(1\ 2\ 3),(1\ 3\ 2);(1)(2\ 3),(1\ 3)(2),(1\ 2)(3)\}, \tag{4}$$

which does not involve the alternation of ligand chirality. On the same line as eq. 1 is concerned with chirality/achirality, eq. 4 is concerned with *RS*-stereogenicity/*RS*-astereogenicity. This means that the three elements other than those of $\mathbf{C}_3$ can be used to evaluate the number of Types II and IV (*RS*-astereogenic). In parallel to the derivation of eq. 3, the number of planted promolecules of Type II and IV (*RS*-astereogenic) can be evaluated by using the following CI-CF:

$$\text{CI-CF}^{(\text{II/IV})}(\mathbf{C}_{3\tilde{v}};b_d) = b_1b_2. \tag{5}$$

Let us further consider the action of the ligand-inversion group represented by

$$\mathbf{C}_{3\hat{I}} \sim \{(1)(2)(3),(1\ 2\ 3),(1\ 3\ 2);\overline{(1)(2)(3)},\overline{(1\ 2\ 3)},\overline{(1\ 3\ 2)}\}, \tag{6}$$

which is concerned with sclerality/asclerality. The discussions described for deriving eqs. 3 and 5 are effective to the $\mathbf{C}_{3\hat{I}}$-group. It follows that the enumeration of planted promolecules of Type I and IV (ascleral) can be conducted by using the following CI-CF:

$$\text{CI-CF}^{(\text{I/IV})}(\mathbf{C}_{3\hat{I}};a_d,c_d) = \frac{1}{3}(a_1^3+2a_3), \tag{7}$$

where the three elements other than those of $\mathbf{C}_3$ in eq. 6 are used to evaluate the added number of Types I and IV (ascleral).

The numbers evaluated by eqs. 3, 5, and 7 commonly contain the number of Type-IV alkyl ligands (i.e., planted promolecules of Type IV). Hence, the next task is to evaluate the number of such Type-IV alkyl ligands. Achiral and *RS*-astereogenic planted promolecules (Type IV) have constitutions such as A_3 and A_2B, where A and B represent achiral ligands (nested planted promolecules). As a result, such planted promolecules of Type IV are represented by the corresponding CI-CF as follows:

$$\text{CI-CF}^{(\text{IV})}(\mathbf{C}_{3v};a_d) = a_1a_2. \tag{8}$$

Compare eq. 8 with eq. 3, where the product a_1c_2 demonstrates the participation of $Ap\overline{p}$ (Type V) along with A_3 and A_2B (Type IV).

We then subtract eq. 8 from eq. 7 for counting planted promolecules of Type I (chiral, *RS*-stereogenic, and ascleral); from eq. 5 for counting those of Type II (chiral and *RS*-astereogenic));

or from eq. 3 for counting those of Type V (achiral and *RS*-stereogenic). Thereby, we obtain the following CI-CFs:

$$\text{CI-CF}^{(\text{I})}(\mathbf{C}_{3\widehat{I}};a_d) = \frac{1}{3}(a_1^3+2a_3)-a_1a_2 \tag{9}$$

$$\text{CI-CF}^{(\text{II})}(\mathbf{C}_{3\widehat{v}};a_d,b_d) = b_1b_2-a_1a_2 \tag{10}$$

$$\text{CI-CF}^{(\text{V})}(\mathbf{C}_{3v};a_d,c_d) = a_1c_2-a_1a_2. \tag{11}$$

Finally, by subtracting eqs. 8–11 from eq. 2, we obtain the following CI-CF for counting planted promolecules of Type III (chiral and *RS*-stereogenic) as follows:

$$\text{CI-CF}^{(\text{III})}(\mathbf{C}_3;a_d,b_d,c_d) = \frac{1}{3}(b_1^3+2b_3)-\frac{1}{3}(a_1^3+2a_3)-(b_1b_2-a_1a_2)-(a_1c_2-a_1a_2), \tag{12}$$

where the two planted promolecules of each enantiomeric pair are counted separately (i.e., under the action of $\mathbf{C}_3$).

3.1.2 Functional Equations for Recursive Calculations

According to previous enumerations of monosubstituted alkanes [21–23], let α_k be the number of achiral monosubstituted alkanes (alkyl ligands as planted promolecules) of carbon content k; let γ_k be the number of monosubstituted alkanes (diploid as planted promolecules) of carbon content k; and let β_k be the number of monosubstituted alkanes (alkyl ligands as steric isomers) of carbon content k. The present target is to subdivide these numbers (α_k, γ_k, and β_k) with referring to the numbers of asymmetric and pseudoasymmetric centers, which are determined by means of Criteria 1 and 2.

Let $\alpha_{k\ell m}$, $\gamma_{k\ell m}$ and $\beta_{k\ell m}$ be respective subdivided numbers with respect to ℓ asymmetric centers and m pseudoasymmetric centers, where they are represented by the following summations:

$$\alpha_k = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\alpha_{k\ell m} \tag{13}$$

$$\gamma_k = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\gamma_{k\ell m} \tag{14}$$

$$\beta_k = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\beta_{k\ell m}. \tag{15}$$

We regard these numbers ($\alpha_{k\ell m}$, $\gamma_{k\ell m}$, and $\beta_{k\ell m}$) as the coefficients of the following generating functions:

$$a(x^d,y^d,z^d) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\alpha_{k\ell m}z^{dm}\right)y^{d\ell}\right)x^{dk} \tag{16}$$

$$c(x^d,y^d,z^d) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\gamma_{k\ell m}z^{dm}\right)y^{d\ell}\right)x^{dk} \tag{17}$$

$$b(x^d,y^d,z^d) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\beta_{k\ell m}z^{dm}\right)y^{d\ell}\right)x^{dk}, \tag{18}$$

where the valuable x is concerned with carbon content, the valuable y is concerned with the number of asymmetric centers, and the valuable z is concerned with the number of pseudoasymmetric centers. We put $\alpha_{000} = 1$, $\gamma_{000} = 1$, and $\beta_{000} = 1$ for treating the respective initial (trivial) cases.

We regard these generating functions as functional equations when we take account of the lowest powers, i.e., $a(x,y,z)$ ($d = 1$ in eq. 16), $c(x^2,y^2,z^2)$ ($d = 2$ in eq. 17 because d should be even), and $b(x,y,z)$ ($d = 1$ in eq. 18).

Suppose that the functional equation $a(x,y,z)$ has been obtained up to carbon content k for inner (nested) planted promolecules. Then, the terms of the $a(x,y,z)$ up to k can be recursively used to enumerate alkyl ligands (planted promolecules) of carbon content $k+1$, where the numbers of asymmetric and pseudoasymmetric centers satisfies $\ell < k$ and $m < k$. Because the resulting functional equation $a(x,y,z)$ is concerned with achiral planted promolecules (Types IV and V) of carbon content $k+1$, the Type-V planted promolecules (eq. 11) causes an increase of pseudoasymmetric centers by one, while Type-IV planted promolecules (eq. 8) has no effects except the increase of carbon content. As a result, the SIs a_1, a_2, and c_2 in eq. 8 (multiplied by x) and eq. 11 (multiplied by xz) are replaced by $a(x,y,z)$, $a(x^2,y^2,z^2)$, and $c(x^2,y^2,z^2)$ so as to give the following functional equation:

$$a(x,y,z) = 1 + xa(x,y,z)a(x^2,y^2,z^2) + xz\left\{a(x,y,z)c(x^2,y^2,z^2) - a(x,y,z)a(x^2,y^2,z^2)\right\}, \quad (19)$$

where the initial value 1 is added to treat a trivial case of hydrogen substitution.

In a similar way, the functional equation $b(x,y,z)$, which is concerned with all types of planted promolecules (Types I–V) of carbon content $k+1$, can be constructed by the data obtained up to carbon content k. For this purpose, we take account of eq. 5 (multiplied by x for Types II and IV because of increasing carbon content 1), eq. 11 (multiplied by xz for Type V because of increasing carbon content 1 and one pseudoasymmetric center) and eqs. 9 and 12 (multiplied by xy for Types I and III because of increasing carbon content 1 and one asymmetric centers). After the SIs a_d, c_d, and b_d in these equations are replaced by $a(x^d,y^d,z^d)$, $c(x^d,y^d,z^d)$, and $b(x^d,y^d,z^d)$, they are summed up to give the following functional equation:

$$\begin{aligned} b(x,y,z) &= 1 + xb(x,y,z)b(x^2,y^2,z^2) + xz\left\{a(x,y,z)c(x^2,y^2,z^2) - a(x,y,z)a(x^2,y^2,z^2)\right\} \\ &\quad + \frac{xy}{3}\left\{b(x,y,z)^3 + 2b(x^3,y^3,z^3)\right\} - xyb(x,y,z)b(x^2,y^2,z^2) \\ &\quad - xy\left\{a(x,y,z)c(x^2,y^2,z^2) - a(x,y,z)a(x^2,y^2,z^2)\right\}, \end{aligned} \quad (20)$$

where the initial value 1 is added to treat a trivial case of hydrogen substitution.

For the purpose of evaluating $c(x^2,y^2,z^2)$, we have to take account of diploids [21]. Although we omit the details of the derivation, we should replace the terms in eqs. 5, 11, and 9 (and eq. 12), i.e., $b(x^d,y^d,z^d)$ by $c(x^{2d},y^{2d},z^{2d})$, $a(x^d,y^d,z^d)$ by $a(x^{2d},y^{2d},z^{2d})$, and $c(x^d,y^d,z^d)$ by $c(x^{2d},y^{2d},z^{2d})$. After the replacement, it is necessary for the equation of Types II and IV (increasing carbon content 2) to be multiplied by x^2; for the equation of Type V (increasing carbon content 2 and two pseudoasymmetric centers) to be multiplied by x^2z^2; as well as for the equation of Types I and III (increasing carbon content 2 and two asymmetric centers) to be multiplied by x^2y^2. By summing up these equations, we obtain the following functional equation:

$$\begin{aligned} c(x^2,y^2,z^2) &= 1 + x^2c(x^2,y^2,z^2)c(x^4,y^4,z^4) \\ &\quad + x^2z^2\{a(x^2,y^2,z^2)c(x^4,y^4,z^4) - a(x^2,y^2,z^2)a(x^4,y^4,z^4)\} \\ &\quad + \frac{x^2y^2}{3}\left\{c(x^2,y^2,z^2)^3 + 2c(x^6,y^6,z^6)\right\} - x^2y^2c(x^2,y^2,z^2)c(x^4,y^4,z^4) \end{aligned}$$

$$-x^2y^2\left\{a(x^2,y^2,z^2)c(x^4,y^4,z^4)-a(x^2,y^2,z^2)a(x^4,y^4,z^4)\right\}, \tag{21}$$

where the initial value 1 is added to treat a trivial case of hydrogen substitution.

The functional equations, $a(x,y,z)$ (eq. 19), $c(x^2,y^2,z^2)$ (eq. 21), and $b(x,y,z)$ (eq. 20), have recursive nature so that they can be used to evaluate the numbers of relevant planted promolecules recursively as the carbon content k is increased successively by one. The resulting generating functions have the forms shown in eqs. 16–18.

3.2 Enumeration of Centroidal Alkanes

In the previous subsection, we have formulated a recursive method of calculating eqs. 16–18 by using $a(x,y,z)$ (eq. 19), $c(x^2,y^2,z^2)$ (eq. 21), and $b(x,y,z)$ (eq. 20). In the present subsection, the results of the recursive calculation are applied to enumerate alkanes (promolecules) of Types I–V on the basis of a tetrahedral skeleton.

3.2.1 Cycle Indices with Chirality Fittingness

Although the previous results concerned with enumeration of promolecules and its application to centroidal alkanes [24, 27] have not involved subdivision into five types, the methodology can be applied to evaluate promolecules of Types I–V distinctly. Thus, we consider the action of the $\mathbf{T}_d$-point group:

$$\begin{aligned}\mathbf{T}_d \;=\; &\{(1)(2)(3)(4),(1\,2)(3\,4),(1\,3)(2\,4),(1\,4)(2\,3),(1)(2\,4\,3),(1\,2\,3)(4),\\ &(1\,3\,4)(2),(1\,4\,2)(3),(1)(2\,3\,4),(1\,2\,4)(3),(1\,3\,2)(4),(1\,4\,3)(2);\\ &\overline{(1)(2\,3)(4)},\overline{(1\,2\,4\,3)},\overline{(1\,3\,4\,2)},\overline{(1\,4)(2)(3)},\overline{(1)(2)(3\,4)},\overline{(1\,2)(3)(4)},\\ &\overline{(1\,3\,2\,4)},\overline{(1\,4\,2\,3)},\overline{(1)(2\,4)(3)},\overline{(1\,2\,3\,4)},\overline{(1\,3)(2)(4)},\overline{(1\,4\,3\,2)}\}\end{aligned} \tag{22}$$

which is represented by its right coset representation $((\mathbf{C}_{3v}\backslash)\mathbf{T}_d)$ according to the four substitution positions of a tetrahedral skeleton. For the purpose of counting promolecules as steric isomers (i.e., Types I–V), we have reported eq. 2 of Ref. 24 derived by Theorem 3 of Ref. 19:

$$\text{CI-CF}^{(\text{I–V})}(\mathbf{T};b_d)=\frac{1}{12}(b_1^4+3b_2^2+8b_1b_3). \tag{23}$$

where two enantiomers of each pair and each achiral promolecules are counted separately.

To count achiral promolecules only (i.e., Types IV and V), we have reported eq. 3 of Ref. 24 as follows:

$$\text{CI-CF}^{(\text{IV/V})}(\mathbf{T}_d;\$_d)=\frac{1}{2}(a_1^2c_2+c_4), \tag{24}$$

where the elements corresponding to reflections in eq. 22 are used according to the first proposition of Theorem 4 of Ref. 19.

Let us next consider the permutation group represented as follows:

$$\begin{aligned}\mathbf{T}_{\tilde{\sigma}} \;=\; &\{(1)(2)(3)(4),(1\,2)(3\,4),(1\,3)(2\,4),(1\,4)(2\,3),(1)(2\,4\,3),(1\,2\,3)(4),\\ &(1\,3\,4)(2),(1\,4\,2)(3),(1)(2\,3\,4),(1\,2\,4)(3),(1\,3\,2)(4),(1\,4\,3)(2);\\ &(1)(2\,3)(4),(1\,2\,4\,3),(1\,3\,4\,2),(1\,4)(2)(3),(1)(2)(3\,4),(1\,2)(3)(4),\\ &(1\,3\,2\,4),(1\,4\,2\,3),(1)(2\,4)(3),(1\,2\,3\,4),(1\,3)(2)(4),(1\,4\,3\,2)\},\end{aligned} \tag{25}$$

which is obtained by omitting the alternation of ligand chirality in $\mathbf{T}_d$ (eq. 22). Note that the action of $\mathbf{T}_{\tilde{\sigma}}$ (eq. 25) is concerned with *RS*-stereogenicity/*RS*-astereogenicity.

On the same line as the derivation of eq. 24 for $\mathbf{T}_d$ (eq. 22), the counterpart CI-CF for $\mathbf{T}_{\tilde{\sigma}}$ (eq. 25) corresponds to *RS*-astereogenic promolecules (i.e., Types II and IV):

$$\text{CI-CF}^{(\text{II/IV})}(\mathbf{T}_{\tilde{\sigma}}; b_d) = \frac{1}{2}(b_1^2 b_2 + b_4), \tag{26}$$

where the elements other than those of $\mathbf{T}$ in eq. 25 are taken into consideration.

Let us finally consider the ligand-inversion group represented as follows:

$$\begin{aligned}\mathbf{T}_{\tilde{I}} \;=\; & \{(1)(2)(3)(4), (1\,2)(3\,4), (1\,3)(2\,4), (1\,4)(2\,3), (1)(2\,4\,3), (1\,2\,3)(4), \\ & (1\,3\,4)(2), (1\,4\,2)(3), (1)(2\,3\,4), (1\,2\,4)(3), (1\,3\,2)(4), (1\,4\,3)(2); \\ & \overline{(1)(2)(3)(4)}, \overline{(1\,2)(3\,4)}, \overline{(1\,3)(2\,4)}, \overline{(1\,4)(2\,3)}, \overline{(1)(2\,4\,3)}, \overline{(1\,2\,3)(4)}, \\ & \overline{(1\,3\,4)(2)}, \overline{(1\,4\,2)(3)}, \overline{(1)(2\,3\,4)}, \overline{(1\,2\,4)(3)}, \overline{(1\,3\,2)(4)}, \overline{(1\,4\,3)(2)}\},\end{aligned} \tag{27}$$

where the latter half (the twelve elements after a semicolon) is obtained by altering the ligand chirality for the former half of elements (i.e., those of $\mathbf{T}$). Note that the action of $\mathbf{T}_{\tilde{I}}$ (eq. 27) is concerned with sclerality/asclerality.

On the same line as the derivation of eq. 24 for $\mathbf{T}_d$ (eq. 22), the counterpart CI-CF for $\mathbf{T}_{\tilde{I}}$ (eq. 27) can be derived so as to count ascleral promolecules (i.e., Types I and IV):

$$\text{CI-CF}^{(\text{I/IV})}(\mathbf{T}_{\tilde{I}}; \$_d) = \frac{1}{12}(a_1^4 + 3c_2^2 + 8a_1a_3), \tag{28}$$

where the twelve elements other than those of $\mathbf{T}$ in eq. 27 are taken into consideration.

The numbers evaluated by eqs. 24, 26, and 28 commonly contain the number of promolecules of Type IV. Hence, the next task is to evaluate the number of such promolecules of Type IV. For this purpose, let us examine the terms appearing in eq. 24. The first term ($a_1^2c_2$) in eq. 24 is related to a pseudoasymmetric promolecule XYp$\overline{\text{p}}$ (e.g., **15**) along with Type-IV promolecules of ABX_2 (e.g., **12**) and A_2X_2 (+ $X_2p\overline{p}$). The Type-IV promolecules correspond to the terms $a_1^2a_2$ and a_2c_2, which contain a duplicated component represented by a_2^2. This means that the first term ($a_1^2c_2$) in eq. 24 should be replaced by $a_1^2a_2 + a_2c_2 - a_2^2$ so as to exclude contamination by pseudoasymmetry. The second term (c_4) in eq. 24 is not related to pseudoasymmetry. Hence, eq. 24 is converted into the following form:

$$\text{CI-CF}^{(\text{IV})}(\mathbf{T}_d; \$_d) = \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \tag{29}$$

for counting Type-IV promolecules.

The combination of the equations derived above gives the following CI-CFs for counting respective *RS*-stereoisomeric types:

$$\text{CI-CF}^{(\text{I})}(\mathbf{T}_{\tilde{I}}; \$_d) = \frac{1}{12}(a_1^4 + 3c_2^2 + 8a_1a_3) - \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \tag{30}$$

$$\text{CI-CF}^{(\text{II})}(\mathbf{T}_{\tilde{\sigma}}; \$_d, b_d) = \frac{1}{2}(b_1^2b_2 + b_4) - \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \tag{31}$$

$$\begin{aligned}\text{CI-CF}^{(\text{III})}(\mathbf{T}; \$_d, b_d) = & \frac{1}{12}(b_1^4 + 3b_2^2 + 8b_1b_3) - \frac{1}{12}(a_1^4 + 3c_2^2 + 8a_1a_3) - \frac{1}{2}(b_1^2b_2 + b_4) \\ & - \frac{1}{2}(a_1^2c_2 + c_4) + (a_1^2a_2 + a_2c_2 - a_2^2 + c_4)\end{aligned} \tag{32}$$

$$\text{CI-CF}^{(\text{V})}(\mathbf{T}_d; \$_d) = \frac{1}{2}(a_1^2c_2 - a_1^2a_2) - \frac{1}{2}(a_2c_2 - a_2^2). \tag{33}$$

Note that the derivations are schematically shown as follows: Type I (eq. 28 minus eq. 29); Type II (eq. 26 minus eq. 29); Type V (eq. 24 minus eq. 29); and Type III (eq.23 minus eqs. 30, 31, and 24).

3.2.2 Functional Equations for Counting Centroidal Alkanes

The CI-CFs for counting centroidal promolecules (eqs. 29–33) should be converted into the corresponding functional equations for counting centroidal alkanes, where each SI is modified so as to accommodate a respective functional equation for counting alkyl ligands (one of eqs. 19–21).

Let $B_{k\ell m}^{(\tau)}$ (τ = I, II, ... V or their combinations) be the number of alkanes (promolecules) of Type τ, which have k carbons, ℓ asymmetric centers and m pseudoasymmetric centers. Let the symbol $B_k^{(\tau)}$ be the summation for each type (τ) represented as follows:

$$B_k^{(\tau)} = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} B_{k\ell m}^{(\tau)}, \tag{34}$$

Then, we regard these numbers $B_{k\ell m}^{(\tau)}$ as the coefficients of the following generating functions:

$$B^{(\tau)}(x^d, y^d, z^d) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} B_{k\ell m}^{(\tau)} z^{dm} \right) y^{d\ell} \right) x^{dk} \tag{35}$$

where the valuable x is concerned with carbon content, the valuable y is concerned with the number of asymmetric centers, and the valuable z is concerned with the number of pseudoasymmetric centers. We put $B_{000}^{(\tau)} = 0$ for treating the respective initial (trivial) cases.

To evaluate the generating functions (eq. 35: τ = I, II, ..., V and $d = 1$), we derive the corresponding functional equations by starting from the CI-CFs (eqs. 29–33). Thus, the SIs a_d, c_d, and b_d in these equations are replaced by $a(x^d, y^d, z^d)$, $c(x^d, y^d, z^d)$, and $b(x^d, y^d, z^d)$ to give the following functional equations:

$$\begin{aligned}
B^{(\mathrm{I})}(x,y,z) &= \frac{xy}{12}\left\{a(x,y,z)^4 + 3c(x^2,y^2,z^2)^2 + 8a(x,y,z)a(x^3,y^3,z^3)\right\} \\
&\quad - \frac{xy}{2}\left\{a(x,y,z)^2 a(x^2,y^2,z^2) + a(x^2,y^2,z^2)c(x^2,y^2,z^2)\right. \\
&\qquad \left. - a(x^2,y^2,z^2)^2 + c(x^4,y^4,z^4)\right\} \qquad (36) \\
B^{(\mathrm{II})}(x,y,z) &= \frac{x}{2}\left\{b(x,y,z)^2 b(x^2,y^2,z^2) + b(x^4,y^4,z^4)\right\} \\
&\quad - \frac{x}{2}\left\{a(x,y,z)^2 a(x^2,y^2,z^2) + a(x^2,y^2,z^2)c(x^2,y^2,z^2)\right. \\
&\qquad \left. - a(x^2,y^2,z^2)^2 + c(x^4,y^4,z^4)\right\} \qquad (37) \\
B^{(\mathrm{III})}(x,y,z) &= \frac{xy}{12}\left\{b(x,y,z)^4 + 3b(x^2,y^2,z^2)^2 + 8b(x,y,z)b(x^3,y^3,z^3)\right\} \\
&\quad - \frac{xy}{12}\left\{a(x,y,z)^4 + 3c(x^2,y^2,z^2)^2 + 8a(x,y,z)a(x^3,y^3,z^3)\right\} \\
&\quad - \frac{xy}{2}\left\{b(x,y,z)^2 b(x^2,y^2,z^2) + b(x^4,y^4,z^4)\right\}
\end{aligned}$$

$$
\begin{aligned}
&-\frac{xy}{2}\left\{a(x,y,z)^2c(x^2,y^2,z^2)+c(x^4,y^4,z^4)\right\}\\
&+xy\left\{a(x,y,z)^2a(x^2,y^2,z^2)+a(x^2,y^2,z^2)c(x^2,y^2,z^2)\right.\\
&\qquad\left.-a(x^2,y^2,z^2)^2+c(x^4,y^4,z^4)\right\} \qquad (38)\\
B^{(\mathrm{IV})}(x,y,z) &= \frac{x}{2}\left\{a(x,y,z)^2a(x^2,y^2,z^2)+a(x^2,y^2,z^2)c(x^2,y^2,z^2)\right.\\
&\qquad\left.-a(x^2,y^2,z^2)^2+c(x^4,y^4,z^4)\right\} \qquad (39)\\
B^{(\mathrm{V})}(x,y,z) &= \frac{xz}{2}\left\{a(x,y,z)^2c(x^2,y^2,z^2)-a(x,y,z)^2a(x^2,y^2,z^2)\right\}\\
&\quad-\frac{xz}{2}\left\{a(x^2,y^2,z^2)c(x^2,y^2,z^2)-a(x^2,y^2,z^2)^2\right\}, \qquad (40)
\end{aligned}
$$

where, to treat the effect of the central carbon atom (i.e., the centroid here), we should consider the multiplication of xy for Types I and III in accord with the increase of carbon content and an asymmetric center; that of x for Types II and IV in accord with the increase of carbon content; and that of xz for Type V in accord with the increase of carbon content and a pseudoasymmetric center.

Suppose that we have obtained $a(x,y,z)=\sum_{k=0}^{\mu}\alpha_k x^k$, $c(x^2,y^2,z^2)=\sum_{k=0}^{\mu}\gamma_k x^{2k}$, and $b(x,y,z)$ = $\sum_{k=0}^{\mu}\beta_k x^k$, where μ is tentatively fixed. On a similar line to the treatment described in Ref. [27], eqs. 36–40 are evaluated as follows. They are introduced into eqs. 36–40 to give $B^{(\tau)(\mu)}(x,y,z)$ (τ = I, II, …, V). Let the symbol coeff$(B^{(\tau)(\mu)}(x,y,z),x^{2\mu+1})$ etc. represent the coefficient of the term $x^{2\mu+1}$ appearing in the equation $B^{(\tau)(\mu)}(x,y,z)$ etc. after expansion. Note that the coefficient is a polynomial containing $y^\ell z^m$. Then, we obtain the following coefficients:

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}B^{(\tau)}_{(2\mu+1)\ell m}z^m\right)y^\ell=\mathrm{coeff}(B^{(\tau)(\mu)}(x,y,z),x^{2\mu+1}) \qquad (41)$$

for odd carbon contents as well as the following coefficients:

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}B^{(\tau)}_{(2\mu+2)\ell m}z^m\right)y^\ell=\mathrm{coeff}(B^{(\tau)(\mu)}(x,y,z),x^{2\mu+2}) \qquad (42)$$

for even carbon contents, where τ represents I, II, …, or V. Note that the powers of y and z are equal to or less than $2\mu+2$. These requirements should be considered in the following programming.

Let $A(x,y,z)$, $C(x,y,z)$, and $B(x,y,z)$ be functional equations for calculating the numbers of achiral, chiral, and total (achiral plus chiral) alkanes, where each pair of two enantiomers and each achiral alkane are respectively counted just once. Because the symbols concerning chiral alkanes, i.e., $B^{(\mathrm{I})}(x,y,z)$ (Type I: chiral/*RS*-stereogenic/ascleral), $B^{(\mathrm{II})}(x,y,z)$ (Type II: chiral/*RS*-astereogenic/scleral), and $B^{(\mathrm{III})}(x,y,z)$ (Type III: chiral/*RS*-stereogenic/scleral), represent the separate counting of two enantiomers of each pair, the functional equations $A(x,y,z)$, $C(x,y,z)$, and $B(x,y,z)$ are calculated as follows:

$$
\begin{aligned}
A(x,y,z) &= B^{(\mathrm{IV})}(x,y,z)+B^{(\mathrm{V})}(x,y,z) \qquad (43)\\
C(x,y,z) &= \frac{1}{2}\left\{B^{(\mathrm{I})}(x,y,z)+B^{(\mathrm{II})}(x,y,z)+B^{(\mathrm{III})}(x,y,z)\right\} \qquad (44)\\
B(x,y,z) &= \frac{1}{2}\left\{B^{(\mathrm{I})}(x,y,z)+B^{(\mathrm{II})}(x,y,z)+B^{(\mathrm{III})}(x,y,z)\right\}+B^{(\mathrm{IV})}(x,y,z)+B^{(\mathrm{V})}(x,y,z) \qquad (45)
\end{aligned}
$$

On the same line as above, we obtain the following coefficients:

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}A_{(2\mu+1)\ell m}z^m\right)y^\ell = \mathrm{coeff}(A(x,y,z)^{(\mu)},x^{2\mu+1}) \quad (46)$$

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}C_{(2\mu+1)\ell m}z^m\right)y^\ell = \mathrm{coeff}(C(x,y,z)^{(\mu)},x^{2\mu+1}) \quad (47)$$

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}B_{(2\mu+1)\ell m}z^m\right)y^\ell = \mathrm{coeff}(B(x,y,z)^{(\mu)},x^{2\mu+1}) \quad (48)$$

for odd carbon contents as well as the following coefficients:

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}A_{(2\mu+2)\ell m}z^m\right)y^\ell = \mathrm{coeff}(A(x,y,z)^{(\mu)},x^{2\mu+2}) \quad (49)$$

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}C_{(2\mu+2)\ell m}z^m\right)y^\ell = \mathrm{coeff}(C(x,y,z)^{(\mu)},x^{2\mu+2}) \quad (50)$$

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}B_{(2\mu+2)\ell m}z^m\right)y^\ell = \mathrm{coeff}(B(x,y,z)^{(\mu)},x^{2\mu+2}) \quad (51)$$

for even carbon contents.

3.2.3 Programming and Implementation

The functional equations $a(x^d,y^d,z^d)$, $c(x^d,y^d,z^d)$, and $b(x^d,y^d,z^d)$ contained in the right-hand sides of eqs. 36–40 have been evaluated respectively by eq. 19, eq. 21, and eq. 20 for alkyl ligands as planted 3D-trees. For the purpose of programming and implementation, the requirements represented by eqs. 41 and 42 as well as eqs. 46–51 should be considered in processes of recursive calculation.

Concretely speaking, suppose that the functional equation $a(x,y,z)$ (eq. 19), $c(x^2,y^2,z^2)$ (eq. 21), and $b(x,y,z)$ (eq. 19) have been recursively calculated up to carbon content k. They are introduced into eqs. 36–40 to count centroidal alkanes. Among the terms appearing in the expanded functional equations, the terms corresponding to x^{2k+1} and x^{2k+2} are adopted as new entries according to the definition of centroidal alkanes (cf. eqs. 41 and 42 as well as eqs. 46–51).

The procedure described in the preceding paragraph is implemented by mean of the Maple programming language and stored with the name "Alkane1-30b.mpl". Although the upper limit of the carbon content (k) is tentatively fixed to be 30, it can be freely selected as far as the capacity of a computer permits.

```
#Alkane1-30b.mpl
axyz := 1 + x*a111*a222 + x*z*(a111*c222 - a111*a222);
cxyz := 1 + x^2*c222*c444 + x^2*z^2*(a222*c444-a222*a444)
 + (1/3)*x^2*y^2*c222^3 + (2/3)*x^2*y^2*c666
 - x^2*y^2*c222*c444 - x^2*y^2*(a222*c444-a222*a444);
bxyz := 1 + x*b111*b222 + x*z*(a111*c222 - a111*a222)
 + (1/3)*x*y*b111^3 + (2/3)*x*y*b333
 - x*y*b111*b222 - x*y*(a111*c222 - a111*a222);

"Alkanes as Centroidal 3D-Trees";

typeI := (x*y/12)*(a111^4 + 3*c222^2 + 8*a111*a333)
 - (x*y/2)*(a111^2*a222 + a222*c222 -a222^2 + c444);
```

```
typeII := (x/2)*(b111^2*b222 + b444)
 - (x/2)*(a111^2*a222 + a222*c222 -a222^2 + c444);
typeIII:= (x*y/12)*(b111^4 + 3*b222^2 + 8*b111*b333)
 - (x*y/12)*(a111^4 + 3*c222^2 + 8*a111*a333)
 - (x*y/2)*(a111^2*c222 + c444) - (x*y/2)*(b111^2*b222 + b444)
 + x*y*(a111^2*a222 + a222*c222 -a222^2 + c444);
typeIV := (x/2)*(a111^2*a222 + a222*c222 - a222^2 + c444);
typeV := (x*z/2)*(a111^2*c222 - a111^2*a222) - (x*z/2)*(a222*c222 - a222^2);

Axh := typeIV + typeV;
Cxh := (1/2)*(typeI + typeII + typeIII);

"Initial Values";
a111 := 1; a222 := 1; a333 :=1; a444 :=1;
c222 := 1; c444 := 1; c666 := 1;
b111 := 1; b222 := 1; b333 := 1; b444 := 1;
asum := 1; csum := 1; bsum := 1;

Ah := x; Ch := 0;
BtypeI := 0; BtypeII := 0; BtypeIII := 0; BtypeIV := x; BtypeV := 0;

"Recursive Calculation";
for k from 1 to 30 by 1 do
Cbxyz:= expand(coeff(bxyz,x^k));
Caxyz:= expand(coeff(axyz,x^k));
Ccxyz:= expand(coeff(cxyz,x^(k*2)));

b1yz := expand(coeff(y*Cbxyz,y)):
b2yz := b1yz: b3yz := b1yz: b4yz := b1yz: subbsum := b1yz:
a1yz := expand(coeff(y*Caxyz,y)):
a2yz := a1yz: a3yz := a1yz: a4yz := a1yz: subasum := a1yz:
c1yz := expand(coeff(y*Ccxyz,y)):
c2yz := c1yz: c3yz := c1yz: subcsum := c1yz:

for l from 1 to degree(Cbxyz,y) by 1 do
CCbxyz:= coeff(Cbxyz, y^l):
bb1yz:= expand(coeff(z*CCbxyz,z)):
bb2yz:= bb1yz: bb3yz:= bb1yz: bb4yz:= bb1yz: subbsum := subbsum + bb1yz:

CCcxyz:= coeff(Ccxyz, y^(2*l)):
cc1yz:= expand(coeff(z*CCcxyz,z)):
cc2yz:= cc1yz: cc3yz:= cc1yz: subcsum := subcsum + cc1yz:

CCaxyz:= coeff(Caxyz, y^l):
aa1yz := expand(coeff(z*CCaxyz,z)):
aa2yz := aa1yz: aa3yz := aa1yz: aa4yz := aa1yz: subasum := subasum + aa1yz:

for m from 1 to degree(CCcxyz,z) by 1 do
CCCcxyz:= coeff(CCcxyz, z^(2*m)):
cc1yz:= cc1yz + CCCcxyz*z^(2*m): cc2yz:= cc2yz + CCCcxyz*z^(4*m):
cc3yz:= cc3yz + CCCcxyz*z^(6*m): subcsum := subcsum + CCCcxyz:
end do:

for n from 1 to degree(CCaxyz,z) by 1 do
CCCaxyz:= coeff(CCaxyz, z^n):
aa1yz:= aa1yz + CCCaxyz*z^n:     aa2yz:= aa2yz + CCCaxyz*z^(2*n):
aa3yz:= aa3yz + CCCaxyz*z^(3*n): aa4yz:= aa4yz + CCCaxyz*z^(4*n):
subasum := subasum + CCCaxyz:
end do:

for p from 1 to degree(CCbxyz,z) by 1 do
CCCbxyz:= coeff(CCbxyz, z^p):
bb1yz:= bb1yz + CCCbxyz*z^p:     bb2yz:= bb2yz + CCCbxyz*z^(2*p):
bb3yz:= bb3yz + CCCbxyz*z^(3*p): bb4yz:= bb4yz + CCCbxyz*z^(4*p):
subbsum := subbsum + CCCbxyz:
end do:

c1yz:= c1yz + cc1yz*y^(2*l): c2yz:= c2yz + cc2yz*y^(4*l):
c3yz:= c3yz + cc3yz*y^(6*l):
a1yz:= a1yz + aa1yz*y^l:     a2yz:= a2yz + aa2yz*y^(2*l):
a3yz:= a3yz + aa3yz*y^(3*l): a4yz:= a4yz + aa4yz*y^(4*l):
b1yz:= b1yz + bb1yz*y^l:     b2yz:= b2yz + bb2yz*y^(2*l):
b3yz:= b3yz + bb3yz*y^(3*l): b4yz:= b4yz + bb4yz*y^(4*l):
end do:

bsum := bsum + subbsum*x^k: asum := asum + subasum*x^k:
csum := csum + subcsum*x^(2*k):
b111 := b111 + b1yz*x^k:     b222 := b222 + b2yz*x^(2*k):
b333 := b333 + b3yz*x^(3*k):  b444 := b444 + b4yz*x^(4*k):
a111 := a111 + a1yz*x^k:     a222 := a222 + a2yz*x^(k*2):
a333 := a333 + a3yz*x^(k*3):  a444 := a444 + a4yz*x^(k*4):
c222 := c222 + c1yz*x^(k*2):  c444 := c444 + c2yz*x^(k*4):
c666 := c666 + c3yz*x^(k*6):

q := 2*k +1:
BtypeI := BtypeI + coeff(typeI,x^q)*x^q + coeff(typeI,x^(q+1))*x^(q+1):
BtypeII := BtypeII + coeff(typeII,x^q)*x^q + coeff(typeII,x^(q+1))*x^(q+1):
BtypeIII := BtypeIII + coeff(typeIII,x^q)*x^q + coeff(typeIII,x^(q+1))*x^(q+1):
BtypeIV := BtypeIV + coeff(typeIV,x^q)*x^q + coeff(typeIV,x^(q+1))*x^(q+1):
BtypeV := BtypeV + coeff(typeV,x^q)*x^q + coeff(typeV,x^(q+1))*x^(q+1):
Ah := Ah + coeff(Axh,x^q)*x^q + coeff(Axh,x^(q+1))*x^(q+1):
Ch := Ch + coeff(Cxh,x^q)*x^q + coeff(Cxh,x^(q+1))*x^(q+1):
end do:

Bh := Ah + Ch:
```

```
"Print Out of Type I (Chiral/RS-Stereogenic/Ascleral)";
for k from 1 to 30 by 1 do
printf("k = %d: ", k);
NtI := expand(coeff(BtypeI,x^k)):
if NtI = 0 then
degNtI := 1; else
degNtI := degree(NtI,z) + 1;
fi:
for m from 1 to degNtI do
printf("m = %d: ", m-1);
NNtI := coeff(z*NtI, z^m):
printf("%d &", expand(coeff(y*NNtI,y)));
for l from 1 to degree(NNtI,y) by 1 do
printf("%d &",
coeff(NNtI,y^l));
end do;
printf("¥¥¥¥ ¥n");
end do;
end do;

(Omitted)
```

In this code named "Alkane1-30b.mpl", the abbreviated symbols for functional equations (as generating functions) are used as follows: `a111` for $a(x,y,z)$ etc.; `c222` for $c(x^2,y^2,z^2)$ etc.; `b111` for $b(x,y,z)$ etc. so that they store calculated values in the form of counting series of generating functions. The symbols `asum`, `csum`, and `bsum` are used to store the series for $a(x,1,1)$, and $c(x^2,1,1)$, and $b(x,1,1)$.

The first part of this code declares three functional equations for alkyl ligands, i.e., `axyz` for $a(x,y,z)$ (eq. 19), `cxyz` for $c(x^2,y^2,z^2)$ (eq. 21), and `bxyz` for $b(x,y,z)$ (eq. 20), as well as five functional equations for alkanes, i.e., `typeI` for $B^{(\mathrm{I})}(x,y,z)$ (eq. 36), `typeII` for $B^{(\mathrm{II})}(x,y,z)$ (eq. 37), `typeIII` for $B^{(\mathrm{III})}(x,y,z)$ (eq. 38), `typeIV` for $B^{(\mathrm{IV})}(x,y,z)$ (eq. 39), `typeV` for $B^{(\mathrm{V})}(x,y,z)$ (eq. 40). In addition, `Ah` for $A(x,y,z)$ (eq. 43) and `Ch` for $C(x,y,z)$ (eq. 44) are involved.

In the paragraph "Initial Values", the initial values for the initial (trivial) alkyl ligands as well as the initial centroidal alkanes. Note that the setting of `Ah := x;` and `BtypeIV := x;` represents their initial values, each of which consists of the first value x ($= 1 \cdot x^1$) for $q = 1$ (i.e., $q = 2k+1$, $k = 0$) and the second value 0 ($= 0 \cdot x^2$) for $q+1 = 2$, because there are no centroidal alkanes of carbon content 2 and we start from $k = 1$ ($q = 3$) in a `do` loop for carbon content k.

The paragraph "Recursive Calculation" of the code shows the `do` loop for carbon content k, in which a nested `do` loop for the number of asymmetric centers (l) and three `do` loops nested further for pseudoasymmetric centers (`m`, `n`, and `p` are used). In each `do` loop, the next coefficients are calculated by using a Maple command `coeff` and added to the end of respective functional equations so as to generate intermediate generating functions. In the last part of the `do` loop for carbon content k, resulting coefficients are stored in counting series represented by `BtypeI` etc. After escaping from the outer `do` loop for k, the code `Bh := Ah + Ch:` calculates $B(x,y,z)$ (eq. 45). The paragraph "Print Out of Type I (Chiral/RS-Stereogenic/Ascleral)" and omitted paragraphs of the code show the print-out of the calculation results. Strictly speaking, k represents the carbon content of an alkyl ligand, while q represents the carbon content of an alkane. In the print-out sections, however, k is used in place of q for the sake of convenience.

We execute the code by inputting the following command on the Maple inputting window:

```
> read "Alkane1-30b.mpl";
```

The above described code gives calculation results according to the indication of its print-out sections. For example, we obtain the following result:

```
k = 19:
```

```
                                                  3          5
                NtI := 19104 y + 380 z y  + 6 y
m = 0: 0 &19104 &0 &0 &0 &6 &¥¥
m = 1: 0 &0 &0 &380 &¥¥
```

for the coefficient of the term x^{19} of $B^{(\mathrm{I})}(x,y,z)$, which is stored as the counting series `BtypeI`. The output of `NtI` means the term:

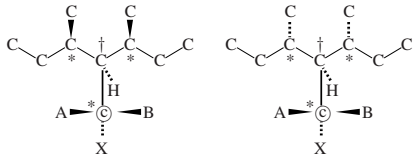
$$x^{19}\left(19104y+380y^3z+6y^5\right), \tag{52}$$

which shows the numbers of Type-I alkanes of of carbon content 19. The last two lines of the output are intended to construct rows of a table with respect to $k=19$; $m=0,1$; and $\ell=0$ to 5 ($x^k y^\ell z^m$) (cf. Table 1 shown below). As found by the code, when the carbon content of alkyl ligands runs from 1 to 30, the carbon content of alkanes runs from 3 to 62. For the sake of page saving, however, calculated values are shown up to 30.

3.2.4 Results and Illustrative Examples

Centroidal Alkanes of Type I Table 1 lists the coefficient $B^{(\mathrm{I})}_{k\ell m}$ of the term $x^k y^\ell z^m$ calculated by means of $B^{(\mathrm{I})}(x,y,z)$ (eq. 36), where each coefficient is stored in the series obtained as `BtypeI` of the code "Alkane1-30b.mpl".

In order to grasp the gist of the data collected in Table 1, it is worthwhile to examine several lower cases of carbon content. For example, the value 380 at the intersection between the ($k=19$, $m=1$)-row and the ($\ell=3$)-column corresponds to the term $380x^{19}y^3z$ (cf. eq. 52). Hence, there exist 380 chiral centroidal alkanes of Type I which have three asymmetric centers and one pseudoasymmetric center according to Criteria 1 and 2. Because the centroid of each of the 380 alkanes is asymmetric, the one pseudoasymmetric center is involved in an achiral alkyl ligand which belongs to Type V (e.g., **31**). It follows that each of the 380 alkanes is represented by the formula **40** or **41**, where the symbols A, B, and X represent a hydrogen atom or alkyl ligands. The alkyl ligands should be selected from achiral alkyl ligands of carbon content 1–8 so as to keep the central atom ⓒ of **40** or **41** being a centroid.



40 **41**

Figure 6: Chiral centroidal alkanes of Type I corresponding to the term $380x^{19}y^3z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbols A, B, and X represent a hydrogen atom or alkyl ligands, which are selected from achiral alkyl ligands of carbon content 1–8 to keep the central atom ⓒ being a centroid. An appropriate enantiomer of a pair is depicted as a representative.

The value 380 of the term $380x^{19}y^3z$ can be verified by using the data of $a(x,y,z)$ (for achiral alkyl ligands) up to x^8 appearing in the following generating function:

$$a(x,y,z)=x+x^2+2x^3+3x^4+5x^5+8x^6+14x^7+23x^8+(39+2y^2z)x^9+\cdots, \tag{53}$$

Table 1: Centroidal Alkanes of Type I (Chiral/*RS*-Stereogenic/Ascleral)[a]

Carbon	No. of Pseudoasym.	No. of Asymmetric Centers (ℓ)											
Content (k)	Centers (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11
$k=1$:	$m=0$:	0											
$k=2$:	$m=0$:	0											
$k=3$:	$m=0$:	0											
$k=4$:	$m=0$:	0											
$k=5$:	$m=0$:	0											
$k=6$:	$m=0$:	0											
$k=7$:	$m=0$:	0	4										
$k=8$:	$m=0$:	0	2										
$k=9$:	$m=0$:	0	14										
$k=10$:	$m=0$:	0	20										
$k=11$:	$m=0$:	0	74										
$k=12$:	$m=0$:	0	104										
$k=13$:	$m=0$:	0	316										
$k=14$:	$m=0$:	0	470										
$k=15$:	$m=0$:	0	1298										
$k=16$:	$m=0$:	0	2002										
$k=17$:	$m=0$:	0	5064										
$k=18$:	$m=0$:	0	7918										
$k=19$:	$m=0$:	0	19104	0	0	0	6						
	$m=1$:	0	0	0	380								
$k=20$:	$m=0$:	0	30060										
	$m=1$:	0	0	0	740								
	$m=2$:	0	0	0	0	0	2						
$k=21$:	$m=0$:	0	69530	0	0	0	22	0	4				
	$m=1$:	0	0	0	2916								
	$m=2$:	0	0	0	0	0	18						
$k=22$:	$m=0$:	0	110614										
	$m=1$:	0	0	0	5184								
	$m=2$:	0	0	0	0	0	34						
$k=23$:	$m=0$:	0	248652	0	0	0	88	0	32				
	$m=1$:	0	0	0	18596								
	$m=2$:	0	0	0	0	0	214						
$k=24$:	$m=0$:	0	397736										
	$m=1$:	0	0	0	33284								
	$m=2$:	0	0	0	0	0	508						
$k=25$:	$m=0$:	0	870538	0	0	0	268	0	168	0	10		
	$m=1$:	0	0	0	96388								
	$m=2$:	0	0	0	0	0	1970						
$k=26$:	$m=0$:	0	1398848										
	$m=1$:	0	0	0	168476								
	$m=2$:	0	0	0	0	0	3998						
$k=27$:	$m=0$:	0	3000730	0	0	0	800	0	718	0	120		
	$m=1$:	0	0	0	464532	0	10424						
	$m=2$:	0	0	0	0	0	13980	0	464				
$k=28$:	$m=0$:	0	4843730										
	$m=1$:	0	0	0	811444	0	19592						
	$m=2$:	0	0	0	0	0	28442	0	1248	0	12		
$k=29$:	$m=0$:	0	10202056	0	0	0	2168	0	2674	0	770	0	32
	$m=1$:	0	0	0	2052328	0	75784						
	$m=2$:	0	0	0	0	0	85782	0	5456	0	76		
	$m=3$:	0	0	0	0	0	0	0	8				
$k=30$:	$m=0$:	0	16528192										
	$m=1$:	0	0	0	3553848	0	134072						
	$m=2$:	0	0	0	0	0	166544	0	11120	0	156		
	$m=3$:	0	0	0	0	0	0	0	56				

[a]Two chiral alkanes of each enantiomeric pair are counted separately.

which is stored in `a111` during the recursive calculation by the code "Alkane1-30b.mpl". Let the partition $[k_1,k_2,k_3]$ represent the carbon contents of A, B, and X under the condition of A≠B, A≠X, B≠X and $k_1+k_2+k_3=9$. Then, the number of enantiomeric pairs is calculated by using the coefficients appearing in the right-side of eq. 53 as follows:

[8,1,0]	$23\times1\times1=23$;	[7,2,0]	$14\times1\times1=14$
[6,3,0]	$8\times2\times1=16$;	[6,2,1]	$8\times1\times1=8$
[5,4,0]	$5\times3\times1=15$;	[5,3,1]	$5\times2\times1=10$
[4,4,1]	$(2+1)\times1=3$;	[4,3,2]	$3\times2\times1=6$

total: 95

It should be noted that the three pairs of butyl ligands (A and B) for the partition [4,4,1] can

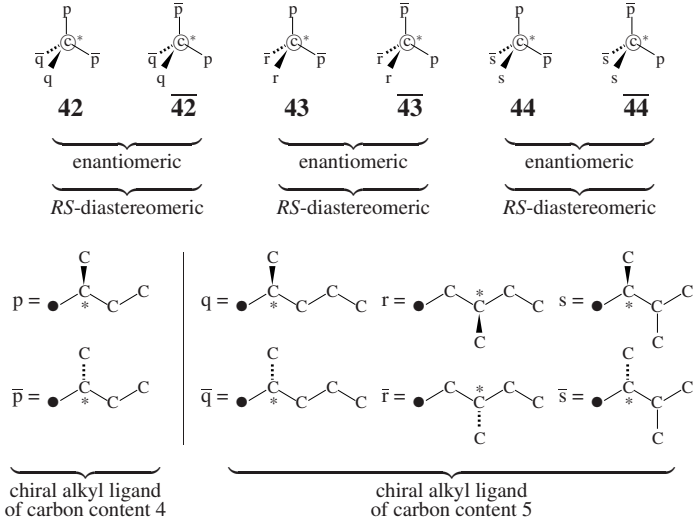


Figure 7: Chiral centroidal alkanes of Type I corresponding to the term $6x^{19}y^5$. Each pair of enantiomers (**42**/**42**, **43**/**43**, or **44**/**44**) is *RS*-diastereomeric at the same time.

be selected from three achiral butyl ligands (cf. $3x^4$ in eq. 53) under the condition of A≠B: i.e., *n*-butyl—isobutyl, *n*-butyl—*tert*-butyl, and isobutyl—*tert*-butyl. Because there exist two enantiomers for each of 95 enantiomeric pairs on the basis of **40** or **41**, we obtain the number of alkanes at issue to be $95 \times 2 \times 2 = 380$, which is equal to the coefficient of the term $380x^{19}y^3z$. Because we can manually depict the achiral isomers of alkanes of carbon content 1–8, we are able to depict the 380 stereoisomers based on **40** and **41** if we would go to such trouble.

We should here emphasize the importance of Criterion 2. The pseudoasymmetric center of **40** (or **41**) is determined at the step of the alkyl ligand of carbon content 9 under Criterion 2. If the same carbon center is examined at the step of the constructed alkane (**40** or **41**), it is determined to be asymmetric, because the corresponding promolecule belongs to Type III. The latter determination is not permitted if we start from Criterion 2. Compare the present case with **11**, which has been determined to be Type III.

The value 6 at the intersection between the ($k = 19$, $m = 0$)-row and the ($\ell = 5$)-column corresponds to the term $6x^{19}y^5$ (cf. eq. 52). This means that there exist six chiral centroidal Type-I alkanes which have five asymmetric centers and no pseudoasymmetric centers according to Criteria 1 and 2. Because there exist one enantiomeric pair of carbon content 4 (p/$\overline{\text{p}}$) and three enantiomeric pairs of carbon content 5 (q/$\overline{\text{q}}$, r/$\overline{\text{r}}$ and s/$\overline{\text{s}}$), we are able to generate six of alkanes depicted in Fig. 7 (**42**–**44** and their enantiomers). It should be noted that the centroid of **42** (or **43** or **44**) is asymmetric because of Type I (chiral/*RS*-stereogenic/ascleral) under Criterion 1. The chiral, *RS*-stereogenic, and ascleral nature of Type I causes the superposition of an enantiomeric relationship onto an *RS*-diastereomeric relationship, as found in each pair of enantiomers (**42**/**42**, **43**/**43**, or **44**/**44**).

From the viewpoint of the revised CIP-system, on the other hand, a reflection operation

converts each *RS*-descriptor for **42**–**44** into the opposite one for the corresponding enantiomers (**$\overline{42}$**–**$\overline{44}$**). This means that the centers (ⓒ) are reflection-variant so as not to be pseudoasymmetric, but to be asymmetric. In spite of the presence of an enantiomeric pair p/$\overline{\text{p}}$, alkanes of Type I (e.g., Fig. 7) are chiral and *not pseudoasymmetric* (according to the CIP system). According to the CIP system, the effect of the pair p/$\overline{\text{p}}$ upon pseudoasymmetry is different between Type I and Types III/V, so that alkanes of Type III (e.g., **11** in Fig. 1) are chiral and pseudoasymmetric and so that alkanes of Type V (e.g., **17** in Fig. 1) are achiral and pseudoasymmetric. This difference implies that the effect of such reflection-invariance as adopted by the revised CIP-system should be re-examined in more detail.

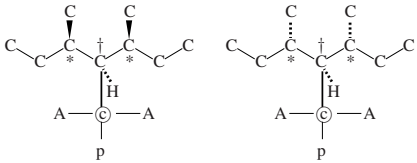
Centroidal Alkanes of Type II The coefficient $B^{(\mathrm{II})}_{k\ell m}$ of the term $x^k y^\ell z^m$ is calculated by means of $B^{(\mathrm{II})}(x,y,z)$ (eq. 37), where each coefficient is stored in the series obtained as `BtypeII` of the code "Alkane1-30b.mpl". The results of calculation are listed in Table 2.

Table 2: Centroidal Alkanes of Type II (Chiral/*RS*-Astereogenic/Scleral)[a]

Carbon Cont. (k)	No. of P. C. (m)	No. of Asymmetric Centers (ℓ)												
		$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12
$k=1$:	$m=0$:	0												
$k=2$:	$m=0$:	0												
$k=3$:	$m=0$:	0												
$k=4$:	$m=0$:	0												
$k=5$:	$m=0$:	0												
$k=6$:	$m=0$:	0												
$k=7$:	$m=0$:	0												
$k=8$:	$m=0$:	0												
$k=9$:	$m=0$:	0	10	2										
$k=10$:	$m=0$:	0	6	2										
$k=11$:	$m=0$:	0	60	22										
$k=12$:	$m=0$:	0	54	24										
$k=13$:	$m=0$:	0	310	252	76	8								
$k=14$:	$m=0$:	0	264	198	40	4								
$k=15$:	$m=0$:	0	1376	1826	1052	220								
$k=16$:	$m=0$:	0	1258	1478	724	160								
$k=17$:	$m=0$:	0	5680	11164	10548	4548	664	32						
$k=18$:	$m=0$:	0	5240	8982	7060	2520	208	8						
$k=19$:	$m=0$:	0	22150	60514	83052	56330	16088	1624						
	$m=1$:	0	0	0	500	544	112							
$k=20$:	$m=0$:	0	21020	50378	59456	34706	7720	624						
	$m=1$:	0	0	0	224	176	16							
$k=21$:	$m=0$:	0	83490	303504	570288	564932	276000	61528	4912	128				
	$m=1$:	0	0	0	2720	3840	1328	64						
$k=22$:	$m=0$:	0	79500	255824	420236	360522	143632	24472	1216	16				
	$m=1$:	0	0	0	2164	2808	840	40						
$k=23$:	$m=0$:	0	303896	1419704	3493328	4717404	3407644	1259832	212368	13040				
	$m=1$:	0	0	0	19600	40104	28352	7464	640					
	$m=2$:	0	0	0	0	0	60	8						
$k=24$:	$m=0$:	0	294300	1227888	2681448	3197852	1981896	606092	79680	3664				
	$m=1$:	0	0	0	13604	23692	12968	2224	80					
	$m=2$:	0	0	0	0	0	32	4						
$k=25$:	$m=0$:	0	1081588	6333264	19768652	34852418	34726192	19178868	5542224	746400	34528	512		
	$m=1$:	0	0	0	92944	246796	257456	113944	18768	512				
	$m=2$:	0	0	0	0	0	560	148						
$k=26$:	$m=0$:	0	1053564	5556870	15564752	24519826	21432540	10081964	2350432	231248	5888	32		
	$m=1$:	0	0	0	77312	184796	167224	60792	7536	144				
	$m=2$:	0	0	0	0	0	500	140						
$k=27$:	$m=0$:	0	3772998	27127012	104713548	232861578	303663676	231380188	99856104	22775032	2380416	90624		
	$m=1$:	0	0	0	474392	1620568	2386768	1696544	592608	93936	5088			
	$m=2$:	0	0	0	0	0	5388	2994	792	64				
$k=28$:	$m=0$:	0	3710798	24200478	84618784	170100714	198297376	132545036	48618208	8923900	673536	15880		
	$m=1$:	0	0	0	380328	1159528	1491368	887356	235216	22528	416			
	$m=2$:	0	0	0	0	0	4112	2240	352	8				
$k=29$:	$m=0$:	0	12949452	112400466	526084244	1439477280	2372569196	2374158472	1422719184	491022828	90437760	7792136	224704	2048
	$m=1$:	0	0	0	2033288	8667216	16929320	16989428	8969200	2340272	242048	4096		
	$m=2$:	0	0	0	0	0	34204	32506	14224	2136				
$k=30$:	$m=0$:	0	12790188	101455558	433682616	1082046376	1614036244	1442261420	754801120	219163840	31822400	1947720	32064	64
	$m=1$:	0	0	0	1780304	6893228	12019120	10501476	4671160	979344	74848	896		
	$m=2$:	0	0	0	0	0	30028	27184	10512	1264				
	$m=3$:	0	0	0	0	0	0	0	8					

[a]Two chiral alkanes of each enantiomeric pair are counted separately.

The value 500 at the intersection between the ($k=19$, $m=1$)-row and the ($\ell=3$)-column corresponds to the term $500x^{19}y^3z$. Hence, there exist 500 chiral centroidal alkanes of Type II which have three asymmetric centers and one pseudoasymmetric center according to Criteria 1 and 2. On a similar line to the formula **40** or **41** in Fig. 6, each of the 500 alkanes is represented by the formula **45** or **46**, where the symbol A represents a hydrogen atom, a methyl ligand, or



45 **46**

Figure 8: Chiral centroidal alkanes of Type II corresponding to the term $500x^{19}y^3z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbol A represents a hydrogen atom, a methyl ligand, or an ethyl ligand, while the symbol p is a chiral ligand with one asymmetric center. The ligands A and p are selected to keep the central atom ⓒ being a centroid. An appropriate enantiomer of a pair is depicted as a representative.

an ethyl ligand, while the symbol p is a chiral ligand with one asymmetric center. The ligands A and p are selected to keep the central atom ⓒ being a centroid.

The value 500 of the term $500x^{19}y^3z$ can be verified as follows. By using the data of $a(x,y,z)$ (eq. 53) and the data of $b(x,y,z)$ up to x^9, we obtain the following generating function for counting chiral alkyl ligands:

$$\begin{aligned}&\frac{1}{2}\{b(x,y,z)-a(x,y,z)\}\\ &\quad = \; yx^4+3yx^5+(8y+2y^2)x^6+(20y+10y^2)x^7\\ &\qquad +(46y+38y^2+4y^3)x^8+(102y+125y^2+28y^3)x^9+\cdots,\end{aligned} \tag{54}$$

where the data are stored by `a111` and `b111` during the recursive calculation by the code "Alkane1-30b.mpl". Note that eq. 54 counts each pair of enantiomers just once. Let the partition $[k_1,k_2,k_2]$ represent the carbon contents of p and A under the condition of $k_1+2k_2=9$. Then, the number of enantiomeric pairs is calculated by using the coefficients of the terms containing y, which appear in the right-side of eq. 54. Thereby we obtain the following numbers for respective partitions:

[9,0,0]	$102\times1\times1=102$;	[7,1,1]	$20\times1\times1=20$
[5,2,2]	$3\times1\times1=3$;		
			total: 125

Because there exist two enantiomers for each of 125 enantiomeric pairs on the basis of **45** or **46**, we obtain the number of alkanes at issue to be $125\times2\times2=500$, which is equal to the coefficient of the term $500x^{19}y^3z$.

Centroidal Alkanes of Type III Table 3 collects the coefficient $B^{(\mathrm{III})}_{k\ell m}$ of each term $x^ky^\ell z^m$, which is calculated by means of $B^{(\mathrm{III})}(x,y,z)$ (eq. 38). Each of the coefficients is stored in the series obtained as `BtypeIII` of the code "Alkane1-30b.mpl".

The value 920 at the intersection between the ($k=19$, $m=1$)-row and the ($\ell=4$)-column corresponds to the term $920x^{19}y^4z$. On the analogy of the formula **40** or **41** in Fig. 6, we can adopt the same alkyl ligand having one pseudoasymmetric center as **40** (or **41**), so that each of the 920 alkanes is represented by one of the formulas **47—50**. The symbols A and B represent

Table 3: Centroidal Alkanes of Type III (Chiral/*RS*-Stereogenic/Scleral)[a]

Carbon	No. of	No. of Asymmetric Centers (ℓ)													
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12	13
$k=1$:	$m=0$:	0													
$k=2$:	$m=0$:	0													
$k=3$:	$m=0$:	0													
$k=4$:	$m=0$:	0													
$k=5$:	$m=0$:	0													
$k=6$:	$m=0$:	0													
$k=7$:	$m=0$:	0													
$k=8$:	$m=0$:	0													
$k=9$:	$m=0$:	0	0	8											
$k=10$:	$m=0$:	0	0	20											
$k=11$:	$m=0$:	0	0	104	24										
$k=12$:	$m=0$:	0	0	192	48										
$k=13$:	$m=0$:	0	0	760	440	64									
$k=14$:	$m=0$:	0	0	1364	984	236	8								
$k=15$:	$m=0$:	0	0	4700	5016	1896	176								
$k=16$:	$m=0$:	0	0	8284	10416	5072	688								
$k=17$:	$m=0$:	0	0	25564	42256	28532	7024	424							
$k=18$:	$m=0$:	0	0	44548	84272	68588	22400	2352	48						
$k=19$:	$m=0$:	0	0	127704	299356	311792	141996	24552	1080						
	$m=1$:	0	0	0	0	920	480	32							
$k=20$:	$m=0$:	0	0	220236	577908	695716	384640	88536	6360						
	$m=1$:	0	0	0	0	2360	1848	288							
$k=21$:	$m=0$:	0	0	596616	1871596	2754112	1961852	639584	80768	2512					
	$m=1$:	0	0	0	0	10512	10024	2368	64						
$k=22$:	$m=0$:	0	0	1027616	3550032	5881020	4875952	1956712	337680	18624	224				
	$m=1$:	0	0	0	0	21576	24296	7232	272						
$k=23$:	$m=0$:	0	0	2660596	10718564	21040956	21347612	11040884	2691752	258528	6272				
	$m=1$:	0	0	0	0	88792	125288	57904	7408	128					
	$m=2$:	0	0	0	0	0	0	52							
$k=24$:	$m=0$:	0	0	4568132	20026004	43478928	49913132	30233240	9122760	1199184	51424				
	$m=1$:	0	0	0	0	182552	303552	178136	35024	1840					
	$m=2$:	0	0	0	0	0	0	224	8						
$k=25$:	$m=0$:	0	0	11387700	57222004	144000688	195831756	145399200	56831760	10683376	797456	14288			
	$m=1$:	0	0	0	0	603032	1205048	925288	268016	23920	256				
	$m=2$:	0	0	0	0	0	0	1464	176						
$k=26$:	$m=0$:	0	0	19511824	105758276	290677692	439055644	370871100	170958464	40163280	4182768	136624	960		
	$m=1$:	0	0	0	0	1176792	2665640	2422648	898816	116944	2400				
	$m=2$:	0	0	0	0	0	0	4036	808						
$k=27$:	$m=0$:	0	0	47178864	289104556	905460132	1582396996	1583140452	895501448	272837256	40466112	2374480	34048		
	$m=1$:	0	0	0	0	3649360	9651328	10865696	5448600	1149312	79776	768			
	$m=2$:	0	0	0	0	0	0	19508	6880	680					
$k=28$:	$m=0$:	0	0	80758776	529921796	1794912392	3436070128	3832143224	2476764136	894183808	166709256	13727408	368944		
	$m=1$:	0	0	0	0	7044240	20822856	26973824	16319056	4482096	483440	14752			
	$m=2$:	0	0	0	0	0	0	49888	24452	4064	112				
$k=29$:	$m=0$:	0	0	190139716	1395543128	5316202664	11572992068	14927093980	11436224808	5076627440	1232594888	146705728	6927984	76352	
	$m=1$:	0	0	0	0	19959840	67836328	104607568	78773096	28794400	4613664	244384	1536		
	$m=2$:	0	0	0	0	0	0	192836	132740	34992	2176				
$k=30$:	$m=0$:	0	0	325250576	2541081904	10388800120	24517843500	34744573964	29781398560	15170974336	4389997616	662254208	44515152	914112	3968
	$m=1$:	0	0	0	0	37690600	140982016	244350432	213267904	94177976	19494688	1519104	19008		
	$m=2$:	0	0	0	0	0	0	449468	392860	137904	14048				
	$m=3$:	0	0	0	0	0	0	0	0	8					

[a]Two chiral alkanes of each enantiomeric pair are counted separately.

a hydrogen atom or an achiral ligand, while the symbol p is a chiral ligand with one asymmetric center. The ligands A, B, and p are so selected as to keep the central atom ⓒ being a centroid. Note that **47** and **48** are *RS*-diastereomeric and **49** and **50** are *RS*-diastereomeric in accord with the Type-III nature of these alkanes.

Let the partition $[k_1,k_2,k_3]$ represent the carbon contents of p, A and B under the condition of A≠B and $k_1+k_2+k_3=9$. Then, the number of enantiomeric pairs is calculated by using the coefficients appearing in the right-side of eq. 53 (for k_2 and k_3) and in the one of eq. 54 (for k_1). The following partitions are effective to maintain the Type-III nature of centroidal alkanes:

[8,1,0]	$46\times1\times1=46$;	[7,2,0]	$20\times1\times1=20$
[6,3,0]	$8\times2\times1=16$;	[6,2,1]	$8\times1\times1=8$
[5,4,0]	$3\times3\times1=9$;	[5,3,1]	$3\times2\times1=6$
[4,5,0]	$5\times1\times1=5$;	[4,4,1]	$1\times3\times1=3$
[4,3,2]	$1\times2\times1=2$;		

total: 115

Because there exist two enantiomers for each of 115 pairs on the basis of one of **47**—**50**, we obtain the number of alkanes at issue to be $115\times2\times4=920$, which is equal to the coefficient of the term $920x^{19}y^4z$.

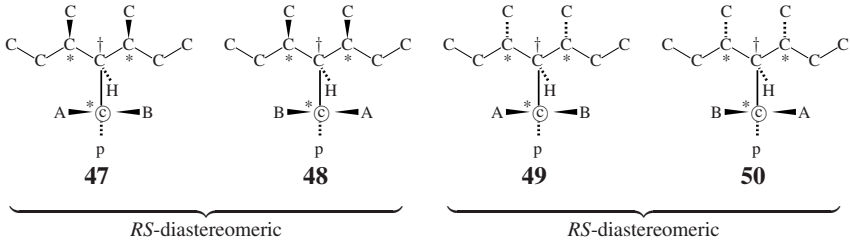


Figure 9: Chiral centroidal alkanes of Type III corresponding to the term $920x^{19}y^4z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbols A and B represent a hydrogen atom or achiral alkyl ligands, while p represents a chiral alkyl ligand with one asymmetric center. The alkyl ligands are selected from alkyl ligands of carbon content 1–8 to keep the central atom ⓒ being a centroid. An appropriate enantiomer of a pair is depicted as a representative.

Centroidal Alkanes of Type IV The coefficient $B^{(\mathrm{IV})}_{k\ell m}$ of the term $x^k y^\ell z^m$ is calculated by means of $B^{(\mathrm{IV})}(x,y,z)$ (eq. 39), where each coefficient is stored in the series named `BtypeIV` in the code "Alkane1-30b.mpl". The results of calculation are listed in Table 4.

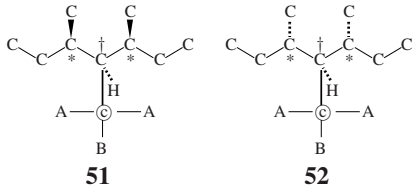


Figure 10: Achiral centroidal alkanes of Type IV corresponding to the term $130x^{19}y^2z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbol A and B represents a hydrogen atom or an alkyl ligand, where A may be equal to B. The ligands A and B are selected to keep the central atom ⓒ being a centroid. An appropriate enantiomer of a pair is depicted as a representative.

To illustrate the generation of alkanes by substituting alkyl ligands, let us examine the value 130 at the intersection between the $(k = 19, m = 1)$-row and the $(\ell = 2)$-column in Table 4, which corresponds to the term $130x^{19}y^2z$. This means that there exist 130 achiral centroidal alkanes of Type IV which have two asymmetric centers and one pseudoasymmetric center according to Criteria 1 and 2. On a similar line to the formula **40** or **41** in Fig. 6, each of the 130 alkanes is represented by the formula **51** or **52** (Fig. 10), where the symbols A and B represents a hydrogen atom or an alkyl ligand. The ligands A and B are selected to keep the central atom ⓒ being a centroid.

Let the partition $[k_1, k_1, k_2]$ represent the carbon contents of A, A and B under the condition that A may be equal to B and we put $2k_1 + k_3 = 9$. Then, the number of constitutional isomers is calculated by using the coefficients appearing in the right-side of eq. 53 (for k_1 and k_2). The following partitions are effective to maintain the Type-IV nature of centroidal alkanes:

Table 4: Centroidal Alkanes of Type IV (Achiral/*RS*-Astereogenic/ascleral)

Carbon	No. of	No. of Asymmetric Centers (ℓ)												
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12
$k=1$:	$m=0$:	1												
$k=2$:	$m=0$:	0												
$k=3$:	$m=0$:	1												
$k=4$:	$m=0$:	1												
$k=5$:	$m=0$:	3												
$k=6$:	$m=0$:	2												
$k=7$:	$m=0$:	7												
$k=8$:	$m=0$:	7												
$k=9$:	$m=0$:	20	0	1										
$k=10$:	$m=0$:	20												
$k=11$:	$m=0$:	55	0	4										
$k=12$:	$m=0$:	60												
$k=13$:	$m=0$:	156	0	12	0	2								
$k=14$:	$m=0$:	162												
$k=15$:	$m=0$:	438	0	33	0	12								
$k=16$:	$m=0$:	471												
$k=17$:	$m=0$:	1239	0	83	0	51	0	4						
$k=18$:	$m=0$:	1319												
$k=19$:	$m=0$:	3498	0	198	0	177	0	32						
	$m=1$:	0	0	130										
	$m=2$:	0	0	0	0	3								
$k=20$:	$m=0$:	3767												
	$m=1$:	0	0	90										
	$m=2$:	0	0	0	0	2								
$k=21$:	$m=0$:	9890	0	455	0	558	0	180	0	8				
	$m=1$:	0	0	588										
	$m=2$:	0	0	0	0	15								
$k=22$:	$m=0$:	10572												
	$m=1$:	0	0	548										
	$m=2$:	0	0	0	0	18								
$k=23$:	$m=0$:	27951	0	1013	0	1607	0	798	0	88				
	$m=1$:	0	0	3132										
	$m=2$:	0	0	0	0	129	0	2						
$k=24$:	$m=0$:	30064												
	$m=1$:	0	0	2696										
	$m=2$:	0	0	0	0	100								
$k=25$:	$m=0$:	79019	0	2200	0	4392	0	3054	0	618	0	16		
	$m=1$:	0	0	11954										
	$m=2$:	0	0	0	0	580	0	10						
$k=26$:	$m=0$:	84798												
	$m=1$:	0	0	11420										
	$m=2$:	0	0	0	0	566								
$k=27$:	$m=0$:	223373	0	4686	0	11423	0	10526	0	3302	0	228		
	$m=1$:	0	0	48356	0	2080								
	$m=2$:	0	0	0	0	3199	0	322	0	14				
$k=28$:	$m=0$:	240364												
	$m=1$:	0	0	44948	0	1424								
	$m=2$:	0	0	0	0	2666	0	112	0	4				
	$m=3$:	0	0	0	0	0	0	4						
$k=29$:	$m=0$:	631477	0	9811	0	28693	0	33582	0	14942	0	1964	0	32
	$m=1$:	0	0	170008	0	9388								
	$m=2$:	0	0	0	0	13157	0	1518	0	82				
	$m=3$:	0	0	0	0	0	0	12						
$k=30$:	$m=0$:	678034												
	$m=1$:	0	0	166688	0	8776								
	$m=2$:	0	0	0	0	12496	0	1136	0	52				
	$m=3$:	0	0	0	0	0	0	44						

[4,4,1]	$3\times1=3$;	[3,3,3]	$2+2=4$
[2,2,5]	$1\times5=5$;	[1,1,7]	$1\times14=14$
[0,0,9]	$1\times39=39$;		
			total: 65

Because the 65 constitutional isomers are achiral and have the formula **51** or **52**, the number of alkanes at issue is calculated to be $65\times2=130$, which is equal to the coefficient of the term $130x^{19}y^2z$.

Centroidal Alkanes of Type V Table 5 lists the coefficient $B^{(\mathrm{V})}_{k\ell m}$ of the term $x^k y^\ell z^m$, which is calculated by means of $B^{(\mathrm{V})}(x,y,z)$ (eq. 40). Each of the coefficients is stored in the series obtained as `BtypeV` of the code "Alkane1-30b.mpl".

The examination of the value 12 at the intersection between the ($k=12$, $m=1$)-row and the

Table 5: Centroidal Alkanes of Type V (Achiral/*RS*-Stereogenic/Scleral)

Carbon	No. of	No. of Asymmetric Centers (ℓ)												
Cont. (k)	P. C. (m)	$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12
$k = 1$:	$m = 0$:	0												
$k = 2$:	$m = 0$:	0												
$k = 3$:	$m = 0$:	0												
$k = 4$:	$m = 0$:	0												
$k = 5$:	$m = 0$:	0												
$k = 6$:	$m = 0$:	0												
$k = 7$:	$m = 0$:	0												
$k = 8$:	$m = 0$:	0												
$k = 9$:	$m = 0$:	0												
$k = 10$:	$m = 0$:	0												
	$m = 1$:	0	0	2										
$k = 11$:	$m = 0$:	0												
	$m = 1$:	0	0	2										
$k = 12$:	$m = 0$:	0												
	$m = 1$:	0	0	12										
$k = 13$:	$m = 0$:	0												
	$m = 1$:	0	0	16										
$k = 14$:	$m = 0$:	0												
	$m = 1$:	0	0	54	0	4								
$k = 15$:	$m = 0$:	0												
	$m = 1$:	0	0	80	0	4								
$k = 16$:	$m = 0$:	0												
	$m = 1$:	0	0	214	0	32								
$k = 17$:	$m = 0$:	0												
	$m = 1$:	0	0	338	0	40								
$k = 18$:	$m = 0$:	0												
	$m = 1$:	0	0	706	0	176	0	8						
$k = 19$:	$m = 0$:	0												
	$m = 1$:	0	0	1160	0	244	0	8						
	$m = 2$:	0	0	0	0	4								
$k = 20$:	$m = 0$:	0												
	$m = 1$:	0	0	2384	0	810	0	80						
	$m = 2$:	0	0	0	0	16								
$k = 21$:	$m = 0$:	0												
	$m = 1$:	0	0	4026	0	1202	0	96						
	$m = 2$:	0	0	0	0	52								
$k = 22$:	$m = 0$:	0												
	$m = 1$:	0	0	7344	0	3330	0	544	0	16				
	$m = 2$:	0	0	0	0	96	0	8						
$k = 23$:	$m = 0$:	0												
	$m = 1$:	0	0	12658	0	5190	0	712	0	16				
	$m = 2$:	0	0	0	0	308	0	24						
$k = 24$:	$m = 0$:	0												
	$m = 1$:	0	0	23152	0	12712	0	2940	0	208				
	$m = 2$:	0	0	0	0	668	0	112						
	$m = 3$:	0	0	0	0	0	0	4						
$k = 25$:	$m = 0$:	0												
	$m = 1$:	0	0	40406	0	20514	0	4124	0	240				
	$m = 2$:	0	0	0	0	1748	0	296						
	$m = 3$:	0	0	0	0	0	0	4						
$k = 26$:	$m = 0$:	0												
	$m = 1$:	0	0	68762	0	44790	0	13796	0	1696	0	32		
	$m = 2$:	0	0	0	0	3060	0	712	0	16				
	$m = 3$:	0	0	0	0	0	0	28						
$k = 27$:	$m = 0$:	0												
	$m = 1$:	0	0	121272	0	74080	0	20380	0	2128	0	32		
	$m = 2$:	0	0	0	0	7772	0	1992	0	64				
	$m = 3$:	0	0	0	0	0	0	38						
$k = 28$:	$m = 0$:	0												
	$m = 1$:	0	0	208618	0	154714	0	58696	0	10652	0	520		
	$m = 2$:	0	0	0	0	14728	0	5052	0	352				
	$m = 3$:	0	0	0	0	0	0	164	0	8				
$k = 29$:	$m = 0$:	0												
	$m = 1$:	0	0	369928	0	260574	0	90276	0	14284	0	584		
	$m = 2$:	0	0	0	0	34324	0	12412	0	992				
	$m = 3$:	0	0	0	0	0	0	274	0	8				
$k = 30$:	$m = 0$:	0												
	$m = 1$:	0	0	607118	0	505024	0	232632	0	56704	0	5064	0	64
	$m = 2$:	0	0	0	0	58860	0	24644	0	3104	0	64		
	$m = 3$:	0	0	0	0	0	0	892	0	80				

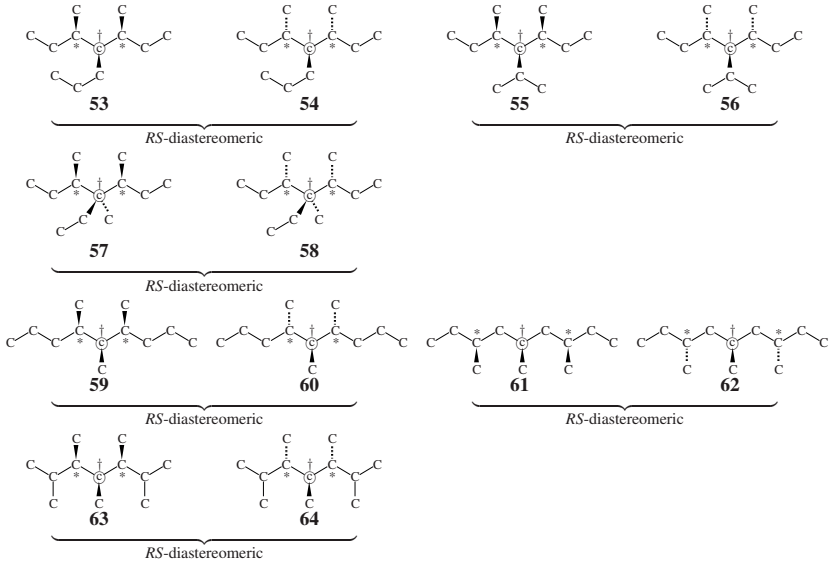


Figure 11: Achiral centroidal alkanes of Type V corresponding to the term $12x^{12}y^2z$. They are typical examples of pseudoasymmetric molecules.

($\ell = 2$)-column of Table 5 (corresponding to the term $12x^{12}y^2z$) is illustrative to understand typical pseudoasymmetric cases. The 12 achiral centroidal alkanes of Type V have two asymmetric centers and one pseudoasymmetric center under Criteria 1 and 2. The total carbon content 12 restricts the carbon contents of involved chiral ligands, so that a pair involved in each of the centroidal alkanes should be selected from one pair of enantiomeric butan-2-yl ligands (carbon content 4) or from three pairs of enantiomeric ligands of carbon content 5 (cf. eq. 54). For the list of these enantiomeric ligands, see the bottom part of Fig. 7. As a result, the 12 achiral centroidal alkanes of Type V have structures shown in Fig. 11.

3.2.5 Comparison with Previous Results

Achiral Centroidal Alkanes The total numbers of achiral centroidal alkanes can be obtained as the coefficients $A_{k\ell m}$ of the term $x^k y^\ell z^m$ appearing in $A(x,y,z)$ (eq. 43), which is stored in the series obtained as `Ah` of the code "Alkane1-30b.mpl". The results of calculation are listed in Table 6. Because we can put

$$A_{k\ell m} = B^{(\mathrm{IV})}_{k\ell m} + B^{(\mathrm{V})}_{k\ell m}, \tag{55}$$

each value of Table 6 can be obtained by summing up corresponding values appearing in Table 4 and Table 5.

The total number of achiral centroidal alkanes of carbon content k is calculated by using eq. 34 as follows:

$$\widehat{A}_k = B^{(\mathrm{IV})}_k + B^{(\mathrm{V})}_k = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} A_{k\ell m}. \tag{56}$$

Table 6: Achiral Centroidal Alkanes (Type IV and Type V)

Carbon	No. of	No. of Asymmetric Centers (ℓ)												
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12
$k=1$:	$m=0$:	1												
$k=2$:	$m=0$:	0												
$k=3$:	$m=0$:	1												
$k=4$:	$m=0$:	1												
$k=5$:	$m=0$:	3												
$k=6$:	$m=0$:	2												
$k=7$:	$m=0$:	7												
$k=8$:	$m=0$:	7												
$k=9$:	$m=0$:	20	0	1										
$k=10$:	$m=0$:	20												
	$m=1$:	0	0	2										
$k=11$:	$m=0$:	55	0	4										
	$m=1$:	0	0	2										
$k=12$:	$m=0$:	60												
	$m=1$:	0	0	12										
$k=13$:	$m=0$:	156	0	12	0	2								
	$m=1$:	0	0	16										
$k=14$:	$m=0$:	162												
	$m=1$:	0	0	54	0	4								
$k=15$:	$m=0$:	438	0	33	0	12								
	$m=1$:	0	0	80	0	4								
$k=16$:	$m=0$:	471												
	$m=1$:	0	0	214	0	32								
$k=17$:	$m=0$:	1239	0	83	0	51	0	4						
	$m=1$:	0	0	338	0	40								
$k=18$:	$m=0$:	1319												
	$m=1$:	0	0	706	0	176	0	8						
$k=19$:	$m=0$:	3498	0	198	0	177	0	32						
	$m=1$:	0	0	1290	0	244	0	8						
	$m=2$:	0	0	0	0	7								
$k=20$:	$m=0$:	3767												
	$m=1$:	0	0	2474	0	810	0	80						
	$m=2$:	0	0	0	0	18								
$k=21$:	$m=0$:	9890	0	455	0	558	0	180	0	8				
	$m=1$:	0	0	4614	0	1202	0	96						
	$m=2$:	0	0	0	0	67								
$k=22$:	$m=0$:	10572												
	$m=1$:	0	0	7892	0	3330	0	544	0	16				
	$m=2$:	0	0	0	0	114	0	8						
$k=23$:	$m=0$:	27951	0	1013	0	1607	0	798	0	88				
	$m=1$:	0	0	15790	0	5190	0	712	0	16				
	$m=2$:	0	0	0	0	437	0	26						
$k=24$:	$m=0$:	30064												
	$m=1$:	0	0	25848	0	12712	0	2940	0	208				
	$m=2$:	0	0	0	0	768	0	112						
	$m=3$:	0	0	0	0	0	0	4						
$k=25$:	$m=0$:	79019	0	2200	0	4392	0	3054	0	618	0	16		
	$m=1$:	0	0	52360	0	20514	0	4124	0	240				
	$m=2$:	0	0	0	0	2328	0	306						
	$m=3$:	0	0	0	0	0	0	4						
$k=26$:	$m=0$:	84798												
	$m=1$:	0	0	80182	0	44790	0	13796	0	1696	0	32		
	$m=2$:	0	0	0	0	3626	0	712	0	16				
	$m=3$:	0	0	0	0	0	0	28						
$k=27$:	$m=0$:	223373	0	4686	0	11423	0	10526	0	3302	0	228		
	$m=1$:	0	0	169628	0	76160	0	20380	0	2128	0	32		
	$m=2$:	0	0	0	0	10971	0	2314	0	78				
	$m=3$:	0	0	0	0	0	0	38						
$k=28$:	$m=0$:	240364												
	$m=1$:	0	0	253566	0	156138	0	58696	0	10652	0	520		
	$m=2$:	0	0	0	0	17394	0	5164	0	356				
	$m=3$:	0	0	0	0	0	0	168	0	8				
$k=29$:	$m=0$:	631477	0	9811	0	28693	0	33582	0	14942	0	1964	0	32
	$m=1$:	0	0	539936	0	269962	0	90276	0	14284	0	584		
	$m=2$:	0	0	0	0	47481	0	13930	0	1074				
	$m=3$:	0	0	0	0	0	0	286	0	8				
$k=30$:	$m=0$:	678034												
	$m=1$:	0	0	773806	0	513800	0	232632	0	56704	0	5064	0	64
	$m=2$:	0	0	0	0	71356	0	25780	0	3156	0	64		
	$m=3$:	0	0	0	0	0	0	936	0	80				

The total numbers $\widehat{A}_k$ ($k = 1$ to 20) have been directly obtained as a generating function and collected in Table 2 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning k = 20 (Table 6) are summed up to give the following result:

$k = 20$:	$m = 0$:	3767							3767
	$m = 1$:	0	0	2474	0	810	0	80	3364
	$m = 2$:	0	0	0	0	18			18
		3767	0	2474	0	828	0	80	7149

The total number 7149 is equal to the value reported previously in Table 2 of Ref. [24].

Moreover, the functional equation for calculating the total numbers (eq. 38 of Ref. [24]) can be derived by starting from eq. 43. When we put $y = z = 1$ in eq. 43, we obtain the following equation:

$$A(x,1,1) = B^{(\mathrm{IV})}(x,1,1) + B^{(\mathrm{V})}(x,1,1) \tag{57}$$

$$= \frac{x}{2}\left\{a(x,1,1)^2 c(x^2,1,1) + c(x^4,1,1)\right\}. \tag{58}$$

The latter equation (eq. 58) can be directly obtained from eq. 24, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. Note that the coefficient of the term x^k in $B^{(\tau)}(x,1,1)$ (T = I, II, ..., V) is equal to the value of $B_k^{(\tau)}$ (eq. 34). By putting $A(x,1,1) = \widehat{A}(x)$, $a(x,1,1) = a(x)$, and $c(x^2,1,1) = c(x^2)$, eq. 58 is converted into the following functional equation:

$$\widehat{A}(x) = \frac{x}{2}\left(a(x)^2 c(x^2) + c(x^4)\right), \tag{59}$$

which is identical with eq. 38 of Ref. [24].

Chiral Centroidal Alkanes The total numbers of chiral centroidal alkanes can be obtained as the coefficients $C_{k\ell m}$ of the term $x^k y^\ell z^m$ appearing in $C(x,y,z)$ (eq. 44), which is stored in the series obtained as `Ch` of the code "Alkane1-30b.mpl". The results of calculation are listed in Table 7. Because we can put

$$C_{k\ell m} = \frac{1}{2}\left\{B^{(\mathrm{I})}_{k\ell m} + B^{(\mathrm{II})}_{k\ell m} + B^{(\mathrm{III})}_{k\ell m}\right\}, \tag{60}$$

each value of Table 7 can be obtained by the half of the sum of corresponding values appearing in Tables 1, 2, and 3.

The total number of chiral centroidal alkanes of carbon content k is calculated by using eq. 34 as follows:

$$\widehat{C}_k = \frac{1}{2}\left\{B_k^{(\mathrm{I})} + B_k^{(\mathrm{II})} + B_k^{(\mathrm{III})}\right\} = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty} C_{k\ell m}. \tag{61}$$

The total numbers $\widehat{C}_k$ ($k = 1$ to 20) have been directly obtained as a generating function and collected in Table 2 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning k = 20 (Table 7) are summed up to give the following result:

$k = 20$:	$m = 0$:	0	25540	135307	318682	365211	196180	44580	3180	1088680
	$m = 1$:	0	0	0	482	1268	932	144		2826
	$m = 2$:	0	0	0	0	0	1			1
		0	25540	135307	319164	366479	197113	44724	3180	1091507

Table 7: Chiral Centroidal Alkanes (Enantiomeric Pairs for Types I, II, and III)

Carbon	No. of	No. of Asymmetric Centers (ℓ)													
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12	13
$k=1$:	$m=0$:	0													
$k=2$:	$m=0$:	0													
$k=3$:	$m=0$:	0													
$k=4$:	$m=0$:	0													
$k=5$:	$m=0$:	0													
$k=6$:	$m=0$:	0													
$k=7$:	$m=0$:	0	2												
$k=8$:	$m=0$:	0	1												
$k=9$:	$m=0$:	0	12	5											
$k=10$:	$m=0$:	0	13	11											
$k=11$:	$m=0$:	0	67	63	12										
$k=12$:	$m=0$:	0	79	108	24										
$k=13$:	$m=0$:	0	313	506	258	36									
$k=14$:	$m=0$:	0	367	781	512	120	4								
$k=15$:	$m=0$:	0	1337	3263	3034	1058	88								
$k=16$:	$m=0$:	0	1630	4881	5570	2616	344								
$k=17$:	$m=0$:	0	5372	18364	26402	16540	3844	228							
$k=18$:	$m=0$:	0	6579	26765	45666	35554	11304	1180	24						
$k=19$:	$m=0$:	0	20627	94109	191204	184061	79045	13088	540						
	$m=1$:	0	0	0	440	732	296	16							
$k=20$:	$m=0$:	0	25540	135307	318682	365211	196180	44580	3180						
	$m=1$:	0	0	0	482	1268	932	144							
	$m=2$:	0	0	0	0	0	1								
$k=21$:	$m=0$:	0	76510	450060	1220942	1659522	1118937	350556	42842	1320					
	$m=1$:	0	0	0	2818	7176	5676	1216	32						
	$m=2$:	0	0	0	0	0	9								
$k=22$:	$m=0$:	0	95057	641720	1985134	3120771	2509792	990592	169448	9320	112				
	$m=1$:	0	0	0	3674	12192	12568	3636	136						
	$m=2$:	0	0	0	0	0	17								
$k=23$:	$m=0$:	0	276274	2040150	7105946	12879180	12377672	6150358	1452076	135784	3136				
	$m=1$:	0	0	0	19098	64448	76820	32684	4024	64					
	$m=2$:	0	0	0	0	0	137	30							
$k=24$:	$m=0$:	0	346018	2898010	11353726	23338390	25947514	15419666	4601220	601424	25712				
	$m=1$:	0	0	0	23444	103122	158260	90180	17552	920					
	$m=2$:	0	0	0	0	0	270	114	4						
$k=25$:	$m=0$:	0	976063	8860482	38495328	89426553	115279108	82289034	31187076	5714888	415997	7400			
	$m=1$:	0	0	0	94666	424914	731252	519616	143392	12216	128				
	$m=2$:	0	0	0	0	0	1265	806	88						
$k=26$:	$m=0$:	0	1226206	12534347	60661514	157598759	230244092	190476532	86654448	20197264	2094328	68328	480		
	$m=1$:	0	0	0	122894	680794	1416432	1241720	453176	58544	1200				
	$m=2$:	0	0	0	0	0	2249	2088	404						
$k=27$:	$m=0$:	0	3386864	37152938	196909052	569160855	943030736	907260320	497679135	147806144	21423324	1232552	17024		
	$m=1$:	0	0	0	469462	2634964	6024260	6281120	3020604	621624	42432	384			
	$m=2$:	0	0	0	0	0	9684	11251	4068	372					
$k=28$:	$m=0$:	0	4277264	52479627	307270290	982506553	1817183752	1982344130	1262691172	451553854	83691396	6871644	184472		
	$m=1$:	0	0	0	595886	4101884	11166908	13931590	8277136	2252312	241928	7376			
	$m=2$:	0	0	0	0	0	16277	26064	13026	2036	62				
$k=29$:	$m=0$:	0	11575754	151270091	960813686	3377839972	6972781716	8650626226	6429473333	2783825134	661516709	77248932	3576360	39200	
	$m=1$:	0	0	0	2042808	14313528	42420716	60798498	43871148	15567336	2427856	124240	768		
	$m=2$:	0	0	0	0	0	59993	112671	76210	18564	1126				
	$m=3$:	0	0	0	0	0	0	0	4						
$k=30$:	$m=0$:	0	14659190	213330317	1487382260	5735423248	13065939872	18093417692	15268099840	7695069088	2210910008	332100964	22273608	457088	1984
	$m=1$:	0	0	0	2667076	22291914	76567604	127425954	108969532	47578660	9784768	760000	9504		
	$m=2$:	0	0	0	0	0	98286	238326	207246	69584	7102				
	$m=3$:	0	0	0	0	0	0	0	32	4					

The total number 1091507 is equal to the value reported previously in Table 2 of Ref. [24].

The functional equation for calculating the total numbers (eq. 40 of Ref. [24]) is regarded as a special case of eq. 44, so that it can be derived by starting from this equation. When we put $y=z=1$ in eq. 44, we obtain the following equation:

$$\begin{aligned} C(x,1,1) &= \frac{1}{2}\left\{B^{(\mathrm{I})}(x,1,1)+B^{(\mathrm{II})}(x,1,1)+B^{(\mathrm{III})}(x,1,1)\right\} \\ &= \frac{x}{24}\left\{b(x,1,1)^4+3b(x^2,1,1)^2+8b(x,1,1)b(x^3,1,1)\right. \\ &\quad \left.-6a(x,1,1)^2c(x^2,1,1)-6c(x^4,1,1)\right\} \end{aligned} \tag{62}$$

By putting $C(x,1,1)=\widehat{C}(x)$, $a(x,1,1)=a(x)$, $c(x^2,1,1)=c(x^2)$, and $b(x,1,1)=b(x)$, eq. 62 is converted into the following functional equation:

$$\widehat{C}(x)=\frac{x}{24}\left\{b(x)^4+3b(x^2)^2+8b(x)b(x^3)-6a(x)^2c(x^2)-6c(x^4)\right\}, \tag{63}$$

which is identical with eq. 40 of Ref. [24].

Achiral Centroidal Alkanes and Enantiomeric Pairs of Chiral Ones Table 8 lists the total numbers of achiral and chiral centroidal alkanes, which are obtained as the coefficients $B_{k\ell m}$ of the term $x^k y^\ell z^m$ appearing in $B(x,y,z)$ (eq. 45). Each of the numbers is stored in the series

Table 8: Achiral Centroidal Alkanes and Enantiomeric Pairs of Chiral Ones

Carbon	No. of	No. of Asymmetric Centers (ℓ)													
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12	13
$k=1$:	$m=0$:	1													
$k=2$:	$m=0$:	0													
$k=3$:	$m=0$:	1													
$k=4$:	$m=0$:	1													
$k=5$:	$m=0$:	3													
$k=6$:	$m=0$:	2													
$k=7$:	$m=0$:	7	2												
$k=8$:	$m=0$:	7	1												
$k=9$:	$m=0$:	20	12	6											
$k=10$:	$m=0$:	20	13	11											
	$m=1$:	0	0	2											
$k=11$:	$m=0$:	55	67	67	12										
	$m=1$:	0	0	2											
$k=12$:	$m=0$:	60	79	108	24										
	$m=1$:	0	0	12											
$k=13$:	$m=0$:	156	313	518	258	38									
$m=1$:		0	0	16											
$k=14$:	$m=0$:	162	367	781	512	120	4								
$m=1$:		0	0	54	0	4									
$k=15$:	$m=0$:	438	1337	3296	3034	1070	88								
$m=1$:		0	80	0	4										
$k=16$:	$m=0$:	471	1630	4881	5570	2616	344								
$m=1$:		0	214	0	32										
$k=17$:	$m=0$:	1239	5372	18447	26402	16591	3844	232							
	$m=1$:	0	0	338	0	40									
$k=18$:	$m=0$:	1319	6579	26765	45666	35554	11304	1180	24						
	$m=1$:	0	0	706	0	176	0	8							
$k=19$:	$m=0$:	3498	20627	94307	191204	184238	79045	13120	540						
	$m=1$:	0	0	1290	440	976	296	24							
	$m=2$:	0	0	0	0	7									
$k=20$:	$m=0$:	3767	25540	135307	318682	365211	196180	44580	3180						
	$m=1$:	0	0	2474	482	2078	932	224							
	$m=2$:	0	0	0	0	18	1								
$k=21$:	$m=0$:	9890	76510	450515	1220942	1660080	1118937	350736	42842	1328					
	$m=1$:	0	0	4614	2818	8378	5676	1312	32						
	$m=2$:	0	0	0	0	67	9	8							
$k=22$:	$m=0$:	10572	95057	641720	1985134	3120771	2509792	990592	169448	9320	112				
	$m=1$:	0	0	7892	3674	15522	12568	4180	136	16					
	$m=2$:	0	0	0	0	114	17	8							
$k=23$:	$m=0$:	27951	276274	2041163	7105946	12880787	12377672	6151156	1452076	135872	3136				
	$m=1$:	0	0	15790	19098	69638	76820	33396	4024	80					
	$m=2$:	0	0	0	0	437	137	56							
$k=24$:	$m=0$:	30064	346018	2898010	11353726	23338390	25947514	15419666	4601220	601424	25712				
	$m=1$:	0	0	25848	23444	115834	158260	93120	17552	1128					
	$m=2$:	0	0	0	0	768	270	226	4						
	$m=3$:	0	0	0	0	0	0	4							
$k=25$:	$m=0$:	79019	976063	8862682	38495328	89430945	115279108	82292088	31187076	5715506	415997	7416			
	$m=1$:	0	0	52360	94666	445428	731252	523740	143392	12456	128				
	$m=2$:	0	0	0	0	2328	1265	1112	88						
	$m=3$:	0	0	0	0	0	0	4							
$k=26$:	$m=0$:	84798	1226206	12534347	60661514	157598759	230244092	190476532	86654448	20197264	2094328	68328	480		
	$m=1$:	0	0	80182	122894	725584	1416432	1255516	453176	60240	1200	32			
	$m=2$:	0	0	0	0	3626	2249	2800	404	16					
	$m=3$:	0	0	0	0	0	0	28							
$k=27$:	$m=0$:	223373	3386864	37157624	196909052	569172278	943030736	907270846	497679135	147809446	21423324	1232780	17024		
	$m=1$:	0	0	169628	469462	2711124	6024260	6301500	3020604	623752	42432	416			
	$m=2$:	0	0	0	0	10971	9684	13565	4068	450					
	$m=3$:	0	0	0	0	0	0	38							
$k=28$:	$m=0$:	240364	4277264	52479627	307270290	982506553	1817183752	1982344130	1262691172	451553854	83691396	6871644	184472		
	$m=1$:	0	0	253566	595886	4258022	11166908	13990286	8277136	2262964	241928	7896			
	$m=2$:	0	0	0	0	17394	16277	31228	13026	2392	62				
	$m=3$:	0	0	0	0	0	0	168	0	8					
$k=29$:	$m=0$:	631477	11575754	151279902	960813686	3377868665	6972781716	8650659808	6429473333	2783840076	661516709	77250896	3576360	39232	
	$m=1$:	0	0	539936	2042808	14583490	42420716	60888774	43871148	15581620	2427856	124824	768		
	$m=2$:	0	0	0	0	47481	59993	126601	76210	19638	1126				
	$m=3$:	0	0	0	0	0	0	286	4	8					
$k=30$:	$m=0$:	678034	14659190	213330317	1487382260	5735423248	13065939872	18093417692	15268099840	7695069088	2210910008	332100964	22273608	457088	1984
	$m=1$:	0	0	773806	2667076	22805714	76567604	127658586	108969532	47635364	9784768	765064	9504	64	
	$m=2$:	0	0	0	0	71356	98286	264106	207246	72740	7102	64			
	$m=3$:	0	0	0	0	0	0	936	32	84					

obtained as `Bh` of the code "Alkane1-30b.mpl". Because we can put

$$B_{k\ell m} = \frac{1}{2}\left\{B^{(\mathrm{I})}_{k\ell m} + B^{(\mathrm{II})}_{k\ell m} + B^{(\mathrm{III})}_{k\ell m}\right\} + B^{(\mathrm{IV})}_{k\ell m} + B^{(\mathrm{V})}_{k\ell m} \tag{64}$$

in agreement with eq. 45, each value of Table 8 can be obtained by starting from corresponding values appearing in Tables 1–5.

The total numbers $\widehat{B}_k$ ($=\sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty} B_{k\ell m}$, $k=1$ to 20) have been directly obtained as a generating function and collected in Table 2 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning k = 20 (Table 8) are summed up to give the following result:

$k=20$:	$m=0$:	3767	25540	135307	318682	365211	196180	44580	3180	1092447
	$m=1$:	0	0	2474	482	2078	932	224		6190
	$m=2$:	0	0	0	0	18	1			19
		3767	25540	137781	319164	367307	197113	44804	3180	1098656

The total number 1098656 is equal to the value reported previously in Table 2 of Ref. [24].

Moreover, the functional equation for calculating the total numbers (eq. 29 of Ref. [24]) can be derived by starting from eq. 45. When we put $y = z = 1$ in eq. 45, we obtain the following equation:

$$\begin{aligned} B(x,1,1) &= \frac{1}{2}\left\{B^{(\mathrm{I})}(x,1,1) + B^{(\mathrm{II})}(x,1,1) + B^{(\mathrm{III})}(x,1,1)\right\} + B^{(\mathrm{IV})}(x,1,1) + B^{(\mathrm{V})}(x,1,1) \\ &= \frac{x}{24}\left\{b(x,1,1)^4 + 3b(x^2,1,1)^2 + 8b(x,1,1)b(x^3,1,1)\right. \\ &\quad \left. + 6a(x,1,1)^2 c(x^2,1,1) + 6c(x^4,1,1)\right\} \end{aligned} \tag{65}$$

By putting $B(x,1,1) = \widehat{B}(x)$, $a(x,1,1) = a(x)$, $c(x^2,1,1) = c(x^2)$, and $b(x,1,1) = b(x)$, eq. 65 is converted into the following functional equation:

$$\widehat{B}(x) = \frac{x}{24}\left\{b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3) + 6a(x)^2 c(x^2) + 6c(x^4)\right\}, \tag{66}$$

which is identical with eq. 29 of Ref. [24].

Under the condition of $y = z = 1$, we obtain the following equation:

$$B^{(\mathrm{I\text{–}V})}(x,1,1) = B^{(\mathrm{I})}(x,1,1) + B^{(\mathrm{II})}(x,1,1) + B^{(\mathrm{III})}(x,1,1) + B^{(\mathrm{IV})}(x,1,1) + B^{(\mathrm{V})}(x,1,1) \tag{67}$$

$$= \frac{x}{12}\left\{b(x,1,1)^4 + 3b(x^2,1,1)^2 + 8b(x,1,1)b(x^3,1,1)\right\} \tag{68}$$

The latter equation (eq. 68) can be directly obtained from eq. 23, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. By putting $B^{(\mathrm{I\text{–}V})}(x,1,1) = \widehat{E}(x)$ and $b(x,1,1) = b(x)$, eq. 68 is converted into the following functional equation:

$$\widehat{E}(x) = \frac{x}{12}\left\{b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3)\right\}, \tag{69}$$

which is identical with eq. 36 of Ref. [24].

3.3 Enumeration of Bicentroidal Alkanes

The categorization into *RS*-stereoisomeric types is not so effective to treat bicentroidal alkanes, because these belong to either Type II or Type IV [29]. Hence, it is sufficient to discuss achiral and chiral bicentroidal alkanes. By using $a(x,y,z)$ (eq. 19), $c(x^2,y^2,z^2)$ (eq. 21), and $b(x,y,z)$ (eq. 20), we enumerate bicentroidal alkanes on the basis of a dumbbell-like skeleton. Although the skeleton has been previously formulated without regard to *RS*-stereoisomeric types [24], its theoretical essence can be applied to the present enumeration after slight modification.

3.3.1 Cycle Indices with Chirality Fittingness

Although the previous results concerned with centroidal alkanes [24, 27] have not taken *RS*-stereoisomeric types, the methodology can be applied to evaluate bicentroidal alkanes. Thus, we consider the action of the **K**-factor group ($\mathbf{K} = \mathbf{D}_{\infty h}/\mathbf{C}_{\infty v}$) and its maximum chiral group ($\mathbf{K}_2$) on the dumbbell-like skeleton:

$$\mathbf{K} \sim \{(1)(2), (1\ 2); \overline{(1)(2)}, \overline{(1\ 2)}\} \tag{70}$$

$$\mathbf{K}_2 \sim \{(1)(2), (1\ 2)\} \tag{71}$$

$$\tag{72}$$

Because bicentroidal alkanes are *RS*-astereogenic, the **K**-group itself can be regarded as a point subgroup and as a ligand-inversion subgroup. This means that it is sufficient to examine only the chiral/achiral nature of bicentroidal alkanes.

On the same line as the derivation of eq. 23 for **T** (contained in eq. 22), we collect products of SIs concerning rotoreflections of $\mathbf{K}_2$ (eq. 71) in order to obtain a CI-CF for counting achiral plus chiral bicentroidal promolecules (i.e., Types II and IV):

$$\text{CI-CF}^{(\text{II/IV})}(\mathbf{K}_2; b_d) = \frac{1}{2}(b_1^2 + b_2), \tag{73}$$

where achiral alkanes and two enantiomers of each pair are counted separately.

On the same line as the derivation of eq. 24 for $\mathbf{T}_d$ (eq. 22), we collect products of SIs concerning rotoreflections of **K** (eq. 70), to obtain a CI-CF for counting achiral bicentroidal alkanes (i.e., Type IV):

$$\text{CI-CF}^{(\text{IV})}(\mathbf{K}; \$_d) = \frac{1}{2}(a_1^2 + c_2). \tag{74}$$

The subtraction of eq. 74 from eq. 73 leaves the CI-CF for counting chiral bicentroidal alkanes (i.e., Type II):

$$\text{CI-CF}^{(\text{II})}(\mathbf{K}; \$_d) = \frac{1}{2}(b_1^2 + b_2 - a_1^2 - c_2) \tag{75}$$

3.3.2 Functional Equations for Counting Bicentroidal Alkanes

Let $\widetilde{B}^{(\tau)}_{k\ell m}$ (τ = II or IV or their combinations) be the number of bicentroidal alkanes (promolecules) of Type T, which have k carbons, ℓ asymmetric centers and m pseudoasymmetric centers. Let the symbol $\widetilde{B}^{(\tau)}_{k}$ be the summation for each type (τ) represented as follows:

$$\widetilde{B}^{(\tau)}_{k} = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \widetilde{B}^{(\tau)}_{k\ell m}. \tag{76}$$

We now regard these numbers $\widetilde{B}^{(\tau)}_{k\ell m}$ as the coefficients of the following generating functions:

$$\widetilde{B}^{(\tau)}(x^d, y^d, z^d) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} \widetilde{B}^{(\tau)}_{k\ell m} z^{dm} \right) y^{d\ell} \right) x^{dk}, \tag{77}$$

where the valuable x is concerned with carbon content, the valuable y is concerned with the number of asymmetric centers, and the valuable z is concerned with the number of pseudoasymmetric centers. We put $\widetilde{B}^{(\tau)}_{000} = 0$ for treating the respective initial (trivial) cases.

To evaluate the generating functions (eq. 77, $d = 1$), we derive the corresponding functional equations by starting from the CI-CFs (eqs. 74 and 75). Thus, the SIs a_d, c_d, and b_d in these equations are replaced by $a(x^d, y^d, z^d)$, $c(x^d, y^d, z^d)$, and $b(x^d, y^d, z^d)$ to give the following functional equations:

$$\widetilde{B}^{(\text{II})}(x,y,z) = \frac{1}{2}\left\{ b(x,y,z)^2 + b(x^2,y^2,z^2) - a(x,y,z)^2 - c(x^2,y^2,z^2) \right\} \tag{78}$$

$$\widetilde{B}^{(\text{IV})}(x,y,z) = \frac{1}{2}\left\{ a(x,y,z)^2 + c(x^2,y^2,z^2) \right\}. \tag{79}$$

Let $\widetilde{A}(x,y,z)$, $\widetilde{C}(x,y,z)$, and $\widetilde{B}(x,y,z)$ be functional equations for calculating the numbers of achiral, chiral, and total (achiral plus chiral) bicentroidal alkanes, where each pair of two enantiomers and each achiral alkane are respectively counted just once. Because the symbol $\widetilde{B}^{(\mathrm{II})}(x,y,z)$ (Type II: chiral/*RS*-astereogenic/scleral) counts two enantiomers of each pair separately, the numbers are calculated as follows:

$$\widetilde{A}(x,y,z) = \widetilde{B}^{(\mathrm{IV})}(x,y,z) = \frac{1}{2}\left\{a(x,y,z)^2 + c(x^2,y^2,z^2)\right\} \tag{80}$$

$$\begin{aligned}\widetilde{C}(x,y,z) &= \frac{1}{2}\widetilde{B}^{(\mathrm{II})}(x,y,z) \\ &= \frac{1}{4}\left\{b(x,y,z)^2 + b(x^2,y^2,z^2) - a(x,y,z)^2 - c(x^2,y^2,z^2)\right\}\end{aligned} \tag{81}$$

$$\begin{aligned}\widetilde{B}(x,y,z) &= \frac{1}{2}\widetilde{B}^{(\mathrm{II})}(x,y,z) + B^{(\mathrm{IV})}(x,y,z) \\ &= \frac{1}{4}\left\{b(x,y,z)^2 + b(x^2,y^2,z^2) + a(x,y,z)^2 + c(x^2,y^2,z^2)\right\}\end{aligned} \tag{82}$$

Suppose that we have obtained $a(x,y,z) = \sum_{k=0}^{\mu} \alpha_k x^k$, $c(x^2,y^2,z^2) = \sum_{k=0}^{\mu} \gamma_k x^{2k}$, and $b(x,y,z) = \sum_{k=0}^{\mu} \beta_k x^k$, where μ is tentatively fixed. They are introduced into eqs. 80–82 so as to give $\widetilde{A}(x,y,z)^{(\mu)}$, $\widetilde{C}(x,y,z)^{(\mu)}$, and $\widetilde{B}(x,y,z)^{(\mu)}$, where the coefficient of the resulting term $x^{2\mu}$ is effective after expansion. Note that the coefficient is a polynomial containing $y^\ell z^m$. Thereby, we obtain the following coefficients:

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\widetilde{A}_{(2\mu)\ell m}z^m\right)y^\ell = \mathrm{coeff}(\widetilde{A}(x,y,z)^{(\mu)}, x^{2\mu}) \tag{83}$$

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\widetilde{C}_{(2\mu)\ell m}z^m\right)y^\ell = \mathrm{coeff}(\widetilde{C}(x,y,z)^{(\mu)}, x^{2\mu}) \tag{84}$$

$$\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\widetilde{B}_{(2\mu)\ell m}z^m\right)y^\ell = \mathrm{coeff}(\widetilde{B}(x,y,z)^{(\mu)}, x^{2\mu}). \tag{85}$$

3.3.3 Programming and Implementation

The recursive calculations of $a(x^d,y^d,z^d)$, $c(x^d,y^d,z^d)$, and $b(x^d,y^d,z^d)$ in the right-hand sides of eqs. 80–82 are the same as described in the code "Alkane1-30b.mpl", although they are omitted. The paragraph "Alkanes as Centroidal 3D-Trees" in the code "Alkane1-30b.mpl" is replaced as follows in the code "BAlkane1-30b.mpl" for calculating bicentroidal alkanes:

```
# BAlkane1-30b.mpl
(omitted)
"Alkanes as Bicentroidal 3D-Trees";
Bxt := (1/4)*(b111^2 + b222 + a111^2 + c222);
Axt := (1/2)*(a111^2 + c222);
Cxt := (1/4)*(b111^2 + b222 - a111^2 - c222);
```

in accord with eqs. 80–82. The storage part from the line "`q := 2*k +1:`" to the line "`end do:`" is replaced as follows:

```
q := 2*k:
Bt := Bt + coeff(Bxt,x^q)*x^q:
At := At + coeff(Axt,x^q)*x^q:
Ct := Ct + coeff(Cxt,x^q)*x^q:
end do:
```

which is in agreement with the bicentroidal nature of alkanes to be counted (cf. eqs. 83–85).

3.3.4 Results and Illustrative Examples

Achiral Bicentroidal Alkanes Table 9 lists the coefficient $\widetilde{A}_{k\ell m}$ of the term $x^k y^\ell z^m$ calculated by means of $\widetilde{A}(x,y,z)$ (eq. 80), where each coefficient is stored in the series obtained as `At` of the code "BAlkane1-30b.mpl".

Table 9: Achiral Bicentroidal Alkanes

Carbon	No. of	No. of Asymmetric Centers (ℓ)												
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12
$k=2$:	$m=0$:	1												
$k=4$:	$m=0$:	1												
$k=6$:	$m=0$:	3												
$k=8$:	$m=0$:	6	0	1										
$k=10$:	$m=0$:	15	0	3										
$k=12$:	$m=0$:	36	0	8	0	2								
$k=14$:	$m=0$:	105	0	20	0	10								
$k=16$:	$m=0$:	276	0	46	0	38	0	4						
$k=18$:	$m=0$:	780	0	102	0	125	0	28						
	$m=1$:	0	0	78										
	$m=2$:	0	0	0	0	3								
$k=20$:	$m=0$:	2145	0	220	0	366	0	148	0	8				
	$m=1$:	0	0	260										
	$m=2$:	0	0	0	0	10								
$k=22$:	$m=0$:	6105	0	461	0	1000	0	614	0	80				
	$m=1$:	0	0	1320										
	$m=2$:	0	0	0	0	78	0	2						
$k=24$:	$m=0$:	17020	0	948	0	2588	0	2224	0	528	0	16		
	$m=1$:	0	0	4416										
	$m=2$:	0	0	0	0	300	0	8						
$k=26$:	$m=0$:	48205	0	1921	0	6430	0	7288	0	2678	0	212		
	$m=1$:	0	0	17360	0	1240								
	$m=2$:	0	0	0	0	1596	0	254	0	14				
$k=28$:	$m=0$:	135460	0	3836	0	15442	0	22226	0	11542	0	1736	0	32
	$m=1$:	0	0	56160	0	4160								
	$m=2$:	0	0	0	0	5886	0	954	0	64				
$k=30$:	$m=0$:	384126	0	7574	0	36099	0	64024	0	44296	0	10528	0	552
	$m=1$:	0	0	197976	0	28032								
	$m=2$:	0	0	0	0	25651	0	7486	0	668	0	12		

The value 6 at the intersection between the ($k=8$, $m=0$)-row and the ($\ell=0$)-column in Table 9 corresponds to the term $6x^8$. Hence, there exist six achiral bicentroidal alkanes (**65**–**70**) which have no asymmetric center and no pseudoasymmetric center, as depicted in Fig. 12.

On the other hand, the value 1 at the intersection between the ($k=8$, $m=0$)-row and the ($\ell=2$)-column in Table 9 corresponds to the term $6x^8y^2$. Hence, there exists one achiral bicentroidal alkane (**71**) which has two asymmetric center and no pseudoasymmetric center (a *meso*-case).

The seven alkanes collected in Fig. 12 have been already illustrated in Fig. 6 of Ref. [24], where they are not itemized with respect to the number of asymmetric centers. The present enumeration discriminates such *meso*-cases as **71** from cases in which two terminal alkyl ligands are alkyl ligands having no asymmetric centers and no pseudoasymmetric centers. As a result, the value $\widetilde{A}_{k00}$ at the intersection between the (k, $m=0$)-row and the ($\ell=0$)-column can be calculated by using the data $\alpha_{(k/2)00}$ (cf. eq. 53), i.e., $\widetilde{A}_{k00}=\alpha_{(k/2)00}(\alpha_{(k/2)00}+1)/2$. For example, we obtain $39\times(39+1)/2=780$, which is equal to the value appearing at the intersection between the ($k=18$, $m=0$)-row and the ($\ell=0$)-column in Table 9.

The total number of achiral bicentroidal alkanes of carbon content k is calculated by using eq. 76 as follows:

$$\widetilde{A}_k=\widetilde{B}_k^{(\mathrm{IV})}=\sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\widetilde{A}_{k\ell m}. \tag{86}$$

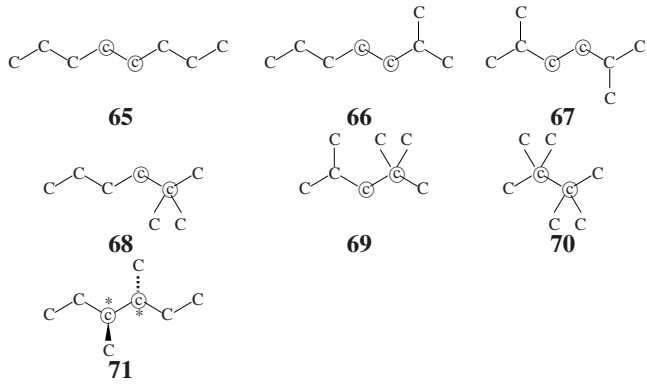


Figure 12: Six achiral bicentroidal alkanes (**65**–**70**) corresponding to the term $6x^8$ as well as one achiral bicentroidal alkane (**71**) corresponding to the term x^8y^2.

The total numbers $\widetilde{A}_k$ ($k = 1$ to 20) have been directly obtained as a generating function and collected in Table 3 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning k = 20 (Table 9) are summed up to give the following result:

$k = 20$:	$m = 0$:	2145	0	220	0	366	0	148	0	8	2887
	$m = 1$:	0	0	260							260
	$m = 2$:	0	0	0	0	10					10
		2145	0	480	0	376	0	148	0	8	3157

The total number 3157 is equal to the value reported previously in Table 3 of Ref. [24].

The numerical confirmation described above can be traced in general. Thus, the functional equation for calculating the total numbers (eq. 56 of Ref. [24]) can be derived by starting from eq. 80. When we put $y = z = 1$ in eq. 80, we obtain the following equation:

$$\widetilde{A}(x,1,1) = \widetilde{B}^{(\mathrm{IV})}(x,1,1) \tag{87}$$

$$= \frac{x}{2}\left\{a(x,1,1)^2 + c(x^2,1,1)\right\} \tag{88}$$

The latter equation (eq. 88) can be directly obtained from eq. 74, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. Note that the coefficient of the term x^k in $\widetilde{B}^{(\mathrm{IV})}(x,1,1)$ is equal to the value of $\widetilde{B}^{(\mathrm{IV})}_k$ (eq. 76). By putting $\widetilde{A}(x,1,1) = \widetilde{A}(x)$, $a(x,1,1) = a(x)$, and $c(x^2,1,1) = c(x^2)$, eq. 88 is converted into the following functional equation:

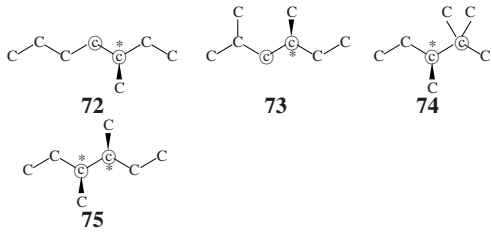
$$\widetilde{A}(x) = \frac{1}{2}\left\{a(x)^2 + c(x^2)\right\}, \tag{89}$$

which is identical with eq. 56 of Ref. [24].

Chiral Bicentroidal Alkanes Table 10 lists the coefficient $\widetilde{C}_{k\ell m}$ of the term $x^k y^\ell z^m$, which is calculated by means of $\widetilde{C}(x,y,z)$ (eq. 81) and stored in the series obtained as `Ct` of the code "BAlkane1-30b.mpl".

Table 10: Enantiomeric Pairs of Chiral Bicentroidal Alkanes

Carbon	No. of	No. of Asymmetric Centers (ℓ)												
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12
$k=2$:	$m=0$:	0												
$k=4$:	$m=0$:	0												
$k=6$:	$m=0$:	0												
$k=8$:	$m=0$:	0	3	1										
$k=10$:	$m=0$:	0	15	9										
$k=12$:	$m=0$:	0	64	80	32	4								
$k=14$:	$m=0$:	0	280	540	400	100								
$k=16$:	$m=0$:	0	1058	2990	3588	1812	304	16						
$k=18$:	$m=0$:	0	3978	15279	26592	21337	7000	784						
	$m=1$:	0	0	0	204	250	56							
$k=20$:	$m=0$:	0	14300	72190	170660	199596	111856	27760	2368	64				
	$m=1$:	0	0	0	880	1464	592	32						
$k=22$:	$m=0$:	0	50710	322521	989540	1574908	1301760	536996	98240	6400				
	$m=1$:	0	0	0	5752	13844	11368	3416	320					
	$m=2$:	0	0	0	0	0	24	4						
$k=24$:	$m=0$:	0	174432	1374896	5316064	11011600	12515456	7709440	2431360	349952	16896	256		
	$m=1$:	0	0	0	24224	77280	94784	48256	8832	256				
	$m=2$:	0	0	0	0	0	192	64						
$k=26$:	$m=0$:	0	595510	5683541	26963340	70175576	104078276	88368528	41760848	10261796	1135472	44944		
	$m=1$:	0	0	0	116876	476580	816980	664408	260008	44856	2544			
	$m=2$:	0	0	0	0	0	1680	1124	360	32				
$k=28$:	$m=0$:	0	1994720	22744736	130028544	414975076	775880728	863793436	566925112	211374724	41496288	3752384	111104	1024
	$m=1$:	0	0	0	461088	2372776	5425472	6235504	3687512	1054624	116864	2048		
	$m=2$:	0	0	0	0	0	9720	11124	5760	1008				
$k=30$:	$m=0$:	0	6634824	88988200	602912676	2311776649	5302623088	7457116880	6440476448	3350078256	1003379072	159741568	11622912	304704
	$m=1$:	0	0	0	1934228	12128606	35181316	53979752	45723560	20829904	4628256	424896	13248	
	$m=2$:	0	0	0	0	0	57404	96156	81960	30176	3744	144		



72 **73** **74**

75

Figure 13: Three chiral bicentroidal alkanes (**72**–**74**) of corresponding to the term $3x^8y$ and one chiral bicentroidal alkane (**75**) of corresponding to the term x^8y^2. An appropriate chiral alkane is depicted as a representative of each pair of enantiomers.

To illustrate the data of Table 10, let us examine the value 3 at the intersection between the ($k=8$, $m=0$)-row and the ($\ell=1$)-column, where the value corresponds to the term $3x^8y$. The value 3 indicates that there exist three pairs of chiral bicentroidal alkanes (**72**–**74**) which have one asymmetric center and no pseudoasymmetric center, as depicted in the first row of Fig. 13. This result can be confirmed by the fact that there exist one enantiomeric pair of chiral butan-2-yl ligands (cf. eq. 54) and three achiral ligands of carbon content 4 (cf. eq. 53).

On the other hand, the value 1 at the intersection between the ($k=8$, $m=0$)-row and the ($\ell=2$)-column in Table 10 corresponds to the term x^8y^2. Hence, there exists one chiral bicentroidal alkane (**75**) which has two asymmetric centers and no pseudoasymmetric center, as shown in the second row of Fig. 13.

The four alkanes collected in Fig. 13 have been already illustrated in Fig. 6 of Ref. [24], where they are not itemized with respect to the number of asymmetric centers. The present enumeration discriminates the cases having one asymmetric center (**72**–**74**) from the case having two asymmetric centers (**75**).

The total number of chiral bicentroidal alkanes of carbon content k is calculated by using

eq. 76 as follows:

$$\widetilde{C}_k = \frac{1}{2}\widetilde{B}_k^{(\mathrm{II})} = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\widetilde{C}_{k\ell m}. \tag{90}$$

The total numbers $\widetilde{C}_k$ ($k = 1$ to 20) have been directly obtained as a generating function and collected in Table 3 of Ref. [24]. They are numerically confirmed by the present itemized enumeration. For example, the rows concerning k = 20 (Table 10) are summed up to give the following result:

$k = 20$:	$m = 0$:	0	14300	72190	170660	199596	111856	27760	2368	64	598794
	$m = 1$:	0	0	0	880	1464	592	32			2968
		0	14300	72190	171540	201060	112448	27792	2368	64	601762

The total number 601762 is equal to the value reported previously in Table 3 of Ref. [24].

In addition to the numerical confirmation, the functional equation for calculating the total numbers (eq. 58 of Ref. [24]) can be algebraically derived by starting from eq. 81. When we put $y = z = 1$ in eq. 81, we obtain the following equation:

$$\begin{aligned}\widetilde{C}(x,1,1) &= \frac{1}{2}\widetilde{B}^{(\mathrm{II})}(x,1,1) \\ &= \frac{1}{4}\left\{b(x,1,1)^2 + b(x^2,1,1) - a(x,1,1)^2 - c(x^2,1,1)\right\}\end{aligned} \tag{91}$$

The latter equation (eq. 91) can be directly obtained from eq. 75, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. By putting $\widetilde{C}(x,1,1) = \widetilde{C}(x)$, $a(x,1,1) = a(x)$, and $c(x^2,1,1) = c(x^2)$, eq. 91 is converted into the following functional equation:

$$\widetilde{C}(x) = \frac{1}{4}\left\{b(x)^2 + b(x^2) - a(x)^2 - c(x^2)\right\}, \tag{92}$$

which is identical with eq. 58 of Ref. [24].

Achiral Bicentroidal Alkanes and Enantiomeric Pairs of Chiral Ones Table 11 lists the coefficient $\widetilde{B}_{k\ell m}$ of the term $x^k y^\ell z^m$ calculated by means of $\widetilde{B}(x,y,z)$ (eq. 82), where each coefficient is stored in the series obtained as `Bt` of the code "BAlkane1-30b.mpl".

The total number of bicentroidal alkanes of carbon content k is calculated by using eq. 76 as follows:

$$\widetilde{B}_k = \frac{1}{2}\widetilde{B}_k^{(\mathrm{II})} + \widetilde{B}_k^{(\mathrm{IV})} = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\widetilde{B}_{k\ell m}. \tag{93}$$

The total numbers $\widetilde{B}_k$ ($k = 1$ to 20) have been directly obtained as a generating function and collected in Table 3 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning k = 20 (Table 11) are summed up to give the following result:

$k = 20$:	$m = 0$:	2145	14300	72410	170660	199962	111856	27908	2368	72	601681
	$m = 1$:	0	0	260	880	1464	592	32			3228
	$m = 2$:	0	0	0	0	10					10
		2145	14300	72670	171540	201436	112448	27940	2368	72	604919

The total number 604919 is equal to the value reported previously in Table 3 of Ref. [24].

Table 11: Achiral Bicentroidal Alkanes and Enantiomeric Pairs of Chiral Ones

Carbon	No. of	No. of Asymmetric Centers (ℓ)												
Cont. (k)	P. C. (m)	$\ell=0$	1	2	3	4	5	6	7	8	9	10	11	12
$k=2$:	$m=0$:	1												
$k=4$:	$m=0$:	1												
$k=6$:	$m=0$:	3												
$k=8$:	$m=0$:	6	3	2										
$k=10$:	$m=0$:	15	15	12										
$k=12$:	$m=0$:	36	64	88	32	6								
$k=14$:	$m=0$:	105	280	560	400	110								
$k=16$:	$m=0$:	276	1058	3036	3588	1850	304	20						
$k=18$:	$m=0$:	780	3978	15381	26592	21462	7000	812						
	$m=1$:	0	0	78	204	250	56							
	$m=2$:	0	0	0	0	3								
$k=20$:	$m=0$:	2145	14300	72410	170660	199962	111856	27908	2368	72				
	$m=1$:	0	0	260	880	1464	592	32						
	$m=2$:	0	0	0	0	10								
$k=22$:	$m=0$:	6105	50710	322982	989540	1575908	1301760	537610	98240	6480				
	$m=1$:	0	0	1320	5752	13844	11368	3416	320					
	$m=2$:	0	0	0	0	78	24	6						
$k=24$:	$m=0$:	17020	174432	1375844	5316064	11014188	12515456	7711664	2431360	350480	16896	272		
	$m=1$:	0	0	4416	24224	77280	94784	48256	8832	256				
	$m=2$:	0	0	0	0	300	192	72						
$k=26$:	$m=0$:	48205	595510	5685462	26963340	70182006	104078276	88375816	41760848	10264474	1135472	45156		
	$m=1$:	0	0	17360	116876	477820	816980	664408	260008	44856	2544			
	$m=2$:	0	0	0	0	1596	1680	1378	360	46				
$k=28$:	$m=0$:	135460	1994720	22748572	130028544	414990518	775880728	863815662	566925112	211386266	41496288	3754120	111104	1056
	$m=1$:	0	0	56160	461088	2376936	5425472	6235504	3687512	1054624	116864	2048		
	$m=2$:	0	0	0	0	5886	9720	12078	5760	1072				
$k=30$:	$m=0$:	384126	6634824	88995774	602912676	2311812748	5302623088	7457180904	6440476448	3350122552	1003379072	159752096	11622912	305256
	$m=1$:	0	0	197976	1934228	12156638	35181316	53979752	45723560	20829904	4628256	424896	13248	
	$m=2$:	0	0	0	0	25651	57404	103642	81960	30844	3744	156		

Moreover, the functional equation for calculating the total numbers (eq. 52 of Ref. [24]) can be derived by starting from eq. 82. When we put $y = z = 1$ in eq. 82, we obtain the following equation:

$$\begin{aligned} \widetilde{B}(x,1,1) &= \frac{1}{2}\widetilde{B}^{(\mathrm{II})}(x,1,1) + \widetilde{B}^{(\mathrm{IV})}(x,1,1) \\ &= \frac{1}{4}\left\{b(x,1,1)^2 + b(x^2,1,1) + a(x,1,1)^2 + c(x^2,1,1)\right\} \end{aligned} \tag{94}$$

By putting $\widetilde{B}(x,1,1) = \widetilde{B}(x)$, $a(x,1,1) = a(x)$, and $c(x^2,1,1) = c(x^2)$, eq. 94 is converted into the following functional equation:

$$\widetilde{B}(x) = \frac{1}{4}\left\{b(x)^2 + b(x^2) + a(x)^2 + c(x^2)\right\}, \tag{95}$$

which is identical with eq. 52 of Ref. [24].

4 Conclusions

A criterion for specifying asymmetric and pseudoasymmetric centers in alkanes has been developed on the basis of three kinds of attributes of *RS*-stereoisomers (chirality, *RS*-stereogenicity, and sclerality), which were formulated by a recently-developed method [29]. The three kinds of attributes are capable of defining five *RS*-stereoisomeric types (Types I–V), so that *RS*-stereogenic promolecules (Type I, III, and V) are divided into chiral (Types I and III) and achiral ones (Type V). After another criterion has been formulated to select entities for the application of the first criterion, the central atom of each promolecule of Types I and III is defined as an asymmetric center, while the central atom of each promolecule of Types V is defined as a pseudoasymmetric center. According to the Criteria, alkyl ligands (equivalently, monosubstituted alkanes) have been regarded as nested planted promolecules, where each participating planted promolecule is categorized into an asymmetric (Types I/III), a pseudoasymmetric (Type V), or a

symmetric one (Types II/IV). Thereby, they have been counted combinatorially with itemization with respect to carbon content (k), to the number of asymmetric carbons (ℓ), as well as to the number of pseudoasymmetric carbons (m). The data of alkyl ligands stored as generating functions have been used to count centroidal and bicentroidal alkanes on the basis of a tetrahedral skeleton, where the criteria are effective to categorize alkanes into Types I–V. Each itemized number has been obtained as the coefficient of the term $x^k y^\ell z^m$ appearing in a respective generating function, which has been derived by following Fujita's proligand method [17–19]. The itemized values up to carbon content 30 have been listed in tabular forms, which are distinctively concerned with Type I, …, or Type V as well as with achiral stereoisomers and chiral stereoisomers.

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[49] The present argument indicates that a pair of p/$\overline{\text{p}}$ for Type V (pseudoasymmetry) is discriminated from pairs of p/$\overline{\text{p}}$ for Type I and III (asymmetry) in agreement with the incapability/capability of generating enantiomers. In other words, the present Criterion reinforces the original conclusion of Prelog and Helmchen's arguments [36]. From this point of view, the "pseudoasymmetry" due to the revised CIP system [37] means that pairs of p/$\overline{\text{p}}$ for Types III and V are discriminated from a pair of p/$\overline{\text{p}}$ for Type I (cf. Fig. 7 below). On the other hand, the vigorous disputation by Hirschmann and Hanson [56] to the Prelog and Helmchen's arguments [36] implies that pairs of p/$\overline{\text{p}}$ for Types I, III, and V exhibit "pseudoasymmetric" nature all together, although cases of Type I have not been explicitly discussed. If pairs of p/$\overline{\text{p}}$ of Types I, III, and V are brought all together, they are not necessary to be discriminated from other proligands in Types I, III, or V. Thus, the Hirschmann and Hanson's argument [56] implies, despite of their intention, that the term "pseudoasymmetry" is no longer necessary because the term "*RS*-stereogenic" is sufficient under the condition that p and $\overline{\text{p}}$ can be discriminated as 3D-objects in isolation. Rigorously speaking, we should adopt Type I, III, or V for an *RS*-stereogenic center in place of the term *asymmetric* or *pseudoasymmetric*. Even in this case, however, such an appropriate criterion as Criterion 2 is necessary to be defined.

[50] Note that the concept of centroidal/bicentroidal trees was originally formulated as graphs by Jordan [57] and applied to the enumeration of trees (as graphs) by Pólya [5, 6].

[51] In the enumeration of alkanes, we have defined a chemical set of terms *promolecule* and *proligands* (*planted promolecules*) and a mathematical set of terms *3D-trees* and *planted 3D-trees* to abstract essential symmetrical properties of a more concrete set of terms *alkanes* and *monosubstituted alkanes* (*alkyl ligands*). See Ref. [21, 24]. To do well with these sets of terms in the present paper, promolecular representations shown in Fig. 1 are used to demonstrate the chemical set, while carbon-skeletal representations demonstrate the mathematical set. Centroidal representations intermediate between the promolecular representations and carbon-skeletal representations.

[52] The term "asymmetric center" has been referred to as an out-dated term that usually should be replaced by "stereogenic center (unit)" or "chirality center" [58]. From the present viewpoint, however, problematic is the transmuted usage of the term "asymmetric center" so as to cover an erroneous connotation "asymmetric center ⊃ pseudoasymmetric center" in place of a more plausible connotation "stereogenic center ⊃ pseudoasymmetric center". The plausible connotation implies that the concept of chirality is a subsidiary concept beneath the concept of stereogenicity, i.e., "stereogenic center = chirality center + pseudoasymmetric center". In contrast, the present methodology is based on the concept of *RS*-stereogenicity which appears in a stereoisogram, independent of the concept of chirality. Hence, we can recognize that "*RS*-stereogenic center = asymmetric center + pseudoasymmetric center", where the term "asymmetric center" is adopted in place of the term "chirality center".

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