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Strength from Weakness: Conformational Divergence between Solid and Solution States of Substituted Cyclitols Facilitated by CH···O Hydrogen Bonding

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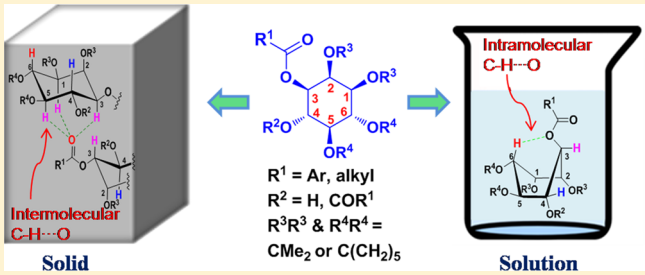
Supporting Information

ABSTRACT: We have investigated the conformational preferences of a series of cyclitol derivatives, namely mono- and diesters of 1,2:5,6-di-*O*-isopropylidene-*myo*-inositol and 1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol, in both solid and solution states. The solid-state conformations were determined by single-crystal X-ray analysis. The solution-state conformations were determined by using NMR. The experimental $^{3}J_{HH}$ values were applied in the Haasnoot−Altona equation to calculate the dihedral angle (ϕ) between the respective vicinal protons. By fixing the dihedral angle between different sets of vicinal protons, the molecules were energy-minimized by MM2 method to visualize their conformation in solution. As the solvent polarities can influence the conformational preference, we have determined the conformations of these molecules in various solvents of different polarities such as benzene-d_6, chloroform-d, acetonitrile-d_3, acetone-d_6, methanol-d_4, and DMSO-d_6. All of the compounds adopted boat conformations in solution irrespective of the solvents, acyl groups, or alkylidene protecting groups. This conformation places H6 and O3 of the cyclitol ring in proximity, such that an intramolecular CH···O hydrogen bond between them stabilizes this otherwise unstable conformation. However, in the solid state, several intermolecular CH···O hydrogen bonds force these molecules to adopt the chair conformation. This study uncovers the role of weak noncovalent interactions in influencing the molecular conformations differentially in different states.



INTRODUCTION

The conformation of molecules present in a substance dictates the properties of the bulk material.[1] For instance, the proper functioning of biomolecules such as peptides,[2] proteins, ligands,[3] carbohydrates, nucleic acids,[4] lipids, etc. depends on the conformation of these biomolecules. In addition, the molecular conformation influences the physical properties of materials.[5] In chemistry, the conformation dictates not only the reactivity but also the selectivity of the reactions. The study of the role of conformation in deciding the reactivity or selectivity in chemical transformations[6] and the factors that affect the conformations is a timely and active area of research. An important area where the correlation between conformation and reactivity or selectivity is actively pursued is carbohydrates.[7] Recently, Bols et al. demonstrated that the conformation of glucopyranosides can be tuned to the $^{1}C_4$ conformation by introducing sterically demanding silyl protecting groups, and as a consequence, the reactivity can be augmented.[8] In addition, the influence of conformation of pyranosides on the selectivity of glycosylation reactions has been demonstrated.[9] Similarly, the conformation has been tuned to modulate the reactivity of cyclitols.[10] For instance, the least reactive 2-OH of *myo*-inositol could be made most reactive by altering the conformation of *myo*-inositol from its normal 5e1a (pentaequatorial monoaxial) to the unusual 5a1e (pentaaxial monoequatorial) conformation through an orthoester lock.[11]

Apart from covalent conformational locks, conformations can also be arrested by attractive or repulsive noncovalent interactions (Figure 1). Strong repulsive steric interactions between bulky silyloxy groups in trans-vicinal orientation in cyclohexanes are known to adopt the otherwise unstable diaxial orientation as a result of conformational flipping.[8,9e] The classical intramolecular OH···O hydrogen-bonding interactions are known to stabilize the diaxial conformation of *cis*-1,3-cyclohexanedicarboxylic acid.[12] Similarly, intramolecular OH···O hydrogen bonding is known to stabilize the otherwise unstable boat conformation (in simple cyclohexane, the boat conformer is energetically less stable, by 7 kcal/mol, than the chair conformer) of *cis*-1,4-cyclohexanediol.[13] As weak interactions are known to mimic or even overpower relatively stronger classical hydrogen bonds at times,[14] it is, in principle, possible for weak hydrogen bonds to stabilize the unusual boat conformations in substituted cyclohexanes. We herein report that weak CH···O hydrogen bonds[15] can also stabilize the otherwise unstable boat conformation in cyclitols. Though there are many examples in the literature suggesting that CH···

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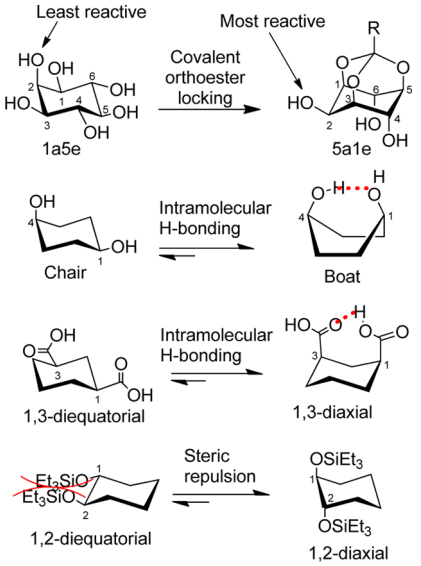


Figure 1. Stabilization of unusual conformations of cyclohexane derivatives by noncovalent interactions and covalent conformational locks.

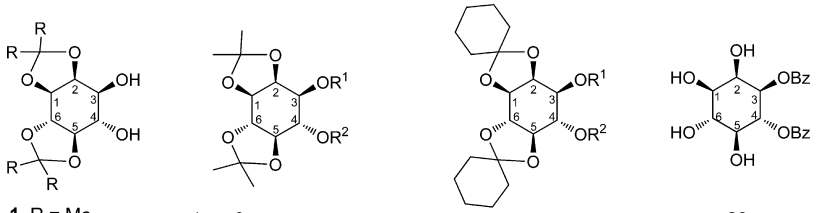
O hydrogen bonds play significant roles in influencing the conformation of small molecules,[16] to the best of our knowledge, stabilization of the boat conformation of cyclohexane rings by CH···O is not known.

RESULTS AND DISCUSSION

We have been interested in the chemistry of cyclitols[10,17] and the role of weak interactions in determining the conformation of cyclitols in solid and solution states.[18] The fact that esters of diketals **1** and **2** are intermediates used for phosphoinositol synthesis prompted us to study their conformations, especially in the solution state, as it is more relevant with respect to reactivity. Though it is easy to study the conformation and the interactions responsible for the conformation in the solid state using single crystal X-ray crystallography, conformational analysis in solution is rather cumbersome. Though the use of the solid-state conformation (crystal structure) to explain the solution-state behavior is widely practiced, often the solution-state conformations differ from the solid-state conformations, pointing out the danger associated with such a practice.[19] ^{1}H NMR spectroscopy is one of the reliable techniques for studying the solution-state conformations.[20] As the Karplus equation relates the dihedral angle (ϕ) between vicinal hydrogens and their $^3J_{HH}$ coupling constants, the dihedral angle can be calculated from the experimental $^3J_{HH}$ values. We have used the Haasnoot−Altona equation,[21] which is the most reliable form of the Karplus equation for studying the solution-state conformation of cyclitol derivatives,[18,22] for the determination of ϕ values of all sets of vicinal protons. The solution-state conformations for these compounds were visualized by energy minimization using MM2 calculations after fixing the dihedral angles between the vicinal protons as those obtained from the NMR method.

In a preliminary communication, we reported conformational studies, in solution and solid states, of di- and monoesters of 1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**3**−**11**; Figure 2).[18a] In solution, these molecules adopt a boat conformation due to intramolecular CH···O hydrogen bonding, but in the solid state, they adopt a chair conformation as a consequence of intermolecular CH···O hydrogen bonding. These interesting and consistent conformational extremities between solid and solution states prompted us to investigate the generality of this phenomenon in otherwise differently protected diketal derivatives. In the present paper, we extend our conformational studies to several di- and monoesters of 1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**12**−**19**) in solution and solid states and generalize our findings by comparing with the conformational preferences of isopropylidene derivatives **3**−**11**.

Conformation of Dibenzoate 12 in Solution. A comparison of dibenzoates **3** and **12** revealed that they adopt identical conformations irrespective of the ketal protecting groups. For instance, the ^{1}H NMR spectra of both compounds showed unusually large coupling constants between H1 and H2 (6.8 Hz in **3** and 7.0 Hz in **12**) and unusually small coupling constants between H3 and H4 (4.4 Hz in **3** nd 3.5 Hz in **12**). The usual $^3J_{H1H2}$ and $^3J_{H3H4}$ values for the chair conformer of *myo*-inositol derivatives are around 2.9 and 9.8 Hz, respectively. All of the other vicinal $^3J_{HH}$ values were also similar between identical vicinal hydrogens of **3** and **12**. The vicinal H−C−C−H dihedral angles (ϕ) were calculated from the $^3J_{HH}$ coupling constants using the Haasnoot−Altona equation,[21] and the conformations of the molecules were mapped by doing energy minimization after fixing the H−C−C−H dihedral angles. The cyclitol rings of both molecules adopt the boat conformation. It



1. R = Me
2. R = $(CH_2)_5$

3. $R^1 = R^2$ = COPh
4. $R^1 = R^2$ = $COCH_3$
5. $R^1 = R^2$ = $COC(CH_3)_3$
6. $R^1 = R^2$ = CONaphthyl
7. $R^1 = R^2$ = COPyrenyl
8. R^1 = $COC(CH_3)_3$, R^2 = H
9. R^1 = COPh, R^2 = H
10. R^1 = CONaphthyl, R^2 = H
11. R^1 = COPyrenyl, R^2 = H

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12. $R^1 = R^2$ = COPh
13. $R^1 = R^2$ = $COC(CH_3)_3$
14. $R^1 = R^2$ = CONaphthyl
15. $R^1 = R^2$ = COPyrenyl
16. R^1 = $COC(CH_3)_3$, R^2 = H
17. R^1 = COPh, R^2 = H
18. R^1 = CONaphthyl, R^2 = H
19. R^1 = COPyrenyl, R^2 = H

Figure 2. *myo*-Inositol derivatives used for conformational studies.

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is strikingly clear that H6 is approaching O3 in this conformation, which suggests the possible stabilization of this conformation by an intramolecular CH···O hydrogen bond between H6 and O3 (Figure 3). The H6 proton is sufficiently

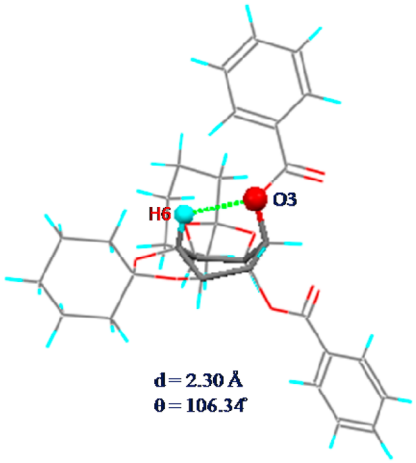

Figure 3. Conformation of dibenzoate **12** in DMSO-d_6. The interacting donor (C6−H6) and acceptor (O3) and the resultant boat form of the cyclitol ring are shown as ball and capped-stick models, respectively, for clarity. d is the distance between the donor H6 and acceptor O3, and θ is the C6−H6···O3 angle.

acidic, due to the attachment of an electronegative oxygen to C6, to be involved in a considerably strong CH···O hydrogen bond. The separation between the interacting atoms H6 and the acceptor O3 is 2.30 Å, which is much smaller than the van der Waals distance (2.72 Å) between them. The angle of approach of 106.3° is well within the accepted limits for effective bonding, as CH···O hydrogen bonding is known to be significant even at smaller angles (down to 90°).[23] Further evidence for the CH···O hydrogen bonding was adduced from the downfield chemical shift of H6 of the cyclitol ring. It is well-known that, as a consequence of CH···O hydrogen bonding, the diamagnetic shielding around the donor H decreases and hence there will be a downfield shift (by $\Delta\delta$ = 0.1−1 ppm) of the donor H.[24] Similar downfield shifts of the H6 proton by 0.42 and 0.47 ppm were observed in the case of benzoates **3** and **12**, respectively, in comparison to H6 of the tetrol **20**, which adopts a normal chair conformation, in the same solvent (CD_3OD). It is clear from the $^3J_{HH}$ values of different sets of vicinal hydrogens in various solvents of different polarity (Table 1) that molecules **3** and **12** adopt the boat conformation in all solvents very consistently, irrespective of the nature of the solvent.

Conformation of Dipivaloate 13, Dinaphthoate 14, and Dipyrenoate 15 in Solution. The conformational preferences of dipivaloate **13**, dinaphthoate **14**, and dipyrenoate **15** were also tested in various solvents of different polarity, and their conformations were compared with the conformation of the corresponding isopropylidene analogues. The coupling constants and corresponding dihedral angles for various vicinal protons of dipivaloate **13** are almost similar in all of the solvents (Table 2). As a representative example, the conformation of dipivaloate **13** was determined in $CDCl_3$ solution (Figure 4A). In addition, the conformation of cyclohexylidene derivative **13** was identical with that of the isopropylidene derivative **5** in all solvents tested. The cyclitol ring of **13** adopted a boat conformation, wherein H6 and O3 are proximally placed. Both the distance (2.11 Å) and angle (115.68°) are comparable to those of **5** (2.19 Å; 119°) and are conducive to CH···O hydrogen bonding between them. It is interesting to note that the H6···O3 distances of pivaloates are the smallest among the compounds studied in this series. As with the dibenzoates and dipivaloates, both dinaphthoate **14** and dipyrenoate **15** also exhibited a boat conformation in the solution state. The coupling constants and dihedral angles for a particular set of vicinal protons (Tables 3 and 4) of **14** and **15** were identical in all of the solvents tested. H6···O3 distances of 2.35 and 2.36 Å were observed in the case of dinaphthoate **14** (in $CDCl_3$) and dipyrenoate **15** (in DMSO-d_6), respectively. In addition, the solution conformations of all of the diesters of 1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol were identical with the solution state conformations of the corresponding isopropylidene derivatives **6** and **7**, respectively. This study revealed that the conformations of similar derivatives (e.g. pivaloates of isopropylidene and cyclohexylidene) were identical irrespective of the type of ketal protecting group. In addition, it is clear from the NMR data (Tables 2−4) that all of the the diesters adopt boat conformation (for the inositol ring), suggesting that the nature or bulkiness of the acyl group is unimportant for the conformation.

Conformation of Monoesters in Solution. Having established the fact that diesters of both 1,2:5,6-di-*O*-isopropylidene-*myo*-inositol and 1,2;5,6-di-*O*-cyclohexylidene-*myo*-inositol adopt similar conformations irrespective of the acyl group and ketal groups, we were curious to know whether monoesters also adopt such conformations in solution. Interestingly, the monoesters **16**−**19** also adopted the boat conformation in solution as the corresponding monoesters **8**−**11** of 1,2:5,6-di-*O*-isopropylidene-*myo*-inositol. In addition,

Table 1. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Dibenzoate 12 and Dibenzoate 3[a]

	12						
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	CD_3OD	C_6D_6	CD_3CN	**3** in DMSO-d_6
H1−C1−C2−H2	7.0 (−6)	6.3 (−14)	6.6 (−8)	6.3 (−14)	6.4 (−12)	6.5 (−10)	6.3 (−14)
H2−C2−C3−H3		3.8 (42)		3.9 (43)	4.1 (41)	4.3 (39)	3.9 (43)
H3−C3−C4−H4		3.5 (44)			4.1 (56)	3.6 (45)	4.4 (55)
H4−C4−C5−H5	9.0 (−159)	9.0 (−159)		8.8 (−167)	9.0 (−169)	8.8 (−158)	8.8 (−157)
H5−C5−C6−H6	10.4 (−167)	10.3 (−167)	10.5 (−166)	10.4 (−168)	10.5 (−166)	10.5 (−166)	10.3 (−167)
H6−C6−C1−H1	7.4 (−167)	7.3 (−166)	7.8 (−171)	7.8 (−171)	7.8 (−171)	7.9 (−172)	7.3 (−166)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ in deg (in parentheses) calculated for the corresponding set of various vicinal protons of the dibenzoate **12** in solvents of different polarities. The $^3J_{HH}$ values of dibenzoate **3** in DMSO-d_6 are given in the last column for easy comparison.

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Table 2. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Dipivaloate 13 and Dipivaloate 5[a]

	13						
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	CD_3OD	C_6D_6	CD_3CN	**5** in $CDCl_3$
H1−C1−C2−H2	5.9 (−21)	6.0 (−19)	5.7 (−25)	5.7 (−25)	5.5 (−26)	5.9 (−21)	6.3 (−15)
H2−C2−C3−H3	5.0 (33)	4.8 (34)	5.1 (32)	5.1 (32)	5.1 (32)	4.7 (35)	4.7 (35)
H3−C3−C4−H4	6.4 (34)	7.0 (27)	6.9 (38)	7.0 (27)	6.9 (38)	6.5 (34)	5.2 (48)
H4−C4−C5−H5	9.8 (−159)	8.8 (−157)	9.7 (−158)	10.0 (−160)	9.9 (−159)	9.9 (−159)	9.0 (−152)
H5−C5−C6−H6	10.1 (−162)		10.1 (−162)	10.0 (−162)	9.9 (−159)	9.9 (−159)	10.3 (−165)
H6−C6−C1−H1	8.6 (177)		8.6 (177)	8.7 (176)	8.5 (178)	8.6 (177)	8.3 (−177)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ in deg (in parentheses) calculated for the corresponding set of various vicinal protons of the dipivaloate **13** in solvents of different polarities. The $^3J_{HH}$ values of dipivaloate **5** in $CDCl_3$ are given in the last column for easy comparison.

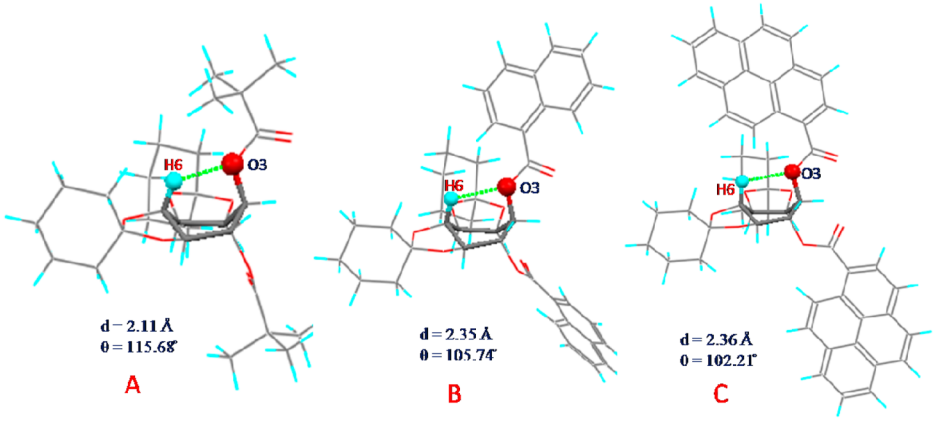

Figure 4. Conformations of (A) dipivaloate **13** in $CDCl_3$, (B) dinaphthoate **14** in $CDCl_3$, and (C) dipyrenoate **15** in DMSO-d_6. The interacting donor (C6−H6) and the acceptor (O3) and the resultant boat form of the cyclitol ring are shown as ball and capped-stick models, respectively, for clarity. d is the distance between the donor H6 and acceptor O3, and θ is the C6−H6···O3 angle.

Table 3. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Dinaphthoate 14 and Dinaphthoate 6[a]

	14						
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	CD_3OD	C_6D_6	CD_3CN	**6** in $CDCl_3$
H1−C1−C2−H2	6.7 (4)	6.7 (4)	6.3 (15)	6.3 (15)	6.7 (4)	6.6 (5)	6.6 (−9)
H2−C2−C3−H3	4.4 (37)	4.7 (39)	3.6 (45)	5.5 (37)	4.6 (36)	4.5 (36)	4.3 (39)
H3−C3−C4−H4	4.4 (55)	5.6 (44)			4.6 (53)		4.3 (56)
H4−C4−C5−H5	9.2(−179)	8.1 (−179)	9.6 (−179)	9.2 (−167)	9.2(−179)	9.4 (−179)	9.4 (−166)
H5−C5−C6−H6	10.3 (−167)		10.3 (−167)	10.2 (−167)	10.2 (−167)	10.2 (−167)	10.2 (−167)
H6−C6−C1−H1	8.0 (−174)		8.1 (−174)	8.2 (−176)	8.0 (−174)	8.3 (−174)	8.0 (−173)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ in deg (in parentheses) calculated for the corresponding set of various vicinal protons of the dinaphthoate **14** in solvents of different polarities. The $^3J_{HH}$ values of dinaphthoate **6** in $CDCl_3$ are given in the last column for easy comparison.

Table 4. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Dipyrenoate 15 and Dipyrenoate 7[a]

	15					
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	C_6D_6	CD_3CN	**7** in DMSO-d_6
H1−C1−C2−H2	6.6 (5)	6.3 (15)	6.4 (10)	6.9 (2)	6.1 (18)	6.1 (−18)
H2−C2−C3−H3		4.5 (36)	3.6 (45)	4.5 (36)	4.3 (39)	4.7 (35)
H3−C3−C4−H4		4.5 (54)		4.5 (54)		5.4 (46)
H4−C4−C5−H5	9.5 (−179)	8.0 (−179)	9.4 (−155)	9.8 (−159)	9.3 (−165)	8.6 (−154)
H5−C5−C6−H6	9.7 (−167)		10.0 (−167)	9.8 (−167)	10.1 (−167)	
H6−C6−C1−H1	8.6 (−179)	6.6 (−164)	8.1 (−179)	7.3 (−179)	8.4 (−179)	7.0 (−164)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ in deg (in parentheses) calculated for the corresponding set of various vicinal protons of the dipyrenoate **15** in solvents of different polarities. The $^3J_{HH}$ values of dipyrenoate **7** in DMSO-d_6 are given in the last column for easy comparison.

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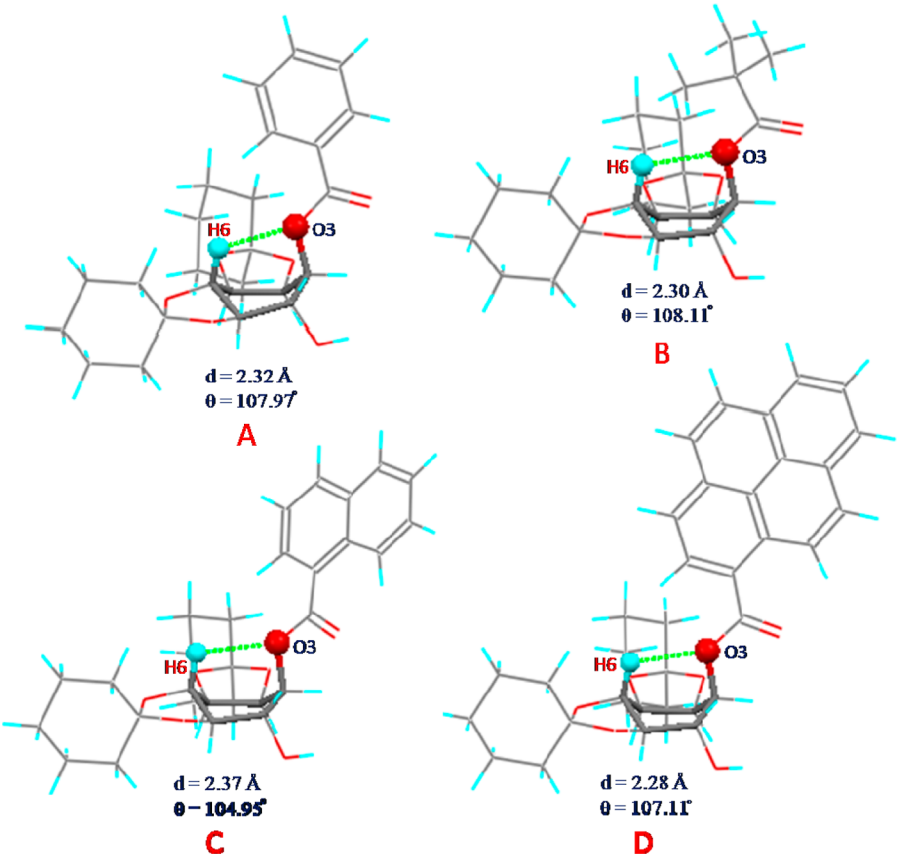

Figure 5. Conformations of (A) monobenzoate **17** in $CDCl_3$ solution, (B) monopivaloate **16** in $CDCl_3$ solution, (C) mononaphthoate **18** in DMSO-d_6 solution, and (D) monopyrenoate **19** in $CDCl_3$ solution. The interacting donor (C6−H6) and the acceptor (O3) and the resultant boat form of the cyclitol ring are shown as ball and capped-stick models respectively, for clarity. d is the distance between the donor H6 and acceptor O3, and θ is the C6−H6···O3 angle.

Table 5. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Monopivaloate 16 and Monopivaloate 8[a]

	16						
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	CD_3OD	C_6D_6	CD_3CN	**8** in DMSO-d_6
H1−C1−C2−H2	6.2 (16)	6.7 (4)	6.5 (10)	6.2 (16)		6.2 (16)	6.7 (−5)
H2−C2−C3−H3	5.0 (33)	4.4 (38)	4.6 (36)	4.7 (35)	4.6 (36)	4.6 (36)	4.2 (40)
H3−C3−C4−H4	5.1 (48)	4.2 (56)	4.6 (55)	5.4 (46)	5.4 (46)	5.3 (48)	4.2 (57)
H4−C4−C5−H5	10.1 (−160)	8.6 (−179)	8.8 (−179)	9.0 (−152)	8.6 (−179)	9.0 (−152)	8.4 (−151)
H5−C5−C6−H6	10.2 (−167)	10.4 (−167)	10.3 (−167)	10.2 (−167)	9.8 (−167)	10.3 (−167)	10.5 (−167)
H6−C6−C1−H1	8.2 (−176)	8.0 (−173)	8.1 (−174)	8.3 (−177)		8.3 (−177)	8.0 (−174)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ in deg (in parentheses) calculated for the corresponding set of various vicinal protons of the monopivaloate **16** in solvents of different polarities. The $^3J_{HH}$ values of monopivaloate **8** in DMSO-d_6 are given in the last column for easy comparison.

consistent with the diesters, the conformation was uniform and consistent in all of the solvents tested irrespective of their polarity. The short H6···O3 contacts were consistent in all the monoesters and were much less than their van der Waals distances. Figure 5 shows the conformations of different monoesters in representative solvents. The respective H6···O3 distances and C6H6···O3 angles for monobenzoate **17**, monopivaloate **16**, mononaphthoate **18**, and monopyrenoate **19** are as follows: 2.32 Å, 107.97°; 2.30 Å, 108.11°; 2.37 Å, 104.95°; 2.28 Å, 107.11°. These are comparable to those of corresponding isopropylidene derivatives: viz. monobenzoate **9** (2.36 Å, 109°), monopivaloate **8** (2.23 Å, 111°), mononaphthoate **10** (2.28 Å, 110°) and monopyrenoate **11** (2.35 Å, 110°) (Tables 5−8).

Conformation of Dibenzoate 12 in the Solid State. The consistent boat conformation of the mono- and diesters of ketals in solution prompted us to investigate their conformational preferences in the solid state. It is possible that, in the solid state wherein the molecules are closely packed, the intermolecular interactions dominate over intramolecular interactions. Hence, the intermolecular interactions will have major roles in the solid-state conformation and packing. We obtained good-quality crystals of **12** from a mixture of hexane and dichloromethane and were analyzed using single-crystal X-ray diffraction. In sharp contrast to the solution-state

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Table 6. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Monobenzoate 17 and Monobenzoate 9[a]

	17						
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	CD_3OD	C_6D_6	CD_3CN	**9** in DMSO-d_6
H1−C1−C2−H2	6.4 (−10)	6.8 (−2)	7.0 (−2)	6.6 (−6)		6.8 (−2)	6.7 (−5)
H2−C2−C3−H3	3.8 (42)	4.0 (41)	3.6 (45)	3.6 (45)		4.0 (41)	4.0 (42)
H3−C3−C4−H4	3.8 (60)		3.9 (59)	3.6 (62)		4.0 (57)	3.9 (59)
H4−C4−C5−H5	8.6 (−167)	8.6 (−167)	8.2 (−167)	8.6 (−167)	8.1 (−167)	8.6 (−167)	8.5 (−152)
H5−C5−C6−H6	10.5 (−166)	10.3 (−167)	10.6 (−167)	10.2 (−167)	10.5 (−167)	10.6 (−167)	10.6 (−167)
H6−C6−C1−H1	7.8 (−172)	7.8 (−172)	7.4 (−172)	7.3 (−179)	7.9 (−173)	7.7 (−171)	7.8 (−171)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ are (in parentheses) calculated for the corresponding set of various vicinal protons of the monobenzoate **17** in solvents of different polarities. The $^3J_{HH}$ values of monobenzoate **9** in DMSO-d_6 are given in the last column for easy comparison.

Table 7. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Mononaphthoate 18 and Mononaphthoate 10[a]

	18						
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	CD_3OD	C_6D_6	CD_3CN	**10** in $CDCl_3$
H1−C1−C2−H2	6.1 (18)	6.0 (19)	6.4 (12)	6.0 (19)	6.3 (15)	6.1 (18)	6.1 (−18)
H2−C2−C3−H3	4.8 (34)	4.1 (41)	4.4 (38)	4.4 (38)	4.4 (38)	4.8 (34)	4.7 (35)
H3−C3−C4−H4	4.8 (51)	4.1 (56)	4.4 (55)	5.2(48)	4.7 (52)	4.8 (51)	4.7 (52)
H4−C4−C5−H5	9.2 (−167)	9.2 (−167)	8.6 (−167)	8.9 (−167)	8.7 (−167)	9.1 (−167)	9.0 (−164)
H5−C5−C6−H6	10.1 (−167)	10.1 (−167)	10.3 (−166)	10.1 (−167)	10.5 (−166)	10.1 (−167)	10.4 (−167)
H6−C6−C1−H1	8.1(−173)	8.1(−173)	8.0 (−174)	8.2 (−176)	8.0 (−173)	8.2 (−176)	8.1(−174)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ in deg (in parentheses) calculated for the corresponding set of various vicinal protons of the mononaphthoate **18** in solvents of different polarities. The $^3J_{HH}$ values of mononaphthoate **10** in $CDCl_3$ are given in the last column for easy comparison.

Table 8. Comparison of the $^3J_{HH}$ Coupling Constants and H−C−C−H Dihedral Angles of Monopyrenoate 19 and Monopyrenoate 11[a]

	19						
H−C−C−H	$CDCl_3$	DMSO-d_6	acetone-d_6	CD_3OD	C_6D_6	CD_3CN	**11** in DMSO-d_6
H1−C1−C2−H2	6.4 (10)	6.3 (15)	6.5 (11)	6.3 (15)	6.4 (10)	6.2 (16)	6.3 (−15)
H2−C2−C3−H3	4.6 (36)	4.2 (41)	4.5 (35)		4.4 (37)	4.8 (34)	4.4 (38)
H3−C3−C4−H4	4.6 (53)	4.5 (55)	4.5 (55)	5.0 (49)	4.4 (55)	4.8 (51)	4.5 (54)
H4−C4−C5−H5	9.6 (−179)	8.9 (−167)	8.6 (−154)	9.0 (−167)	8.6 (−167)	9.1 (−153)	8.9 (−161)
H5−C5−C6−H6	10.1 (−167)	10.1 (−167)	10.4 (−167)	10.1 (−167)	10.3 (−167)	10.3 (−167)	10.3 (−167)
H6−C6−C1−H1	8.3 (−177)	8.0 (−173)	8.0 (−173)	8.2 (−176)	7.7 (−172)	8.2 (−176)	8.0 (−173)

[a] $^3J_{HH}$ values in Hz obtained from ^{1}H NMR and dihedral angles ϕ in deg (in parentheses) calculated for the corresponding set of various vicinal protons of the mononaphthoate **19** in solvents of different polarities. The $^3J_{HH}$ values of mononaphthoate **11** in DMSO-d_6 are given in the last column for easy comparison.

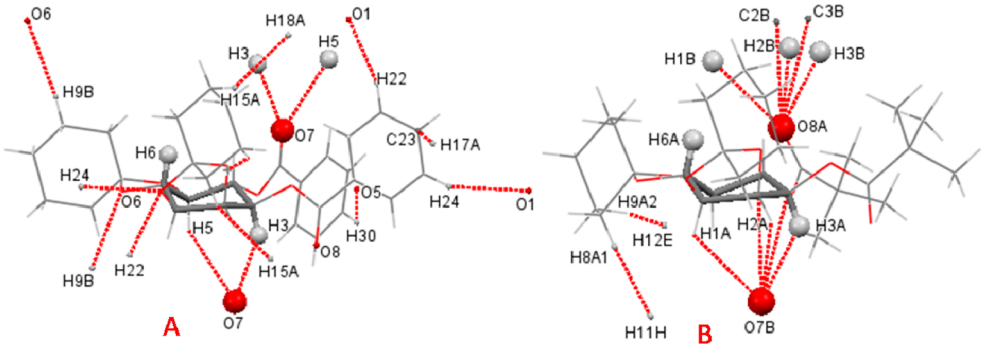

Figure 6. Conformations of (A) dibenzoate **12** and (B) dipivaloate **13** in the solid state. The interacting atoms and the resultant chair form of the cyclitol ring are shown as ball and capped-stick models, respectively, for clarity.

conformation, the cyclitol ring of dibenzoate **12** adopted a chair conformation in the solid state (Figure 6A). In the solution conformation, the C3 end of the cyclitol ring approaches the C6 end, which facilitates an intramolecular CH···O hydrogen bond between H6 and O3. In the solid state, the C3 end of the cyclitol ring is held in an orientation opposite to the C6 end.

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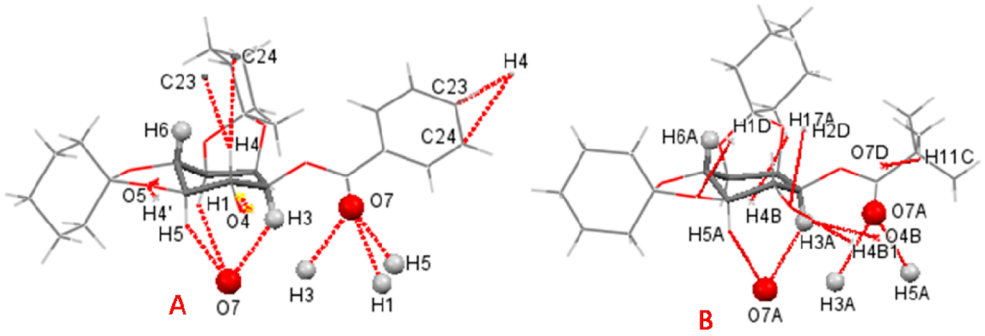

Figure 7. Conformations of (A) monobenzoate **17** and (B) monopivaloate **16** in the solid state. The interacting atoms and the resultant chair form of the cyclitol ring are shown as ball and capped-stick models, respectively, for clarity.

The main interaction responsible for this conformation is the C3−H3···O7 hydrogen bond with the carbonyl oxygen of the C4-benzoate of a neighboring molecule. Also, it is worth noting that this is the strongest CH···O bonding in the crystal with the shortest H···O distance of 2.37 Å. This interaction is further supplemented by three other CH···O contacts made by the carbonyl oxygen (O8) of C3-benzoate (C6H6···O8, C14H14B···O8, and C8H8B···O8). Apart from these interactions, many other CH···O hydrogen bonds are involved in the stabilization of the crystal (Table S1, Supporting Information). It is clear that, as in the case of dibenzoate **3**,[18a] the solid-state conformation of **12** is dictated by several intermolecular CH···O hydrogen bonds.

Conformation of Dipivaloate 13 in the Solid State. Dipivaloate **13** crystallizes in the *Cc* space group with four molecules in the asymmetric unit. In all of the conformers, the cyclitol rings adopted a chair conformation. In all of these conformers H1, H2, and H3 of the inositol ring are in CH···O hydrogen bonds with the carbonyl oxygen of a different neighboring conformer (Figure 6B). It should be noted that the H3···O═C contact is the shortest in all of the conformers, suggesting that the main function of the carbonyl oxygen is to arrest the conformation of the cyclitol ring of a neighboring molecule as a chair by pulling the C3 end of the cyclitol ring opposite to the C6 end. In conformer A, the C3 is held by a C3AH3A···O7B (2.46 Å) hydrogen bond to a neighboring B conformer, as a result of which the cyclitol ring is held in a chair conformation. In the B conformer, C3 is held by C3BH3B···O8A (2.47 Å) hydrogen bond to the carbonyl oxygen of a neighboring A conformer. Conformers C and D show disorders in the *tert*-butyl groups of the pivaloyl unit at C3. The conformer C adopts a chair conformation as a result of the intermolecular C3CH3C···O8D hydrogen bond (2.45 Å), and conformer D adopts a chair conformation as a result of the C3DH3D···O8C (2.49 Å) hydrogen bond. The intermolecular CH···O hydrogen bonding (Table S2, Supporting Information) and the chair conformation adopted by the dipivaloate **13** is identical with those of dipivaloate **5** in the solid state.

Conformation of Monoesters in the Solid State. While the solid-state conformations of diesters are dictated by several intermolecular CH···O hydrogen bonds, the presence of one free hydroxyl group in monoesters, which can form strong intermolecular OH···O hydrogen bonds, can mask any weak interaction such as CH···O hydrogen bonding. Though such intermolecular interactions are less likely in dilute solutions, they can be powerful in the solid state. In order to compare the solid state conformations of monoesters with that of diesters and with their solution conformation, we have done single crystal X-ray analysis of several monoesters as well.

*Conformation of Monobenzoate **17** in the Solid State.* Monobenzoate **17** forms a centrosymmetric hydrogen-bonded dimer with a neighboring molecule. The cyclitol ring of monobenzoate **17** also adopts a chair conformation in the solid state. The carbonyl oxygen (O7) forms trifurcated CH···O hydrogen bonds with C1−H1, C3−H3, and C5−H5 hydrogens, which collectively assist to pull the C3 end away from the C6 end of the cyclitol ring, preventing its boat conformation (Figure 7A). In addition, these weak interactions facilitate the formation of another centrosymmetric dimer. It is worth noting that a C3H3···O7 hydrogen bond consistent with that in diesters is present, which assists in the chair conformation in the solid state (Table S4, Supporting Information). Though the monobenzoate **17** adopts a chair conformation, similar to that of **9** in the solid state, their intermolecular hydrogen-bonding patterns are different. While trifurcated CH···O hydrogen bonds are responsible for the chair conformation of monobenzoate **17**, the OH···O hydrogen bond also plays a significant role in pulling the C3 end of the cyclitol ring opposite to the C6 end in case of monobenzoate **9**.

*Conformation of Monopivaloate **16** in the Solid State.* As in the case of dipivaloate **13**, the monopivaloate **16** also crystallizes with four molecules in the asymmetric unit. The cyclitol ring of each of these conformers adopts a chair conformation, in line with other esters and dipivaloate **13**. The hydroxyl group of each conformer is involved in intermolecular OH···O hydrogen bonds. In each of the four conformers, the carbonyl oxygen is involved in a CH···O hydrogen bond with H3 of a neighboring conformer, forming a pseudocentrosymmetric dimer. These two mutually complementing CH···O hydrogen bonds force the C3 end opposite to the C6 end, arresting the conformation of the cyclitol ring in chair form. Other noncovalent interactions involved in stabilizing the crystal structure are given in Table S3 (Supporting Information).

*Conformation of Monopyrenoate **19** in the Solid State.* Monopyrenoate **19** crystallizes in the *P*1 space group with two symmetrically independent molecules of **19** and two molecules of dichloromethane in the asymmetric unit (Figure 8). The cyclitol ring in both conformers of **19** adopts a chair conformation. Each of the conformers makes centrosymmetric OH···O hydrogen bonds with an identical conformer. As with solid-state structures of other esters, the C3H3···O7 hydrogen bonding is intact in both the conformers. Thus, the mutually complementary CH···O hydrogen bonds between carbonyl oxygen and H3 of two neighboring molecules stabilize the chair

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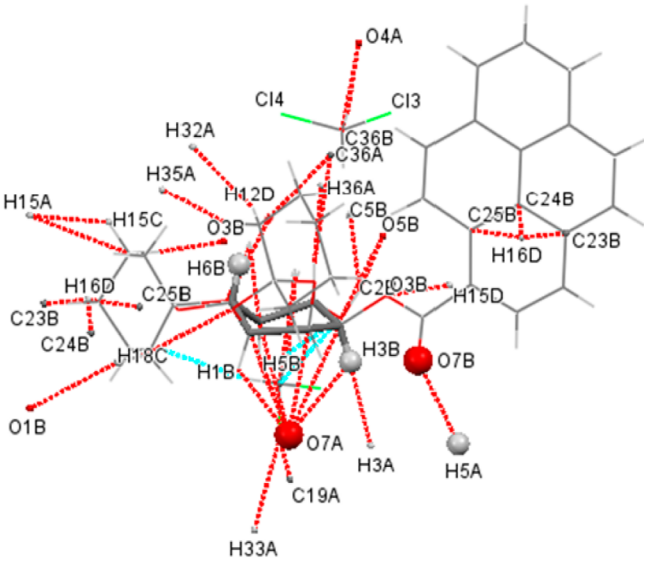

Figure 8. Conformation of monopyrenoate **19** in the solid state. The interacting atoms in intermolecular CH···O hydrogen bonding and the chair form of the cyclitol ring are shown in ball and capped-stick models respectively, for clarity.

conformation. As with other structures of this series, several intermolecualr interactions stabilize the chair conformation of **19** in the solid state (Table S5, Supporting Information). However, its isopropylidene derivative **11** adopts a boat conformation in the solid state.

CONCLUSION

We have successfully shown the consistent conformational extremities between solution and solid states of a series of cyclitol derivatives. While in the solution state these molecules adopt a boat conformation irrespective of the nature of the solvent and the nature and number of acyl groups, in the solid state all of these molecules adopt a chair conformation. The solution conformation is stabilized by a lone intramolecular CH···O hydrogen bond, but the solid-state conformation is dictated by several intermolecular CH···O hydrogen bonds. Though our evidence suggests that intramolecular CH···O hydrogen bonds are involved in the solution conformation, whether this CH···O bond is a cause or consequence of the boat conformation is a question yet to be resolved. The inherent nature of these molecules to adopt the boat conformation in isolation (dilute solution) by virtue of intramolecular CH···O or other structural constraints is challenged by several intermolecular hydrogen bonds, and thus the compound is compelled to adopt the chair conformation in the solid state. Hence, undoubtedly the conformation is dictated by intermolecular CH···O hydrogen bonds in the solid state. Knowledge of molecular conformations and the factors affecting the conformation are important, as properties, reactivities, etc. depend on the conformations of molecules. Our study shows that even a weak noncovalent interaction can influence the conformation of molecules differently in different states: viz., solution and solids. This study also cautions against the practice of depending on the crystal structure to explain the solution-state behavior of molecules.

EXPERIMENTAL SECTION

General Methods. Chromatograms were visualized under UV light and by dipping plates into either phosphomolybdic acid in MeOH or anisaldehyde in ethanol, followed by heating. ^{1}H NMR, COSY, NOESY, and HMQC spectra were recorded on a 500 MHz NMR spectrometer. Proton chemical shifts are reported in ppm (δ) relative to the internal standard tetramethylsilane (TMS, δ 0.0 ppm) or to the solvent reference relative to TMS employed as the internal standard ($CDCl_3$, δ 7.26 ppm; D_2O, δ 4.79 ppm). Data are reported as follows: chemical shift (multiplicity (singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m)), coupling constants (Hz), integration, and peak identification). All NMR signals were assigned on the basis of ^{1}H NMR, ^{13}C NMR, COSY, and HMQC experiments. ^{13}C spectra were recorded with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard. All NMR data were collected at 25 °C. The concentration of the compounds for ^{1}H NMR was 5 mg per 0.5 mL, and for ^{13}C NMR it was 20 mg per 0.5 mL. Melting points were determined using a melting point apparatus and are uncorrected. Flash column chromatography was performed using 200−400 mesh silica gel. All reactions were carried out under an argon or nitrogen atmosphere employing oven-dried glassware.

X-ray intensity data measurements of freshly grown crystals of **12**, **13**, **16**, and **17** were carried out at 293−296 K and those of **19** at 110 K on a Bruker-KAPPA APEX II CCD diffractometer with graphite-monochromated (λ(Mo Kα) = 0.71073 Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. Data were collected with a scan width of 0.3° at different settings of φ (0, 90, and 180°), keeping the sample to detector distance fixed at 40 mm and the detector position (2θ) fixed at 24°. The X-ray data collection was monitored by the SMART program. All data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs. SHELX-97 was used for the structure solution and full-matrix least-squares refinement on F^2. Molecular and packing diagrams were generated using Mercury 3.1. Geometrical calculations were performed using SHELXTL and PLATON.

Determination of the Structure in Solution. $^3J_{HH}$ values for the cyclitol ring protons were measured from ^{1}H NMR spectra. By using the Haasnoot−Altona equations the corresponding ϕ values were calculated. The structures were then energy minimized after fixing the ϕ values to the vicinal protons by the MM2 method using the ChemBio3D Ultra 12.0 platform.

*(±)-3,4-Di-O-benzoyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**3**).* To a cooled solution of (±)-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**1**;[25] 0.26 g, 1 mmol) in dry pyridine (5 mL) were added benzoyl chloride (0.24 mL, 2.1 mmol) and a catalytic amount of DMAP (10 mg). The reaction mixture was stirred for 2 h at room temperature. When TLC showed the complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (50 mL), and this solution was then washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 25% ethyl acetate in petroleum ether (R_f 0.34) as eluent, to give (±)-3,4-di-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**3**)[26] as a white solid (0.402 g, 86%), which was crystallized from a mixture of dichloromethane and hexane (2/1, v/v) by slow evaporation.

Mp: 186−188 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 1.337 (s, 3H, CH_3), 1.343 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 4.01 (dd, J = 10.2, 8.8 Hz, *H*-5), 4.18 (dd, J = 10.2, 7.8 Hz, *H*-6), 4.55 (dd, J = 7.8, 6.3 Hz, *H*-1), 4.78 (dd, J = 6.3, 3.9 Hz, *H*-2), 5.56−5.59 (m, 2H, *H*-3 and *H*-4), 7.47−8.02 (m, 10H, Ar-*H*). ^{1}H NMR (400 MHz, C_6D_6): δ 1.13 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 3.67 (dd, J = 9.9, 9.0 Hz, *H*-5), 4.19 (dd, J = 7.4, 6.9 Hz, *H*-1), 4.40−4.47 (m, 2H, *H*-2 and *H*-6), 5.82 (t, J = 4.4, *H*-3), 6.09

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(dd, J = 9.0, 4.4 Hz, *H*-4), 6.90−8.18 (m, 10H, Ar-*H*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 3.89 (dd, J = 10.3, 8.0 Hz, *H*-5), 4.32 (dd, J = 10.3, 7.3 Hz, *H*-6), 4.53 (dd, J = 7.3, 6.8 Hz, *H*-1), 4.73 (dd, J = 6.8, 3.9 Hz, *H*-2), 5.60−5.70 (m, 2H, *H*-3 and *H*-4), 7.26−8.10 (m, 10H, Ar-*H*). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.31 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 4.11 (dd, J = 10.5, 8.8 Hz, *H*-5), 4.30 (dd, J = 10.5, 7.8 Hz, *H*-6), 4.65 (dd, J = 7.8, 6.6 Hz, *H*-1), 4.86 (dd, J = 6.6, 3.9 Hz, *H*-2), 5.63−5.67 (m, 2H, *H*-3 and *H*-4), 7.49−7.99 (m, 10H, Ar-*H*). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.28 (s, 6H, 2 × CH_3), 1.41 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 4.08 (dd, J = 10.3, 8.8 Hz, *H*-5), 4.14 (dd, J = 10.3, 7.3 Hz, *H*-6), 4.57 (dd, J = 7.3, 6.3 Hz, *H*-1), 4.78 (dd, J = 6.3, 3.9 Hz, *H*-2), 5.51 (dd, J = 8.8, 4.4 Hz, *H*-4), 5.5 (dd, J = 4.4, 3.9 Hz, *H*-3), 7.52−8.32 (m, 10H, Ar-*H*). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.23 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 3.80 (dd, J = 10.5, 8.3 Hz, *H*-5), 4.19 (dd, J = 10.5, 7.8 Hz, *H*-6), 4.42 (dd, J = 7.8, 6.8 Hz, *H*-1), 4.63 (dd, J = 6.8, 3.9 Hz, *H*-2), 5.47−5.53 (m, 2H, *H*-3 and *H*-4), 7.36−7.97 (m, 10H, Ar-*H*). ^{1}H NMR (500 MHz, CD_3CN): δ 1.22 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 3.90 (dd, J = 10.5, 8.8 Hz, *H*-5), 4.12 (dd, J = 10.5, 7.9 Hz, *H*-6), 4.42 (dd, J = 7.9, 6.5 Hz, *H*-1), 4.65 (dd, J = 6.5, 4.1 Hz, *H*-2), 5.47−5.52 (m, 2H, *H*-3 and *H*-4), 7.40−7.95 (m, 10H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.82 (CH_3), 26.62 (CH_3), 26.96 (CH_3), 27.01 (CH_3), 72.67 (C-3 or C-4), 73.64 (C-4 or C-3), 74.04 (C-2), 76.37 (C-5), 76.43 (C-1), 77.64 (C-6), 111.34 (ketal carbon), 113.14 (ketal carbon), 128.34, 128.44, 129.25, 129.87, 129.97 (aromatic C), 133.35 (C-ipso), 164.86 (*C*O), 165.06 (*C*O). Anal. Calcd for $C_{26}H_{28}O_8$: C, 66.66; H, 6.02. Found: C, 66.45; H, 6.27.

*(±)-3,4-Di-O-acetyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**4**).* To a cooled solution of diketal **1** (0.26 g, 1 mmol) in dry pyridine (5 mL) were added acetic anhydride (0.28 mL, 3 mmol) and a catalytic amount of DMAP (10 mg). The reaction mixture was stirred for 2 h at room temperature. When TLC showed complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (50 mL), and this solution was then washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 25% ethyl acetate in petroleum ether (R_f 0.33) as eluent, to give (±)-3,4-di-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**4**) as a white solid (0.313 g, 91%), which was crystallized from a mixture of chloroform and petroleum ether (2/1 v/v).

Mp: 158−160 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 1.23 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.98 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 3.63 (dd, J = 10.5, 9.3 Hz, *H*-5), 3.85 (dd, J = 10.5, 8.0 Hz, *H*-6), 4.31 (dd, J = 8.0, 6.4 Hz, *H*-1), 4.47 (dd, J = 6.4, 3.7 Hz, *H*-2), 5.06−5.09 (m, 2H, *H*-3 and *H*-4). ^{1}H NMR (500 MHz C_6D_6): δ 1.15 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.35 (s, 6H, 2 × CH_3), 1.59 (s, 3H, $COCH_3$), 1.66 (s, 3H, $COCH_3$), 3.45 (dd, J = 10.4, 9.2 Hz, *H*-5), 4.03 (dd, J = 7.9, 6.5 Hz, *H*-1), 4.17 (dd, J = 6.5, 4.4 Hz, *H*-2), 4.21 (dd, J = 10.4, 7.9 Hz, *H*-6), 5.35 (t, J = 4.4 Hz, *H*-3), 5.67 (dd, J = 9.2, 4.4 Hz, *H*-4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 2.04 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 3.55 (dd, J = 10.5, 8.8 Hz, *H*-5), 3.98 (dd, J = 10.5, 7.9 Hz, *H*-6), 4.31 (dd, J = 7.9, 6.7 Hz, *H*-1), 4.43 (dd, J = 6.7, 4.2 Hz, *H*-2), 5.11 (dd, J = 4.2, 3.8 Hz, *H*-3), 5.17 (dd, J = 8.8, 3.8 Hz, *H*-4). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.17 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.927 (s, 3H, $COCH_3$), 1.93 (s, 3H, $COCH_3$), 3.64 (dd, J = 10.5, 8.7 Hz, *H*-5), 3.89 (dd, J = 10.5, 7.9 Hz, *H*-6), 4.35 (dd, J = 7.9, 6.5 Hz, *H*-1), 4.43 (dd, J = 6.5, 4.1 Hz, *H*-2), 5.02 (dd, J = 4.3, 4.1 Hz, *H*-3), 5.05 (dd, J = 8.7, 4.3 Hz, *H*-4). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.27 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.05 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 3.77 (dd, J = 10.4, 9.1 Hz, *H*-5), 3.85 (dd, J = 10.4, 7.9 Hz, *H*-6), 4.41 (dd, J = 7.9, 6.4 Hz, *H*-1), 4.48 (dd, J = 6.4, 4.5 Hz, *H*-2), 5.08 (dd, J = 9.1, 5.0 Hz, *H*-4), 5.13 (dd, J = 5.0, 4.5 Hz, *H*-3). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.25 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.99 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 3.52 (dd, J = 10.5, 8.7 Hz, *H*-5), 3.93 (dd, J = 10.5, 7.9 Hz, *H*-6), 4.26 (dd, J = 7.9, 6.7 Hz, *H*-1), 4.39 (dd, J = 6.7, 4.1 Hz, *H*-2), 5.05 (dd, J = 4.1, 3.9 Hz, *H*-3), 5.08 (dd, J = 8.7, 3.9 Hz, *H*-4). ^{1}H NMR (500 MHz, CD_3CN): δ 1.33 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 2.06 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 3.69 (dd, J = 10.5, 9.3 Hz, *H*-5), 3.98 (dd, J = 10.5, 8.1 Hz, *H*-6), 4.38 (dd, J = 8.1, 6.4 Hz, *H*-1), 4.51 (dd, J = 6.4, 3.6 Hz, *H*-2), 5.16−5.18 (m, 2H, *H*-3 and *H*-4). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 19.48, 19.57, 19.92, 20.00, 20.06, 20.44, 20.53, 23.72, 24.35, 25.76, 26.20, 26.44, 71.15, 72.07, 72.85, 73.63, 75.18, 76.01, 76.43, 77.26, 110.25 (ketal carbon), 111.99 (ketal carbon), 168.37 (*C*O), 168.76 (*C*O). Anal. Calcd for $C_{16}H_{24}O_8$: C, 55.81; H, 7.02. Found: C, 55.51; H, 7.26.

*(±)-3,4-Di-O-pivaloyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**5**).* To a cooled solution of diketal **1** (0.26 g, 1 mmol) in dry pyridine (5 mL) were added pivaloyl chloride (0.61 mL, 5 mmol) and a catalytic amount of DMAP (10 mg). The reaction mixture was stirred for 2 h at room temperature. When TLC showed complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (50 mL), and the solution was then washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 25% ethyl acetate in petroleum ether (R_f 0.30) as eluent, to give (±)-3,4-di-*O*-pivaloyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**5**) as a white solid (0.35 g, 82%), which was crystallized from a mixture of chloroform and petroleum ether (1/4 v/v).

Mp: 144−146 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 1.092 (s, 9H, 3 × CH_3), 1.096 (s, 9H, 3 × CH_3), 1.22 (s, 3H, CH_3), 1.31 (s, 6H, CH_3), 1.40 (s, 3H, CH_3), 3.59 (dd, J = 10.1, 9.7 Hz, *H*-5), 3.79 (dd, J = 10.1, 8.5 Hz, *H*-6), 4.27 (dd, J = 8.5, 5.6 Hz, *H*-1), 4.48 (dd, J = 5.6, 4.9 Hz, *H*-2), 5.03 (dd, J = 6.7, 4.9 Hz, *H*-3), 5.18 (dd, J = 9.7, 6.7 Hz, *H*-4). ^{1}H NMR (500 MHz, C_6D_6): δ 1.25 (s, 3H, CH_3), 1.27 (s, 9H, 3 × CH_3), 1.32 (s, 9H, 3 × CH_3), 1.39 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 3.40 (dd, J = 10.0, 9.8 Hz, *H*-5), 4.06 (dd, J = 8.6, 5.5 Hz, *H*-1), 4.16 (dd, J = 10.0, 8.6 Hz, *H*-6), 4.43 (dd, J = 5.5, 4.9 Hz, *H*-2), 5.31 (dd, J = 6.9, 4.9 Hz, *H*-3), 5.89 (dd, J = 9.8, 6.9 Hz, *H*-4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (s, 9H, 3 × CH_3), 1.15 (s, 9H, 3 × CH_3), 1.25 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.47 (dd, J = 10.3, 9.0 Hz, *H*-5), 3.92 (dd, J = 10.3, 8.3 Hz, *H*-6), 4.26 (dd, J = 8.3, 6.3 Hz, *H*-1), 4.45 (dd, J = 6.3, 4.7 Hz, *H*-2), 5.00 (dd, J = 5.2, 4.7 Hz, *H*-3), 5.20 (dd, J = 9.0, 5.2 Hz, *H*-4). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.05 (s, 9H, 3 × CH_3), 1.06 (s, 9H, 3 × CH_3), 1.17 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 3.63 (dd, J = 10.1, 9.4 Hz, *H*-5), 3.84 (dd, J = 10.1, 8.4 Hz, *H*-6), 4.33 (dd, J = 8.4, 5.9 Hz, *H*-1), 4.46 (dd, J = 5.9, 4.7 Hz, *H*-2), 4.99 (dd, J = 6.2, 4.7 Hz, *H*-3), 5.15 (dd, J = 9.4, 6.2 Hz, *H*-4). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.06 (s, 18H, 6 × CH_3), 1.18 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 3.68 (dd, J = 10.1, 9.2 Hz, *H*-5), 3.75 (dd, J = 10.1, 8.3 Hz, *H*-6), 4.32 (dd, J = 8.3, 5.7 Hz, *H*-1), 4.4 (dd, J = 5.7, 4.7 Hz, *H*-2), 5.03 (dd, J = 6.5, 4.7 Hz, *H*-3), 5.10 (dd, J = 9.2, 6.5 Hz, *H*-4). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.10 (s, 9H, 3 × CH_3), 1.11 (s, 9H, 3 × CH_3), 1.24 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 3.46 (dd, J = 10.2, 9.1 Hz, *H*-5), 3.87 (dd, J = 10.2, 8.4 Hz, *H*-6), 4.22 (dd, J = 8.4, 6.1 Hz, *H*-1), 4.43 (dd, J = 6.1, 4.7 Hz, *H*-2), 4.97 (dd, J = 5.4, 4.7 Hz, *H*-3), 5.14 (dd, J = 9.1, 5.4 Hz, *H*-4). ^{1}H NMR (500 MHz, CD_3CN): δ 1.08 (s, 9H, 3 × CH_3), 1.09 (s, 9H, 3 × CH_3), 1.21 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 3.58 (dd, J = 10.2, 9.4 Hz, *H*-5), 3.83 (dd, J = 10.2, 8.4 Hz, *H*-6), 4.24 (dd, J = 8.4, 5.9 Hz, *H*-1), 4.44 (dd, J = 5.9, 4.7 Hz, *H*-2), 5.00 (dd, J = 6.0, 4.7 Hz, *H*-3), 5.12 (dd, J = 9.4, 6.0 Hz, *H*-4). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 26.92, 27.02, 27.26, 27.39, 27.50, 27.85, 39.00, 39.04, 72.23, 72.33, 72.78, 73.96, 74.72, 75.89, 76.21, 76.57, 76.72, 76.94,

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76.96, 78.00, 78.83, 110.89 (ketal carbon), 112.84 (ketal carbon), 177.22 (CO), 177.34 (CO). Anal. Calcd for $C_{22}H_{36}O_8$: C, 61.66; H, 8.47. Found: C, 61.37; H, 8.28.

*(±)-3,4-Di-O-naphthoyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**6**).* To a solution of 1-naphthoic acid (0.37 g 2.2 mmol) in dry DCM (15 mL) were added EDC·HCl (0.42 g, 2.2 mmol) and DMAP (0.007 g, 0.1 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. The diketal **1** (0.26 g, 1 mmol) was added to the above solution, and the mixture was stirred at room temperature for 24 h. When TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was concentrated under reduced pressure, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was then washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 20% ethyl acetate in petroleum ether as eluent, to give (±)-3,4-di-*O*-naphthoyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**6**) as a white solid (0.32 g, 56%).

Mp: 160−162 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 0.86 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 3.41 (dd, J = 10.2, 9.4 Hz, *H*-5), 3.89 (dd, J = 8.0, 6.3 Hz, *H*-1), 4.17−4.21 (m, 2H, *H*-2 and *H*-6), 5.70 (dd, J = 5.0, 4.7 Hz, *H*-3), 6.01 (dd 9.4, 5.0 Hz, *H*-4), 7.07−7.64 (m, 10H, naph-*H*), 8.30 (d, J = 7.0 Hz, 1H, naph-*H*), 8.61 (d, J = 7.0 Hz, 1H, naph-*H*), 9.30 (d, J = 8.0 Hz, 1H, naph-*H*), 9.58 (d, J = 8.0 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 3.87 (dd, J = 10.2, 9.4 Hz, *H*-5), 4.25 (dd, J = 10.2, 8.0 Hz, *H*-6), 4.47 (dd, J = 8.0, 6.6 Hz, *H*-1), 4.75 (dd, J = 6.6, 4.3 Hz, *H*-2), 5.72 (t, J = 4.3 Hz, *H*-3), 5.78 (dd, J = 9.4, 4.3 Hz, *H*-4), 7.40−8.24 (m, 12H, naph-*H*), 8.80 (d, J = 9.0 Hz, 1H, naph-*H*), 8.91 (d, J = 9.0 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.22 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 4.05 (dd, J = 10.3, 9.5 Hz, *H*-5), 4.17 (dd, J = 10.3, 8.1 Hz, *H*-6), 4.55 (dd, J = 8.1, 6.2 Hz, *H*-1), 4.83 (dd, J = 6.2, 3.8 Hz, *H*-2), 5.74−5.77 (m, 2H, *H*-3 and *H*-4), 7.43−8.70 (m, 13H, naph-*H*),), 8.80 (d, J = 9.0 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.33 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 4.11−4.18 (m, 2H, *H*-5 and *H*-6), 4.59 (dd, J = 7.4, 6.0 Hz, *H*-1), 4.87 (dd, J = 6.0, 4.7 Hz, *H*-2), 5.76 (dd, J = 8.6, 5.7 Hz, *H*-4), 5.85 (dd, J = 5.7, 4.7 Hz, *H*-3), 7.57−8.76 (m, 14H, naph-*H*). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.29 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.85 (dd, J = 10.2, 9.1 Hz, *H*-5), 4.18 (dd, J = 10.2, 8.0 Hz, *H*-6), 4.43 (dd, J = 8.0, 6.5 Hz, *H*-1), 4.73 (dd, J = 6.5, 4.5 Hz, *H*-2), 5.69 (dd, J = 4.7, 4.5 Hz, *H*-3), 5.75 (dd, J = 9.1, 4.7 Hz, *H*-4), 7.42−8.21 (m, 12H, naph-*H*), 8.76 (d, J = 8.0 Hz, 1H, naph-*H*), 8.83 (d, J = 8.0 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, CD_3OD): δ 1.35 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 4.04 (dd, J = 10.2, 9.6 Hz, *H*-5), 4.20 (dd, J = 10.2, 8.3 Hz, *H*-6), 4.52 (dd, J = 8.3, 6.0 Hz, *H*-1), 4.84 (dd, J = 6.0, 4.0 Hz, *H*-2), 5.80−5.84 (m, 2H, *H*-3 and *H*-4), 7.54−8.23 (m, 14H, naph-*H*). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.29 (CH_3), 26.78 (CH_3), 26.90 (CH_3), 27.18 (CH_3), 32.07, 55.80, 68.47, 72.24, 73.19, 74.60, 75.58, 78.23, 110.07 (ketal carbon), 112.05 (ketal carbon), 124.72, 124.84, 124.87, 125.54, 125.63, 126.50, 126.98, 127.98, 128.04, 128.79, 130.30, 130.38, 133.36, 133.38, 133.97, 134.00 (aromatic C), 165.22 (CO), 165.74 (CO). Anal. Calcd for $C_{34}H_{32}O_8$: C, 71.82; H, 5.67. Found: C, 71.55; H, 5.38.

*(±)-3,4-Di-O-pyrenoyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**7**).* To a solution of pyrene-1-carboxylic acid (0.045 g, 0.18 mmol) in dry DCM (15 mL) were added EDC·HCl (0.03 g, 0.16 mmol) and DMAP (0.001 g, 0.007 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. The diketal **1** (0.02 g, 0.077 mmol) was added to the above solution, and the mixture was stirred at room temperature for 24 h. When TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was concentrated under reduced pressure, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was then washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 20% ethyl acetate in petroleum ether as eluent, to give (±)-3,4-di-*O*-pyrenoyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**7**) as a yellow solid (0.03 g, 54%).

Mp: 140−142 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 1.11 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.36 (s, 6H, 2 × CH_3), 3.76 (dd, J = 9.9, 9.5 Hz, *H*-5), 4.18 (dd, J = 7.9, 6.3 Hz, *H*-1), 4.50−4.55 (m, 2H, *H*-2 and *H*-6), 6.14 (t, J = 4.8, *H*-3), 6.43 (dd, J = 9.5 Hz, 5.0, *H*-4), 7.45−7.72 (m, 13H, pyr-*H*), 7.76 (d, J = 9.2 Hz, 1H, pyr-*H*), 8.64 (d, J = 8.0, 1H, pyr-*H*), 8.90 (d, J = 8.0 Hz, 1H, pyr-*H*), 9.40 (d, J = 9.5 Hz, 1H, pyr-*H*), 9.66 (d, J = 9.5 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 6H, 2 × CH_3), 1.49 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 4.01 (dd, J = 10.4, 8.7 Hz, *H*-5), 4.40 (dd, J = 10.4, 8.0 Hz, *H*-6), 4.56 (dd, J = 8.0, 6.6 Hz, *H*-1), 4.86 (dd, J = 6.6, 4.2 Hz, *H*-2), 5.92 (t, J = 4.2 Hz, *H*-3), 5.96 (dd, J = 8.7, 4.2 Hz, *H*-4), 7.93−8.16 (m, 14H, pyr-*H*), 8.58 (d, J = 8.5 Hz, 1H, pyr-*H*), 8.68 (d, J = 8.0 Hz, 1H, pyr-*H*), 9.12 (d, J = 9.5 Hz, 1H, pyr-*H*), 9.22 (d, J = 9.5 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.27 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 4.19 (dd, J = 10.1, 9.6 Hz, *H*-5), 4.30 (dd, J = 10.1, 8.1 Hz, *H*-6), 4.63 (dd, J = 8.1, 6.2 Hz, *H*-1), 4.95 (dd, J = 6.2, 3.6 Hz, *H*-2), 5.93−5.95 (m, 2H, *H*-3 and *H*-4), 7.95−8.23 (m, 13H, pyr-*H*), 8.61 (d, J = 8.0 Hz, 1H, pyr-*H*), 8.66 (d, J = 8.0 Hz, 1H, pyr-*H*), 9.01 (d, J = 9.5 Hz, 1H, pyr-*H*), 9.10 (d, J = 9.5 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.42 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 4.28−4.36 (m, 2H, *H*-5 and *H*-6), 4.72 (dd, J = 7.0, 6.1 Hz, *H*-1), 5.04 (dd, J = 6.1, 4.7 Hz, *H*-2), 5.98 (dd, J = 8.6, 5.4 Hz, *H*-4), 6.07 (dd, J = 5.4, 4.7 Hz, *H*-3), 8.27−8.73 (m, 16H, pyr-*H*), 9.04 (d, J = 9.5 Hz, 1H, pyr-*H*), 9.12 (d, J = 9.5 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.33 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 3.99 (dd, J = 10.3, 9.0 Hz, *H*-5), 4.32 (dd, J = 10.3, 7.9 Hz, *H*-6), 4.52 (dd, J = 7.9, 6.3 Hz, *H*-1), 4.85 (dd, J = 6.3, 4.3 Hz, *H*-2), 5.88 (dd, J = 4.6, 4.3 Hz, *H*-3), 5.92 (dd, J = 9.0, 4.6 Hz, *H*-4), 7.95−8.13 (m, 14H, pyr-*H*), 8.60 (d, J = 8.5 Hz, 1H, pyr-*H*), 8.66 (d, J = 8.0 Hz, 1H, pyr-*H*), 9.08 (d, J = 9.5 Hz, 1H, pyr-*H*), 9.13 (d, J = 9.5 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, CD_3OD): δ 1.42 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 4.18 (dd, J = 10.1, 9.7 Hz, *H*-5), 4.30 (dd, J = 10.1, 8.4 Hz, *H*-6), 4.61 (dd, J = 8.4, 5.8 Hz, *H*-1), 4.97 (dd, J = 5.8, 4.0 Hz, *H*-2), 6.02−6.04 (m, 2H, *H*-3 and *H*-4), 7.97−8.23 (m, 14H, pyr-*H*), 8.64 (d, J = 8.0 Hz, 1H, pyr-*H*), 8.65 (d, J = 8.0 Hz, 1H, pyr-*H*), 8.94 (d, J = 9.5 Hz, 1H, pyr-*H*), 8.95 (d, J = 9.5 Hz, 1H, pyr-*H*). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.32 (CH_3), 26.84 (CH_3), 26.95 (CH_3), 27.18 (CH_3), 72.54, 73.49, 74.38, 75.70, 78.32, 110.17 (ketal carbon), 112.15 (ketal carbon), 123.03, 123.67, 123.83, 124.35, 124.45, 126.46, 126.66, 126.86, 126.92, 127.04, 128.24, 128.31, 129.36, 130.20, 130.33, 134.12 (Aromatic C), 165.65 (CO), 166.15 (CO). Anal. Calcd for $C_{46}H_{36}O_8$: C, 77.08; H, 5.06. Found: C, 77.25; H, 5.29.

*(±)-3-O-Pivaloyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**8**).* To a cooled solution of diketal **1** (0.26 g, 1 mmol) in dry pyridine (5 mL) were added pivaloyl chloride (0.12 mL, 1.0 mmol) and catalytic amount of DMAP (10 mg). The reaction mixture was stirred for 2 h at room temperature. When TLC showed complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (50 mL), and the solution was washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 15% ethyl acetate in petroleum ether (R_f 0.30) as eluent, to give (±)-3-*O*-pivaloyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**8**) as a white solid (0.23 g, 67%).

Mp: 95−97 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 1.13 (s, 9H, 3 × CH_3), 1.22 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 3.38 (dd, J = 10.4, 8.8 Hz, *H*-5), 3.75 (dd, J = 10.4, 8.3 Hz, *H*-6), 3.78 (dd, J = 8.8, 5.3 Hz, *H*-4), 4.25 (dd, J = 8.3, 6.2 Hz, *H*-1). 4.46 (dd, J = 6.2, 4.5 Hz, *H*-2), 4.84 (dd, J = 5.3, 4.5 Hz, *H*-3). ^{1}H NMR (500 MHz, C_6D_6): δ 1.24 (s, 3H, CH_3), 1.28 (s, 9H, 3 × CH_3),

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1.47 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.39 (dd, J = 9.8, 8.8 Hz, *H*-5), 4.08−4.16 (m, 3H, *H*-1, *H*-4, *H*-6) 4.43 (dd, J = 5.8, 4.6 Hz, *H*-2), 5.15 (dd, J = 4.8, 4.6 Hz, *H*-3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9H, 3 × CH_3), 1.26 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 3.40 (dd, J = 10.4, 8.8 Hz, *H*-5), 3.81 (dd, J = 10.4, 8.2 Hz, *H*-6), 3.97 (dd, J = 8.8, 5.0 Hz, *H*-4), 4.27 (dd, J = 8.2, 6.3 Hz, *H*-1), 4.50 (dd, J = 6.3, 4.5 Hz, *H*-2), 4.85 (dd, J = 5.0, 4.5 Hz, *H*-3). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.21 (s, 9H, 3 × CH_3), 1.30 (s, 3H, CH_3), 1.367 (s, 3H, CH_3), 1.372 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.80−2.90 (br s, 1H, C4-OH), 3.54 (dd, J = 10.5, 8.4 Hz, *H*-5), 3.90 (dd, J = 8.4, 4.4 Hz, *H*-4), 3.92 (dd, J = 10.5, 8.1 Hz, *H*-6), 4.43 (dd, J = 8.1, 6.6 Hz, *H*-1), 4.57 (dd, J = 6.6, 4.3 Hz, *H*-2), 4.96 (dd, J = 4.4, 4.3 Hz, *H*-3). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.16 (s, 9H, 3 × CH_3), 1.25 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 3.46 (dd, J = 10.5, 8.4 Hz, *H*-5), 3.69 (ddd, J = 8.4, 5.1, 4.2 Hz, *H*-4), 3.79 (dd, J = 10.5, 8.0 Hz, *H*-6), 4.36 (dd, J = 8.0, 6.7 Hz, *H*-1). 4.45 (dd, J = 6.7, 4.2 Hz, *H*-2), 4.86 (dd, J = 4.2, 4.1 Hz, *H*-3), 5.76 (d, J = 5.1 Hz, 1H, C4-OH). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.14 (s, 9H, 3 × CH_3), 1.23 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 3.34 (dd, J = 10.4, 8.8 Hz, *H*-5), 3.75 (dd, J = 10.4, 8.3 Hz, *H*-6), 3.92 (dd, J = 8.8, 5.3 Hz, *H*-4), 4.21 (dd, J = 8.3, 6.2 Hz, *H*-1). 4.45 (dd, J = 6.2, 4.5 Hz, *H*-2), 4.82 (dd, J = 5.3, 4.5 Hz, *H*-3). ^{1}H NMR (500 MHz, CD_3OD): δ 1.20 (s, 9H, 3 × CH_3), 1.28 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.43 (dd, J = 10.4, 8.8 Hz, *H*-5), 3.81 (dd, J = 10.4, 8.3 Hz, *H*-6), 3.83−3.86 (m, 1H, *H*-4), 4.28 (dd, J = 8.3, 6.2 Hz, *H*-1), 4.48 (dd, J = 6.2, 4.5 Hz, *H*-2), 4.89 (dd, J = 5.1, 4.5 Hz, *H*-3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 25.19 (CH_3), 27.07 (CH_3), 27.08 (CH_3), 27.24 (CH_3), 27.43 (CH_3), 39.13, 72.35, 74.15, 75.33, 76.70, 78.33, 78.75, 110.79 (ketal carbon), 112.67 (ketal carbon), 178.28 (*C*O). Anal. Calcd for $C_{17}H_{28}O_7$: C, 59.29; H, 8.19. Found: C, 59.56; H, 7.96.

*(±)-3-O-Benzoyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**9**).* To a cooled solution of diketal **1** (0.26 g, 1 mmol) in dry pyridine (5 mL) were added benzoyl chloride (0.12 mL, 1.05 mmol) and a catalytic amount of DMAP (10 mg). The reaction mixture was stirred for 2 h at room temperature. When TLC showed complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (50 mL), and the solution was washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 30% ethyl acetate in petroleum ether (R_f 0.20) as eluent, to give (±)-3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**9**)[27] as a white solid (0.22 g, 61%), which was crystallized from a mixture of chloroform and petroleum ether (1/1 v/v).

Mp: 182−184 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 1.22 (s, 6H, 2 × CH_3), 1.34 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 3.51 (dd, J = 10.6, 8.6 Hz, *H*-5), 3.92−3.96 (m, 2H, *H*-4 and *H*-6), 4.36 (dd, J = 7.7, 6.6 Hz, *H*-1), 4.57 (dd, J = 6.6, 4.1 Hz, *H*-2), 5.18 (dd, J = 4.2, 4.1 Hz, *H*-3), 7.39−7.97 (m, 5H, Ar-*H*). ^{1}H NMR (500 MHz, C_6D_6): δ 0.96 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 3.31 (dd, J = 10.6, 8.3 Hz, *H*-5), 3.96−4.01 (m, 2H, *H*-4 and *H*-1), 4.17 (dd, J = 10.6, 7.8 Hz, *H*-6), 4.22 (dd, J = 6.6, 4.1 Hz, *H*-2), 5.28 (dd, J = 4.1, 3.9 Hz, *H*-3), 6.84−8.08 (m, 5H, Ar-*H*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 3.52 (dd, J = 10.6, 8.6 Hz, *H*-5), 4.00 (dd, J = 10.6, 7.8 Hz, *H*-6), 4.15 (dd, J = 8.6, 4.1 Hz, *H*-4), 4.38 (dd, J = 7.8, 6.6 Hz, *H*-1), 4.60 (dd, J = 6.6, 4.2 Hz, *H*-2), 5.20 (dd, J = 4.2, 4.1 Hz, *H*-3), 7.38−8.03 (m, 5H, Ar-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.14 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.266 (s, 3H, CH_3), 1.270 (s, 3H, CH_3), 3.54 (dd, J = 10.6, 8.3 Hz, *H*-5), 3.95−4.00 (m, 2H, *H*-4 and *H*-6), 4.41 (dd, J = 7.0, 6.7 Hz, *H*-1), 4.56 (dd, J = 6.7, 4.0 Hz, *H*-2), 5.18 (dd, J = 4.0, 3.8 Hz, *H*-3), 7.40−7.94 (m, 5H, Ar-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.20 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.381 (s, 3H, CH_3), 1.384 (s, 3H, CH_3), 3.58 (dd, J = 10.6, 8.5 Hz, *H*-5), 3.90 (ddd, J = 8.5, 5.0, 3.9 Hz, *H*-4), 3.95 (dd, J = 10.6, 7.8 Hz, *H*-6), 4.46 (dd, J = 7.8, 6.7 Hz, *H*-1), 4.58 (dd, J = 6.7, 4.0 Hz, *H*-2), 5.20 (dd, J = 4.0, 3.9 Hz, *H*-3), 5.90 (d, J = 5.0 Hz, 1H, C4-OH), 7.55−7.99 (m, 5H, Ar-*H*). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.24 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 3.47 (dd, J = 10.6, 8.6 Hz, *H*-5), 3.94 (dd, J = 10.6, 7.8 Hz, *H*-6) 4.10 (dd, J = 8.6, 4.2 Hz, *H*-4), 4.32 (dd, J = 7.8, 6.5 Hz, *H*-1), 4.56 (dd, J = 6.5, 4.3 Hz, *H*-2), 5.17 (dd, J = 4.3, 4.2 Hz, *H*-3), 7.38−7.99 (m, 5H, Ar-*H*). ^{1}H NMR (500 MHz, CD_3OD): δ 1.30 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 3.58 (dd, J = 10.6, 8.7 Hz, *H*-5), 4.01 (dd, J = 10.6, 8.0 Hz, *H*-6) 4.07 (dd, J = 8.7, 4.4 Hz, *H*-4), 4.41 (dd, J = 8.0, 6.5 Hz, *H*-1), 4.64 (dd, J = 6.5, 4.3 Hz, *H*-2), 5.26 (dd, J = 4.4, 4.3 Hz, *H*-3), 7.53−8.04 (m, 5H, Ar-*H*). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 24.91 (CH_3), 26.56 (CH_3), 26.88 (CH_3), 26.97 (CH_3), 70.97, 73.46, 75.62, 76.08, 77.31, 78.60, 109.73 (ketal carbon), 111.18 (ketal carbon), 128.52, 128.80, 129.22, 129.36, (aromatic C), 133.52 (C-ipso), 164.54 (CO). Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.93; H, 6.44.

*(±)-3-O-Naphthoyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**10**).* To a solution of 1-naphthoic acid (0.18 g 1.1 mmol) in dry DCM (15 mL) were added EDC·HCl (0.21 g, 1.1 mmol) and DMAP (0.007 g, 0.1 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. The diketal **1** (0.26 g, 1 mmol) was added to the above solution, and the mixture was stirred at room temperature for 24 h. When TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was concentrated under reduced pressure, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was then washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 30% ethyl acetate in petroleum ether as eluent, to give (±)-3-*O*-naphthoyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**10**) as a white solid (0.24 g, 58%), which was crystallized from a mixture of ethyl acetate and petroleum ether (1/1 v/v).

Mp: 151−153 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 1.24 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 3.52 (dd, J = 10.4, 8.9 Hz, *H*-5), 3.90 (dd, J = 10.4, 8.2 Hz, *H*-6), 4.04 (dd, J = 8.9, 5.1 Hz, *H*-4), 4.37 (dd, J = 8.2, 6.2 Hz, *H*-1), 4.67 (dd, J = 6.2, 4.5 Hz, *H*-2), 5.30 (dd, J = 4.5, 5.1 Hz, *H*-3), 7.44−7.52 (m, 3H, naph), 7.85 (d, J = 8.0 Hz, 1H, naph), 8.02 (d, J = 8.5 Hz, 1H, naph-*H*), 8.14−8.16 (m, 1H, naph-*H*), 8.82 (d, J = 8.5 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, C_6D_6): δ 1.22 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 3.51 (dd, J = 10.5, 8.7 Hz, *H*-5), 4.20 (dd, J = 8.0, 6.3 Hz, *H*-1), 4.29 (dd, J = 8.7, 4.7 Hz, *H*-4), 4.35 (dd, J = 10.5, 8.0 Hz, *H*-6), 4.56 (dd, J = 6.3, 4.4 Hz, *H*-2), 5.59 (dd, J = 4.7, 4.4 Hz, *H*-3), 7.13−7.69 16 (m, 5H, naph-*H*), 8.51−8.53 (m, 1H, naph-*H*), 9.56 (d, J = 8.5 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 2.62 (d, J = 3.0 Hz, 1H, C4-OH), 3.52 (dd, J = 10.4, 9.0 Hz, *H*-5), 3.96 (dd, J = 10.4, 8.1 Hz, *H*-6), 4.25 (ddd, J = 9.0, 4.7, 3.0 Hz, *H*-4), 4.38 (dd, J = 8.1, 6.1 Hz, *H*-1), 4.69 (dd, J = 6.1, 4.7 Hz, *H*-2), 5.29 (t, J = 4.7 Hz, *H*-3), 7.43−7.56 16 (m, 3H, naph-*H*), 7.82 (d, J = 8.0 Hz, 1H, naph-*H*), 7.98 (d, J = 8.0 Hz, 1H, naph-*H*), 8.19−8.21 (m, 1H, naph-*H*), 8.90 (d, J = 8.5 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.32 (s, 6H, 2 × CH_3), 1.41 (s, 6H, 2 × CH_3), 3.69 (dd, J = 10.5, 8.6 Hz, *H*-5), 4.07 (dd, J = 10.5, 8.0 Hz, *H*-6), 4.22 (ddd, J = 8.6, 4.4, 4.4 Hz, *H*-4), 4.55 (dd, J = 8.0, 6.4 Hz, *H*-1), 4.78 (dd, J = 6.4, 4.4 Hz, *H*-2), 5.17 (d, J = 4.4 Hz, 1H, C4-OH), 5.45 (t, J = 4.4 Hz, *H*-3), 7.59−7.67 (m, 3H, naph-*H*), 8.02 (d, J = 7.5 Hz, 1H, naph-*H*), 8.20 (d, J = 8.0 Hz, 1H, naph-*H*), 8.29 (dd, J = 8.0, 7.5 Hz 1H, naph-*H*), 8.98 (d, J = 8.5 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.25 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.40 (s, 6H, 2 × CH_3), 3.60 (dd, J = 10.4, 9.2 Hz, *H*-5), 3.89 (dd, J = 10.4, 8.1 Hz, *H*-6), 4.01 (ddd, J = 9.2, 5.1, 4.5 Hz, *H*-4), 4.45 (dd, J = 8.1, 6.3 Hz, *H*-1), 4.66 (dd, J = 6.3, 4.5 Hz, *H*-2), 5.33 (t, J = 4.5 Hz, *H*-3), 5.93 (d, J = 5.1 Hz, 1H, C4-OH), 7.60−7.68 (m, 3H, naph-*H*), 8.05 (d, J = 7.5 Hz, 1H, naph-*H*), 8.17−8.24 (m, 2H, naph-*H*), 8.80 (d, J = 8.5 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.26 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 2.64 (d, J = 3.3 Hz, 1H,

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C4-OH), 3.47 (dd, J = 10.4, 9.0 Hz, *H*-5), 3.89 (dd, J = 10.4, 8.2 Hz, *H*-6), 4.19 (ddd, J = 9.0, 5.2, 3.3 Hz, *H*-4), 4.32 (dd, J = 8.2, 6.1 Hz, *H*-1), 4.65 (dd, J = 6.1, 4.6 Hz, *H*-2), 5.27 (dd, J = 5.2, 4.6 Hz, *H*-3), 7.45−7.55 (m, 3H, naph-*H*), 7.84 (d, J = 8.0 Hz, 1H, naph-*H*), 8.00 (d, J = 8.0 Hz, 1H, naph-*H*), 8.17 (dd, J = 7.0, 7.5 Hz 1H, naph-*H*), 8.85 (d, J = 9.0 Hz, 1H, naph-*H*). ^{1}H NMR (500 MHz, CD_3OD): δ 1.32 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 3.57 (dd, J = 10.3, 9.1 Hz, *H*-5), 3.96 (dd, J = 10.3, 8.2 Hz, *H*-6), 4.15 (ddd, J = 9.1, 5.3, 4.8 Hz, *H*-4), 4.23 (d, J = 4.8 Hz, 1H, C4-OH), 4.42 (dd, J = 8.2, 6.1 Hz, *H*-1), 4.72 (dd, J = 6.1, 4.5 Hz, *H*-2), 5.39 (dd, J = 5.3, 4.5 Hz, *H*-3), 7.60−7.68 (m, 3H, naph-*H*), 8.02 (d, J = 8.5 Hz, 1H, naph-*H*), 8.16−8.26 (m, 3H, naph-*H*). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.10 (CH_3), 26.89 (CH_3), 26.94 (CH_3), 70.71, 73.80, 75.45, 75.96 77.71, 78.26 109.59 (ketal carbon), 111.08 (ketal carbon), 124.89, 125.10, 126.44, 127.88, 128.72, 130.13, 130.45, 133.39, 133.57 (aromatic C), 165.64 (CO). Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.39; H, 6.61.

*(±)-3-O-Pyrenoyl-1,2:5,6-di-O-isopropylidene-myo-inositol (**11**).* To a solution of pyrene-1-carboxylic acid (0.023 g, 0.09 mmol) in dry DCM (15 mL) were added EDC·HCl (0.013 g, 0.07 mmol) and DMAP (0.001 g, 0.007 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. The diketal **1** (0.02 g, 0.077 mmol) was added to the above solution, and the mixture was stirred at room temperature for 24 h. When TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was concentrated under reduced pressure, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was then washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 30% ethyl acetate in petroleum ether as eluent, to give (±)-3-*O*-pyrenoyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**11**) as a yellow solid (0.019 g, 51%), which was crystallized from a mixture of ethyl acetate and petroleum ether (3/1 v/v) by slow evaporation.

Mp: 170−172 °C. ^{1}H NMR (500 MHz, CD_3OD): δ 1.27 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.38 (s, 6H, 2 × CH_3), 3.58 (dd, J = 10.3, 9.0 Hz, *H*-5), 3.99 (dd, J = 10.3, 8.1 Hz, *H*-6), 4.13 (dd, J = 9.0, 5.0 Hz, *H*-4), 4.42 (dd, J = 8.1, 6.3 Hz, *H*-1), 5.41 (dd, J = 5.0, 4.7 Hz, *H*-3), 8.00 (t, J = 8.0 Hz, 1H, pyr-*H*), 8.06 (d, J = 8.0 Hz, 1H, pyr-*H*), 8.15−8.18 (m, 3H, pyr-*H*), 8.22 (d, J = 7.7 Hz, 2H, pyr-*H*) 8.58 (d, J = 8.1 Hz, 1H, pyr-*H*) 9.17 (d, J = 9.5 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, C_6D_6): δ 1.05 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.32 (s, 6H, 2 × CH_3), 3.38 (dd, J = 10.5, 8.6 Hz, *H*-5), 4.07 (dd, J = 7.9, 6.4 Hz, *H*-1), 4.19 (dd, J = 8.6, 4.4 Hz, *H*-4), 4.28 (dd, J = 10.5, 7.9 Hz, *H*-6), 4.43 (dd, J = 6.4, 4.3 Hz, *H*-2), 5.51 (dd, J = 4.4, 4.3 Hz, *H*-3), 7.54 (d, J = 8.9 Hz, 1H, pyr-*H*), 7.57−7.64 (m, 2H, pyr-*H*), 7.66 (d, J = 8.9 Hz, 1H, pyr-*H*), 7.76−7.78 (m, 2H, pyr-*H*), 7.90 (d, J = 9.4 Hz, 1H, pyr-*H*), 8.78 (d, J = 8.1 Hz, 1H, pyr-*H*), 9.68 (d, J = 9.4 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.58 (dd, J = 10.4, 8.9 Hz, *H*-5), 4.06 (dd, J = 10.4, 8.0 Hz, *H*-6), 4.33 (dd, J = 8.9, 4.6 Hz, *H*-4), 4.43 (dd, J = 8.0, 6.2 Hz, *H*-1), 4.76 (dd, J = 6.2 Hz, 4.6, *H*-2), 5.40 (t, J = 4.6 Hz, *H*-3), 7.98−8.21 (m, 7H, pyr-*H*), 8.62 (d, J = 8.1, 1H, pyr-*H*), 9.24 (d, J = 9.4 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.15 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.28 (s, 6H, 2 × CH_3), 3.60 (dd, J = 10.5, 8.6 Hz, *H*-5), 4.03 (dd, J = 10.5, 8.0 Hz, *H*-6), 4.16 (dd, J = 8.6, 4.5 Hz, *H*-4), 4.46 (dd, J = 8.0, 6.4 Hz, *H*-1), 4.71 (dd, J = 6.4, 4.3 Hz, *H*-2), 5.42 (dd, J = 4.5, 4.3 Hz, *H*-3), 8.01−8.30 (m, 7H, pyr-*H*), 8.61 (d, J = 8.1 Hz, 1H, pyr-*H*), 9.21 (d, J = 9.4 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 3.69 (dd, J = 10.3, 8.9 Hz, *H*-5), 4.02 (dd, J = 10.3, 8.0 Hz, *H*-6), 4.14 (ddd, J = 8.9, 5.2, 4.5 Hz, *H*-4), 4.55 (dd, J = 8.0, 6.3 Hz, *H*-1), 4.77 (dd, J = 6.3, 4.4 Hz, *H*-2), 5.49 (dd, J = 4.5, 4.4 Hz, *H*-3), 6.05 (d, J = 5.2 Hz, 1H, C4-OH), 8.22 (t, J = 7.6 Hz, 1H, pyr-*H*), 8.32 (d, J = 8.9 Hz, 1H, pyr-*H*), 8.35−8.50 (m, 5H, pyr-*H*), 8.68 (d, J = 8.1 Hz, 1H, pyr-*H*), 9.21 (d, J = 9.4 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.28 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.39 (s, 6H, 2 × CH_3), 2.68 (d, J = 3.7 Hz, 1H, C4-OH), 3.52 (dd, J = 10.3, 8.9 Hz, *H*-5), 3.98 (dd, J = 10.3, 8.1 Hz, *H*-6), 4.28 (ddd, J = 8.9, 5.0, 3.7 Hz, *H*-4), 4.37 (dd, J = 8.1, 6.1 Hz, *H*-1), 4.72 (dd, J = 6.1, 4.7 Hz, *H*-2), 5.38 (dd, J = 5.0, 4.7 Hz, *H*-3), 8.01−8.06 (m, 4H, pyr-*H*), 8.14−8.24 (m, 3H, pyr-*H*), 8.61 (d, J = 1H, 8.1, pyr-*H*), 9.20 (d, J = 1H, 9.4 Hz, pyr-*H*). ^{1}H NMR (500 MHz, CD_3OD): δ 1.35 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.64 (dd, J = 10.3, 8.9 Hz, *H*-5), 4.03 (dd, J = 10.3, 8.3 Hz, *H*-6), 4.24 (ddd, J = 8.9, 5.2, 4.9 Hz, *H*-4), 4.28 (d, J = 4.9 Hz, 1H, C4-OH), 4.46 (dd, J = 8.3, 6.0 Hz, *H*-1), 4.79 (dd, J = 6.0, 4.6 Hz, *H*-2), 5.49 (dd, J = 5.2, 4.6 Hz, *H*-3), 8.17 (t, J =1H, 7.7 Hz, pyr-*H*), 8.23 (d, J = 1H, 8.9 Hz, pyr-*H*), 8.32−8.41 (m, 5H, pyr-*H*), 8.70 (d, J = 1H, 8.1 Hz, pyr-*H*), 9.24 (d, J = 1H, 9.4 Hz, pyr-*H*). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.12 (CH_3), 26.91 (CH_3), 26.95 (CH_3), 26.98 (CH_3), 70.84, 70.89, 75.70, 76.04, 77.75, 78.36, 109.66 (ketal carbon), 111.12 (ketal carbon), 123.00, 123.25, 123.88, 124.21, 124.51, 126.46, 126.76, 126.85, 127.15, 128.28, 129.57, 129.76, 129.85, 130.19, 130.55, 133.93, 133.57 (aromatic C), 166.05 (CO). Anal. Calcd for $C_{29}H_{28}O_7$: C, 71.30; H, 5.78. Found: C, 71.05; H, 5.49.

*(±)-3,4-Di-O-benzoyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**12**).* To a cooled solution of (±)-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**2**;[28] 0.2 g, 0.58 mmol) in dry pyridine (5 mL) were added benzoyl chloride (0.15 mL, 1.29 mmol) and a catalytic amount (10 mg) of DMAP. The reaction mixture was stirred for 2 h at room temperature. When TLC showed complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was then concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (20 mL), and the solution was then washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 25% ethyl acetate in petroleum ether (R_f 0.34) as eluent, to give (±)-3,4-di-*O*-benzoyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**12**)[29] as a white solid (0.2 g, 62%), which was crystallized from hexane and dichloromethane (8/2, v/v) by slow evaporation.

Mp: 153−155 °C. IR: 2939, 1716, 1452, 1323, 1276, 1166, 1111, 1066, 1026, 931, 709 cm^{-1}. ^{1}H NMR (500 MHz, CD_3OD): δ 1.39−1.77 (m, 20H, Cyclo-*H*), 4.06 (dd, J = 10.4, 8.8 Hz, *H*-5), 4.22 (dd, J = 10.4, 7.8 Hz, *H*-6), 4.59 (dd, J = 7.8, 6.3 Hz, *H*-1), 4.81 (dd, J = 6.3, 3.9 Hz, *H*-2), 5.57−5.60 (m, 2H, *H*-3 and *H*-4), 7.49−7.53 (m, 4H, Ar-*H*), 7.64 (t, J = 7.4 Hz, 2H, Ar-*H*). 8.03 (d, J = 7.5 Hz, 2H, Ar-*H*), 8.06 (d, J = 7.5 Hz, 2H, Ar-*H*). ^{1}H NMR (500 MHz, C_6D_6): δ 1.46−1.71 (m, 20H, Cyclo-*H*), 3.79 (dd, J = 10.5, 9.0 Hz, *H*-5), 4.28 (dd, J = 7.8, 6.4 Hz, *H*-1), 4.42 (dd, J = 6.4, 4.1 Hz, *H*-2), 4.55 (dd, J = 10.5, 7.8 Hz, *H*-6), 5.86 (t, J = 4.1 Hz, *H*-3), 6.09 (dd, J = 9.0, 4.1 Hz, *H*-4), 6.92−6.97 (m, 4H, Ar-*H*), 7.01−7.06 (m, 2H, Ar-*H*), 8.03−8.05 (m, 2H, Ar-*H*), 8.18−8.20 (m, 2H, Ar-*H*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35−1.75 (m, 20H, Cyclo-*H*), 3.91 (dd, J = 10.4, 9.0 Hz, *H*-5), 4.34 (dd, J = 10.4, 7.4 Hz, *H*-6), 4.55 (dd, J = 7.4, 7.0 Hz, *H*-1), 4.73 (m, 1H, *H*-2), 5.62−5.63 (m, *H*-3 and *H*-4), 7.45−7.49 (m, 4H, Ar-*H*), 7.60 (t, J = 7.2 Hz, 2H, Ar-*H*), 8.08 (dd, 6.6, 5.7 Hz, 4H, Ar-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.36−1.75 (m, 20H, Cyclo-*H*), 4.14 (t, J = 10.5 Hz, *H*-5), 4.34 (dd, J = 10.5, 7.8 Hz, *H*-6), 4.68 (dd, J = 7.8, 6.6 Hz, *H*-1), 4.89 (bs, 1H, *H*-2), 5.64−5.66 (m, 2H, *H*-3 and *H*-4), 7.55 (m, 4H, Ar-*H*), 7.67 (d, J = 6.5 Hz, 2H, Ar-*H*), 8.08 (t, J = 7.7 Hz, 4H, Ar-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.30−1.70 (m, 20H, Cyclo-*H*), 4.08 (dd, J = 10.3, 9.0 Hz, *H*-5), 4.16 (dd, J = 10.3, 7.3 Hz, *H*-6), 4.57 (dd, J = 7.3, 6.3 Hz, *H*-1), 4.79 (dd, J = 6.3, 3.8 Hz, *H*-2), 5.45 (dd, J = 9.0, 3.5 Hz, *H*-4), 5.4 (dd, J = 3.8, 3.5 Hz, *H*-3), 7.56 (t, J = 7.3 Hz, 4H, Ar-*H*), 7.67−7.71 (m, 2H, Ar-*H*), 7.97 (d, J = 7.5 Hz, 2H, Ar-*H*), 8.01 (d, J = 7.6 Hz, 2H, Ar-*H*). ^{1}H NMR (500 MHz, CD_3CN): δ 1.37−1.77 (m, 20H, Cyclo-*H*), 4.03 (dd, J = 10.5, 8.8 Hz, *H*-5), 4.25 (dd, J = 10.5, 7.9 Hz, *H*-6), 4.54 (dd, J = 7.9, 6.5 Hz, *H*-1), 4.76 (dd, J = 6.5, 4.3 Hz, *H*-2), 5.54 (dd, J = 8.8, 3.6 Hz, *H*-4), 5.61 (dd, J = 4.3, 3.6 Hz, *H*-3), 7.54 (dd, J = 7.5, 7.3 Hz, 4H, Ar-*H*), 7.65−7.69 (m, 2H, Ar-*H*), 8.04 (d, J = 7.3 Hz, 2H, Ar-*H*), 8.06 (d, J = 7.3 Hz, 2H, Ar-*H*). ^{13}C NMR (125 MHz, acetone-d_6): δ 24.72, 24.77, 34.02, 36.19, 36.36, 36.40, 72.95 (C-3 or C-4), 73.77 (C-4 or C-3), 73.90 (C-2), 75.47 (C-5), 76.23 (C-1), 77.99 (C-6), 111.14 (ketal carbon), 112.92 (ketal

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carbon), 128.59, 128.61, 129.57, 129.60, 129.70 (Ar-*C*), 133.39 (C-ipso), 133.47, 164.36 (CO), 164.86 (CO). Anal. Calcd for $C_{32}H_{36}O_8$: C, 70.06; H, 6.61. Found: C, 70.26; H, 6.78.

*(±)-3,4-Di-O-pivaloyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**13**).* To a cooled solution of diketal **2** (0.2 g, 0.58 mmol) in dry pyridine (5 mL) were added pivaloyl chloride (0.16 mL, 1.29 mmol) and a catalytic amount (10 mg) of DMAP. The reaction mixture was stirred for 2 h at room temperature. When TLC showed complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (20 mL), and the solution was then washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography using 15% ethyl acetate in petroleum ether (R_f 0.45) as eluent, to give (±)-3,4-di-*O*-pivaloyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**13**) as a white solid (0.22 g, 76%), which was crystallized from a mixture of chloroform and petroleum ether (1/6 v/v) by slow evaporation.

Mp: 120−122 °C. IR: 2935, 1730, 1450, 1367, 1280, 1165, 1101, 1035, 933 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 1.22 (s, 9H, 3 × CH_3), 1.23 (s, 9H, 3 × CH_3), 1.75−1.44 (m, 20H, Cyclo-*H*), 3.68 (t, *J* = 10.0 Hz, *H*-5), 3.87 (dd, *J* = 10.0, 8.7 Hz, *H*-6), 4.39 (dd, *J* = 8.7, 5.7 Hz, *H*-1), 4.62 (dd, *J* = 5.7, 5.1 Hz, *H*-2), 5.13 (dd, *J* = 7.0, 5.1 Hz, *H*-3), 5.32 (dd, *J* = 10.0, 7.0 Hz, *H*-4). ^1H NMR (500 MHz, C_6D_6): δ 1.18 (s, 9H, 3 × CH_3), 1.24 (s, 9H, 3 × CH_3), 1.43−1.68 (m, 20H, Cyclo-*H*), 3.34 (t, *J* = 9.9 Hz, *H*-5), 4.00 (dd, *J* = 8.5, 5.5 Hz, *H*-1), 4.05 (dd, *J* = 9.9, 8.5 Hz, *H*-6), 4.40 (dd, *J* = 5.5, 5.1 Hz, *H*-2), 5.18 (dd, *J* = 6.9, 5.1 Hz, *H*-3), 5.78 (dd, *J* = 9.9, 6.9 Hz, *H*-4). ^1H NMR (500 MHz, $CDCl_3$): δ 1.23 (s, 9H, 3 × CH_3), 1.24 (s, 9H, 3 × CH_3), 1.40−1.74 (m, 20H, Cyclo-*H*), 3.51 (dd, *J* = 10.1, 9.8 Hz, *H*-5), 3.92 (dd, *J* = 10.1, 8.6 Hz, *H*-6), 4.32 (dd, *J* = 8.6, 5.9 Hz, *H*-1), 4.57 (dd, *J* = 5.9, 5.0 Hz, *H*-2), 5.06 (dd, *J* = 6.4, 5.0 Hz, *H*-3), 5.20 (dd, *J* = 9.8, 6.4 Hz, *H*-4). ^1H NMR (500 MHz, acetone-d_6): δ 1.21 (s, 9H, 3 × CH_3), 1.22 (s, 9H, 3 × CH_3), 1.41−1.75 (m, 20H, Cyclo-*H*), 3.75 (dd, *J* = 10.1, 9.7 Hz, *H*-5), 3.93 (dd, *J* = 10.1, 8.6 Hz, *H*-6), 4.46 (dd, *J* = 8.6, 5.7 Hz, *H*-1), 4.63 (dd, *J* = 5.7, 5.1 Hz, *H*-2), 5.14 (dd, *J* = 6.9, 5.1 Hz, *H*-3), 5.35 (dd, *J* = 9.7, 6.9 Hz, *H*-4). ^1H NMR (500 MHz, DMSO-d_6): δ 1.39 (s, 9H, 3 × CH_3), 1.40 (s, 9H, 3 × CH_3), 1.50−1.64 (m, 20H, Cyclo-*H*), 3.71- 3.78 (m, 1H, *H*-5 and *H*-6), 4.38 (dd, *J* = 6.7, 6.0 Hz, *H*-1), 4.50 (dd, *J* = 6.0, 4.8 Hz, *H*-2), 5.10 (dd, *J* = 7.0, 4.8 Hz, *H*-3), 5.20 (dd, *J* = 8.8, 7.0 Hz, *H*-4). ^1H NMR (500 MHz, CD_3CN): δ 1.20 (s, 18H, 6 × CH_3), 1.38−1.74 (m, 20H, Cyclo-*H*), 3.66 (t, *J* = 9.9, *H*-5), 3.89 (dd, *J* = 9.9, 8.6 Hz, *H*-6), 4.34 (dd, *J* = 8.6, 5.9 Hz, *H*-1), 4.56 (dd, *J* = 5.9, 4.7 Hz, *H*-2), 5.09 (dd, *J* = 6.5, 4.7 Hz, *H*-3), 5.25 (dd, *J* = 9.9, 6.5 Hz, *H*-4). ^{13}C NMR (125 MHz, acetone-d_6): δ 23.80, 24.77, 26.28, 26.38, 26.50, 26.59, 34.20, 36.09, 36.27, 37.43, 38.37, 71.88, 72.05, 73.85, 74.96, 75.75, 78.94 (Ins-*C*), 110.34 (ketal-*C*), 112.27 (ketal-*C*), 176.23 (CO), 176.36 (CO). Anal. Calcd for $C_{28}H_{44}O_8$: C, 66.12; H, 8.72. Found: C, 66.29; H, 8.81.

*(±)-3,4-Di-O-naphthoyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**14**).* To a solution of 1-naphthoic acid (0.37 g, 2.2 mmol) in dry DCM (20 mL) were added EDC·HCl (0.42 g, 2.2 mmol) and DMAP (0.012 g, 0.1 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. The diketal **2** (0.34 g, 1 mmol) was added to the above solution, and the mixture was stirred at room temperature for 24 h. When TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was then concentrated, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 20% ethyl acetate in petroleum ether as eluent, to give (±)-3,4-di-*O*-naphthoyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**14**) as a white solid (0.41 g, 63%).

Mp: 90−92 °C. IR: 2929, 1724, 1510, 1448, 1367, 1278, 1240, 1193, 1126, 1014, 912, 779 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 1.30−1.77 (m, 20H, Cyclo-*H*), 4.07 (dd, *J* = 10.2, 9.2 Hz, *H*-5), 4.20 (dd, *J* = 10.2, 8.2 Hz, *H*-6), 4.57 (dd, *J* = 8.2, 6.3 Hz, *H*-1), 4.90 (dd, *J* = 5.5, 4.0 Hz, *H*-2), 5.81−5.85 (m, 2H, *H*-3 and *H*-4), 7.50−7.55 (m, 6H, naph-*H*), 7.91−7.94 (m, 2H, naph-*H*), 8.09 (t, *J* = 9.0 Hz, 2H, naph-*H*), 8.18 (d, *J* = 7.0 Hz, 1H, naph-*H*), 8.23 (d, *J* = 7.0 Hz, 1H, naph-*H*), 8.72 (d, *J* = 7.7 Hz, 1H, naph-*H*), 8.85−8.87 (m, 1H, naph-*H*). ^1H NMR (500 MHz, C_6D_6): δ 1.46−1.74 (m, 20H, Cyclo-*H*), 3.81 (dd, *J* = 10.2, 9.2 Hz, *H*-5), 4.27 (dd, *J* = 8.0, 6.7 Hz, *H*-1), 4.52−4.56 (m, 2H, *H*-2 and *H*-6), 6.01 (t, *J* = 4.6 Hz, *H*-3), 6.28 (dd, *J* = 10.2, 4.6 Hz, *H*-4), 6.99−7.04 (m, 2H, naph-*H*), 7.14−7.18 (m, 2H, naph-*H*), 7.26−7.29 (m, 1H, naph-*H*), 7.46−7.55 (m, 4H, naph-*H*), 8.18 (dd, *J* = 6.4, 0.8 Hz, 1H, naph-*H*), 8.48 (dd, *J* = 6.4, 0.8 Hz, 1H, naph-*H*), 9.19 (d, *J* = 8.7 Hz, 1H, naph-*H*), 9.46 (d, *J* = 8.7 Hz, 1H, naph-*H*). ^1H NMR (500 MHz, $CDCl_3$): δ 1.44−1.79 (m, 20H, Cyclo-*H*), 3.94 (dd, *J* = 10.3, 9.2 Hz, *H*-5), 4.33 (dd, *J* = 10.3, 8.0 Hz, *H*-6), 4.56 (dd, *J* = 8.0, 6.7 Hz, *H*-1), 4.85 (dd, *J* = 6.7, 4.4 Hz, *H*-2), 5.81 (t, *J* = 4.4 Hz, *H*-3), 5.88 (dd, *J* = 9.2, 4.3 Hz, *H*-4), 7.51−8.61 (m, 6H, naph-*H*), 7.90 (dd, *J* = 7.2, 6.1 Hz, 2H, naph-*H*), 8.05 (t, *J* = 8.2 Hz, 2H, naph-*H*), 8.20 (d, *J* = 7.2 Hz, 1H, naph-*H*), 8.31 (d, *J* = 7.2 Hz, 1H, naph-*H*), 8.85 (d, *J* = 8.6 Hz, 1H, naph-*H*), 9.01 (d, *J* = 8.6 Hz, 1H, naph-*H*). ^1H NMR (500 MHz, acetone-d_6): δ 1.31−1.78 (m, 20H, Cyclo-*H*), 4.18 (dd, *J* = 10.3, 9.6 Hz, *H*-5), 4.32 (dd, *J* = 10.3, 8.1 Hz, *H*-6), 4.70 (dd, *J* = 8.1, 6.3 Hz, *H*-1), 4.99 (dd, *J* = 6.3, 3.6 Hz, *H*-2), 5.89−5.90 (m, 2H, *H*-3 and *H*-4), 7.59−7.65 (m, 6H, naph-*H*), 8.01−8.03 (m, 2H, naph-*H*), 8.18−8.20 (m, 2H, naph-*H*), 8.27 (d, *J* = 7.2 Hz, 1H, naph-*H*), 8.82−8.84 (m, 2H, naph-*H*), 8.96 (d, *J* = 8.2 Hz, 1H, naph-*H*). ^1H NMR (500 MHz, DMSO-d_6): δ 1.34−1.72 (m, 20H, Cyclo-*H*), 4.10−4.16 (m, 2H, *H*-5 and *H*-6), 4.59 (t, *J* = 6.7 Hz, *H*-1), 4.88 (dd, *J* = 6.7, 4.7 Hz, *H*-2), 5.71 (dd, *J* = 8.1, 5.6 Hz, *H*-4), 5.82 (dd, *J* = 5.6, 4.7 Hz, *H*-3), 7.60−8.67 (m, 6H, naph-*H*), 8.04−8.06 (m, 2H, naph-*H*), 8.19−8.25 (m, 4H, naph-*H*), 8.62−8.64 (m, 1H, naph-*H*), 8.75−8.77 (m, 1H, naph-*H*). ^1H NMR (500 MHz, CD_3CN): δ 1.37−1.78 (m, 20H, Cyclo-*H*), 4.06 (dd, *J* = 10.2, 9.4 Hz, *H*-5), 4.22 (dd, *J* = 10.2, 8.3 Hz, *H*-6), 4.54 (dd, *J* = 8.3, 6.6 Hz, *H*-1), 4.99 (dd, *J* = 6.6, 4.5 Hz, *H*-2), 5.80−5.85 (m, 2H, *H*-3 and *H*-4), 7.57−7.62 (m, 6H, naph-*H*), 7.98−7.99 (m, 2H, naph-*H*), 8.14−8.15 (m, 2H, naph-*H*), 8.23−8.24 (m, 2H, naph-*H*), 8.76 (d, *J* = 9.6 Hz, 1H, naph-*H*), 8.81 (d, *J* = 7.2 Hz, 1H, naph-*H*). ^{13}C NMR (125 MHz, acetone-d_6): δ 23.49, 23.56, 23.61, 23.80, 24.75, 24.77, 34.22, 36.21, 36.38, 36.87, 72.78, 73.75, 74.22, 75.22, 76.16, 78.59 (Ins-*C*), 111.04 (ketal-*C*), 112.89 (ketal-*C*), 124.66, 124.71, 125.35, 125.57, 126.36, 126.37, 126.50, 126.67, 127.73, 127.79, 128.68, 130.14, 130.57, 131.22, 133.66, 133.79,133.91, 133.97 (Ar-*C*), 165.50 (CO), 166.01 (CO). Anal. Calcd for $C_{40}H_{40}O_8$: C, 74.06; H, 6.21. Found: C, 74.30; H, 6.08.

*(±)-3,4-Di-O-pyrenoyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**15**).* To a solution of pyrene-1-carboxylic acid (0.31 g, 1.29 mmol) in dry DCM (20 mL) were added EDC·HCl (0.24 g, 1.29 mmol) and DMAP (0.007 g, 0.058 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. To this solution was added the diketal **2** (0.2 g, 0.58 mmol), and the mixture was stirred at room temperature for 24 h. When the TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was concentrated, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The mixture was purified by flash column chromatography using 20% ethyl acetate in petroleum ether as an eluent, to give (±)-3,4-di-*O*-pyrenoyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**15**) as a yellow solid (0.29 g, 62%), which was crystallized from a mixture of toluene and hexane (1/1, v/v).

Mp: 143−145 °C. IR: 2933, 1716, 1595, 1508, 1452, 1367, 1253, 1226, 1126, 1083, 1043, 914, 846, 709 cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 1.51−1.84 (m, 20H, Cyclo-*H*), 3.97 (t, *J* = 9.8 Hz, *H*-5), 4.37 (dd, *J* = 7.3, 6.9 Hz, *H*-1), 4.67−4.72 (m, 2H, *H*-2 and *H*-6), 6.26 (t, *J* = 4.5 Hz, *H*-3), 6.51 (dd, *J* = 9.8 Hz, 4.5 Hz, *H*-4), 7.59−7.67 (m, 4H, pyr-*H*), 7.70−7.80 (m, 7H, pyr-*H*), 7.84 (d, *J* = 9.4 Hz, 2H, pyr-*H*), 7.91 (d, *J* = 9.4 Hz, 1H, pyr-*H*), 8.74 (d, *J* = 8.0 Hz,1H, pyr-*H*), 9.00 (d, *J* = 8.0 Hz, 1H, pyr-*H*), 9.52 (d, *J* = 9.4 Hz, 1H, pyr-*H*), 9.78 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^1H NMR (500 MHz, $CDCl_3$): δ 1.29−1.85 (m,

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20H, Cyclo-*H*), 4.08 (dd, *J* = 9.7, 9.5 Hz, *H*-5), 4.47 (dd, *J* = 9.7, 8.6 Hz, *H*-6), 4.65 (dd, *J* = 8.6, 6.6 Hz, *H*-1), 4.96 (bs,1H, *H*-2), 6.00−6.06 (m, 2H, *H*-3, *H*-4), 8.06−8.12 (m, 5H, pyr-*H*), 8.26−8.17 (m, 9H, pyr-*H*), 8.67 (d, *J* = 8.0 Hz, 1H, pyr-*H*), 8.77 (d, *J* = 8.0 Hz, 1H, pyr-*H*), 9.18 (d, *J* = 9.4 Hz, 1H, pyr-*H*), 9.32 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.59−1.85 (m, 20H, Cyclo-*H*), 4.32 (dd, *J* = 10.0, 9.4 Hz, *H*-5), 4.44 (dd, *J* = 10.0, 8.1 Hz, *H*-6), 4.78 (dd, *J* = 8.1, 6.4 Hz, *H*-1), 5.11 (dd, *J* = 6.4, 3.6 Hz, *H*-2), 6.06−6.08 (m, 2H, *H*-3 and *H*-4), 8.11−8.15 (m, 2H, pyr-*H*), 8.19−8.26 (m, 4H, pyr-*H*), 8.31−8.40 (m, 8H, pyr-*H*), 8.75 (d, *J* = 8.1 Hz, 1H, pyr-*H*), 8.80 (d, *J* = 8.1 Hz, 1H, pyr-*H*), 9.15 (d, *J* = 9.4 Hz, 1H, pyr-*H*), 9.27 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.30−1.78 (m, 20H, Cyclo-*H*), 4.25−4.30 (m, 2H, *H*-5 and*H*-6), 4.67 (dd, *J* = 6.6, 6.3, Hz, *H*-1), 5.01 (dd, *J* = 6.3, 4.5 Hz, *H*-2), 5.90 (dd, *J* = 8.0, 4.5 Hz, *H*-4), 6.01 (t, *J* = 4.5 Hz, *H*-3), 8.15−8.16 (m, 2H, pyr-*H*), 8.26 (bs, 4H, pyr-*H*), 8.32−8.42 (m, 8H, pyr-*H*), 8.67 (d, *J* = 7.8 Hz, 1H, pyr-*H*), 8.98 (d, *J* = 9.4 Hz, 1H, pyr-*H*), 9.10 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^{1}H NMR (500 MHz, CD_3CN): δ 1.58−1.96 (m, 20H, Cyclo-*H*), 4.18 (dd, *J* = 10.1, 9.3 Hz, *H*-5), 4.31 (dd, *J* = 10.1, 8.4 Hz, *H*-6), 4.61 (dd, *J* = 8.4, 6.1 Hz, *H*-1), 4.97 (dd, *J* = 6.1, 4.3 Hz, *H*-2), 5.97−6.03 (m, 2H, *H*-3 and *H*-4), 8.06−8.10 (m, 4H, pyr-*H*), 8.15−8.18 (m, 2H, pyr-*H*), 8.22−8.33 (m, 8H, pyr-*H*), 8.66−8.69 (m, 2H, pyr-*H*), 9.00 (d, *J* = 9.4 Hz, 1H, pyr-*H*), 9.40 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^{13}C NMR (125 MHz, acetone-d_6): δ 23.51, 23.59, 23.63, 23.82, 24.78, 34.30, 36.29, 36.41, 36.95, 73.11, 74.05, 74.41, 75.40, 76.28, 78.75 (Ins-*C*), 111.15 (ketal-*C*), 112.95 (ketal-*C*), 123.01, 124.24, 124.33, 124.46, 124.51, 124.58, 126.31, 126.56, 127.08, 127.12, 128.25, 128.58, 129.38, 129.42, 129.81, 130.28, 131.03, 134.53, 134.59 (Ar−C), 165.97 (*C*O), 166.44 (*C*O). Anal. Calcd for $C_{52}H_{44}O_8$: C, 78.37; H, 5.57. Found: C, 78.57; H, 5.63.

*(±)-3-O-Pivaloyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**16**).* To a cooled solution of diketal **2** (0.34 g, 1 mmol) in dry pyridine (10 mL) were added pivaloyl chloride (0.12 mL, 1.0 mmol) and a catalytic amount (10 mg) of DMAP. The reaction mixture was stirred for 1.5 h at room temperature. When TLC showed complete disappearance of the starting material, the reaction was quenched by adding a few drops of water and the mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (20 mL), and the solution was then washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography using 15% ethyl acetate in petroleum ether (R_f 0.35) as eluent, to give (±)-3-*O*-pivaloyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**16**) as a white solid (0.1 g, 73%).

Mp: 181−183 °C. IR: 3479, 2933, 1718, 1456, 1367, 1280, 1165, 1101, 1068, 933, 773 cm^{-1}. ^{1}H NMR (500 MHz, CD_3OD): δ 1.26 (s, 9H, 3 × C*H*$_3$), 1.45−1.72 (m, 20H, Cyclo-*H*), 3.49 (dd, *J* = 10.2, 9.0 Hz, *H*-5), 3.83 (dd, *J* = 10.2, 8.3 Hz, *H*-6), 3.92 (dd, *J* = 9.0, 5.4 Hz, *H*-4), 4.36 (dd, *J* = 8.3, 6.2 Hz, *H*-1), 4.59 (dd, *J* = 6.2, 4.7 Hz, *H*-2), 4.94 (dd, *J* = 5.4, 4.7 Hz, *H*-3). ^{1}H NMR (C_6D_6, 500 MHz): δ: 1.21 (s, 9H, 3 × C*H*$_3$), 1.72−1.92 (m, 20H, Cyclo-*H*), 3.27 (dd, *J* = 8.7, 8.6 Hz, *H*-5), 3.99−4.01 (m, 3H, *H*-1, *H*-4, *H*-6) 4.35−4.36 (m, 1H, *H*-2), 4.98 (dd, *J* = 5.4, 4.6 Hz, *H*-3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (s, 9H, 3 × C*H*$_3$), 1.57−1.76 (m, 20H, Cyclo-*H*), 3.46 (dd, *J* = 10.2, 10.1 Hz, *H*-5), 3.84 (dd, *J* = 10.2, 8.2 Hz, *H*-6), 4.08−4.11 (m, 1H, *H*-4), 4.35 (dd, *J* = 8.2, 6.2 Hz, *H*-1), 4.60 (dd, *J* = 6.2, 5.0 Hz, *H*-2), 4.91 (dd, *J* = 5.1, 5.0 Hz, *H*-3). ^{1}H NMR (acetone-d_6, 500 MHz): δ 1.23 (s, 9H, 3 × C*H*$_3$), 1.40−1.72 (m, 20H, Cyclo-*H*), 3.54 (dd, *J* = 10.3, 8.8 Hz, *H*-5), 3.90 (dd, *J* = 10.3, 8.1 Hz, *H*-6), 3.95 (ddd, *J* = 8.4, 4.65, 4.6 Hz, *H*-4), 4.43 (dd, *J* = 8.1, 6.5 Hz, *H*-1), 4.60 (dd, *J* = 6.5, 4.6 Hz, *H*-2), 4.85 (d, *J* = 4.65 Hz, 1H, C4-O*H*), 4.96 (t, *J* = 4.6 Hz, *H*-3). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.16 (s, 9H, 3 × C*H*$_3$), 1.34−1.62 (m, 20H, Cyclo-*H*), 3.46 (dd, *J* = 10.4, 8.6 Hz, *H*-5), 3.71 (dd, *J* = 8.6, 4.2 Hz, *H*-4), 3.75 (dd, *J* = 10.4, 8.0 Hz, *H*-6), 4.35 (dd, *J* = 8.0, 6.7 Hz, *H*-1), 4.47 (dd, *J* = 6.7, 4.4 Hz, *H*-2), 4.84 (t, *J* = 4.4 Hz, *H*-3), 5.75 (d, *J* = 4.8 Hz, 1H, C4-O*H*). ^{1}H NMR (500 MHz, CD_3CN): δ 1.24 (s, 9H, 3 × C*H*$_3$), 1.39−1.70 (m, 20H, Cyclo-*H*), 3.45 (dd, *J* = 10.3, 9.0 Hz, *H*-5), 3.70 (d, *J* = 4.7 Hz, 1H, C4-O*H*), 3.81 (dd, *J* = 10.3, 8.3 Hz, *H*-6), 3.88 (ddd, *J* = 9.0, 5.3, 4.7 Hz, *H*-4), 4.30 (dd, *J* = 8.3, 6.2 Hz, *H*-1) 4.53 (dd, *J* = 6.2, 4.6 Hz, *H*-2), 4.90 (dd, *J* = 5.3, 4.6 Hz, *H*-3). ^{13}C NMR (125 MHz, acetone-d_6): δ 23.47, 23.50, 23.56, 23.73, 24.82, 24.85, 26.56, 33.89, 36.36, 36.40, 36.90, 38.36, 71.61, 75.28, 76.20, 77.98, 78.48 (Ins-*C*), 110.21 (ketal-*C*), 111.73 (ketal-*C*), 176.70 (*C*O). Anal. Calcd for $C_{23}H_{36}O_7$: C, 65.07; H, 8.55. Found: C, 65.25; H, 8.39.

*(±)-3-O-Benzoyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**17**).* To a cooled solution of diketal **2** (0.34 g, 1 mmol) in dry pyridine (10 mL) were added benzoyl chloride (0.12 mL, 1.0 mmol) and a catalytic amount (10 mg) of DMAP. The reaction mixture was stirred for 2 h at room temperature. The reaction was quenched by adding a few drops of water, and the mixture was then concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (20 mL), and the solution was then washed successively with 10% ascorbic acid solution, saturated sodium bicarbonate solution, water, and finally brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using 30% ethyl acetate in petroleum ether (R_f 0.30) as eluent, to give (±)-3-*O*-benzoyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**17**)[30] as a white solid (0.22 g, 61%), which was crystallized from a mixture of chloroform and petroleum ether (1/2 v/v).

Mp: 172−174 °C. IR: 3527, 2943, 1708, 1450, 1367, 1278, 1047, 1159, 1114, 1047, 910, 850, 713 cm^{-1}. ^{1}H NMR (500 MHz, CD_3OD): δ 1.37−1.69 (m, 20H, Cyclo-*H*), 3.63 (dd, *J* = 10.2, 8.6 Hz, *H*-5), 4.05−4.09 (m, 2H, *H*-4 and *H*-6), 4.48 (dd, *J* = 7.3, 6.6 Hz, *H*-1), 4.68 (dd, *J* = 6.6, 3.6 Hz, *H*-2), 5.31 (t, *J* = 3.6 Hz, *H*-3), 7.53 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.65 (dd, *J* = 7.3, 7.2 Hz, 1H, Ar-*H*), 8.07 (d, *J* = 7.5 Hz, 2H, Ar-*H*). ^{1}H NMR (500 MHz, C_6D_6): δ 1.40−1.72 (m, 20H, Cyclo-*H*), 3.57 (dd, *J* = 10.5, 8.1 Hz, *H*-5), 4.22−4.4.25 (m, 2H, *H*-4 and *H*-1), 4.39 (dd, *J* = 10.5, 7.9 Hz, *H*-6), 4.41−4.43 (m, 1H, *H*-2), 5.48−5.49 (m, 1H, *H*-3), 7.00 (bs, 2H, Ar-*H*), 7.06 (m, 1H, Ar-*H*), 8.21 (dd, *J* = 7.2,1.2 Hz, 2H, Ar-*H*). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.42−1.73 (m, 20H, Cyclo-*H*), 3.61 (dd, *J* = 10.5, 8.6 Hz, *H*-5), 4.10 (dd, *J* = 10.5, 7.8 Hz, *H*-6), 4.23 (dd, *J* = 8.6, 3.8 Hz, *H*-4), 4.47 (dd, *J* = 7.8, 6.4 Hz, *H*-1), 4.68 (dd, *J* = 6.4, 3.8 Hz, *H*-2), 5.29 (t, *J* = 3.8 Hz, *H*-3), 7.49 (dd, *J* = 7.8, 7.6 Hz, 2H, Ar-*H*), 7.62 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 8.10 (d, *J* = 7.4 Hz, 2H, Ar-*H*). ^{1}H NMR (500 MHz, acetone-d_6): δ 1.31−1.70 (m, 20H, Cyclo-*H*), 3.69 (dd, *J* = 10.6, 8.2 Hz, *H*-5), 4.11−4.16 (m, 2H, *H*-4 and *H*-6), 4.56 (dd, *J* = 7.4, 7.0 Hz, *H*-1), 4.71 (dd, *J* = 7.0, 3.6 Hz, *H*-2), 5.06 (d, *J* = 4.4 Hz, 1H, 4-O*H*), 5.34 (dd, *J* = 3.9, 3.6 Hz, *H*-3), 7.56 (dd, *J* = 7.8, 7.6 Hz, 2H, Ar-*H*), 7.68 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 8.07 (dd, *J* = 7.1, 1.3 Hz, 2H, Ar-*H*). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.40−1.61 (m, 20H, Cyclo-*H*), 3.59 (dd, *J* = 10.3, 8.6 Hz, *H*-5), 3.88−3.90 (m, 1H, *H*-4), 3.98 (dd, *J* = 10.3, 7.8 Hz, *H*-6), 4.46 (dd, *J* = 7.8, 6.8 Hz, *H*-1), 4.58 (dd, *J* = 6.8, 4.0 Hz, *H*-2), 5.20−5.22 (m, 1H, *H*-3), 5.92 (d, *J* = 5.0 Hz, 1H, C4-O*H*), 7.57 (dd, *J* = 7.5, 7.3 Hz, 2H, Ar-*H*), 7.68 (t, *J* = 7.3 Hz,1H, Ar-*H*), 7.98 (d, *J* = 7.5 Hz, 2H, Ar-*H*). ^{1}H NMR (500 MHz, CD_3CN): δ 1.40−1.61 (m, 20H, Cyclo-*H*), 3.59 (dd, *J* = 10.6, 8.6 Hz, *H*-5), 4.04 (dd, *J* = 10.6, 7.7 Hz, *H*-6) 4.06 (dd, *J* = 8.6, 4.0 Hz, *H*-4), 4.42 (dd, *J* = 7.7, 6.8 Hz, *H*-1), 4.64 (dd, *J* = 6.8, 4.0 Hz, *H*-2), 5.27 (t, *J* = 4.0 Hz, *H*-3), 7.57 (dd, *J* = 7.8, 7.6 Hz, 2H, Ar-*H*), 7.68 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.57 (dd, *J* = 7.8, 7.6 Hz, 2H, Ar-*H*). ^{13}C NMR (125 MHz, acetone-d_6): δ 23.58, 23.63, 24.82, 33.98, 36.32, 36.37, 36.46, 71.99, 73.46, 76.13, 76.57, 77.60, 78.83 (Ins-*C*), 110.74 (ketal-*C*), 112.04 (ketal-*C*), 128.55, 129.55, 130.15 (aromatic C), 133.21 (C-ipso), 164.75 (*C*O). Anal. Calcd for $C_{25}H_{32}O_7$: C, 67.55; H, 7.26. Found: C, 67.40; H, 7.33.

*(±)-3-O-Naphthoyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**18**).* To a solution of 1-naphthoic acid (0.18 g, 1.1 mmol) in dry DCM (20 mL) were added EDC·HCl (0.21 g, 1.1 mmol) and DMAP (0.012 g, 0.1 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. The diketal **2** (0.34 g, 1 mmol) was added to the above solution, and the mixture was stirred at room temperature for 24 h. When TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was then concentrated, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product thus obtained was purified by

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flash column chromatography using 30% ethyl acetate in petroleum ether as eluent, to give (±)-3-*O*-naphthoyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**18**) as a white solid (0.27 g, 55%).

Mp: 131−133 °C. IR: 3446, 2931, 1718, 1512, 1448, 1367, 1278, 1242, 1195, 1130, 1051, 910, 781 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 1.36−1.69 (m, 20H, Cyclo-*H*), 3.63 (dd, *J* = 10.1, 8.9 Hz, *H*-5), 4.00 (dd, *J* = 10.1, 8.2 Hz, *H*-6), 4.17 (dd, *J* = 8.9, 5.2 Hz, *H*-4), 4.48 (dd, *J* = 8.2, 6.0 Hz, *H*-1), 4.80 (dd, *J* = 6.0, 4.4 Hz, *H*-2), 5.42 (dd, *J* = 5.2, 4.4 Hz, *H*-3), 7.57−7.64 (m, 3H, naph-*H*), 7.98 (d, *J* = 7.9 Hz, 1H, naph-*H*), 8.14 (d, *J* = 7.9 Hz, 1H, naph-*H*), 8.24 (d, *J* = 7.3 Hz, 1H, naph-*H*), 8.94 (d, *J* = 8.5 Hz, 1H, naph-*H*). ^1H NMR (500 MHz, C_6D_6): δ 1.13−1.74 (m, 20H, Cyclo-*H*), 3.46−3.49 (m, 1H, *H*-5), 4.15 (dd, *J* = 8.2, 5.8 Hz, *H*-1), 4.26 (dd, *J* = 10.3, 8.2 Hz, *H*-4 and *H*-6), 4.52−4.53 (m, 1H, *H*-2), 5.52−5.53 (m, 1H, *H*-3), 7.05−9.44 (m, 7H, naph-*H*). ^1H NMR (500 MHz, $CDCl_3$): δ 1.42−1.71 (m, 20H, Cyclo-*H*), 2.72 (d, *J* = 3.0 Hz, 1H, C4-OH), 3.59 (dd, *J* = 10.1, 9.2 Hz, *H*-5), 4.02 (dd, *J* = 10.1, 8.1 Hz, *H*-6), 4.34 (m, 1H, *H*-4), 4.46 (dd, *J* = 8.1, 6.1 Hz, *H*-1), 4.79 (dd, *J* = 6.1, 4.8 Hz, *H*-2), 5.38 (t, *J* = 4.8 Hz, *H*-3), 7.53−9.01 (m, 7H, naph-*H*). ^1H NMR (500 MHz, acetone-d_6): δ 1.43−1.70 (m, 20H, Cyclo-*H*), 3.70 (dd, *J* = 10.3, 8.6 Hz, *H*-5), 4.07 (dd, *J* = 10.3, 8.0 Hz, *H*-6), 4.25 (ddd, *J* = 8.6, 4.45, 4.4, *H*-4), 4.56 (dd, *J* = 8.0, 6.4 Hz, *H*-1), 4.81 (dd, *J* = 6.4, 4.4 Hz, *H*-2), 5.09 (d, *J* = 4.45 Hz, 1H, C4-O*H*), 5.46 (t, *J* = 4.4 Hz, *H*-3), 7.62−7.67 (m, 3H, naph-*H*), 8.04 (d, *J* = 7.5 Hz,1H, naph-*H*), 8.20 (d, *J* = 8.0 Hz,1H, naph-*H*), 8.28 (d, *J* = 7.2 Hz, 1H, naph-*H*), 9.00 (d, *J* = 8.6 Hz, 1H, naph-*H*). ^1H NMR (500 MHz, DMSO-d_6): δ 1.31−1.62 (m, 20H, Cyclo-*H*), 3.60 (dd, *J* = 10.1, 9.2 Hz, *H*-5), 3.89 (dd, *J* = 10.1, 8.1 Hz, *H*-6), 4.01 (ddd, *J* = 9.2, 5.1, 4.1 Hz, *H*-4), 4.46 (dd, *J* = 8.1, 6.0 Hz, *H*-1), 4.67 (dd, *J* = 6.0, 4.1 Hz, *H*-2), 5.33 (t, *J* = 4.1 Hz, *H*-3), 5.93 (d, *J* = 5.1 Hz, 1H, C4-O*H*), 7.61−7.68 (m, 3H, naph-*H*), 8.06 (d, *J* = 7.5 Hz, 1H, naph-*H*), 8.17 (d, *J* = 6.9 Hz, 1H, naph-*H*), 8.22 (d, *J* = 8.0 Hz, 1H, naph-*H*), 8.81 (d, *J* = 8.0 Hz, 1H, naph-*H*). ^1H NMR (500 MHz, CD_3CN): δ 1.45−1.71 (m, 20H, Cyclo-*H*), 3.59 (dd, *J* = 10.1, 9.1 Hz, *H*-5), 3.89 (d, *J* = 4.2 Hz, 1H, C4-O*H*), 3.96 (dd, *J* = 10.1, 8.2 Hz, *H*-6), 4.15 (ddd, *J* = 9.1, 4.8, 4.2 Hz, *H*-4), 4.41 (dd, *J* = 8.2, 6.1 Hz, *H*-1), 4.73 (dd, *J* = 6.1, 4.8 Hz, *H*-2), 5.38 (t, *J* = 4.8 Hz, *H*-3), 7.62−7.68 (m, 3H, naph-*H*), 8.02 (d, *J* = 8.1 Hz, 1H, naph-*H*), 8.17 (d, *J* = 8.1 Hz, 1H, naph-*H*), 8.25 (d, *J* = 7.2 Hz, 1H, naph-*H*), 8.91 (d, *J* = 8.5 Hz, 1H, naph-*H*). ^{13}C NMR (125 MHz, acetone-d_6): δ 23.48, 23.54, 23.58, 23.76, 24.79, 24.83, 34.15, 36.37, 36.42, 36.85, 71.68, 73.82, 76.05, 76.43, 78.17, 78.38 (Ins-*C*), 110.58 (ketal-*C*), 111.93 (ketal-*C*), 124.70, 125.74, 126.32, 127.25, 127.61, 128.63, 130.29, 131.20, 133.44, 133.97 (aromatic C), 166.00 (*C*O). Anal. Calcd for $C_{29}H_{34}O_7$: C, 70.43; H, 6.93. Found: C, 70.18; H, 6.71.

*(±)-3-O-Pyrenoyl-1,2:5,6-di-O-cyclohexylidene-myo-inositol (**19**).* To a solution of pyrene-1-carboxylic acid (0.155 g, 0.645 mmol) in dry DCM (20 mL) were added EDC·HCl (0.124 g, 0.645 mmol) and DMAP (0.007 g, 0.058 mmol). The mixture was stirred at room temperature under an argon atmosphere for 15 min. To this solution was added the diketal **2** (0.2 g, 0.58 mmol), and the mixture was stirred at room temperature for 24 h. When TLC showed complete disappearance of the starting material, the reaction mixture was filtered and washed well with ethyl acetate. The filtrate was concentrated, and the resulting residue was dissolved in ethyl acetate (30 mL). The ethyl acetate layer was washed with water (2 × 20 mL) and brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The mixture was purified by flash column chromatography using 30% ethyl acetate in petroleum ether as an eluent, to ive (±)-3-*O*-pyrenoyl-1,2:5,6-di-*O*-cyclohexylidene-*myo*-inositol (**19**) as a yellow solid (0.18 g, 54%), which was crystallized from a mixture of dichloromethane and petroleum ether (3/1 v/v).

Mp: 132−134 °C. IR: 3437, 2931, 1712, 1597, 1448, 1367, 1251, 1228, 1130, 1087, 1049, 910, 848 cm^{-1}. ^1H NMR (500 MHz, CD_3OD): δ 1.31−1.77 (m, 20H, Cyclo-*H*), 3.68 (dd, *J* = 10.1, 9.0 Hz, *H*-5), 4.10 (dd, *J* = 10.1, 8.2 Hz, *H*-6), 4.25 (dd, *J* = 9.0, 5.0 Hz, *H*-4), 4.52 (dd, *J* = 8.2, 6.3 Hz, *H*-1), 4.85 (bs, 1H, 2-*H*), 5.51−5.53 (m, 1H, *H*-3), 8.13 (t, *J* = 7.6 Hz, 1H, pyr-*H*), 8.18 (d, *J* = 8.9 Hz, 1H, pyr-*H*), 8.27−8.30 (m, 3H, pyr-*H*), 8.35 (d, *J* = 7.6 Hz, 2H, pyr-*H*), 8.69 (d, *J* = 8.1 Hz,1H, pyr-*H*) 9.28 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^1H NMR (500 MHz, C_6D_6): δ 1.23−1.77 (m, 20H, Cyclo-*H*), 3.54 (dd, *J* = 10.3, 8.6 Hz, *H*-5), 4.22 (dd, *J* = 7.7, 6.4 Hz, *H*-1), 4.33 (dd, *J* = 8.6, 4.4 Hz, *H*-4), 4.39 (dd, *J* = 10.3, 7.7 Hz, *H*-6), 4.59 (dd, *J* = 6.4, 4.4 Hz, *H*-2), 5.63 (t, *J* = 4.4 Hz, *H*-3), 7.64 (d, *J* = 8.9 Hz,1H, pyr-*H*), 7.70 (t, *J* = 7.6 Hz, 1H, pyr-*H*), 7.75 (dd, *J* = 8.6, 6.5 Hz, 2H, pyr-*H*), 7.87 (d, *J* = 7.6 Hz, 2H, pyr-*H*), 8.01 (d, *J* = 9.4 Hz,1H, pyr-*H*), 8.88 (d, *J* = 8.1 Hz, 1H, pyr-*H*), 9.76 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^1H NMR (500 MHz, $CDCl_3$): δ 1.42−1.73 (m, 20H, Cyclo-*H*), 3.65 (dd, *J* = 10.1, 9.6 Hz, *H*-5), 4.12 (dd, *J* = 10.1, 8.3 Hz, *H*-6), 4.44 (dd, *J* = 9.6, 4.6 Hz, *H*-4), 4.43 (dd, *J* = 8.3, 6.4 Hz, *H*-1), 4.85 (dd, *J* = 6.4, 4.6 Hz, *H*-2), 5.49 (t, *J* = 4.6 Hz, *H*-3), 8.08−8.10 (m, 2H, pyr-*H*), 8.18−8.30 (m, 5H, pyr-*H*), 8.70 (d, *J* = 8.1 Hz, 1H, pyr-*H*), 9.33 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^1H NMR (500 MHz, acetone-d_6): δ 1.53−1.71 (m, 20H, Cyclo-*H*), 3.75 (dd, *J* = 10.4, 8.6 Hz, *H*-5), 4.17 (dd, *J* = 10.4, 8.0 Hz, *H*-6), 4.33 (ddd, *J* = 8.6, 4.55, 4.5, *H*-4), 4.60 (dd, *J* = 8.0, 6.5 Hz, *H*-1), 4.88 (dd, *J* = 6.5, 4.5 Hz, *H*-2), 5.12 (d, *J* = 4.55 Hz, C4-O*H*), 5.57 (t, *J* = 4.5 Hz, *H*-3), 8.18−9.37 (m, 9H, pyr-*H*). ^1H NMR (500 MHz, DMSO-d_6): δ 1.26−1.66 (m, 20H, Cyclo-*H*), 3.64 (dd, *J* = 10.1, 8.9 Hz, *H*-5), 3.98 (dd, *J* = 10.1, 8.0 Hz, *H*-6), 4.11 (ddd, *J* = 8.9, 5.1, 4.2 Hz, *H*-4), 4.50 (dd, *J* = 8.0, 6.3 Hz, *H*-1), 4.74 (dd, *J* = 6.3, 4.2 Hz, *H*-2), 5.44 (t, *J* = 4.2 Hz, *H*-3), 5.98 (d, *J* = 5.1 Hz, 1H, C4-OH), 8.17−8.62 (m, 9H, pyr-*H*). ^1H NMR (500 MHz, CD_3CN): δ 1.52−1.74 (m, 20H, Cyclo-*H*), 3.63 (dd, *J* = 10.3, 9.1 Hz, *H*-5), 3.94 (d, *J* = 4.6 Hz, 1H, C4-O*H*), 4.04 (dd, *J* = 10.3, 8.2 Hz, *H*-6), 4.24 (ddd, *J* = 9.1, 4.8, 4.6 Hz, *H*-4), 4.45 (dd, *J* = 8.1, 6.2 Hz, *H*-1), 4.80 (dd, *J* = 6.2, 4.8 Hz, *H*-2), 5.49 (m, 1H, *H*-3), 8.16 (t, *J* = 7.6 Hz, 1H, pyr-*H*), 8.22 (d, *J* = 8.9 Hz, 1H, pyr-*H*), 8.31−8.35 (m, 3H, pyr-*H*), 8.40 (dd, *J* = 7.5, 1.3 Hz, 1H, pyr-*H*), 8.69 (d, *J* = 9.4 Hz, 1H, pyr-*H*), 9.25 (d, *J* = 9.4 Hz, 1H, pyr-*H*). ^{13}C NMR (125 MHz, acetone-d_6): δ 23.49, 23.55, 23.59, 23.78, 24.79, 24.84, 34.15, 36.39, 36.54, 36.82, 54.03 (trapped CH_2Cl_2), 71.83, 73.89, 76.26, 76.51, 78.16, 78.52 (Ins-*C*), 110.66 (ketal-*C*), 111.98 (ketal-*C*), 123.72, 123.94, 124.35, 124.84, 126.35, 126.58, 126.67, 127.22, 128.56, 129.37, 129.79, 130.41, 130.90, 131.13, 134.44 (aromatic C), 166.37 (CO). Anal. Calcd for $C_{36}H_{38}Cl_2O_7$: C, 66.16; H, 5.86. Found: C, 66.28; H, 5.92.

Crystal Data for Dibenzoate 12: refined formula $C_{32}H_{36}O_8$, formula weight *M* = 548.61, colorless block, 1.0 × 0.2 × 0.15 mm^3, monoclinic, space group $P2_1/c$, unit cell dimensions and volume *a* = 23.1620(10), *b* = 11.5821(5), *c* = 11.2981(4) Å, and *V* = 2975.2(2) $Å^3$, no. of formula units in the unit cell *Z* = 4, *T* = 293(2) K, $2\theta_{max}$ = 55.00°, calculated density ρ_{calcd} = 1.225 g cm^{-3}, *F*(000) = 1168, linear absorption coefficient μ 0.087 mm^{-1}, 21494 reflections collected, 5232 unique reflections (R_{int} = 0.0879), multiscan absorption correction, T_{min} = 0.9176, T_{max} = 0.9870, no. of parameters 361, no. of restraints 0, GOF = 1.090, R1 = 0.0509, wR2 = 0.1202, *R* indices based on 3551 reflections with $I > 2\sigma(I)$ (refinement on F^2), $\Delta\rho_{max}$ = 0.001 e $Å^{-3}$, $\Delta\rho_{min}$ = 0.000 e $Å^{-3}$.

Crystal Data for Dipivaloate 13: refined formula $C_{28}H_{44}O_8$, formula weight *M* = 508.63, colorless block, 0.2 × 0.15 × 0.1 mm^3, monoclinic, space group *Cc*, unit cell dimensions and volume *a* = 46.9596(11), *b* = 12.7191(3), *c* = 20.5382(5) Å, and *V* = 11725.9(5) $Å^3$, no. of formula units in the unit cell *Z* = 16, *T* = 296(2) K, $2\theta_{max}$ = 41.82°, calculated density ρ_{calcd} = 1.152 g cm^{-3}, *F*(000) = 4416, linear absorption coefficient μ 0.083 mm^{-1}, 47729 reflections collected, 18731 unique reflections (R_{int} = 0.2434), multiscan absorption correction, T_{min} = 0.9836, T_{max} = 0.9917, no. of parameters 1279, no. of restraints 3, GOF = 0.966, R1 = 0.0552, wR2 = 0.1328, *R* indices based on 4869 reflections with $I > 2\sigma(I)$ (refinement on F^2), $\Delta\rho_{max}$ = 0.035 e $Å^{-3}$, $\Delta\rho_{min}$ = 0.010 e $Å^{-3}$.

Crystal Data for Monopivaloate 16: refined formula $C_{23}H_{36}O_7$, formula weight *M* = 424.52, colorless block, 0.2 × 0.15 × 0.1 mm^3, triclinic, space group $P\bar{1}$, unit cell dimensions and volume *a* = 17.077(3), *b* = 17.490 (3), *c* = 17.638(3) Å, and *V* = 4505.5(12) $Å^3$, no. of formula units in the unit cell *Z* = 8, *T* = 296(2) K, $2\theta_{max}$ = 55.52°, calculated density ρ_{calcd} = 1.252 g cm^{-3}, *F*(000) = 1840, linear absorption coefficient μ 0.091 mm^{-1}, 65964 reflections collected, 15812 unique reflections (R_{int} = 0.2986), multiscan absorption correction, T_{min} = 0.9820, T_{max} = 0.9909, no. of parameters 1085, no. of restraints 1, GOF = 0.920, R1 = 0.0662, wR2 = 0.1501, *R* indices based on 3670 reflections with $I > 2\sigma(I)$ (refinement on F^2). $\Delta\rho_{max}$ = 0.076 e $Å^{-3}$, $\Delta\rho_{min}$ = 0.012 e $Å^{-3}$.

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Crystal Data for Monobenzoate 17: refined formula $C_{25}H_{32}O_7$, formula weight M = 444.51, colorless block, 0.2 × 0.15 × 0.1 mm^3, monoclinic, space group $P2_1/c$, unit cell dimensions and volume a = 12.150 (5), b = 10.181(5), c = 18.898(5) Å, and V = 2326.6(16) Å^3, no. of formula units in the unit cell Z = 4, T = 293(2) K, $2\theta_{max}$ = 51.56°, calculated density ρ_{calcd} = 1.269 g cm^{-3}, $F(000)$ = 952, linear absorption coefficient μ 0.092 mm^{-1}, 17782 reflections collected, 4104 unique reflections (R_{int} = 0.1073), multiscan absorption correction, T_{min} = 0.9818, T_{max} = 0.9909, no. of parameters 294, no. of restraints 1, GOF = 1.022, R1 = 0.0565, wR2 = 0.1370, R indices based on 2405 reflections with $I > 2\sigma(I)$ (refinement on F^2). $\Delta\rho_{max}$ = 0.002 e Å^{-3}, $\Delta\rho_{min}$ = 0.000 e Å^{-3}.

Crystal Data for Monopyrenoate 19: refined formula $C_{36}H_{38}Cl_2O_7$, formula weight M = 653.56, colorless block, 0.2 × 0.15 × 0.1 mm^3, triclinic, space group $P\bar{1}$, unit cell dimentions and volume a = 12.0165(3), b = 16.3915(4), c = 18.4237(4) Å, and V = 3165.08(13) Å^3, no. of formula units in the unit cell Z = 4, T = 110(2) K, $2\theta_{max}$ = 56.28°, calculated density ρ_{calcd} = 1.372 g cm^{-3}, $F(000)$ = 1376, linear absorption coefficient μ 0.255 mm^{-1}, 45336 reflections collected, 11083 unique reflections (R_{int} = 0.0830), multiscan absorption correction, T_{min} = 0.9507, T_{max} = 0.9749, no. of parameters 819, no. of restraints 2, GOF = 1.052, R1 = 0.0455, wR2 = 0.1064, R indices based on 7448 reflections with $I > 2\sigma(I)$ (refinement on F^2). $\Delta\rho_{max}$ = 0.001 e Å^{-3}, $\Delta\rho_{min}$ = 0.000 e Å^{-3}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables showing prominent noncovalent interactions in the crystal structure of **12**, **13**, **16**, **17**, and **19**, figures giving ^{1}H NMR, ^{13}C NMR, DEPT, and 2D NMR spectra for **3**−**19**, and CIF files giving crystallographic data for **12**, **13**, **16**, **17**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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