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Cyclodextrin Host as a Supramolecular Catalyst in Nonpolar Solvents: Stereoselective Synthesis of (*E*)-3-Alkylideneoxindoles

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ABSTRACT

Heptakis(6-*O*-triisopropylsilyl)-β-cyclodextrin (TIPS-β-CD) effectively formed inclusion complexes with oxindole and its derivatives as guests in nonpolar solvents. Their inclusion complex formation was remarkably affected by the position and size of substituents on the oxindole ring of the guest. The Knoevenagel condensation reaction of these oxindoles with cinnamaldehyde to give 3-alkylideneoxindoles was accelerated with enhanced *E*/*Z* selectivities in the presence of catalytic amounts of TIPS-β-CD.

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1. Introduction

In the past decades, a wide variety of host–guest and supramolecular systems have been applied to organic synthesis, due to their great potential for dramatically improving the reactivity and selectivity.[1] In particular, much effort has been devoted to catalytic reactions utilizing supramolecular host systems.[2] Cyclodextrins (CDs) and their derivatives incorporate guest molecules of an appropriate size and shape into their sub-nanoscaled cavities to form inclusion complexes in aqueous and polar media.[3] By utilizing the substrate incorporation within the cavities, CDs can catalyze a variety of chemical reactions as a supramolecular catalyst.[2b,c,4] However, in most cases, catalytic reactions using CDs were limited to aqueous media and several kinds of polar organic media. On the other hand, catalytic reactions in nonpolar solvents with CDs were rarely carried out. Recently, our research group reported that 6-*O*-modified CDs, such as heptakis(6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (TBDMS-β-CD) and heptakis(6-*O*-triisopropylsilyl)-β-cyclodextrin (TIPS-β-CD), effectively formed inclusion complexes with aromatic compounds in nonpolar solvents.[5] We also found that TBDMS-β-CD functioned as a catalyst for the photodimerization of coumarin in nonpolar solvents via the incorporation of coumarin within the CD cavity.[6] These findings prompted us to investigate the scope of catalytic reactions with CDs in nonpolar solvents.

Under these backgrounds, we focused on oxindole which contains a benzene ring fused with cyclic amide, and is a prominent structure moiety found in a number of bioactive natural products and pharmaceutically important compounds.[7] Based on the CPK-modeling studies, we expected that oxindole should be effectively incorporated within the CD cavity in nonpolar solvents. The Knoevenagel condensation reaction of oxindoles with aldehyde has been widely utilized for the preparation of 3-alkylideneoxindoles which act as valuable intermediates in the synthesis of indole alkaloids and drug candidates.[8,9] However, this reaction often required high reaction temperature and produced 3-alkylideneoxindoles with poor *E/Z* selectivity.[10] Thus, more efficient and stereoselective synthesis of 3-alkylideneoxindoles via Knoevenagel condensation reaction is highly required.

Herein, we report the effective inclusion complex formation between 6-*O*-modified CDs and oxindoles in nonpolar solvents, and the facile stereoselective synthesis of (*E*)-3-alkylideneoxindoles via Knoevenagel condensation reaction of oxindoles with cinnamaldehyde using 6-*O*-modified CDs as a supramolecular catalyst in nonpolar solvents.

2. Results and Discussion

2.1. The formation of inclusion complexes of 6-O-modified CDs and oxindoles

First, we examined the inclusion ability of 6-*O*-modified CDs towards oxindole and its derivatives (Scheme 1). Figure 1 shows the ^{1}H NMR spectral changes of TIPS-β-CD upon addition of oxindole

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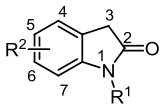


	R^1	R^2
1a	H	H
1b	H	5-Cl
1c	H	6-Cl
1d	H	5-F
1e	H	5-Br
1f	Me	H
1g	Ph	H

Scheme 1. Oxindole **1a** and its derivatives **1b-g** used in this study.

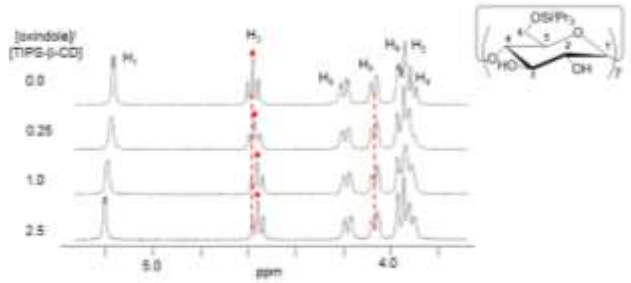
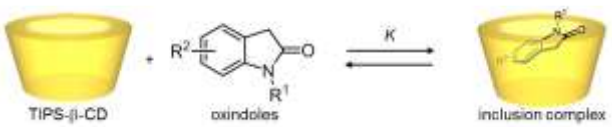


Figure 1. ^{1}H NMR spectral changes observed for TIPS-β-CD (1.0×10^{-3} M) in benzene-d_6 upon addition of oxindole **1a** at 25 °C.

1a in benzene-d_6. A shift of the H_3 proton signal of TIPS-β-CD was observed upon addition of **1a**, suggesting the formation of a TIPS-β-CD–**1a** complex in benzene-d_6. Job plots using a NMR method (see Figure S16(a), Supporting Information) showed a maximum at a [TIPS-β-CD]/[**1a**] molar ratio of 1:1, clearly indicating that TIPS-β-CD forms a 1:1 complex with **1a**. In the case of TBDMS-β-CD, similar ^{1}H NMR spectral changes upon addition of **1a** were observed (Figure S2). Table 1 summarizes the association constants between TIPS-β-CD (or TBDMS-β-CD) and oxindoles in benzene-d_6. TIPS-β-CD showed an approximately 8 times higher association constant with **1a** than TBDMS-β-CD (Table 1, entries 1 and 2). This trend is consistent with the case where pyrene was used as a guest.[5b] The inclusion complex formation between TIPS-β-CD and the oxindole derivatives was remarkably affected by the position and size of substituents on the oxindole ring of the guest. In particular, the position of the chlorine substituent on the oxindole ring had large effect on inclusion complex formation: 5-chloro-2-oxindole **1b** exhibited a 10 times higher association constant with TIPS-β-CD than 6-chloro-2-oxindole **1c**. The size of the halogen substituent at the C-5 position of oxindole also had a significant effect on inclusion complex formation (Table1, entries 3, 5, and 6). The association constant increased with a decrease in the size of the halogen substituent at the C-5 position of oxindole. Here, 5-fluoro-2-oxindole **1d** showed almost the same association constant with TIPS-β-CD as nonsubstituted oxindole **1a**, suggesting that the size of the guest molecule rather than its polarity may govern inclusion complex formation with TIPS-β-CD. Different from these oxindole derivatives, *N*-methyloxindole **1f** formed a 1:2 inclusion complex with TIPS-β-CD with a high association constant of more than 1×10^8 M^{-2}, suggesting a good spatial fit of the *N*-methyloxindole molecule within the TIPS-β-CD dimer cavity. On the other hand, *N*-phenyloxindole **1g** bearing a larger substituent group did not form an inclusion complex with TIPS-β-CD (Table 1, entry 8). These results indicate that inclusion complex formation between TIPS-β-CD and the oxindole derivatives in benzene-d_6 is mainly affected by the spatial fit of the guest molecule into the CD cavity, which is also discussed in more detail below.

Table 1. Association constants between TIPS-β-CD and oxindoles in benzene-d_6 at 25 °C.



entry	oxindoles	R^1	R^2	association constant[a] K (M^{-1})
1	**1a**	H	H	1700 ± 800
2[b]	**1a**	H	H	220 ± 30
3	**1b**	H	5-Cl	320 ± 80
4	**1c**	H	6-Cl	33 ± 10
5	**1d**	H	5-F	1800 ± 470
6	**1e**	H	5-Br	29 ± 3
7	**1f**	Me	H	$(3.1 \pm 0.9) \times 10^8$ [c]
8	**1g**	Ph	H	~ 0 [d]

[a] Determined by a NMR titration method.
[b] Association constant with TBDMS-β-CD.
[c] Association constant for 2:1 (TIPS-β-CD:**1f**) complex, in M^{-2}.
[d] No shift of ^{1}H NMR signals of TIPS-β-CD was observed.

In a cyclohexane-d_{12} solvent, an upfield shift of the H_5 signal as well as a downfield shift of the H_3 signal of TIPS-β-CD upon addition of **1a** was observed (see Figure S1, Supporting Information), and an association constant between TIPS-β-CD and **1a** estimated from the ^{1}H NMR spectral changes (1:1 stoichiometry, K = 19000 ± 7000 M^{-1}) was higher than that in the benzene-d_6 solvent. This observation shows that the inclusion complex between TIPS-β-CD and **1a** is formed in cyclohexane-d_{12} more effectively than in benzene-d_6.

The crystalline structure of an inclusion complex of TIPS-β-CD with *N*-methyloxindole **1f** in benzene was determined by an X-ray diffraction method (Figure 2). The crystalline structure shows that one *N*-methyloxindole molecule is included within the cavity of the TIPS-β-CD dimer in a similar mode to the complex between TIPS-β-CD and pyrene or (*S*)-1-(1-naphthyl)ethylamine in benzene-d_6.[5b,c] Interestingly, the carbonyl oxygen of the oxindole molecule forms hydrogen bonds with the secondary hydroxy groups of the CDs. This observation suggests that the hydrogen bonds between **1f** and TIPS-β-CD play a key role in forming a stable inclusion complex between them. Although the X-ray analyses of crystals of the inclusion complexes between TIPS-β-CD and **1a-e** in benzene have yet to be successful, the hydrogen bonds between the carbonyl oxygens of these oxindoles and the OH groups of TIPS-β-CD, which were suggested by the shifts of the OH proton signals of the CD upon addition of oxindoles (see Figure S1, Supporting Information), seem to affect their inclusion complex formation.

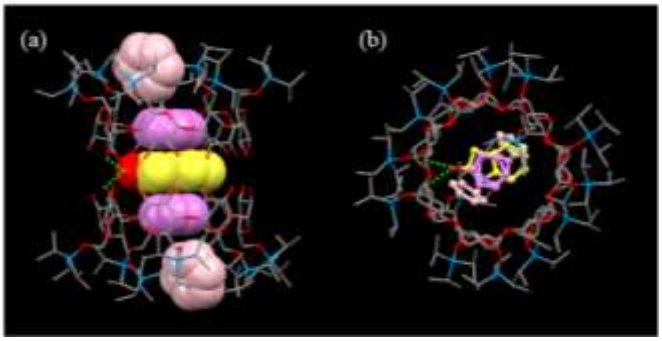


Figure 2. Crystal structure of TIPS-β-CD–**1f** inclusion complex. (a) Side view. TIPS-β-CD is shown with a cylinder representation, whereas **1f** and benzene are shown with space-filling representations. Hydrogen atoms in all compounds are omitted for clarity. (b) Top view. TIPS-β-CD is shown with a cylinder representation, whereas **1f** and benzene are shown with ball-and-stick representations. Color labels: gray, carbon in TIPS-β-CD; cyan, silicon; red, oxygen; yellow, **1f**; violet, benzene molecules interacting with **1f**; pink, benzene molecules incorporated near the C-6 position of TIPS-β-CD; green dot line, hydrogen bonds between a carbonyl oxygen of **1f** and hydroxy groups of TIPS-β-CD.

The formation of inclusion complexes between TIPS-β-CD and **1a-e** in benzene was ascertained by the NOESY measurement. In the NOESY spectra of the inclusion complexes between TIPS-β-CD and **1a**, **b** and **d** in benzene-d_6 (see Figures S17, 18 and 20, Supporting Information), cross peaks were clearly observed between the H_3 protons of TIPS-β-CD and all protons of these oxindoles whereas cross peaks between the H_5 protons of the host and the guest protons were scarcely observed. This observation indicates that these guests are incorporated within the cavity of TIPS-β-CD with their molecular planes almost perpendicular to the axis of TIPS-β-CD. In the NOESY spectra of inclusion complexes of TIPS-β-CD with **1c** and **e**, cross peaks were clearly observed between the H_3 protons of TIPS-β-CD and the H_3, H_4 and $H_{5/6}$ protons of these oxindoles, but the correlations were scarcely observed between the H_3 protons of TIPS-β-CD and the H_7 protons of these oxindoles, suggesting that these guests are incorporated within the cavity with their molecular planes almost parallel to the axis of TIPS-β-CD cavity (see Figure S19 and 21, Supporting Information). These results clearly indicate that the inclusion mode of the guest within the CD cavity depends on the size and position of substituent on the oxindole ring. Larger association constants between TIPS-β-CD and oxindoles **1a**, **b** and **d** in benzene compared to those between TIPS-β-CD and **1c** and **e** can be explained by considering the higher stability of the former inclusion complexes compared to the latter complexes due to the better spatial fit into the CD cavity. The difference in the association constant with TIPS-β-CD between **1b** and **1d**, which showed similar inclusion mode within the CD cavity, may indicate that **1d** penetrate deeper into the CD cavity than **1b**, while keeping the similar inclusion mode to **1b**. On the other hand, no correlation between the protons of TIPS-β-CD and the protons of the *N*-phenyl-oxindole **1g** was observed.

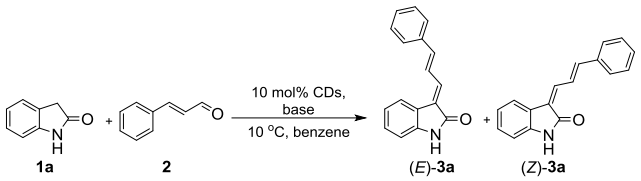
2.2. Knoevenagel condensation reaction of oxindoles with cinnamaldehyde

Next, the Knoevenagel condensation reaction of **1a** with cinnamaldehyde **2** in the presence of TIPS-β-CD or TBDMS-β-CD was examined under various reaction conditions. We used benzene, in which the inclusion complex formation between **1a** and TIPS-β-CD or TBDMS-β-CD was clearly observed, as a solvent. Cinnamaldehyde was chosen as the model reactant for the following reasons: (1) the extensively-conjugated system should increase the reaction rate by stabilizing the transition state and the product; (2) it is easy to determine the product distribution by ^{1}H NMR spectra; and (3) it forms no inclusion complex with TIPS-β-CD in benzene.

In the presence of TIPS-β-CD and TBDMS-β-CD, the *E*/*Z* selectivity of the resulting 3-alkylideneoxindole **3a** as well as the reaction rate was improved dramatically (Table 2, entries 1-3). Time course studies on the reaction of **1a** with **2** in the presence and absence of 0.1 equiv. (10 mol%) of TIPS-β-CD clearly indicated that TIPS-β-CD functions as a catalyst for this reaction. The *E*/*Z* ratio of the resulting **3a** was almost constant during the reaction. (see Figure S23).

TBDMS-α-CD and TBDMS-γ-CD, which did not form an inclusion complex with **1a** in benzene, also remarkably accelerated the reaction but exhibited no effect on the *E*/*Z* selectivity (see Table S1). This result suggests that the hydroxy groups on the CD ring participate in the large acceleration of the reaction. Actually, when the reaction was carried out in the presence of 10 mol% permethylated β-CD which has no free hydroxy group and forms no inclusion complex with oxindole in benzene, neither the large acceleration of the reaction rate nor the improvement in the *E*/*Z* selectivity was observed (see Table S1, entry 2). By screening of the

Table 2. Knoevenagel Condensation Reaction of Oxindole **1a** with Cinnamaldehyde **2** under various conditions.[a]



entry	Reaction Conditions			conv.	**3a**[b]
	CDs	base (mol %)	time (h)	(%)[b]	*E* : *Z* [c]
1	without	DBU (20)	40	62	47 : 53
2	TBDMS-β-CD	DBU (20)	4	99	71 : 29
3	TIPS-β-CD	DBU (20)	2	99	78 : 22
4	TIPS-β-CD	NEt_3 (50)	40	~ 0	-
5	TIPS-β-CD	DIPEA (50)	40	~ 0	-
6	TIPS-β-CD	pyrrolidine (20)	40	44	45 : 55
7	TIPS-β-CD	^{t}BuOK (50)	3	99	82 : 18
8	without	^{t}BuOK (50)	3	99	67 : 33
9[d]	TIPS-β-CD	^{t}BuOK (50)	2	99	93 : 7
10[e]	TIPS-β-CD	^{t}BuOK (50)	12	99	76 : 24

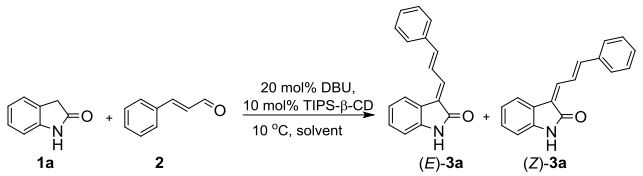
[a] Reaction conditions: **1a** (20 μmol), **2** (24 μmol), CDs (2 μmol), base (4 or 10 μmol), 2 mL benzene, at 10 °C.
[b] The both products (*E*)- and (*Z*)-**3a** form no inclusion complex with TIPS-β-CD in benzene.
[c] Determined by ^{1}H NMR.
[d] In the presence of 0.4 μmol TIPS-β-CD (2 mol% against **1a**).
[e] At rt.

base, it became clear that in the presence of weak bases such as NEt_3 (p*K*a = 9.0)[11] and *N*,*N*-diisopropylethylamine (DIPEA p*K*a = 8.5)[11], no reaction occurred (Table 2, entries 4 and 5). On the other hand, the reaction proceeded well in the presence of a stronger base such as DBU (p*K*a = 13.9)[11] (Table 2, entry 3). When ^{t}BuOK (p*K*a ≈ 18) was used as a base, the reaction proceeded faster even in the absence of TIPS-β-CD. The addition of TIPS-β-CD (10 mol% against **1a**) in this reaction system clearly increased the *E*/*Z* selectivity (Table 2, entries 7 and 8). A decrease in the addition amount of TIPS-β-CD to 2 mol% further increased the *E*/*Z* selectivity (Table 2, entry 9). An alkoxide ion generated by the reaction of the OH group of TIPS-β-CD with some portion of ^{t}BuOK may participate in the increase in the *E*/*Z* selectivity. When polar solvents such as chloroform, THF and methanol were used, the formation of TIPS-β-CD–**1a** complex was barely observed spectroscopically, and neither the reaction rate nor the *E*/*Z* selectivity was appreciably enhanced in the presence of TIPS-β-CD (Table 3, entries 3-5). This is contrary to the case of benzene solvent where a remarkable improvement in the reaction rate and the *E*/*Z* selectivity by TIPS-β-CD was observed. These results indicate that benzene is the optimal solvent for this reaction from the viewpoints of the reaction rate and *E*/*Z* selectivity (Table 3, entry 1)

Based on these results, the reactions of various oxindole derivatives **1b-g** with cinnamaldehyde were examined in the presence of TIPS-β-CD using benzene as the solvent and DBU as the base (Table 4). The reactions of *N*-unsubstituted oxindoles **1a-e** with cinnamaldehyde in the presence of TIPS-β-CD afforded the corresponding (*E*)-3-alkylideneoxindoles with enhanced reaction rates and moderate to good stereoselectivity. In particular, when **1c** was used as the substrate, a large increase in the *E*/*Z* selectivity by TIPS-β-CD was observed; consequently, this reaction gave the (*E*)-isomer in 87 % yield. Although there is no clear relationship between the *E*/*Z* selectivity and the association constant between TIPS-β-CD and the oxindole derivative, it appears that a small difference in the inclusion mode of the oxindole derivative within the TIPS-β-CD cavity may largely affect the *E*/*Z* selectivity. Interestingly, in the reaction of **1f** and cinnamaldehyde, the presence of TIPS-β-CD caused a change in the product selectivity from (*E*)-selectivity to (*Z*)-

selectivity. The 2:1 inclusion complex formed between TIPS-β-CD and **1f** may participate in the (*Z*)-selective reaction. As expected, when the reaction of cinnamaldehyde with **1g**, which formed no complex with TIPS-β-CD, was carried out, the *E*/*Z* selectivity was not changed by the addition of TIPS-β-CD (Table 4, entry 7).

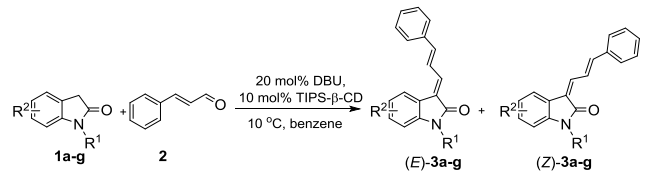
Table 3. Knoevenagel Condensation of Oxindole **1a** with Cinnamaldehyde **2** in Various Solvents.[a]



entry	solvent	time (h)[b]	conv. (%)[b,c]	*E* : *Z* [b,c]
1	benzene	2 (40)	99 (62)	78 : 22 (47 : 53)
2	cyclohexane	4 (12)	99 (99)	77 : 23 (71 : 29)
3	chloroform	20 (40)	82 (42)	78 : 22 (70 : 30)
4	THF	20 (40)	75 (55)	65 : 35 (52 : 48)
5	methanol	1 (1)	99 (99)	51 : 49 (51 : 49)

[a] Reaction conditions: **1a** (20 μmol), **2** (24 μmol), CDs (2 μmol), DBU (4 μmol), 2 mL solvent, at 10 °C.
[b] The values in parentheses are reaction time, conversion, and *E*/*Z* ratio of the product in the absence of TIPS-β-CD respectively.
[c] Determined by ^{1}H NMR.

Table 4. Knoevenagel Condensation of Oxindoles **1a-g** with Cinnamaldehyde **2** in the Presence of TIPS-β-CD.[a]



entry	oxindoles	time[b] (h)	conv. (%)[b,c]	product distribution[b,c] *E* : *Z*
1	**1a**	3 (40)	99 (62)	78 : 22 (47 : 53)
2	**1b**	2 (40)	99 (94)	65 : 35 (44 : 56)
3	**1c**	5 (40)	99 (80)	87 : 13 (62 : 38)
4	**1d**	3 (40)	99 (85)	56 : 44 (35 : 65)
5	**1e**	12 (40)	99 (64)	72 : 28 (52 : 48)
6	**1f**	20 (20)	95 (65)	39 : 61 (71 : 29)
7	**1g**	20 (20)	85 (53)	62 : 38 (62 : 38)

[a] Reaction conditions: **1a-g** (20 μmol), **2** (24 μmol), CDs (2 μmol), DBU (4 μmol), 2 mL benzene, at 10 °C.
[b] The values in parentheses are reaction time, conversion, and *E*/*Z* ratio of the product in the absence of TIPS-β-CD respectively.
[c] Determined by ^{1}H-NMR.

On the basis of these results, we can speculate that the enhancement of *E*-isomer selectivity by TIPS-β-CD and TBDMS-β-CD is due to the change in steric hindrance surrounding the oxindole molecules, which is caused by their incorporation within the cavities of the CD hosts. The hydrogen bondings between the carbonyl oxygen of incorporated oxindoles and the OH groups of the CD host as well as the incorporation of oxindoles within the CD cavity may produce larger steric hindrance on the carbonyl group side at the C-3 position of oxindoles than on the aromatic group side. Besides, the rate acceleration of the reactions of **1a-e** with **2** by the CDs may be explained by considering the acceleration of nucleophilic addition of the oxindole carbanions to the carbonyl group of **2** and the dehydration of the resulting alcohol intermediates by the CDs. The addition of the oxindole carbanion to **2** would be enhanced by bringing these substrates close together through the hydrogen bonds between OH groups of CD and carbonyl oxygen of **2** as well as the inclusion of oxindole molecules within the CD cavity. On the other hand, the hydrogen bonds between the OH groups of the CDs and the alcohol intermediates would accelerate the elimination of water from the alcohols to give 3-alkylideneoxindoles.[12] Thus, the 6-*O*-modified CDs can successfully function as a catalyst for the Knoevenagel condensation reaction of oxindoles and aldehydes.

3. Conclusion

In summary, we have demonstrated that TIPS-β-CD and TBDMS-β-CD effectively form inclusion complexes with oxindole and its derivatives in nonpolar solvents. The inclusion behavior of these 6-*O*-modified CDs was remarkably affected by the position and size of substituents on the oxindole ring of the guest. Furthermore, we showed that a facile synthesis of (*E*)-3-alkylideneoxindoles via stereoselective Knoevenagel condensation reaction of oxindoles with cinnamaldehyde was successfully carried out by using TIPS-β-CD as a supramolecular catalyst in nonpolar solvents. In particular, the reaction of oxindole with cinnamaldehyde in the presence of TIPS-β-CD in benzene proceeded with high *E*/*Z* selectivity. This reaction can be applied to 5- and 6-substituted oxindoles as well as to intact oxindole, thus providing structurally diverse 3-alkylideneoxindoles from readily available starting materials. To the best of our knowledge, this is the first example of stereocontrolled reaction using CD derivatives as a supramolecular catalyst in nonpolar solvents. Further studies on the application of CDs as a supramolecular catalyst are now in progress in our laboratory.

4. Experimental Section

4.1. Determination of association constants by NMR spectroscopy.

In complexation of heptakis(6-*O*-triisopropylsilyl)-β-cyclodextrin (TIPS-β-CD) host with oxindole 1a and its derivatives 1b-e in benzene-d_6 or cyclohexane-d_{12} at 25 °C, a solution of host molecule (600 μL, 1.0 mM) was titrated in a NMR tube with increasing amounts of the guest stock solution. The titration curves (changes in the chemical shift of the host protons (Δδ) against the guest/host concentration ratio) were analyzed by a non-linear least-squares curve fitting method to generate association constants (*K*) of the host-guest complexes. In complexation of TIPS-β-CD (host) with *N*-methyloxindole **1f** (guest) in benzene-d_6 at 25 °C, the exchange of complexed and uncomplexed hosts was slow on the NMR time scale. Thus, the association constant (*K*) was determined by using integration of the NMR signals for complexed and uncomplexed hosts.

4.2. Experimental procedure for Job plots.

In complexation of TIPS-β-CD (host) with oxindoles (guest) in benzene-d_6, Job plots were carried out at 25 °C by monitoring the changes in the chemical shift of the host protons (Δδ) in a series of solutions with varying host/guest ratios but with the total concentration of the host and guest kept constant, or monitoring the changes in the integral values of the proton signals of free and complexing hosts in a series of solutions with varying host/guest ratios but the total concentration of the host and the guest kept constant. In the former case, the relative concentration of the host-guest complex estimated from the Δδ·[host] value was plotted against {[host]/([host] + [guest])}. In the latter case, the concentration of the host-guest complex estimated from the total host concentration and the integral ratio of the proton signal of complexing host to that of total host was plotted against {[host]/([host] + [guest])}.

4.3. Knoevenagel condensation reaction of oxindoles with cinnamaldehyde.

A mixture of oxindoles (2.0×10^{-2} mmol), cinnamaldehyde, a base and a prescribed amount of TIPS-β-CD was stirred in solvents (2 mL) at 10 °C. After the removal of solvent *in vacuo*, the residue was analyzed by ^{1}H-NMR to determine the reaction conversion and product distributions. The product was isolated by silica gel column chromatography with a hexane/ethyl acetate (4:1, v/v) eluent.

4.4. Analytics.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL NMR system (400 MHz) in DMSO-d_6 and the chemical shifts in ppm refer to DMSO (δ_H 2.50, δ_C 39.52) as an internal standard. The following abbreviations were used for chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. NMR signal assignments were based on additional 2D-NMR spectroscopy (e.g., COSY, NOESY, HSQC and HMBC).

4.5. Analytical data of the products

4.5.1. (Z)-3-(3'-Phenylallylidene)indolin-2-one ***((Z)-3a)****.* ^{1}H NMR (DMSO-d_6) δ 6.81 (d, *J* = 7.7 Hz, 1 H), 6.96 (dd, *J* = 7.3, 7.3 Hz, 1 H), 7.18 (dd, *J* = 7.3, 7.7 Hz, 1 H), 7.18 (d, *J* = 15.8 Hz, 1 H), 7.38 (d, *J* = 7.3 Hz, 2 H), 7.41–7.47 (m, 2 H), 7.57–7.60 (m, 4 H), 8.48 (dd, *J* = 11.3, 15.8 Hz, 1 H), 10.5 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 109.5 (d, 7-Ar), 120.0 (d, 5-Ar), 121.1 (s, Ar), 123.7 (d, 9-CH=CH), 124.0 (d, 4-Ar), 125.4 (s, C=CH), 127.4 (d, Ar), 129.0 (d, Ar), 129.1 (d, 6-Ar), 129.4 (d, Ar), 135.5 (d, 8-CH=C), 136.2 (s, Ar), 141.1 (s, Ar), 142.2 (d, 10-CH=CH), 168.3 (s, C=O). IR : 1686.11 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{13}NO$: 247.0997, found 247.0996.

4.5.2. (E)-3-(3'-Phenylallylidene)indolin-2-one ***((E)-3a)****.* ^{1}H NMR (DMSO-d_6) δ 6.86 (d, *J* = 7.7 Hz, 1 H), 7.01 (dd, *J* = 7.7, 7.7 Hz, 1 H), 7.23 (dd, *J* = 7.7, 7.7 Hz, 1 H), 7.30 (d, *J* = 12.2 Hz, 1 H), 7.35–7.47 (m, 4 H), 7.57–7.60 (m, 4 H), 7.75 (dd, *J* = 12.2, 14.9 Hz, 1 H), 7.79–7.82 (m, 2 H), 7.99 (d, *J* = 7.7 Hz, 1 H), 10.5 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 109.8 (d, 7-Ar), 121.5 (d, 5-Ar), 122.1 (s, Ar), 123.3 (d, 9-CH=CH), 124.2 (d, 4-Ar), 125.8 (s, C=CH), 128.1 (d, Ar), 128.9 (d, Ar), 129.2 (d, 6-Ar), 129.7 (d, Ar), 134.5 (d, 8-CH=C), 135.9 (s, Ar), 142.2 (s, Ar), 144.5 (d, 10-CH=CH), 168.9 (s, C=O). IR : 1698.19 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{13}NO$: 247.0997, found 247.0996.

4.5.3. (Z)-3-(3'-Phenylallylidene)-5-chloro-indolin-2-one ***((Z)-3b)****.* ^{1}H NMR (DMSO-d_6) δ 6.81(d, *J* = 8.1 Hz, 1 H), 7.17–7.22 (m, 2 H), 7.37–7.46 (m, 3 H), 7.60 (d, *J* = 13.3 Hz, 2 H), 7.69–7.72 (m, 2 H), 8.45 (dd, *J* = 11.3, 15.8 Hz, 1 H), 10.7 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 110.9, 120.0, 123.8, 124.4, 125.4, 125.5, 127.6, 128.3, 129.1, 129.7, 136.0, 137.5, 139.7, 143.4, 168.1 (s, C=O). IR : 1704.13 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{12}ClNO$: 281.0667, found 281.0606.

4.5.4. (E) -3-(3'-Phenylallylidene)-5-chloro-indolin-2-one ***((E)-3b)****.* ^{1}H NMR (DMSO-d_6) δ 6.85 (d, *J* = 8.6 Hz, 1 H), 7.27 (dd, *J* = 2.2, 8.2 Hz, 1 H), 7.36 (d, *J* = 12.2 Hz, 1 H), 7.39–7.48 (m, 4 H), 7.75 (dd, *J* = 12.2, 15.4 Hz, 1 H), 7.86 (d, *J* = 7.2 Hz, 2 H), 8.07 (d, *J* = 2.2 Hz, 1 H), 10.6 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 110.9, 123.2, 123.6, 123.6, 124.5, 125.7, 128.5, 128.7, 128.9, 129.9, 135.8, 136.6, 140.9, 146.3, 168.7. IR : 1702.52 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{12}ClNO$: 281.0667, found 281.0611.

4.5.5. (Z)-3-(3'-Phenylallylidene)-6-chloro-indolin-2-one ***((Z)-3c)****.* ^{1}H NMR (DMSO-d_6) δ 6.83 (d, *J* = 1.4 Hz, 1 H), 7.01 (dd, *J* = 1.4, 8.2 Hz, 1 H), 7.21 (d, *J* = 15.4 Hz, 1 H), 7.31–7.47 (m, 3 H), 7.58–7.61 (m, 3 H), 7.62 (d, *J* = 11.3 Hz, 1 H), 8.48 (dd, *J* = 11.3, 15.4 Hz, 1 H), 10.7 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 109.5, 120.9, 121.4, 122.6, 123.8, 124.2, 127.5, 129.1, 129.6, 133.0, 136.1, 136.6, 142.2, 143.0, 168.2. IR : 1683.96 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{12}ClNO$: 281.0667, found 281.0606.

4.5.6. (E)-3-(3'-Phenylallylidene)-6-chloro-indolin-2-one ***((E)-3c)****.* ^{1}H NMR (DMSO-d_6) δ 6.87 (d, *J* = 1.8 Hz, 1H), 7.03 (dd, *J* = 1.8, 8.1 Hz, 1 H), 7.32–7.46 (m, 5 H), 7.71 (dd, *J* = 12.7, 15.4 Hz, 1 H), 7.80–7.82 (m, 2 H), 8.02 (d, *J* = 8.7 Hz, 1 H), 10.6 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 109.7, 121.0, 121.0, 123.1, 124.6, 125.4, 128.2, 128.9, 129.8, 133.3, 135.4, 135.8, 143.5, 145.4, 168.8. IR : 1706.91 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{12}ClNO$: 281.0667, found 281.0604.

4.5.7. (Z)-3-(3'-Phenylallylidene)-5-fluoro-indolin-2-one ***((Z)-3d)****.* ^{1}H NMR (DMSO-d_6) δ 6.77–6.80 (m, 1 H), 6.98–7.04 (m, 1 H), 7.12 (d, *J* = 15.8 Hz, 1 H), 7.34–7.52 (m, 6 H), 7.61 (d, *J* = 7.3 Hz, 2 H), 7.66 (d, *J* = 11.3 Hz, 1 H), 8.46 (dd, *J* = 11.3, 15.4 Hz, 1 H), 10.5 (s, 1 H). IR : 1702.41 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{12}FNO$: 265.0903, found 265.0906.

4.5.8. (E)-3-(3'-Phenylallylidene)-5-fluoro-indolin-2-one ***((E)-3d)****.* ^{1}H NMR (DMSO-d_6) δ 6.81–6.85 (m, 1 H), 7.04–7.09 (m, 1 H), 7.33–7.70 (m, 4 H), 7.75 (dd, *J* = 12.2, 14.9 Hz, 1 H), 7.88 (d, *J* = 6.8 Hz, 2 H), 7.94–7.97 (m, 1 H), 10.5 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 110.2 (*J* = 7.7 Hz), 111.4 (*J* = 25.8 Hz), 115.3 (*J* = 23.8 Hz), 122.9 (*J* = 8.6 Hz), 123.1, 125.3 (*J* = 2.9 Hz), 128.4, 128.9, 129.9, 135.8, 136.2, 138.4 (*J* = 1.9 Hz), 146.0, 158.0 (*J* = 234.6 Hz), 168.9. IR : 1704.53 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{12}FNO$: 265.0903, found 265.0902.

4.5.9. (E)-3-(3'-Phenylallylidene)-5-bromo-indolin-2-one ***((E)-3e)****.* ^{1}H NMR (DMSO-d_6) δ 6.81 (d, *J* = 8.2 Hz, 1 H), 7.34–7.47 (m, 7 H), 7.73 (dd, *J* = 12.7, 14.5 Hz, 1 H), 7.85 (d, *J* = 7.3 Hz, 1 H), 8.14 (s, 1 H), 10.6 (s, 1 H). ^{13}C NMR (DMSO-d_6) δ 111.5, 113.4, 123.2, 124.1, 124.4, 126.2, 128.5, 128.9, 129.9, 131.6, 135.8, 136.6, 141.3, 146.3, 168.6. IR : 1702.93 (C=O). HRMS (EI) *m/z* calcd. for $C_{17}H_{12}BrNO$: 325.0102, found 325.0098.

4.5.10. (Z)- N-Methyl-3-(3'-phenylallylidene)-indolin-2-one ***((Z)-3f)****.* ^{1}H NMR (DMSO-d_6) δ 3.18 (s, 3 H), 6.98 (d, *J* = 8.2 Hz, 1 H), 7.03 (dd, *J* = 6.8, 7.7 Hz, 1 H), 7.21 (d, *J* = 15.8 Hz, 1 H), 7.28 (dd, *J* = 7.7, 8.2 Hz, 1 H), 7.39 (d, *J* = 6.8 Hz, 1 H), 7.43–7.46 (m, 2 H), 7.58–7.61 (m, 3 H), 7.64 (d, *J* = 4.6 Hz, 1H), 8.50 (dd, *J* = 12.6, 15.9 Hz, 1 H). ^{13}C NMR (DMSO-d_6) δ 25.6, 108.5, 119.7, 121.7, 122.7, 123.9, 124.4, 127.4, 129.0, 129.1, 129.5, 135.9, 136.2, 142.2, 142.6, 166.4. IR : 1705.13 (C=O). HRMS (EI) *m/z* calcd. for $C_{18}H_{15}NO$: 261.1154, found 261.1150.

4.5.11. (E)-N-Methyl-3-(3'-phenylallylidene)-indolin-2-one ***((E)-3f)****.* ^{1}H NMR (DMSO-d_6) δ 3.19 (s, 3 H), 7.04 (d, *J* = 7.7 Hz), 7.09 (dd, *J* = 7.7, 7.7 Hz), 7.33 (dd, *J* = 7.7, 7.7 Hz), 7.35–7.47 (m, 5 H), 7.73–7.82 (m, 3 H), 8.04 (d, *J* = 7.7 Hz). ^{13}C NMR (DMSO-d_6) δ 25.9, 108.5, 121.3, 122.0, 123.2, 123.9, 124.8, 128.1, 128.9, 129.2, 129.8, 135.1, 135.9, 143.3, 145.0, 167.4. IR : 1698.44 (C=O). HRMS (EI) *m/z* calcd. for $C_{18}H_{15}NO$: 261.1154, found 261.1148.

4.5.12. (E)-N-Phenyl-3-(3'-phenylallylidene)-indolin-2-one ***((E)-3g)****.* ^{1}H NMR (DMSO-d_6) δ 6.79 (d, *J* = 7.7 Hz, 1 H), 7.16 (dd, *J* = 7.7, 7.7 Hz, 1 H), 7.28 (dd, *J* = 7.7, 7.7 Hz, 1 H), 7.40–7.50 (m, 7 H), 7.51 (s, 1 H), 7.56–7.61 (m, 2 H), 7.82–7.89 (m, 3 H), 8.17 (d, *J* = 7.7 Hz, 1 H). ^{13}C NMR (DMSO-d_6) δ 109.0, 121.5, 122.7, 123.2, 124.2, 124.4, 126.9, 127.9, 128.3, 129.0, 129.2, 129.6, 130.0, 134.4, 135.8, 136.2, 142.8, 145.8, 166.9. IR : 1699.82 (C=O). HRMS (EI) *m/z* calcd. for $C_{23}H_{17}NO$: 323.1310, found 323.1313.

4.6. Crystal structure determination.

X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å). Direct methods (SIR-2002) were used to determine the structure.[13] All calculations were performed with the observed reflections [$I > 2\sigma(I)$] using the CrystalStructure crystallographic software package,[14] except for refinement, which was performed using SHELXL-97.[15] All of the non-hydrogen atoms were refined with anisotropic displacement parameters except carbon atoms of benzene molecules placed out of the TIPS-β-CD, which were refined isotropically because of their relatively high thermal parameters. Hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. *N*-methyloxindole molecule within the TIPS-β-CD dimer was refined over two sites with occupancy ratios of 0.55 and 0.45. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no.CCDC-924901 (TIPS-β-CD–**1f** inclusion complex). Copies of the data can be obtained free of charge on application to CCDC,12 Union Road, Cambridge CB2 1EZ, UK (fax: þ44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary Material

Supplementary data associated with this article can be found, in the online version, at.

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