Multicenter Homogeneous Dendritic Catalysts: The Higher the Generation, the Better the Reactivity and Selectivity? – A Comparative Study of the Catalytic Efficiency of Dendrimeric [1,1′-Binaphthalene]-2,2′-diol-Derived Catalysts

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

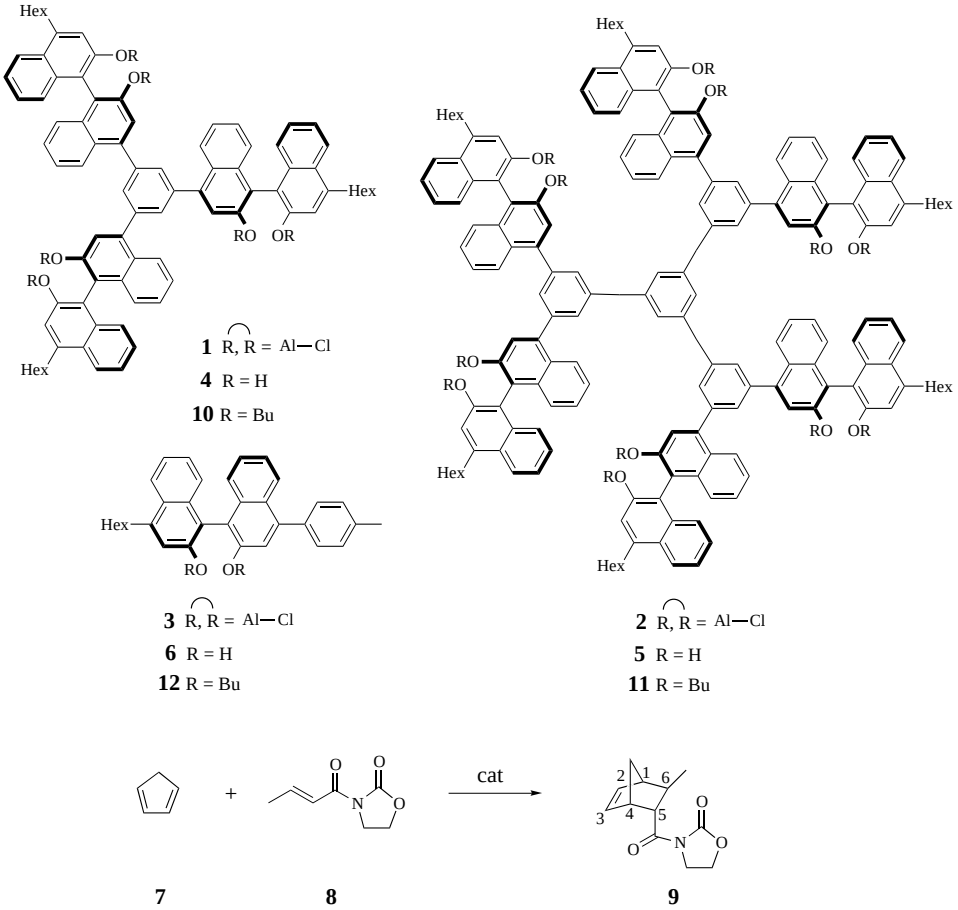
The G0 and G1 generations of optically active, multicenter 1,1′-binaphthalene-based dendritic ligands **4** and **5** constructed on a rigid oligo(arylene) framework were prepared by divergent synthesis. Their corresponding aluminum complexes **1** and **2**, respectively, were shown to possess slightly better reactivity and enantioselectivity than those of a monomeric 1,1′-binaphthalene catalyst **3** in the *Diels–Alder* reaction between cyclopentadiene and 3-[(*E*)-but-2-enoyl]-oxazolidin-2-one.

1. Introduction. – The design of soluble dendrimeric catalysts [1] having multiple catalytic centers has recently become a topic of interest. There are several advantages associated with the use of such soluble catalytic systems as compared to their monomeric counterparts. First, they enable the catalyzed reactions to be carried out under homogeneous conditions with optimal efficiency, and, after the reaction, catalyst recovery and/or product isolation can be simplified through nano-filtration [1e,f] or precipitation [1d,g]. Second, the presence of multiple catalytic centers in close vicinity may sometimes result in positive cooperativity with enhanced catalyst reactivity [1a,d,g,h] and may even offer better reaction selectivity [1j]. Third, transition metal-based dendrimeric catalysts are found to possess better thermal stability than corresponding monomeric ones [1d,g]. Despite these developments, a comparative study on the effect of degree of oligomerization (*i.e.*, dendrimer generation) on catalyst reactivity and selectivity is still lacking. Herein, we wish to report our findings based on the study of multicenter, homogeneous, optically active [1,1′-binaphthalene]-2,2′-diol-derived (BINOL) aluminum-based dendrimeric catalysts **1** and **2**, and their monomeric analogue **3**. Binaphthol-based dendrimers with a single binaphthol unit at the dendritic core had been reported before [2].

Earlier investigations [1c,f,i] indicated that the length and flexibility of the branch and brancher units of the dendrimer skeleton had an important effect on the overall performance of the catalyst. In this study, we would like to evaluate the dendrimeric effect on catalyst properties of multicenter, structurally rigid dendritic catalysts. Such

[1]) An '*Areas of Excellence Scheme*' established under the University Grants Committee of the Hong Kong SAR.

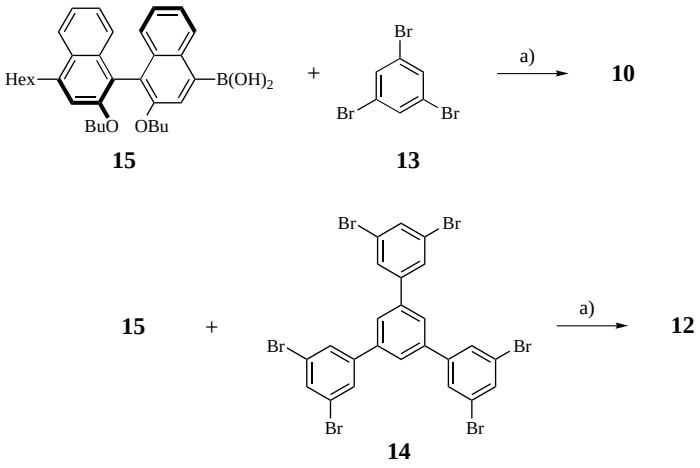
compounds were prepared by attaching BINOL catalytic units on the surface of a conformationally restrained oligo(arylene) dendritic skeleton [3]. Modeling studies suggested that the catalytic centers had relatively large separation and, therefore, their intramolecular interactions can be avoided. Such a catalyst design would, therefore, enable one to evaluate the dendrimeric effect without the interference of such intramolecular catalytic-site interactions. Hexyl groups were grafted onto the surface of the dendrimers to improve their solubility property in order to ensure that the catalyzed reactions were conducted under homogeneous conditions. The target aluminum-based catalysts **1**–**3** were generated *in situ* by mixing Me_2AlCl with the corresponding metal-free ligands **4**–**6** [4]. The catalyzed reaction chosen in this study was the *Diels–Alder* reaction between cyclopenta-1,3-diene (Cp) **7** and 3-[(*E*)-but-2-enoyl]oxazolidin-2-one (**8**) [5].



2. Synthesis. – Initially, the binaphthol groups in the ligands **4**–**6** were protected as their corresponding butyl ethers (*i.e.*, **10**–**12**). The divergent synthetic approach was employed for their synthesis [6]. Conceptually, this method involved the attachment of

multiple copies of a BINOL derivative to the surface of a polyfunctional oligo(arylene) dendritic core. A survey of the literature suggested 1,3,5-tribromobenzene (**13**) and 1,3,5-tris-(3,5-dibromophenyl)benzene (**14**) [3] were the ideal central core units. The chiral building block was the (*S*)-binaphthol-derived boronic acid **15** reported by us in another study [7]. Hence, commercially available 1,3,5-tribromobenzene (**13**) and the boronic acid **15** were reacted under *Suzuki* coupling conditions (2M Na_2CO_3, $Pd(PPh_3)_4$, EtOH/toluene, 80°) [8] to give the G0 dendrimer **10** G0–$(OBu)_6$ as a glassy solid in 73% yield (*Scheme 1*) after chromatographic purification. In a similar manner, treatment of **14** with the boronic acid **15** provided the G1 dendrimer **12** (G1–$(OBu)_{12}$ in 47% yield. No other defective side products due to incomplete coupling were detected.

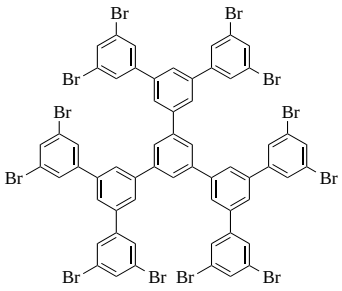
Scheme 1



a) Na_2CO_3, $Pd(PPh_3)_4$, EtOH/toluene.

Attempts were also made to prepare the higher-generation G2 dendritic ether G2–$(OBu)_{24}$. As the corresponding dodecabromo core **16** was not immediately available, an alternative route involving coupling between a bis(binaphthyl) benzene-boronic acid **17** and the hexabromide **14** was tried. Thus, *Suzuki* coupling of the boronic acid **15** with 3,5-dibromo-1-(trimethylsilyl)benzene (**18**) [9] afforded a bis(binaphthyl) dendron **19** in 52% yield (*Scheme 2*). Unfortunately, despite numerous attempts, reaction of **19** with various iodinating agents (*e.g.*, iodine monochloride) failed to produce the corresponding aryl iodide **20**, which was a key intermediate required for the preparation of the boronic acid **17**. In the end, we decided not to pursue the synthesis of the G2 analogue G2–$(OBu)_{24}$.

A monomeric BINOL analogue **6** was required as a reference standard to compare the catalytic and chiroptical properties of the dendritic catalysts. To minimize the variation of steric and electronic factors, the model compound **6** chosen had an hexyl chain at C(4) and a tolyl group at C(4′). This compound as well as its dibutoxy analogue **12** have also been reported earlier [7].



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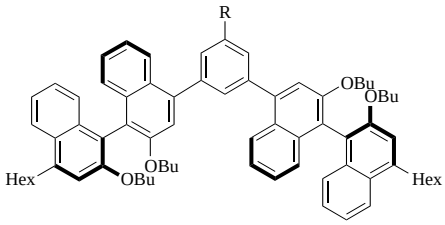
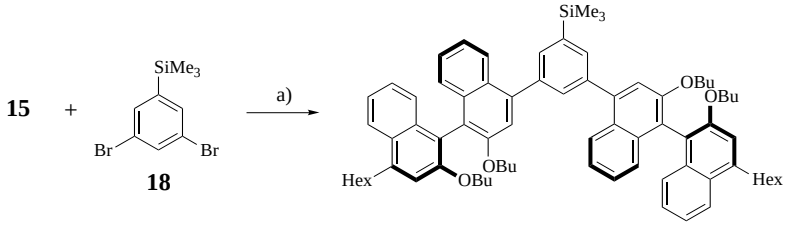


17 R = $B(OH)_2$
20 R = I

Scheme 2



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19

a) Na_2CO_3, $Pd(PPh_3)_4$, EtOH/toluene.

The Bu protecting groups of the dendrimeric ethers **10** and **11** were then dismantled by reaction with BBr_3 in CH_2Cl_2. In this manner, the G0 ligand **4** (G0−$(OH)_6$) and G1 ligand **5** (G1−$(OH)_{12}$) were obtained both in 99% yields, respectively, from their corresponding ethers after chromatographic purification.

3. Characterization. – 3.1. *^{1}H-NMR Spectroscopy.* The G0−$(OBn)_6$ dendrimer **10** contains three chiral (*S*)-binaphthyl ether units and has a pseudo C_3 symmetry. One of the characteristic signals in the ^{1}H-NMR spectrum of compound **10** was a sharp *singlet* (δ 8.03) attributed to the three magnetically equivalent aromatic H-atoms of the central core (*Fig. 1*). The chemical-shift value was consistent with that of the G1 oligo(arylene) dendrimer described by *Miller et al.* [3]. Moreover, the relative integrations of the various regions were consistent with the symmetrically structure of G0−$(OBn)_6$ **10**.

For the first-generation dendritic ether G1−$(OBn)_{12}$ **11**, the aromatic H-atom signals due to the oligo(arylene) skeleton were distinguishable and assignable in its ^{1}H-NMR spectrum. Thus, the three equivalent aryl H-atoms of the core ring appeared as a *singlet* (δ 8.26), while the H-atoms of the three internal aromatic rings were nonequivalent and appeared as two *singlets* (δ 7.91 and 8.15) with a relative integration of 1:2. Again, the relative integration of the central aryl H-atoms matched well to those of the H-atoms of the Bu hexyl groups.

When the ^{1}H-NMR spectra of the dendritic BINOL ligands **4** and **5** were compared to those of the butoxy analogs **10** and **11**, the ^{1}H signals due to the Bu groups were

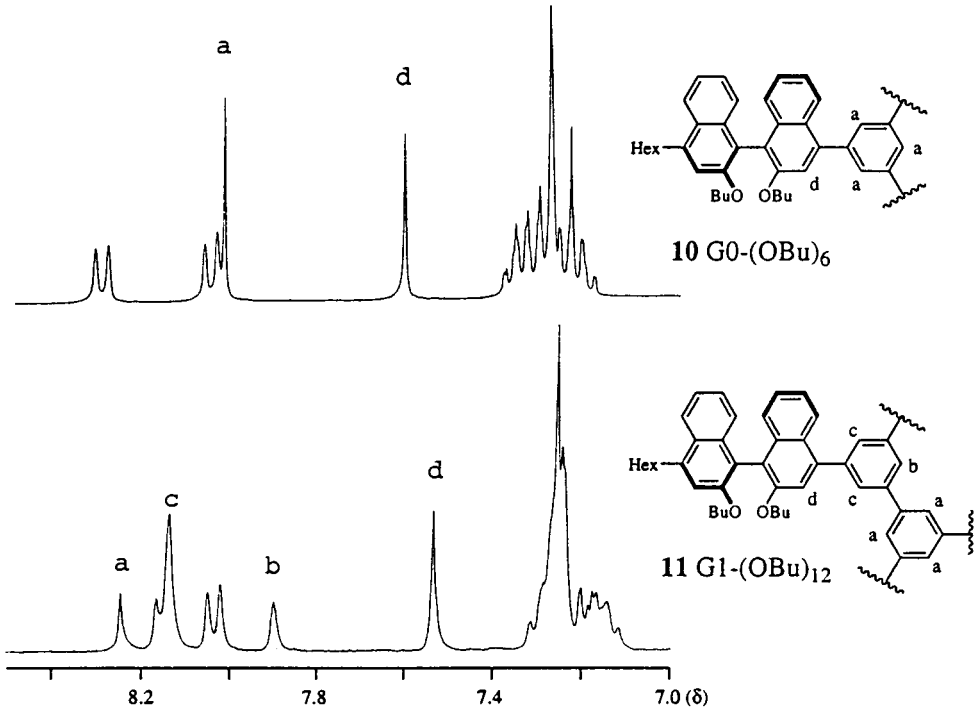

Fig. 1. *The aromatic region of the* ^{1}*H-NMR spectra of G0−(OBu)*$_6$ (**10**) *and G1−(OBu)*$_{12}$ (**11**).

absent, thus providing an evidence for the complete deprotection. Interestingly, the phenolic H-atoms of the binaphthol units in these dendritic ligands were non-equivalent and appeared as two sharp *singlets* at δ 5.10 and 5.17 for both compounds. In sharp contrast to the observed diastereomerism due to the newly formed chiral axis found in structurally similar binaphthol oligomers [7], this dendritic series of compounds apparently did not exist as a mixture of diastereoisomers, as all the ^{1}H-NMR signals were well-resolved and had little sign of signal multiplicity. Thus, it appeared that, in all these dendrimers and dendritic ligands, the C−C bonds connecting the aromatic rings were freely rotating at room temperature.

3.2. *Gel-Permeation Chromatography.* The purities of the products were examined by gel-permeation chromatography (GPC). The GPC chromatograms of each dendrimer exhibited a sharp peak with decreasing retention time from G0−(OH)$_6$ (**4**), G0−(OBu)$_6$ (**10**), G1−(OH)$_{12}$ (**5**), and G1−(OBu)$_{12}$ (**11**; *Fig. 2*). Based on polystyrenes as the calibration standards, the estimated molecular weights of these dendrimer species from GPC measurement were usually smaller than their theoretical values, an observation that was consistent with the compact nature of the dendritic structures. The mass-spectral data of these dendritic species were also in good agreement with the proposed structures.

3.3. *Chiroptical Properties.* The chiroptical properties of all dendrimers, **4**, **5**, **10**, **11**, and **19**, and the model compounds **6** and **12** were examined by polarimetry (*Table 1*).

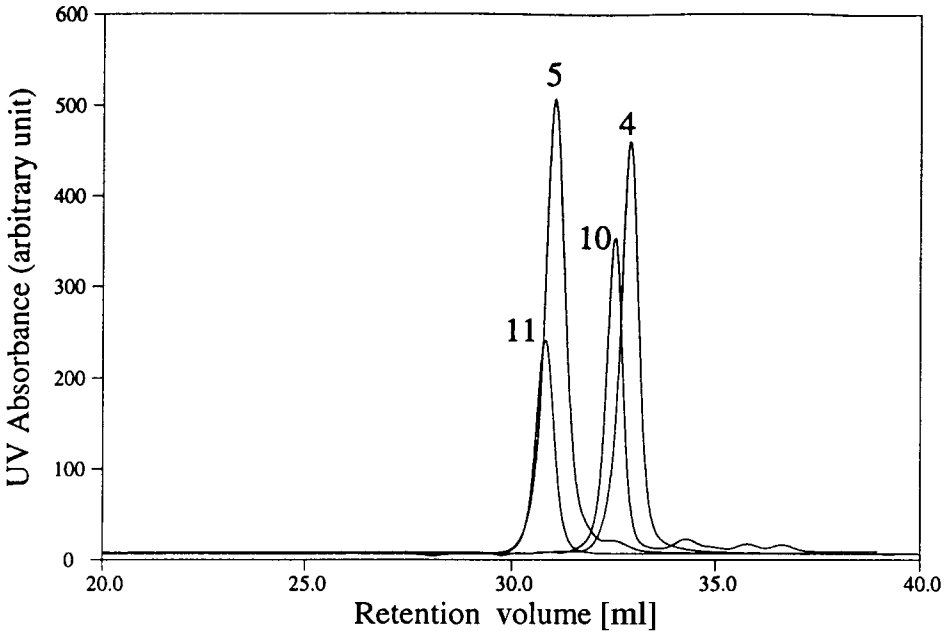

Fig. 2. *GPC Chromatogram of G0–(OBu)$_6$* (**10**), *G1–(OBu)$_{12}$* (**11**), *G0–(OH)$_6$* (**4**), *and G1–(OH)$_{12}$* (**5**)

Table 1. *Optical-Rotation Values of the* O-*Bu Derivatives* **10**, **11**, **12**, *and* **19**, *and of the Binaphthols* **4**, **5**, *and* **6**

Compound	No. of BINOL subunits	$[\alpha]_D^{25}$ (in $CHCl_3$)	Molar rotation	Molar rotation/BINOL
12	1	– 55.2 ($c = 2.17$)[a])	– 316	– 316
19	2	– 63.4 ($c = 0.79$)	– 704	– 352
10	3	– 86.7 ($c = 0.63$)	– 1316	– 439
11	6	– 71.8 ($c = 0.63$)	– 2288	– 381
6	1	– 30.4 ($c = 0.39$)[a])	– 140	– 140
4	3	– 56.8 ($c = 0.81$)	– 671	– 224
5	6	– 46.7 ($c = 0.33$)	– 1174	– 196

[a]) Data from [7].

The molar rotations of the *O*-Bu series **10**, **11**, **12**, and **19** were approximately proportional to the number of chiral binaphthyl units, and the molar rotation contribution per binaphthyl unit was roughly constant (– 372). This trend also held for the binaphthol series **4**, **5**, and **6**, although the molar-rotation contribution per binaphthol unit was lower (– 186). These results were similar to those reported earlier for chiral, sterically noncongested dendrimers [10], suggesting that each binaphthyl unit in these dendrimers had very similar chemical environment.

4. Kinetics and Enantioselectivity of Dendritic Binaphthol-Aluminum-Complex-Catalyzed *Diels–Alder* Reaction. – In the past, a number of publications on the application of optically active binaphthols as chiral ligands in asymmetric synthesis

have appeared [11]. In fact, most of these catalyzed reactions proceeded with good reactivity and enantioselectivity. In this study, we decided to choose the *Diels–Alder* reaction [5] between cyclopentadiene (Cp, **7**) and 3-[(*E*)-but-2-enoyl]oxazolidin-2-one (**8**) as the model reaction, because this reaction had a moderate reaction rate at room temperature to allow easy monitoring of its progress. Furthermore, the reaction catalyzed by chiral monomeric binaphthol-derived aluminum catalysts was found to proceed with relatively poor enantioselectivity [5b], and, hence, one could detect the enhanced enantioselectivity of the dendritic catalysts more easily in case of a positive dendrimeric effect.

The monomeric **3**, and dendrimeric catalysts, **1** and **2**, were prepared by stirring a mixture of the corresponding binaphthol ligands and Me_2AlCl (1 mol-equiv. per binaphthol unit) in anhydrous CH_2Cl_2 under N_2 for 30 min before the start of the *Diels–Alder* reaction. The reaction was initiated by addition of a CH_2Cl_2 solution of Cp (**7**) and the dienophile **8** to the above solution. The homogeneous reaction mixture was stirred under N_2 at $25.0 \pm 0.1°$ in a constant-temperature bath, and the progress was monitored by ^{1}H-NMR spectroscopy (see *Exper. Part* for details). The initial rate of the *Diels–Alder* reaction was obtained from the slope of a plot of product concentration [**9**] against the reaction time (*Fig. 3*). The *endo*/*exo* product ratios were obtained from ^{1}H-NMR spectroscopic measurements, while the enantiomeric excesses of the major *endo* adduct were determined by chiral high-performance liquid chromatography (HPLC).

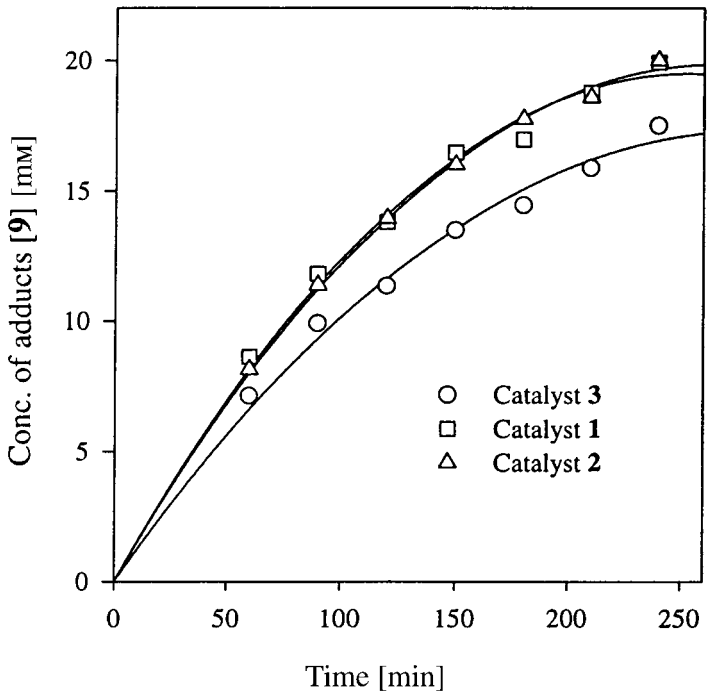

Fig. 3. *Kinetic plots of the* Diels–Alder *reaction promoted by catalysts* **1**, **2**, *and* **3** ([**7**] = 100 mM; [**8**] = 33 mM)

The kinetic data and the conditions for the various trials were summarized (*Table 2*). Examination of the kinetic profiles showed that the reactivities per BINOL of the G0–$(OH)_6$ and G1–$(OH)_{12}$ derived catalysts, **1** and **2**, respectively, were the same, and were *ca.* 25% higher than that of the monomeric analogue **3**. The chiral inductions of all catalyzed reactions were poor (ee < 20%). However, both dendritic catalysts exhibited slightly better enantioselectivity and *endo*-selectivity as compared to those of the monomeric catalyst. This finding was similar to those reported by *Soai* and co-workers [1i], in which the product enantioselectivity was independent of the catalyst generation, when the catalytic centers were placed on the surface of a rigid framework and were devoid of intramolecular interactions. The slightly enhanced catalytic reactivity of the dendritic catalysts as compared to the monomeric species was unexpected. We speculated this could be due to a slight difference of substituent patterns (4-monosubstituted *vs.* 3,5-disubstituted) on the aryl ring at C(4).

Table 2. *The* Diels–Alder *Reaction of Cp* (**7**) *and 3-[(*E*)-but-2-enoyl]oxazolidin-2-one* (**8**) *Catalyzed by Aluminum-BINOL Complexes* **1**–**3** ([**7**] = 100 mM; [**8**] = 33 mM)

Catalyst	No. of BINOL units	[Catalyst] [mM]	[BINOL] [mM]	Initial rate of reaction [mM/h]	Rate/ [Catalyst] [h^{-1}]	Rate/ [BINOL] [h^{-1}]	*endo*/*exo* Ratio	% ee (Config.)
3	1	3.6	3.6	7.3	2.0	2.0	80 : 20	10 (2*S*,3*R*)
1	3	1.2	3.6	9.2	7.7	2.6	95 : 5	13 (2*S*,3*R*)
2	6	0.6	3.6	9.0	15.0	2.5	90 : 10	16 (2*S*,3*R*)

5. Conclusions. – In this paper, we reported the preparation of a series of structurally rigid, lower-generation, multicenter, homogeneous dendritic ligands for a comparative study of their efficiency and selectivity in an asymmetric *Diels–Alder* reaction. In the absence of intramolecular interactions among the catalytic centers, the catalyst reactivity and reaction enantioselectivity were found to be independent of dendrimer generation. Slightly improved reactivity and enantioselectivity of these dendritic catalysts, as compared to those of the monomeric catalyst, was noted.

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Experimental Part

1. *General*. All nonaqueous reactions were carried out under dry N_2 with flame-dried glassware. All reactions were monitored by TLC performed on *Merck* precoated silica-gel *60F*$_{254}$ plates, and compounds were visualized with a spray of 5% (*w*/*v*) dodecamolybdophosphoric acid in EtOH and subsequent heating. Flash chromatography (FC): on columns of *MN* silica gel 60 (230–400 mesh). Unless otherwise stated, all chemicals were purchased from commercial suppliers and used without further purification. All solvents were reagent grade. CH_2Cl_2 was distilled from P_2O_5 and stored over 3 Å (4–8 mesh) molecular sieves. Cyclopentadiene was freshly distilled before use. THF and benzene were freshly distilled from Na/benzophenone ketyl under N_2. Gel-permeation chromatography (*Stragel HR4*, *HR3*, *HR2*, and *HR1 SEC* columns; 7.8 × 300 mm in serial): with THF as solvent on a *Waters HPLC 510* pump equipped with a *Waters 486* tunable UV-absorbance detector. Separation of the enantiomers of the *Diels-Alder* adducts was performed on a *Chiralcel OD HPLC* columns (*Daicel Chemical Industries*, Ltd.). M.p.: *Reichert* microscope apparatus; uncorrected. $[\alpha]_D^{25}$: at 589 nm and at

25° on a *Perkin-Elmer 341* digital polarimeter. ^{1}H- (300 MHz) and ^{13}C-NMR (75.5 MHz) spectra: *Bruker DPX-300* spectrometer; all measurements carried out at r.t. in $CDCl_3$ with TMS as internal standard unless otherwise specified; chemical shifts in ppm in δ scale downfield from TMS. MS: *Bruker APEX 47e FTMS* or a *Finnigan MAT 95* spectrometer by the fast-atom-bombardment (FAB) method; the molecular mass reported in each case is the most abundant molecular isotopic peak for the compound. Elemental analyses were carried out either at Shanghai Institute of Organic Chemistry, Academy of Science, China or MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, Middlesex, United Kingdom.

2. *Synthesis of Binaphthyl-Based Dendritic Ethers* **10** *and* **11**. *[(S)-2,2′-Dibutoxy-4′-hexyl-1,1′-binaphthalen-4-yl]boronic Acid*. BuLi (0.78 ml, 1.6M in hexane, 1.25 mmol) was added to a soln. of (*S*)-4-bromo-2,2′-dibutoxy-4′-hexyl-1,1′-binaphthalene [7] (0.35 g, 0.62 mmol) in dry THF (10 ml) at −78°. After 15 min, Me_3B (0.14 ml, 1.23 mmol) was added in one portion to the mixture. The soln. was then warmed to r.t. for 1 h and quenched with dil. HCl soln. The mixture was extracted with AcOEt (50 ml), washed with H_2O and sat. NaCl solns., dried (Na_2SO_4), and filtered. The solvents were removed *in vacuo* to give crude **15**, which was used immediately in the *Suzuki* coupling reaction without characterization.

1,3,5-Tris(2,2′-dibutoxy-4′-hexyl-1,1′-binaphthalen-4-yl)benzene (**10**). A heterogeneous mixture of **15** (prepared from (*S*)-4-bromo-2,2′-dibutoxy-4′-hexyl-1,1′-binaphthalene (0.40 g, 0.71 mmol)), 1,3,5-tribromobenzene (**13**, 0.06 g, 0.19 mmol) in the presence of $[Pd(PPh_3)_4]$ (0.07 g, 0.06 mmol) in EtOH/toluene (20 ml, 1:1 (*v*/*v*)), and aq. Na_2CO_3 (2 ml, 2.0M) was refluxed for 24 h. The mixture was cooled to r.t. and extracted with AcOEt (50 ml). The mixture was washed with dil. HCl (1M) and sat. NaCl solns., dried (Na_2SO_4), and filtered. The org. layer was concentrated *in vacuo*, and the residue was purified by FC (silica gel; hexane/CH_2Cl_2 6:1) to give **10** (0.21 g, 73%). Glassy solid. M.p. 78–80°. R_f (hexane/CH_2Cl_2 3:1) 0.57. $[\alpha]_D^{25} = -86.7$ ($c = 0.63$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.60–0.68 (*m*, 18 H); 0.91–1.07 (*m*, 21 H); 1.34–1.57 (*m*, 30 H); 1.81–1.92 (*m*, 6 H); 3.10–3.26 (*m*, 6 H); 3.90–4.08 (*m*, 12 H); 7.20–7.40 (*m*, 21 H); 7.62 (*s*, 3 H); 8.03 (*s*, 3 H); 8.06 (*d*, $J = 8.4$, 3 H); 8.30 (*d*, $J = 8.4$ Hz, 3 H). ^{13}C-NMR ($CDCl_3$): 13.56; 13.66; 14.14; 18.74; 18.80; 22.72; 29.57; 30.91; 31.49; 31.83; 33.59; 69.62; 116.40; 117.50; 118.93; 120.91; 123.16; 123.64; 123.82; 125.63; 126.00; 126.25; 126.40; 127.54; 127.83; 130.98; 134.78; 135.01; 140.44; 140.88; 141.15; 154.16; 154.22. FAB-MS: 1520 (90, $[M+H]^+$). Anal. calc. for $C_{108}H_{126}O_6$: C 85.33, H 8.35; found: C 85.21, H 8.37.

1,3,5-Tris[3,5-bis(2,2′-dibutoxy-4′-hexyl-1,1′-binaphthalen-4-yl)phenyl]benzene (**11**). A heterogeneous mixture of **15** (prepared from (*S*)-4-bromo-2,2′-dibutoxy-4′-hexyl-1,1′-binaphthalene) (0.71 g, 1.3 mmol), *1,3,5-tris(3,5-dibromophenyl)benzene* (**14** [3]; 0.10 g, 0.13 mmol) in the presence of $[Pd(PPh_3)_4]$ (0.03 g, 0.02 mmol) in EtOH/toluene (20 ml, 1:1 (*v*/*v*)), and aq. Na_2CO_3 (2 ml, 2.0M) was refluxed for 24 h. The mixture was cooled to r.t. and extracted with AcOEt (50 ml). The mixture was washed with diluted HCl (1M) and sat. NaCl solns., dried (Na_2SO_4), and filtered. The org. layer was concentrated *in vacuo*, and the residue was purified by FC (silica gel; hexane/CH_2Cl_2 4:1) to give **11** (0.19 g, 47%). Glassy solid. M.p. 109–110°. R_f (hexane/CH_2Cl_2 2:1) 0.29. $[\alpha]_D^{25} = -71.8$ ($c = 0.63$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.53–0.64 (*m*, 36 H); 0.86–0.99 (*m*, 42 H); 1.31–1.59 (*m*, 60 H); 1.80–1.91 (*m*, 12 H); 3.10–3.25 (*m*, 12 H); 3.87–4.04 (*m*, 24 H); 7.13–7.34 (*m*, 42 H); 7.55 (*s*, 6 H); 7.91 (*s*, 3 H); 8.04 (*d*, $J = 8.4$, 6 H); 8.15 (*s*, 6 H); 8.16 (*d*, $J \approx 8$, 6 H); 8.26 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$) 13.54; 13.65; 14.14; 18.72; 18.75; 22.72; 29.56; 30.90; 31.45; 31.83, 33.58; 69.56; 116.38; 117.26; 118.93; 120.88; 123.13; 123.65; 123.75; 125.64; 125.98; 126.17; 126.40; 127.54; 127.78; 128.35; 131.32; 134.76; 134.94; 140.36; 140.80; 141.12; 141.92; 142.85; 154.13. FAB-MS: 3190 (100, $[M+H]^+$). Anal. calc. for $C_{228}H_{258}O_{12}$: C 85.83, H 8.15, found: C 86.00, H 8.39.

1,3-Bis(2,2′-dibutoxy-4′-hexyl-1,1′-binaphthalen-4-yl)-5-(trimethylsilyl)benzene (**19**). A heterogeneous mixture of **15** (prepared from (*S*)-4-bromo-2,2′-dibutoxy-4′-hexyl-1,1′-binaphthalene (0.41 g, 0.73 mmol)) and 1,3-dibromo-5-(trimethylsilyl)benzene (**18** [8]; 0.08 g, 0.26 mmol) in the presence of $[Pd(PPh_3)_4]$ (0.03 g, 0.02 mmol) in EtOH/toluene (20 ml, 1:1 (*v*/*v*)), and aq. Na_2CO_3 (2 ml, 2.0M) was refluxed for 24 h. The mixture was cooled to r.t. and extracted with AcOEt (50 ml). The mixture was washed with diluted HCl (1M) and sat. NaCl solns., dried (Na_2SO_4), and filtered. The org. layer was concentrated *in vacuo*, and the residue was purified by FC (silica gel; hexane/CH_2Cl_2 5:1) to give **19** (0.15 g, 52%). Oil. R_f (hexane/CH_2Cl_2 3:1) 0.53. $[\alpha]_D^{25} = -63.4$ ($c = 0.79$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.43 (*s*, 9 H); 0.62 (*t*, $J = 7.5$, 6 H); 0.66 (*t*, $J = 7.5$, 6 H); 0.91–1.07 (*m*, 14 H); 1.30–1.60 (*m*, 20 H); 1.82–1.92 (*m*, 4 H); 3.10–3.26 (*m*, 4 H); 3.90–4.04 (*m*, 8 H); 7.17–7.36 (*m*, 14 H); 7.49 (*s*, 2 H); 7.88 (*s*, 3 H); 8.04–8.10 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): −0.88; 13.56; 13.66; 14.15; 18.73; 18.79; 22.72; 29.57; 29.70; 30.91; 31.45; 31.53; 31.83; 33.59; 69.56; 69.66; 116.44; 117.37; 119.01; 120.70; 123.16; 123.51; 123.80; 125.61; 125.89; 126.00; 126.14; 126.42; 127.64; 127.83; 132.45; 134.01; 134.78; 134.91; 140.35; 140.39; 141.34; 154.13. FAB-MS: 1111 (100, $[M+H]^+$). Anal. calc. for $C_{77}H_{94}O_4Si$: C 83.19, H 8.52; found: C 83.09, H 8.46.

3. *General Procedure for the Synthesis of the (*S*)-Ligands* **4** *and* **5**. A mixture of the (*S*)-binaphthyl ether and BBr_3 (1.0M in CH_2Cl_2, 3 mol-equiv. per binaphthyl unit) in anh. CH_2Cl_2 (10 ml) was stirred at 0° for 2 h. The reaction was quenched with 1M HCl soln. (20 ml) and extracted with AcOEt (50 ml). The org. layers were washed with sat. NaCl soln., dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was then purified by FC.

1,3,5-Tris(4′-hexyl-2,2′-dihydroxy-1,1′-binaphthalen-4-yl)benzene (**4**). This compound was prepared as a white solid (0.11 g, 99%) from **10** (0.14 g, 0.09 mmol) and BBr_3 (0.80 ml, 0.80 mmol) in CH_2Cl_2 (10 ml), and purified by FC (silica gel; hexane/AcOEt 12:1). M.p. 155–157°. R_f (hexane/AcOEt 3:1) 0.30. $[\alpha]_D^{25} = -56.8$ ($c = 0.81$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.94 (*t*, *J* = 7.2, 9 H); 1.33–1.48 (*m*, 12 H); 1.48–1.60 (*m*, 6 H); 1.83–1.93 (*m*, 6 H); 3.16 (*t*, *J* = 7.8, 6 H); 5.10 (*s*, 3 H); 5.17 (*s*, 3 H); 7.24–7.46 (*m*, 21 H); 7.61 (*s*, 3 H); 8.03 (*s*, 3 H); 8.10 (*d*, *J* = 8.4, 3 H); 8.28 (*d*, *J* = 8.4, 3 H). ^{13}C-NMR ($CDCl_3$): 14.14; 22.68; 29.60; 30.52; 31.78; 33.20; 108.70; 111.10; 117.49; 119.01; 123.80; 124.36; 124.41; 124.88; 124.98; 126.57; 127.12; 127.47; 127.84; 128.20; 130.88; 133.90; 134.25; 140.41; 142.91; 143.30; 152.31; 152.38. FAB-MS: 1183 (100, $[M+H]^+$). Anal. calc. for $C_{84}H_{78}O_6$: C 85.25, H 6.64; found: C 85.59, H 6.69.

1,3,5-Tris[3,5-bis(4′-hexyl-2,2′-dihydroxy-1,1′-binaphthalen-4-yl)phenyl]benzene (**5**). This compound was prepared as a white solid (0.11 g, 99%) from **11** (0.14 g, 0.04 mmol) and BBr_3 (0.72 ml, 0.72 mmol) in CH_2Cl_2 (10 ml), and purified by FC (silica gel; hexane/AcOEt 5:1). M.p. 219–222°. R_f 0.43 (hexane/AcOEt 2:1). $[\alpha]_D^{25} = -46.7$ ($c = 0.33$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.94 (*t*, *J* = 7.2, 18 H); 1.33–1.48 (*m*, 24 H); 1.48–1.60 (*m*, 12 H); 1.81–1.93 (*m*, 12 H); 3.16 (*t*, *J* = 7.8, 12 H); 5.10 (*s*, 6 H); 5.17 (*s*, 6 H); 7.23–7.40 (*m*, 42 H); 7.57 (*s*, 6 H); 7.92 (*s*, 3 H); 8.09 (*d*, *J* = 8.4, 6 H); 8.18 (*s*, 6 H); 8.19 (*d*, *J* = 8.1, 6 H); 8.26 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 14.14; 22.67; 29.60; 30.52; 31.78; 33.19; 108.73; 111.10; 117.47; 118.86; 123.78; 124.33; 124.83; 125.00; 126.21; 126.62; 127.15; 127.46; 127.92; 128.15; 128.37; 130.89; 133.91; 134.20; 140.93; 141.39; 142.39; 143.02; 143.23; 152.26; 152.36. FAB-MS: 2518 (100, $[M+H]^+$). Anal. calc. for $C_{180}H_{162}O_{12}$: C 85.89, H 6.49; found: C 85.87, H 6.66.

4. *Kinetics Experiments. General Procedure for the Preparation of the Various Binaphthyl-Derived Aluminum Complexes* **1**–**3** *for Use in the* Diels–Alder *Reaction*. A mixture of the ligands **4**–**6** (0.11 mol-equiv. of binaphthol units with respect to *3-[(*E*)-but-2-enoyl]oxazolidin-2-one* (**8**) and Me_2AlCl (1 mol-equiv. per binaphthol units, 1.0M in hexane) in anh. CH_2Cl_2 (5.0 ± 0.1 ml) was stirred under N_2 at 25.0 ± 0.1° in a constant-temp. bath for 30 min. The *Diels–Alder* reaction was then initiated by the addition of a stock soln. (4.0 ± 0.1 ml) containing Cp (**7**; 100 mM) and **8** (33 mM).

General Procedure for Monitoring the Formation of Cycloadduct 3-[(6-methylbicylo[2.2.1]hept-2-en-5-yl)carbonyl]oxazolidin-2-one (**9**). All reaction mixtures were stirred under N_2 at 25.0 ± 0.1° in a constant-temp. bath, and reactions were monitored by taking aliquots (0.2 ml) at recorded times and quenching with H_2O (50 µl). The mixture was then diluted with AcOEt, and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was subjected to ^{1}H-NMR analysis. The relative integrations of ^{1}H signals arising from the Me group of **8** (*d*, δ 1.97) and one of the olefinic H-atoms of **9** (*m*, δ 6.25–6.35) were used as markers to determine the ratio of **8** to **9**. The *endo*/*exo* ratio of **9** was determined by ^{1}H-NMR integration of the relevant ^{1}H-NMR signals (*endo* isomer: δ 5.79; *exo* isomer: 6.15), and the enantiomeric excess of the *endo* adduct was determined by chiral HPLC on a *Chiralcel OD* column according to the method described in [12].

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