Syntheses and Properties of a New Type of Lewis Acids Incorporating Linked Bisphenoxide Moiety

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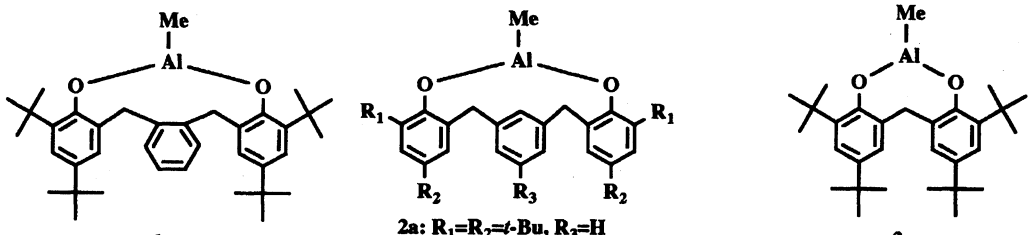
Several ligands for a new type of Lewis acid, which incorporates two linked phenols, were synthesized and the reaction of these ligands with trimethylaluminum quantitatively gave Lewis acids. These Lewis acids were found to be an efficient promoter for the rearrangement of epoxides to carbonyl compounds as well as a useful protector of acetophenone against hydride-reduction. The VT-NMR spectrum and NOESY spectrum of a 1 : 1 complex of Lewis acid **2a** (methyl[2,2′-(*m*-xylene-α,α'-diyl)bis(4,6-di-*t*-butylphenoxido)aluminum and acetophenone provided data on the structure of a complex of acetophenone and **2a**.

Bulky oxygenophilic organoaluminum reagents have been recognized as a highly useful Lewis acid in selective organic synthesis and have also been used in other areas of chemistry.[1—3] However, known types of Lewis acid are usually made up of methylaluminum bisphenoxide type molecules that have a molecular cleft for the recognition of oxygen-containing guest molecules by acid-base complex formation, and have been used as a protective group for less hindered carbonyl groups.[4—7] In a previous study, we developed a new type of Lewis acid that contained the linked bisphenol moiety shown below.[8] Recently Schaverien[9] and Okuda[10] reported titanium alkoxide complexes that contain a bidentate bis(phenoxy) ligand[11—15] as catalyst for olefin oligo-polymerization. These studies also showed the usefulness of this new type of Lewis acid, which contains two phenols that are connected with a linker moiety. In this study, we will discuss the synthesis and properties of methyl[2,2′-(*o*-xylene-α,α'-diyl)bis(phenoxido)]aluminum (**1**) and methyl-[*m*-xylene-α,α'-diylbis(phenoxido)]aluminum (**2a**, **2b**, **2c**, **2d**, and **2e**) and methyl[2,2′-methylene-bis(phenoxido)]-aluminum (**3**) (Chart 1).

Results and Discussion

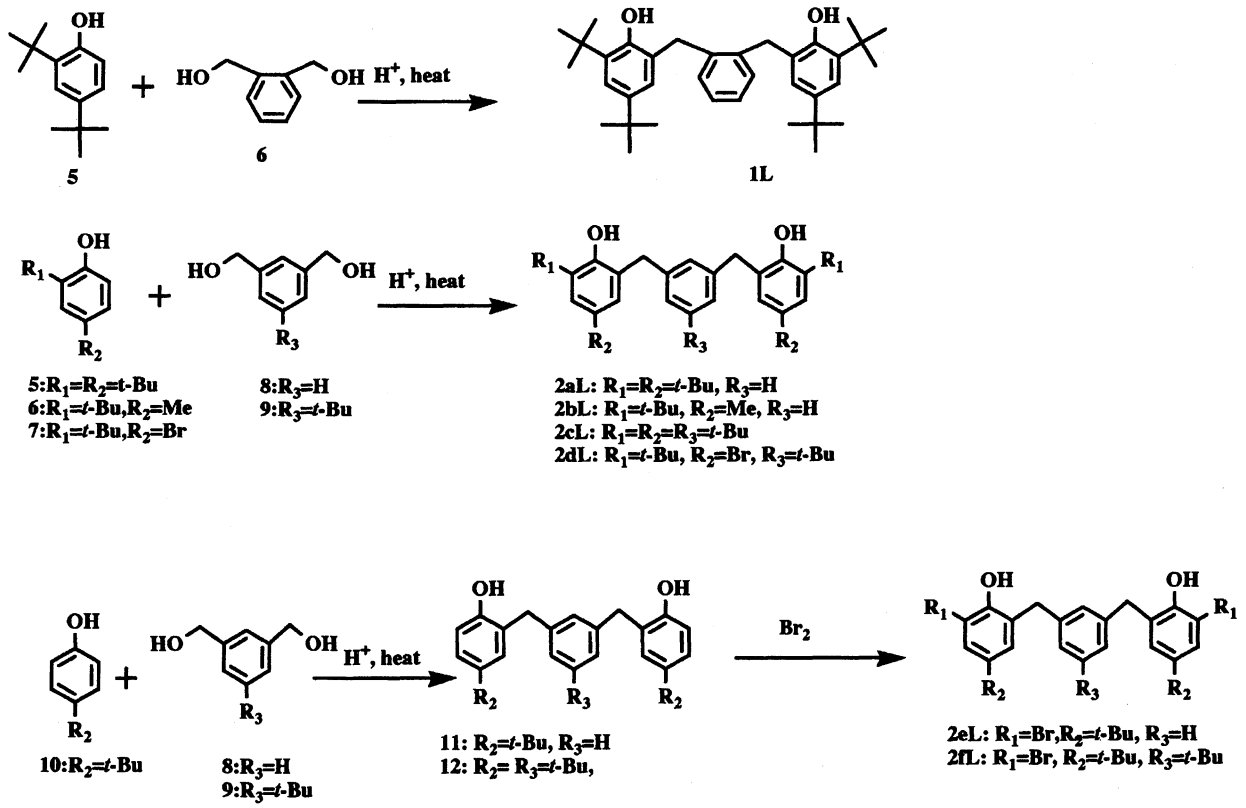
Xylene-α,α'-diylbisphenoxide type ligands were synthesized as follows: 1,2-Bis(3,5-di-*t*-butylsalicyl)benzene (**1L**) was obtained by the condensation reaction of commercially available α,α'-dihydroxy-*o*-xylene with an excess of 2,4-di-*t*-butylphenol in 39% yield. 1,3-Bis(3,5-di-*t*-butylsalicyl)benzene (**2aL**), 1,3-bis(3-*t*-butyl-5-methylsalicyl)-benzene (**2bL**), 1,3-bis(3,5-di-*t*-butylsalicyl)-5-*t*-butylbenzene (**2cL**), and 1,3-bis(5-bromo-3-*t*-butylsalicyl)-5-*t*-butylbenzene (**2dL**) were also synthesized by the acid catalyzed condensation of *m*-bis(hydroxymethyl)benzene (**8**) or 1-*t*-butyl-3,5-bis(hydroxymethyl)benzene (**9**) with 2,4-di-*t*-butylphenol or 2-*t*-butyl-2-methylphenol or with 4-bromo-2-*t*-butylphenol in 69, 39, 44, and 34% yield, respectively (Scheme 1). The acid catalyzed condensation of *p*-*t*-butylphenol and 1,3-bis(hydroxymethyl)benzene (**8** or **9**) gave 1,3-bis(5-*t*-butylsalicyl)benzene (**11**) and 1,3-bis(5-*t*-butylsalicyl)-5-*t*-butylbenzene (**12**) in 34 and 40% yield, respectively. Bisphenol derivatives **11** and **12** were brominated to give 1,3-bis(3-bromo-5-*t*-butylsalicyl)benzene (**2eL**) and 1,3-bis(3-bromo-5-*t*-butylsalicyl)-5-*t*-butylbenzene (**2fL**) in 93 and 94% yield, respectively. 2,4-Di-*t*-butylphenol was



1 **3**

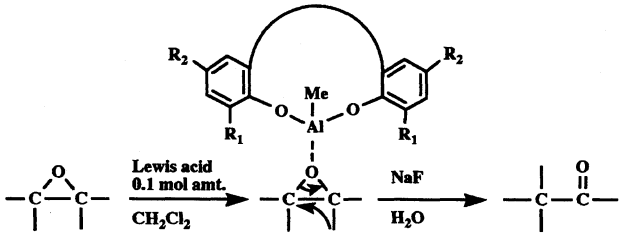
2a: R_1=R_2=*t*-Bu, R_3=H
2b: R_1=*t*-Bu, R_2=Me, R_3=H
2c: R_1=R_2=R_3=*t*-Bu
2d: R_1=*t*-Bu, R_2=Br, R_3=*t*-Bu
2e: R_1=Br, R_2=*t*-Bu, R_3=H

Chart 1.



Scheme 1. Syntheses of ligands **1L**, **2aL**, **2bL**, **2cL**, **2dL**, **2eL**, and **2fL**.

treated with formaldehyde in the presence of 10% aqueous sodium hydroxide to give 2,4-di-*t*-butyl-6-(hydroxymethyl)-phenol (**13**) in 58% yield followed by condensation with 2,4-di-*t*-butylphenol to give 2,2′-methylenebis(4,6-di-*t*-butylphenol) (**3L**) in 61% yield. 2,2′-Methylenebis(4-*t*-butylphenol) (**14**) was brominated to give **15** in 77% yield. Ether **16** was then obtained by the treatment of **15** in 84% yield. **15** was treated with *t*-butyllithium to give bisphenol compound **17** in 61% yield (Scheme 2).

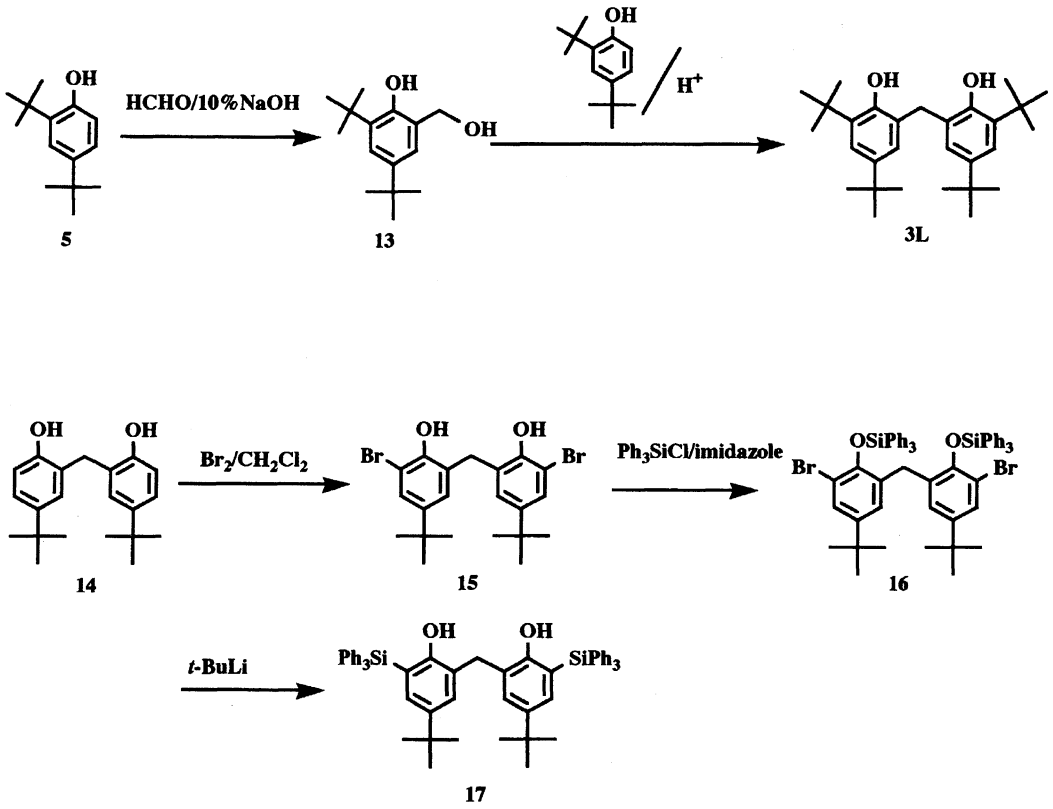


(1)

Preparation of Lewis Acids. The addition of a commercially available solution of trimethylaluminum in hexane into a solution of ligand **1L** with absolute dichloromethane at room temperature in an argon atmosphere gave methyl [2,2′-*o*-xylene-α,α'-diylbis(4,6-di-*t*-butylphenoxide)]aluminum (**1**), of which formation was confirmed by ^{1}H NMR measurement. The ^{1}H NMR spectrum showed a clean singlet at −1.56 ppm, which corresponded to the methyl group that was connected to the aluminum atom.[16] Two sets of broad singlets at 3.60 and 4.80 ppm corresponded to methylene protons. ^{1}H NMR also showed clean signals of aromatic protons at 7.20—7.55 ppm and no resonance for the phenolic OH groups, which is consistent with the formation of desired cyclic Lewis acid (**1**). Other types of Lewis acids (**2a**, **2b**, **2c**, **2d**, **2e**, and **3**) were also synthesized by the same procedure and their structures were confirmed by their ^{1}H NMR spectra. The ^{1}H NMR signal of the methyl group connected with the aluminum atom of the other Lewis acids showed a sharp singlet in a high magnetic field (−0.32——1.62 ppm) (Table 1). In regard to the ^{1}H NMR spectrum of Lewis acid **3**, the resonance of the methylene proton between the two phenols showed two types of doublets at 3.60 and 4.40 ppm (J = 14 Hz). These signals indicate that Lewis acid **3** has a small cyclic structure and only one fixed structure at room temperature. On the other hand, the ^{1}H NMR spectra of Lewis acids (**2a**, **2b**, **2c**, and **2d**) showed two types of doublets near 4 ppm. The chemical shifts of these two methylene signals were very close to each other. This was caused by the fact that the xylene-α,α'-diyl type linker moieties were longer than that of the methylene bridge, which led the

Table 1. ^{1}H Data of New Type of Lewis Acids

Lewis acid	δ (AlMe)/ppm	δ (Ar–CH$_2$–Ar)/ppm	
1	−1.55	3.63	4.82
2a	−1.52	4.03	4.05
2b	−1.56	3.97	3.98
2c	−1.61	3.98	4.02
2d	−1.62	3.95	3.96
2e	−0.71	3.53	
3	−0.32	3.60	4.40



Scheme 2. Syntheses of ligands **3L**, **15**, and **17**.

flexibility of cyclic Lewis acid **2a** and its derivatives. This indicates that Lewis acid **2a** and its derivatives have a more flexible structure than Lewis acid **1**. Other ligands (**14**, **15**, **17**, and **2fL**) were synthesized to obtain other new types of Lewis acids. In this study, however, we obtained a mixture of many kinds of Lewis acid when trimethylaluminum was added to a solution of other ligands (**14**, **15**, **17**, and **2fL**). In addition, the molecular weight of **2a** was measured by cryoscopy in benzene to confirm its structure.[17] The molecular weight obtained (MW 548.6) corresponds closely to the value (MW 554.8) calculated for a monomeric species.

We studied the rearrangement of epoxides to carbonyl compounds (as indicated in Eq. 1) to analyze the properties of these new types of Lewis acids. Table 2 shows the results for the transformation of *trans*-stilbene oxide with Lewis acid in dichloromethane under various conditions. The reaction of *trans*-stilbene oxide with these new types of Lewis acid (0.1 mol amt.) at room temperature gave rearranged diphenylacetaldehyde in a quantitative yield. On the other hand, when *trans*-stilbene oxide was treated with Lewis acid (0.1 mol amt.) at low temperature (−50 °C), rearrangement was achieved only at a low conversion level (4—14% yield). These results can be attributed to the stronger coordination of carbonyl oxygen than the oxygen of epoxide.[18] The stoichiometric use of Lewis acid was therefore necessary in the quantitative rearrangement of the epoxide at −50 °C (Entries 3, 6, 10, 14, 18, 21, and 25). When the reactions were done at a lower temperature (−80 °C), a difference in reactivity between these types of Lewis acids was observed. **2b** and **2d** have good reactivity even at −80 °C (Entries 7 and 19). The low conversion of *trans*-stilbene oxide with **2c** at −80 °C is because the steric hindrance of the *t*-butyl group at the 5-position of the benzene bridge prevented the approach of the epoxide. The smallness of the hollow of Lewis acid (**3**) also decreased the conversion yield of *trans*-stilbene oxide at −80 °C (Entry 26). The results of the experiment when *cis*-stilbene oxide was used as a substrate are listed in Table 3. 2, 2-Diphenylacetaldehyde was obtained as the major product at room temperature. On the other hand, the yields of benzyl phenyl ketone increased at −50 °C in some cases. The migration of hydride and the phenyl shift occurred competitively in these reactions. When these reactions were done at −80 °C, the yields of 2,2-diphenylacetaldehyde and benzyl phenyl ketone were low and the amount of recovered *cis*-stilbene oxide was small (Entries 4, 12, 20, 24, and 28). In these experiments, benzophenone was obtained as a major product. The formation mechanism of benzophenone are currently being studied.

NMR Study of Lewis Acid. Solution NMR studies were done in $CDCl_3$ to obtain structural data on Lewis acid **2a** and that of the complex of **2a** with acetophenone. Typical ^{1}H NMR spectra of Lewis acid **2a**, without or with an equimolar amount of acetophenone, are shown in Fig. 1. The resonance of the methylene bridge of Lewis acid (**2a**) was observed at 4.07 ppm as a singlet at −60 °C (Fig. 1B). This indicates that **2a** is flexible enough to do its ring inversion even at −60 °C. When an equimolar amount of acetophenone was added to this **2a** solution, the signals of the methylene protons were found as four doublets at 3.81, 3.93, 4.03, and 4.22 ppm at −60 °C (Fig. 1C). This was caused by

Table 2. Lewis Acid-Catalyzed Rearrangements of *trans*-Stilbene Oxide

Entry	Lewis acid	Amount of Lewis acid	Conditions	Aldehyde	Recovered epoxide
		mol amt. ×100	°C	% yield	% yield
1	**1**	10	R.T.	92	0
2	**1**	10	−50	11	69
3	**1**	100	−50	85	0
4	**1**	100	−80	28	70
5	**2a**	10	R.T.	97	Trace
6	**2a**	10	−50	7	63
7	**2a**	100	−50	95	0
8	**2a**	100	−80	85	0
9	**2b**	10	R.T.	98	0
10	**2b**	10	−50	8	81
11	**2b**	100	−50	95	0
12	**2b**	100	−80	91	0
13	**2c**	10	R.T.	98	Trace
14	**2c**	10	−50	4	94
15	**2c**	100	−50	95	0
16	**2c**	100	−80	5	88
17	**2d**	10	R.T.	94	0
18	**2d**	10	−50	10	84
19	**2d**	100	−50	97	0
20	**2d**	100	−80	94	0
21	**2e**	10	R.T.	85	0
22	**2e**	10	−50	3	97
23	**2e**	100	−50	37	63
24	**2e**	100	−80	11	88
25	**3**	10	R.T.	94	0
26	**3**	10	−50	4	80
27	**3**	100	−50	53	39
28	**3**	100	−80	7	88

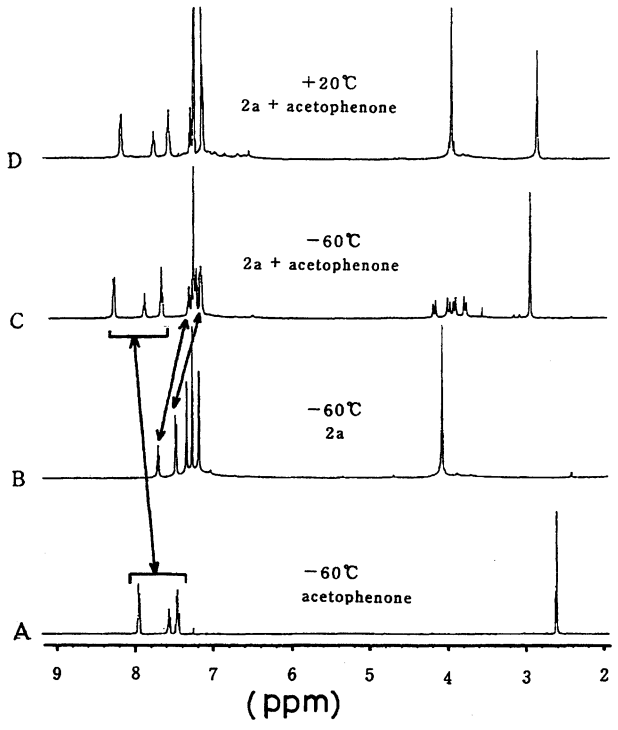


Fig. 1. 500 MHz ^{1}H NMR of acetophenone in $CDCl_3$ at −60 °C (A), **2a** at −60 °C (B), **2a**+acetophenone at −60 °C (1 mol amt.) (C) and **2a**+acetophenone at 20 °C (D).

the fact that the structure of the **2a**–acetophenone complex at −60 °C was tightly fixed and that the C_2 symmetry of **2a** was lost. The signal for the methyl group of acetophenone at 2.61 ppm shifted to 2.97 ppm at −60 °C. On the other hand, a signal for the methyl group of acetophenone appeared at 2.87 ppm (Fig. 1D). Under these conditions, there was a rapid reversible equilibrium on the NMR time scale between the 1 : 1 complex (**2a**–acetophenone) and free **2a** and acetophenone at room temperature. The ^{13}C NMR spectrum of this mixture under the same conditions as described above showed that the resonance of the carbonyl carbon of acetophenone at 197.5 shifted to 211.3 ppm.[19—21] The temperature dependent partial ^{1}H NMR spectra of this complex in $CDCl_3$ (Fig. 2) showed that the conformational inversion is slow at low temperatures but rapid at higher ones. The free energy barriers ($\Delta G^{\neq}$)[22] for the conformational inversion of the two kinds of methylene protons (Ha and Hb) were 48.1 and 49.0 kJ mol^{-1}. The nuclear Overhauser and exchange Spectroscopy (NOESY)[23] measurement of the 1 : 1 mixture of acetophenone and **2a** at −60 °C showed the following results (Fig. 3): NOE cross peaks were observed between the methyl protons connected to aluminum and the following protons: (A) aromatic proton (Ha) of *m*-xylene-α,α'-diyl moiety, (B) aromatic proton (Hb), (C) aromatic proton (Hc) of *m*-xylene-α,α'-diyl moiety, (D) methyl protons of acetophenone, and (E) one methylene proton (He) of the *m*-xylene-

Table 3. Lewis Acid-Catalyzed Rearrangements of *cis*-Stilbene Oxide

Entry	Lewis acid	Amount of Lewis acid	Conditions	Aldehyde	Ketone	Recovered epoxide
		mol amt. ×100	°C	% yield	% yield	% yield
1	**1**	10	R.T.	54	31	0
2	**1**	10	−50	18	18	38
3	**1**	100	−50	84	16	0
4	**1**	100	−80	0	24	42
5	**2a**	10	R.T.	50	22	0
6	**2a**	10	−50	19	13	35
7	**2a**	100	−50	83	17	0
8	**2a**	100	−80	42	16	22
9	**2b**	10	R.T.	74	26	0
10	**2b**	10	−50	10	2	88
11	**2b**	100	−50	53	9	0
12	**2b**	100	−80	15	24	0
13	**2c**	10	R.T.	65	35	0
14	**2c**	10	−50	7	3	88
15	**2c**	100	−50	49	41	10
16	**2c**	100	−80	24	34	12
17	**2d**	10	R.T.	74	26	0
18	**2d**	10	−50	10	2	88
19	**2d**	100	−50	88	12	0
20	**2d**	100	−80	12	45	0
21	**2e**	10	R.T.	49	24	0
22	**2e**	10	−50	12	5	57
23	**2e**	100	−50	18	7	36
24	**2e**	100	−80	9	4	50
25	**3**	10	R.T.	33	21	37
26	**3**	10	−50	8	3	89
27	**3**	100	−50	44	13	38
28	**3**	100	−80	0	16	47

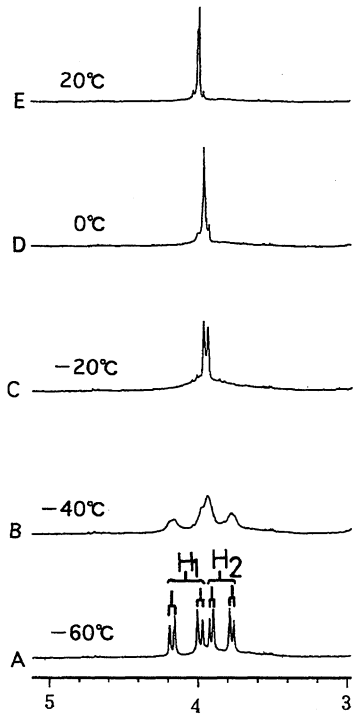


Fig. 2. Temperature dependent partial ^{1}H NMR spectra of **2a**+acetophenone (1 mol amt.) in $CDCl_3$ (500 MHz).

α,α'-diyl moiety. (Fig. 4). NOE cross peaks were observed between the *ortho*- and *meta*-protons of acetophenone and *t*-butyl protons of Lewis acid (**2a**). (F) No NOE was observed between the methyl protons of acetophenone and aromatic protons of the Lewis acid (**2a**). This may be because the methyl group that is connected to the aluminum of Lewis acid (**2a**) holds a position in the inside space that is formed by Lewis acid (**2a**) and methyl group (D) of the acetophenone neighbors on the methyl group (Al–Me) of Lewis acid (**2a**). One potential and speculative structure is shown in Fig. 4 to explain these results. On the other hand, when cyclohexyl phenyl ketone was used as a guest molecule, the signals of the guest in ^{1}H and ^{13}C NMR spectra showed no change. Here, a bulky group (cyclohexyl group) could not be accommodated in the inner space formed by Lewis acid (**2a**), thereby demonstrating the discrimination properties of Lewis acid (**2a**) (i.e. acetophenone from cyclohexyl phenyl ketone). This was also supported by the following experiments.

Selective Protection against Reductive Reagents by Using Lewis Acid. Treatment of a mixture of an equiv molar amount of cyclohexyl phenyl ketone and acetophenone in dichloromethane with diisobutylaluminum hydride (DIBAH) (1 equiv) at −78 °C for 1 h gave cyclohexylphenylmethanol and 1-phenylethanol in a quantitative combined yield (ratio of these alcohols = 42/58). On the other hand, the treatment of these two ketones with an equimolar amt. of Lewis acid (**2a**)

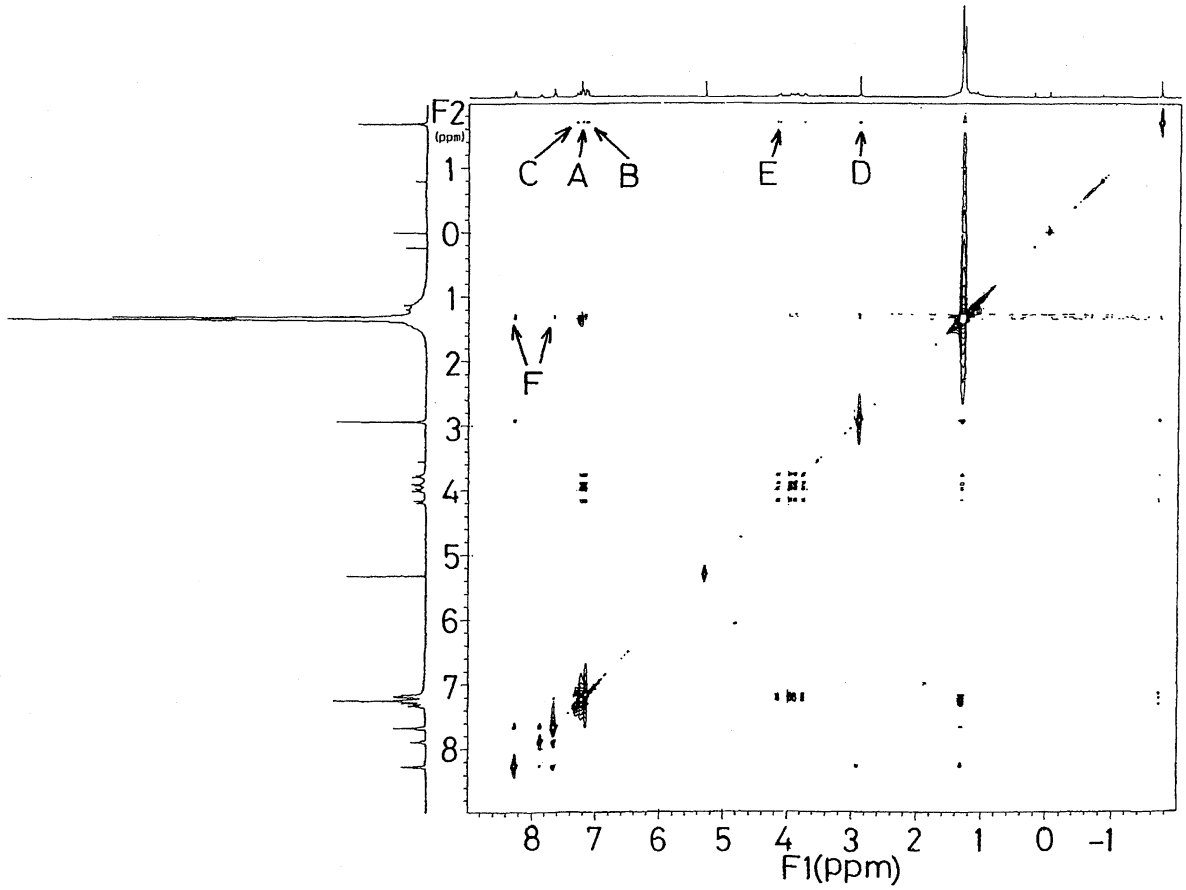


Fig. 3. ^{1}H NOESY spectrum (1000 ms mixing time, 500 MHz) of **2a**+acetophenone (1 mol amt.) in $CDCl_3$ at −60 °C.

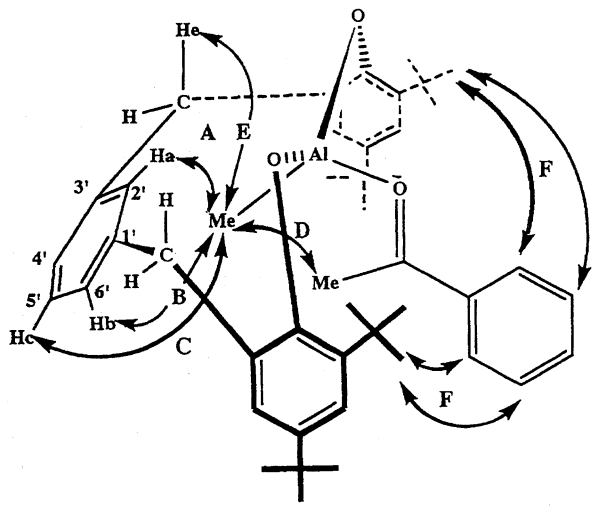


Fig. 4. A speculative structure of a complex of **2a** and acetophenone.

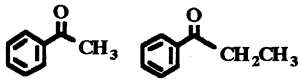
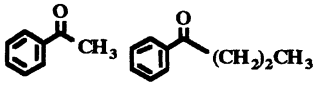
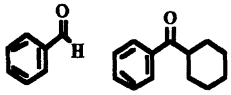
and the addition of DIBAH resulted in a high level of selectivity (cyclohexylphenylmethanol: 1-phenyethanol = 84/16; 78% total yield). Various types of Lewis acid (**2a**, **2b**, **2c**, and **2d**) were an effective and selecting protecting group for acetophenone against DIBAH (Table 4), with Lewis acid **2b** being the most efficient protector for acetophenone. Lewis acids **1** and **3**, however, showed no protecting function for acetophenone against DIBAH reduction. On the other hand, the selective protection of benzaldehyde using **2a**, **2b**, **2c**, and **2d** was unsuccessful (Entries 13, 14, 15, 16, and 17). This may be because aldehyde obtains a high level of reactivity by forming aldehyde–Lewis acid complexes against hydride attack.[6]

Experimental

General. The melting points are uncorrected. NMR spectra were recorded at 500 MHz on a Varian INOVA 500 instrument. Signals were expressed as ppm down field from the tetramethylsilane that was used as an internal standard (δ value in $CDCl_3$) unless otherwise noted. IR (KBr disk) and mass spectra (70 eV) were obtained on a Hitachi EPI-S2 and on a JEOL AX-350 spectrometers, respectively. Elemental analyses were done using a Perkin–Elmer PE2400-II CHNS/O Analyzer. Column chromatography was done using silica gel (Merck, Cat. No. 7734 or 9385) without any pretreatment. Dichloromethane (CH_2Cl_2) and chloroform were dried over P_4O_{10}, and were freshly distilled before use. The trimethylaluminum in hexane used was commercially available. Cryoscopy was done using a Sansyo Beckmann's thermometer.

General Procedure for the Preparation of Linked Bisphenols 1L, 2aL, 2bL, 2cL, 2dL, 2eL, and 3L. 1,2-Bis(3,5-di-*t*-butylsalicyl)benzene (1L). A mixture of 1,2-bis(hydroxymethyl)benzene (1.5 g, 11 mmol), 2,4-di-*t*-butylphenol (22.7 g, 110 mmol), and *p*-toluenesulfonic acid (0.2 g) was heated at 110 °C for 5 h under a nitrogen atmosphere. After being cooled to room temperature, it was steam-distilled to remove unreacted 2,4-di-*t*-butylphenol. The residue obtained was chromatographed on silica gel (Wako C-200; hexane/ethyl acetate = 15/1) to give **1L** (2.2 g,

Table 4. Selective Reduction of Ketones

Entry	Ketones	Lewis acid	Hydride[a)]	Yield[b)]	Ratio[c)]
1		**1**	DIBAH	88	1.4/1
2		**2a**	DIBAH	78	1/5.3
3		**2a**	$AlBr_2H$[d)]	54	1/12
4		**2b**	DIBAH	73	1/16
5		**2c**	DIBAH	80	1/4
6		**2d**	DIBAH	82	1/7
7		**3**	DIBAH	75	1.3/1
8		$AlMe_3$	DIBAH	91	1.4/1
9		**2a**	DIBAH	82	1/2
10		**2a**	$AlBr_2H$	63	1/1.2
11		**2a**	DIBAH	86	1/2.1
12		**2a**	$AlBr_2H$	48	1/2.3
13		**2a**	DIBAH	93	1/1.5
14		**2a**	$AlBr_2H$	76	1.6/1
15		**2b**	DIBAH	92	1/1.5
16		**2c**	DIBAH	81	1/2
17		**2d**	DIBAH	76	1/1.1

a) One equivalent of reducing reagents was used. b) Combined yields of the obtained alcohols. c) The ratio of two alcohols were determined by ^{1}H NMR. d) Prepared from $LiAlH_4$ (1 mol amt.) and anhydrous $AlBr_3$ (3 mol amt.) in absolute ether at 0 °C for 30 min.

39%).

1L: Colorless powder (hexane), mp 176—179 °C; IR 3560, 2957, 1480, 1362, 1213, 880, and 743 cm^{-1}; ^{1}H NMR δ = 1.33 (18H, s), 1.40 (18H, s), 4.00 (4H, s, –CH_2–), 4.58 (2H, s, –OH), 6.90 (2H, d, J = 2.4 Hz), 7.07 (2H, dd, J = 3.2, 5.7 Hz), 7.20 (2H, dd, J = 3.2, 5.7 Hz), and 7.24 (2H, d, J = 2.4 Hz); ^{13}C NMR δ = 150.43, 142.62, 137.52, 135.70, 129.16, 127.32, 125.28, 124.92, 122.58, 34.74, 34.37, 34.26, 31.61, and 29.95; MS *m/z* 514 (M^+; 100%). Found: C, 83.98; H, 9.87%. Calcd for $C_{36}H_{50}O_2$: C, 83.99; H, 9.79%.

1,3-Bis(3,5-di-*t*-butylsalicyl)benzene (2aL). Bisphenol (**2aL**) was obtained by the reaction of 1,3-bis(hydroxymethyl)benzene (1.5 g, 11 mmol) with 2,4-di-*t*-butylphenol (22.7 g, 110 mmol) in 69% yield.

2aL: Colorless powder (hexane), mp 158—162 °C; IR 3530, 2954, 1497, 883, and 794 cm^{-1}; ^{1}H NMR δ = 1.29 (18H, s), 1.37 (18H, s), 3.95 (4H, s, –CH_2–), 4.58 (2H, s, –OH), 7.00 (2H, d, J = 2 Hz), 7.08 (1H, dd, J = 7.6, 1.4 Hz), 7.12 (1H, dd, J = 1.4, 1.4 Hz), 7.22 (2H, d, J = 2.2 Hz), and 7.25 (1H, dd, J = 7.6, 7.6 Hz); ^{13}C NMR δ = 150.50, 142.42, 139.88, 135.79, 129.47, 128.68, 126.93, 125.75, 125.63, 122.67, 37.63, 34.74, 34.25, 31.65, and 29.91; MS *m/z* 514 (M^+; 100%). Found: C, 83.98; H, 9.87%. Calcd for $C_{36}H_{50}O_2$: C, 83.99; H, 9.79%.

1,3-Bis(3-*t*-butyl-5-methylsalicyl)benzene (2bL). Bisphenol (**2bL**) was obtained by the reaction of 1,3-bis(hydroxymethyl)benzene (0.8 g, 6.26 mmol) with 2-*t*-butyl-4-methylphenol (10.1 g, 62.6 mmol) in 39% yield.

2bL: Colorless viscous oil; IR 3554, 3000, 2956, 1603, 1475, 860, 758, and 706 cm^{-1}; ^{1}H NMR δ = 1.38 (18H, s), 2.25 (6H, s), 3.93 (4H, s, –CH_2–), 4.58 (2H, s, –OH), 6.85 (1H, s), 6.79 (2H, d, J = 2.4 Hz), 7.00 (2H, d, J = 2.4 Hz), 7.10 (2H, d, J = 7.6 Hz), 7.12 (1H, s), and 7.25 (2H, dd, J = 7.6, 7.6 Hz); ^{13}C NMR δ = 150.56, 139.81, 136.44, 129.48, 129.20, 129.09, 128.71, 126.92, 126.47, 122.32, 37.09, 34.42, 29.45, and 20.83; MS *m/z* 430 (M^+; 100%). Found: C, 83.70; H, 8.63%. Calcd for $C_{30}H_{38}O_2$: C, 83.67; H, 8.89%.

5-*t*-Butyl-1,3-bis(3,5-di-*t*-butylsalicyl)benzene (2cL). Bisphenol (**2cL**) was obtained by the reaction of 5-*t*-butyl-1,3-bis(hydroxymethyl)benzene (3.0 g, 15.4 mmol) with 2,4-di-*t*-butylphenol (31.7 g, 154 mmol) in 44% yield.

2cL: Colorless prisms (hexane), mp 140.5—141.5 °C; IR 3556, 2960, 1594, 1477, 877, and 794 cm^{-1}; ^{1}H NMR δ = 1.23 (9H, s), 1.27 (18H, s), 1.37 (18H, s), 3.94 (4H, s, –CH_2–), 4.58 (2H, s, –OH), 6.85 (1H, s), 6.95 (2H, d, J = 2.4 Hz), 7.10 (2H, s), and 7.21 (2H, d, J = 2.4 Hz); ^{13}C NMR δ = 152.42, 150.47, 142.36, 139.24, 135.72, 125.86, 125.69, 125.54, 124.00, 122.51, 37.64, 34.76, 34.66, 34.24, 31.64, 31.25, and 29.88; MS *m/z* 570 (M^+; 100%). Found: C, 84.10; H, 10.05%. Calcd for $C_{40}H_{58}O_2$: C, 84.15; H, 10.24%.

1,3-Bis(5-bromo-3-*t*-butylsalicyl)-5-*t*-butylbenzene (2dL). Bisphenol (**2dL**) was obtained by the reaction of 5-*t*-butyl-1,3-bis-(hydroxymethyl)benzene (0.49 g, 2.53 mmol) with 4-bromo-2-*t*-butylphenol (5.82 g, 25.3 mmol) in 34% yield.

2dL: Colorless powder (hexane), mp 126—128 °C; IR 3540, 2958, 1604, 1589, 1485, 866, 760, and 704 cm^{-1}; ^{1}H NMR δ = 1.22 (9H, s), 1.35 (18H, s), 3.92 (4H, s, –CH_2–), 4.72 (2H, s, –OH), 6.90 (1H, s), 6.79 (2H, d, J = 2.4 Hz), 7.00 (2H, d, J = 2.4 Hz), 7.10 (4H, m), and 7.29 (2H, d, J = 2.4 Hz); ^{13}C NMR δ = 153.08, 152.04, 139.03, 138.36, 131.07, 128.76, 128.44, 125.57, 124.21, 112.72, 37.05, 34.76, 34.72, 31.21, and 29.52; MS *m/z* 616 (M^+; 100%). Found: C, 62.55; H, 6.65%. Calcd for $C_{32}H_{40}Br_2O_2$: C, 62.35; H, 6.54%.

1,3-Bis(5-*t*-butylsalicyl)benzene (11). A mixture of 1,3-bis-(hydroxymethyl)benzene (1.0 g, 7.2 mmol), 4-*t*-butylphenol (20.0 g, 133 mmol) and *p*-toluenesulfonic acid (0.2 g) was heated at 110 °C for 5 h under a nitrogen atmosphere. After the same procedure described for the synthesis of **1aL**, we obtained **11** in 47% yield.

11: Colorless powder (hexane), mp 152—153 °C; IR 3520,

2956, 1605, 1506, 1463, 825, and 706 cm^{-1}; ^1H NMR δ = 1.27 (18H, s), 3.95 (4H, s, $-CH_2-$), 4.56 (2H, s, –OH), 6.71 (2H, d, J = 8.1 Hz), 6.87 (1H, dd, J = 1.2, 1.2 Hz), 7.05 (2H, d, J = 2.4 Hz), 7.12 (2H, dd, J = 8.3, 2.4 Hz), and 7.13 (2H, d, J = 2.4 Hz); MS m/z 402 (M^+; 34%) and 57 (100). Found: C, 83.32; H, 8.40%. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51%.

1,3-Bis(3-bromo-5-*t*-butylsalicyl)benzene (2eL). To a solution of **11** (0.50 g, 1.24 mmol) in $CHCl_3$ (20 ml) was added bromine (0.44g, 2.73 mmol) in $CHCl_3$ (2 ml) at 0 °C over a period of 1 h, and the mixture was stirred for 30 min at room temperature. This reaction mixture was then poured into 20 g of ice and the organic layer was separated. The organic layer obtained was washed with water and brine and then dried over anhydrous sodium sulfate and concentrated. The yellow residue was chromatographed on silica gel (Kiesel gel-60; hexane/ethyl acetate = 30/1) to give **2eL** (647 mg, 93%).

2eL: Colorless viscous oil: IR 3521, 2960, 1605, 1576, 1481, 868, 758, and 710 cm^{-1}; ^1H NMR δ = 1.23 (18H, s), 3.97 (4H, s, $-CH_2-$), 5.40 (2H, s, –OH), 7.05 (2H, d, J = 2.4 Hz), 7.06 (2H, dd, J = 7.6, 1.2 Hz), 7.11 (1H, dd, J = 1.2, 1.2 Hz), 7.19 (1H, dd, J = 7.6, 7.6 Hz), and 7.30 (2H, d, J = 2.4 Hz); ^{13}C NMR δ = 147.83, 144.49, 140.24, 129.18, 128.38, 127.93, 127.46, 126.76, 126.49, 110.18, 36.98, 34.16, and 31.37; MS m/z 560 (M^+; 100%). Found: C, 59.86; H, 5.65%. Calcd for $C_{28}H_{32}Br_2O_2$: C, 60.02; H, 5.76%.

5-*t*-Butyl-1,3-bis(5-*t*-butylsalicyl)benzene (12). A mixture of 1-*t*-butyl-3,5-bis(hydroxymethyl)benzene (2.0 g, 10.3 mmol), 4-*t*-butylphenol (20.0 g, 133 mmol), and *p*-toluenesulfonic acid (0.2 g) was heated at 110 °C for 5 h under a nitrogen atmosphere. After the same procedure described for the synthesis of **1a**, **12** was obtained in 40% yield.

12: Colorless powder (hexane), mp 141—143 °C; IR 3514, 2962, 1599, 1506, 1464, 822, 759, and 712 cm^{-1}; ^1H NMR δ = 1.25 (27H, s), 3.93 (4H, s, $-CH_2-$), 4.58 (2H, s, –OH), 6.70 (2H, d, J = 8.3 Hz), 6.87 (1H, dd, J = 1.2, 1.2 Hz), 7.09 (2H, d, J = 2.4 Hz), 7.12 (2H, dd, J = 8.3, 2.4 Hz), and 7.13 (2H, d, J = 2.4 Hz); MS m/z 458 (M^+; 73%) and 83 (100). Found: C, 83.52; H, 9.40%. Calcd for $C_{32}H_{42}O_2$: C, 83.79; H, 9.23%.

1,3-Bis(3-bromo-5-*t*-butylsalicyl)-5-*t*-butylbenzene (2fL). To a solution of **12** (1.50 g, 3.27 mmol) in $CHCl_3$ (20 ml) was added bromine (1.15 g, 7.19 mmol) in $CHCl_3$ (2 ml) at 0 °C over a period of 1 h, and this was stirred for 30 min at room temperature. By the same procedure described for the synthesis of **2dL**, **2fL** was obtained in 94% yield.

2fL: Colorless viscous oil; IR 3521, 2960, 1599, 1577, 1481, 866, 735, and 712 cm^{-1}; ^1H NMR δ = 1.22 (18H, s), 1.27 (9H, s), 3.96 (4H, s, $-CH_2-$), 5.39 (2H, s, –OH), 6.88 (1H, dd, J = 1.2, 1.2 Hz), 7.03 (2H, d, J = 2.4 Hz), 7.13 (2H, d, J = 1.2 Hz), and 7.29 (2H, d, J = 2.4 Hz); MS m/z 616 (M^+; 100%). Found: C, 62.55; H, 6.65%. Calcd for $C_{32}H_{40}Br_2O_2$: C, 62.35; H, 6.54%.

2,4-Di-*t*-Butyl-6-(hydroxymethyl)phenol (13). To a solution of 2,4-di-*t*-butylphenol (**5**, 3.3 g, 16 mmol) in methanol (2 ml), 10% aqueous NaOH (10 ml) was added with ice cooling. Then a formaldehyde solution (37%, 4 g) was added dropwise over a period of 10 min and the solution was stirred at 45 °C for 5 h under a nitrogen atmosphere. After being cooled to room temperature, the reaction mixture was acidified by adding 10% HCl (20 ml) and was extracted with $CHCl_3$. The organic layer was washed with a saturated NaCl solution and then water, and dried over Na_2SO_4. The solvent was removed and the residue (3 g) was crystallized from hexane (15 ml) to give **13** (2.2 g, 58%) as colorless prism.

13: Colorless crystal; IR 3427, 3188, 2966, 2867, 1483, 997, 879, 723, and 649 cm^{-1}; ^1H NMR δ = 1.29 (9H, s), 1.43 (9H, s), 2.02 (1H, t, J = 6 Hz, $-CH_2O\underline{H}$), 4.86 (2H, d, J = 6 Hz, $-C\underline{H_2}OH$), 6.90 (1H, d, J = 2.6 Hz), 7.28 (1H, d, J = 2.6 Hz), and 7.53 (1H, s, –O<u>H</u>); MS m/z 236 (M^+; 21%) and 202 (100). Found: C, 76.46; H, 10.52%. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23%.

2,2′-Methylenebis(4,6-di-*t*-butylphenol) (3L). Bisphenol (**3L**) was obtained by the reaction of **13** (2.2 g, 9.3 mmol), with 2,4-di-*t*-butylphenol (10 g, 48.5 mmol) in 59% yield.

3L: Colorless prism (hexane), mp 149—151 °C; IR 3531, 2954, 2906, 1479, 883, and 798 cm^{-1}; ^1H NMR δ = 1.28 (18H, s), 1.41 (18H, s), 3.93 (2H, s, $-CH_2-$), 5.87 (2H, s, –OH), 7.15 (2H, d, J = 2.4 Hz), and 7.19 (2H, d, J = 2.4 Hz); ^{13}C NMR δ = 149.87, 142.96, 135.50, 126.04, 125.15, 122.53, 34.63, 34.26, 32.52, 31.58, and 30.05; MS m/z 424 (M^+; 67%) and 220 (100). Found: C, 82.32; H, 10.73%. Calcd for $C_{29}H_{44}O_2$: C, 82.02; H, 10.44%.

2,2′-Methylenbis(4-*t*-butylphenol) (14). **14** was obtained by the reaction of 4-*t*-butyl-2-(hydroxymethyl)phenol (1.5 g, 8.4 mmol) with 4-*t*-butvlphenol (12.5 g, 84 mmol) in 71% yield.[24]

14: Colorless powder (hexane), mp 190—193 °C; IR 3580, 2905, 2867, 1510, 1480, 880, and 677 cm^{-1}; ^1H NMR δ = 1.28 (18H, s), 3.96 (2H, s, $-CH_2-$), 6.76 (2H, d, J = 8.3 Hz), 6.79 (2H, s, –OH), 7.10 (2H, dd, J = 8.3, 2.4 Hz), and 7.31 (2H, d, J = 2.4 Hz); MS m/z 312 (M^+; 44%) and 297 (100). Found: C, 80.69; H, 9.15%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

2,2′-Methylenebis(6-bromo-4-*t*-butylphenol) (15). To a solution of **14**[24] (2.25 g, 7.2 mmol) in CCl_4 (10 ml), bromine (2.3 g, 14.6 mmol) in CH_2Cl_2 (10 ml) was added over a period of 30 min at 0 °C and the mixture was stirred for 1 h. **15** in 77% yield was obtained after the same procedure used for the synthesis of **2dL**.

15: Pale yellow powder (hexane), mp 137—138 °C, IR 3444, 3608, 2962, 1589, 1471, 1429, 1290, 1241, 1107, 910, and 871 cm^{-1}; ^1H NMR δ = 1.25 (18H, s), 4.00 (2H, s, $-CH_2-$), 6.02 (2H, s), 7.18 (2H, d, J = 2 Hz), and 7.32 (2H, d, J = 2 Hz); MS m/z 470 (M^+; 50%) and 57 (100). Found: C, 53.77; H, 5.64%. Calcd for $C_{21}H_{26}Br_2O_2$: C, 53.64; H, 5.57%.

Bis[3-bromo-5-*t*-butyl-2(triphenylsilyl)phenyl]methane (16). To the solution of phenol (**15**) (2.53 g, 5 mmol) and imidazole (1.22 g, 18 mmol) in *N*,*N*-dimethylformamide (30 ml) was added triphenylsilylchloride (4.42 g, 15 mmol). The resulting solution was stirred for 9 h at room temperature, poured into saturated $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was washed with a saturated $NaHCO_3$ solution again, dried over Na_2SO_4, and concentrated. The obtained residue was put on a silica-gel column and chromatographed (hexane/ethyl acetate = 10/1) to give **16** (4.48 g) in 84% yield.

16: Pale yellow powder (hexane), mp 167—169 °C; IR 3069, 2959, 1589, 1473, 1429, 1290, 1240, 1115, 775, 740, and 519 cm^{-1}; ^1H NMR δ = 1.12 (18H, s), 3.37 (2H, s, $-CH_2-$), 6.35 (2H, d, J = 2.5 Hz), 7.21 (2H, d, J = 2.5 Hz), 7.27 (12H, dd, J = 7.5, 7.5 Hz), 7.39 (6H, dddd, J = 7.5, 7.5, 2.5, 2.5 Hz), 7.48 (12H, dd, J = 7.5, 2.5 Hz); MS m/z 986 (M^+; 30%). Found: C, 69.50; H, 5.55%. Calcd for $C_{57}H_{54}Br_2O_2Si_2$: C, 69.36; H, 5.51%.

2,2′-Methylenebis[4-*t*-butyl-6-(triphenylsilyl)phenol] (17). To a solution of **16** (1.0 g, 1.0 mmol) in absolute THF (13 ml) was added dropwise 1.57 M (1 M = 1 mol dm^{-3}) pentane solution of *t*-butyllithium (2.9 ml, 4.5 mmol) over a period of 5 min at 0 °C and this was stirred for 1.5 h at room temperature. The reaction mixture was poured into a saturated ammonium chloride solution and was extracted with CH_2Cl_2. The organic layers were combined and dried over Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel (ethyl acetate/hexane = 1/10) to give **17** (0.51 g, 61%).

17: Colorless prism (hexane); mp 239—245 °C; IR 3504,

3444, 3068, 2962, 1589, 1479, 1429, 1282, 1240, 1115, 742, 700, and 500 cm^{-1}; ^1H NMR δ = 1.14 (18H, s), 3.88 (2H, s, $-CH_2-$), 5.79 (2H, s, –OH), 7.08 (2H, d, J = 2.5 Hz), 7.30 (12H, dd, J = 7.5, 7.5 Hz), 7.34 (2H, d, J = 2.5 Hz), 7.39 (6H, dddd, J = 7.5, 7.5, 1.5, 1.5 Hz), and 7.56 (12H, dd, J = 7.5, 1.5 Hz); MS m/z 828 (M^+;5%) and 672 (100). Found: C, 82.15; H, 6.63%. Calcd for $C_{57}H_{56}O_2Si_2$: C, 82.56; H, 6.80%.

General Procedure for the Preparation of Lewis Acids 1,2a, 2b,2c,2d,2e, and 3. 1,2-Bis(3,5-di-*t*-butylsalicyl)benzene (**1L**) (51.4 mg, 0.1 mmol) was placed in a two-necked flask and air was removed under reduced pressure (133.322 Pa) and purged by argon gas. This operation were repeated three times, then this reaction flask was heated at 90 °C for 1 h to remove moisture completely and was cooled to room temperature. Air-free CH_2Cl_2 (5 ml) was injected by a syringe. An 1.0 M hexane solution of trimethylaluminum (0.1 cm^3, 0.1 mmol) was added to this solution and it was stirred for 1 h at room temperature. This solution was used as a CH_2Cl_2 solution of Lewis acid without further purification. To check the purity of the Lewis acid solution, the solvent of the Lewis acid was replaced from CH_2Cl_2 to $CDCl_3$ and we measured it by ^1H NMR. The ^1H NMR spectra of these new types of Lewis acids were as follows.

1: ^1H NMR δ = −1.56 (3H, s, Al–CH_3), 1.35 (18H, s), 1.36 (18H, s), 3.60 (2H, br s, $-CH_2-$), 4.80 (2H, br s, $-CH_2-$), 7.17 (1H, d, J = 2.5 Hz), 7.29 (2H, d, J = 2.5 Hz), 7.39 (2H, dd, J = 5.7, 3.6 Hz), and 7.48 (2H, dd, J = 5.7, 3.6 Hz); ^{13}C NMR δ = 152.84, 140.61, 138.11, 138.07, 133.21, 132.02, 127.16, 125.58, 123.18, 35.23, 34.93, 34.25, 31.83, 30.15, and −10.31.

2a: ^1H NMR δ = −1.55 (3H, s, Al–CH_3), 1.33 (18H, s), 1.43 (18H, s), 4.03 (2H, d, J = 16 Hz), 4.05 (2H, d, J = 16 Hz), 7.12 (1H, d, J = 2.6 Hz), 7.32 (2H, dd, J = 1.9, 1.9 Hz), 7.34 (2H, d, J = 2.6 Hz), 7.42 (2H, dd, J = 7.6, 1.9 Hz), and 7.64 (1H, dd, J = 7.6, 7.6 Hz); ^{13}C NMR δ = 154.03, 147.56, 140.90, 138.76, 136.40, 129.93, 126.38, 125.56, 123.59, 118.06, 40.63, 35.17, 34.21, 31.77, 30.71, and −10.30.

2b: ^1H NMR δ = −1.56 (3H, s, Al–CH_3), 1.42 (18H, s), 2.30 (6H, s), 3.97 (2H, d, J = 16 Hz), 3.98 (2H, d, J = 16 Hz), 6.93 (1H, d, J = 2.3 Hz), 7.09 (2H, d, J = 2.3 Hz), 7.29 (1H, dd, J = 1.9, 1.9 Hz), 7.40 (2H, dd, J = 7.6, 1.9 Hz), and 7.61 (1H, dd, J = 7.6, 7.6 Hz); ^{13}C NMR δ = 154.23, 147.48, 139.53, 136.53, 129.98, 129.35, 127.66, 127.31, 127.15, 118.09, 40.19, 34.86, 30.66, 20.83, and −10.29.

2c: ^1H NMR δ = −1.61 (3H, s, Al–CH_3), 1.30 (9H, s), 1.34 (18H, s), 1.44 (18H, s), 3.98 (2H, d, J = 16 Hz), 4.02 (2H, d, J = 16 Hz), 7.09 (1H, dd, J = 1.5, 1.5 Hz), 7.10 (2H, d, J = 2.6 Hz), 7.31 (2H, d, J = 2.6 Hz), and 7.40 (2H, d, J = 1.5 Hz); ^{13}C NMR δ = 160.56, 154.25, 147.58, 140.74, 138.72, 127.35, 126.53, 125.56, 123.44, 114.31, 40.74, 35.41, 35.18, 34.21, 31.77, 30.87, 30.69, and −10.28.

2d: ^1H NMR δ = −1.63 (3H, s, Al–CH_3), 1.31 (18H, s), 1.39 (18H, s), 3.95 (2H, d, J = 16 Hz), 3.96 (2H, d, J = 16 Hz), 7.04 (1H, dd, J = 1.9, 1.9 Hz), 7.25 (2H, d, J = 2.3 Hz), 7.37 (2H, d, J = 2.3 Hz), and 7.42 (2H, d, J = 1.9 Hz); ^{13}C NMR δ = 161.58, 155.89, 146.78, 142.24, 131.11, 129.59, 129.36, 127.92, 114.03, 111.13, 39.58, 35.58, 35.16, 34.21, 30.85, 30.34, and −10.29.

2e: ^1H NMR δ = −0.71 (3H, s, Al–CH_3), 1.39 (18H, s), 3.53 (4H, s), 7.13—7.19 (5H, m), and 7.23—7.27 (3H, d, m).

3: ^1H NMR δ = −0.32 (3H, s, Al–CH_3), 1.26 (18H, s), 1.33 (18H, s), 3.60 (2H, d, J = 14 Hz), 4.40 (2H, d, J = 14 Hz), 7.11 (2H, d, J = 2.3 Hz), and 7.23 (2H, d, J = 2.3 Hz). The ^{13}C NMR spectra of **2e** and **3** could not be obtained, because of their instability.

General Procedure for the Reaction of Lewis Acids 1,2a, 2b,2c,2d,2e, and 3 with *trans*-Stilbene Oxide. An 1.0 M solution of trimethylaluminum (0.1 cm^3, 0.1 mmol) was added to a solution of 1,2-bis(3,5-di-*t*-butylsalicyl)benzene (**1L**) 51.4 mg, 0.1 mmol) in absolute CH_2Cl_2 (5 ml) at room temperature in an argon atmosphere and this solution was stirred at this temperature for 1 h and then *trans*-stilbene oxide (196 mg, 1 mmol) in absolute CH_2Cl_2 (2 ml) was poured into this flask at −50 °C. The mixture was stirred at −50 °C for 1 h and treated with NaF (17 mg, 0.4 mmol) followed by water (0.1 ml) at this temperature. The solution was stirred vigorously at −50 °C for 30 min and filtered. The filtrate was concentrated and the obtained residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give diphenyl acetaldehyde (190 mg, 97%).

General Procedure for the Reaction of Lewis Acids 1,2a,2b, 2c,2d,2e, and 3 with *cis*-Stilbene Oxide. An 1.0 M solution of trimethylaluminum (0.1 ml, 0.1 mmol) was added to a solution of 1,2-bis(3,5-di-*t*-butylsalicyl)benzene (**1L**) (51.4 mg, 0.1 mmol) in absolute CH_2Cl_2 (5 ml) at room temperature in an argon atmosphere and this solution was stirred at this temperature for 1 h and then *cis*-stilbene oxide (196 mg, 1 mmol) in absolute CH_2Cl_2 (2 ml) was poured into this flask at −80 °C. The mixture was stirred at −50 °C for 1 h and treated with NaF (17 mg, 0.4 mmol) followed by water (0.1 ml) at this temperature. The solution was stirred vigorously at −50 °C for 30 min and filtered. The filtrate was concentrated and the obtained residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give benzyl phenyl ketone (47 mg, 24%), benzophenone (60 mg, 33%), and *cis*-stilbene oxide (82 mg, 42%).

General Procedure for the Selective Reduction of Ketones. An 1.0 M hexane solution of trimethylaluminum (0.2 ml, 0.2 mmol) was added to a solution of 1,3-bis(3,5-di-*t*-butylsalicyl)benzene (**2aL**) (103 mg, 0.2 mmol) in absolute CH_2Cl_2 (5 ml) and the resulting solution was stirred at room temperature for 1 h in an argon atmosphere. After this was cooled to −78 °C, a mixture of acetophenone (24 mg, 0.2 mmol) and cyclohexyl phenyl ketone (37.6 mg, 0.2 mmol) in absolute diethyl ether (1 ml) was added at −78 °C, and an 1 M hexane solution of diisobutylaluminum hydride (0.2 ml, 1 equiv) was added to this solution using a syringe. The mixture was stirred for 1 h at −78 °C and was then poured into 10% aqueous HCl solution, extracted with ether, and dried over anhydrous sodium sulfate. The evaporation of solvents and the purification of the residue by column chromatography on silica gel (hexane/ethyl acetate as an eluent) gave 36.5 mg (96%) of cyclohexylphenylmethanol and 4.5 mg (18%) of 1-phenylethanol.

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