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ALKYLATION OF PHENOL BY MYRTENOL

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Alkylation of phenol by myrtenol in the presence of aluminum phenoxide and aluminum isopropoxide was studied in the temperature range 120–160°C. The reaction occurred with the formation of an array of alkylated phenols. Isomerization of the terpene substituent as a result of rearrangements of the bicyclic myrtenol structure was observed. The side reaction of myrtenol reduction occurred during the alkylation in the presence of aluminum isopropoxide. A significant number of compounds with two aromatic moieties was formed in the presence of aluminum phenoxide.

Keywords: phenol, myrtenol, organoaluminum catalysts, alkylation.

Terpenophenols are known to exhibit a variety of biological activities [1–3]. The presence of isoprenyl substituents modifies the role of the aromatic compounds, mainly by increasing their lipophilicity. This enhances the retention of the prenylphenols in lipid cell membranes and the penetration through them [4]. The structure of the terpene substituent and the terpenophenol in general can determine the type of activity. In this respect, studies elucidating the relationship between the alkylation conditions and the resulting products are interesting. The goal of such investigations is to find the parameters that facilitate the selective production of compounds with a given structure.

Herein the influence of two organoaluminum catalysts, aluminum phenoxide and aluminum isopropoxide, on the products formed by alkylation of phenol (**1**) with myrtenol (**2**) (Scheme 1) is evaluated taking into account various thermal regimes and reagent ratios. According to the literature [5–8], both catalysts are *ortho*-orienting.

Phenol, aluminum phenoxide, and aluminum diisopropoxide-phenoxide were alkylated by myrtenol at 120, 140, and 160°C. The catalysts were aluminum phenoxide $(PhO)_3Al$ and aluminum isopropoxide $(i\text{-}PrO)_3Al$. $(PhO)_3Al$ was produced *in situ* by reacting phenol with metallic Al. $(i\text{-}PrO)_3Al$ was transformed during the reaction into the mixed aluminum alkoxide-phenoxide by reaction of equimolar amounts of phenol and $(i\text{-}PrO)_3Al$.

The alkylation with an equimolar ratio of aluminum alkoxides and myrtenol was carried out for 3 h with practically complete conversion of myrtenol regardless of the nature of the organoaluminum component. The reaction with a catalytic amount of the aluminum alkoxides occurred at temperatures of at least 160°C and continued for 8-15 h. The conversion of myrtenol was 50–60%. The reaction products were a mixture of O- and C-alkylated phenols and myrtenol derivatives (numbering of C atoms is given for convenience of reading spectra). These were monoalkylated phenols (**3**, **4**); cyclic ethers (**5**, **8**); a linear ether (**9**); substituted phenols (**10**–**16**); dialkylated phenols **17** (chromone and *o*-substituted), **18** and **19** (*ortho* and *o*-substituted), **20** and **21** (*ortho*- and *para*-substituted); *ortho*-disubstituted phenol (**22**); myrtenol derivatives (**22–27**); and myrtenol derivatives with two aromatic cores (**28–33**) (Scheme 1).

A variety of structures for the terpene substituent was noted in the alkylation products. The presence of a strained cyclobutane moiety in the 2,6,6-trimethylcyclo[3.1.1]heptane skeleton of myrtenol was reflected in the chemical behavior of this compound. The myrtenol structure can undergo Wagner–Meerwein rearrangement, the small ring of the bicyclic terpene can open, and a Nametkin rearrangement can occur in the presence of electrophilic reagents, Bronsted and Lewis acids and as a result of thermal treatment [9–11]. The presence of the double bond in the allyl position of myrtenol makes the hydroxyl proton labile and explains the high reactivity of this terpene alcohol.

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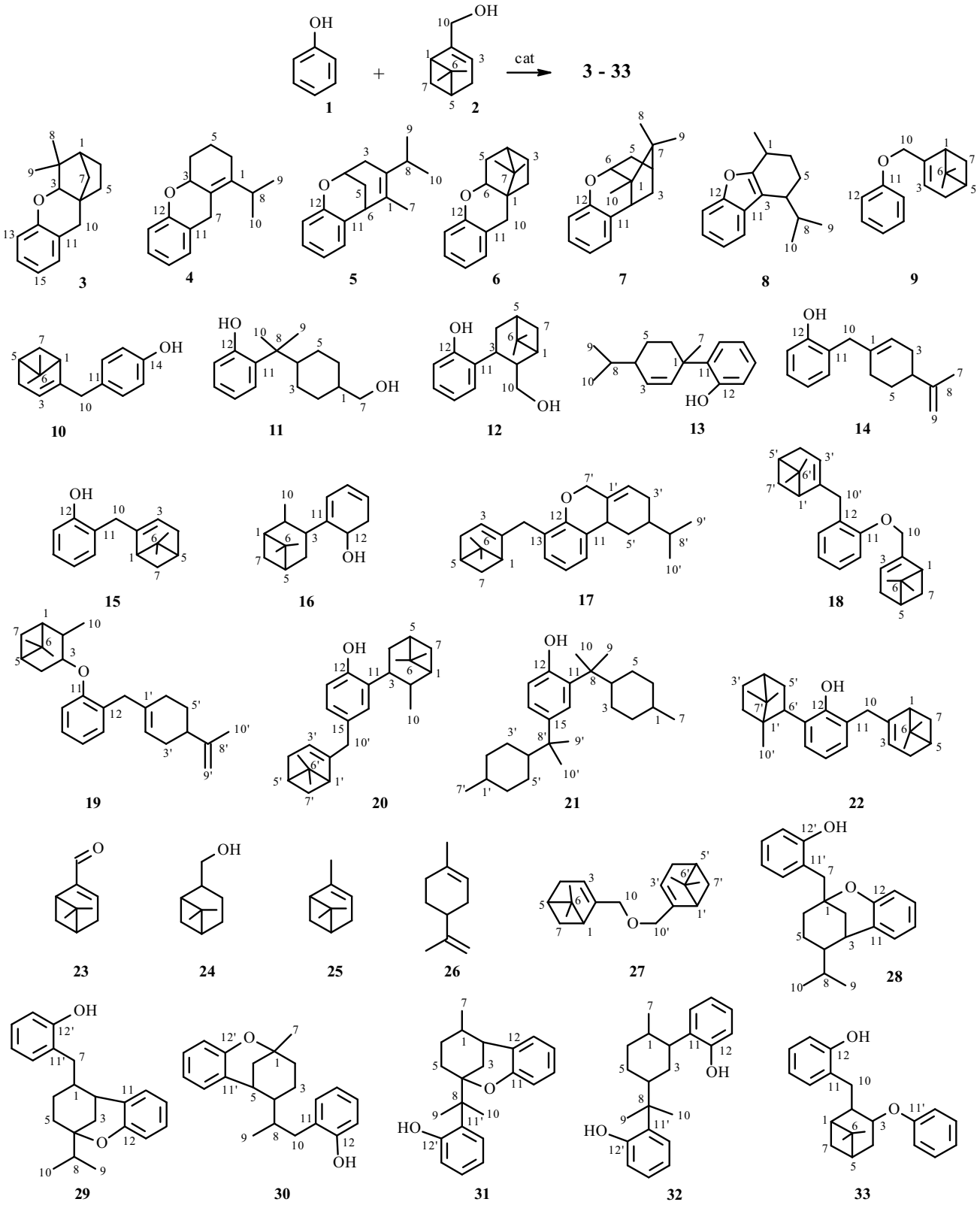


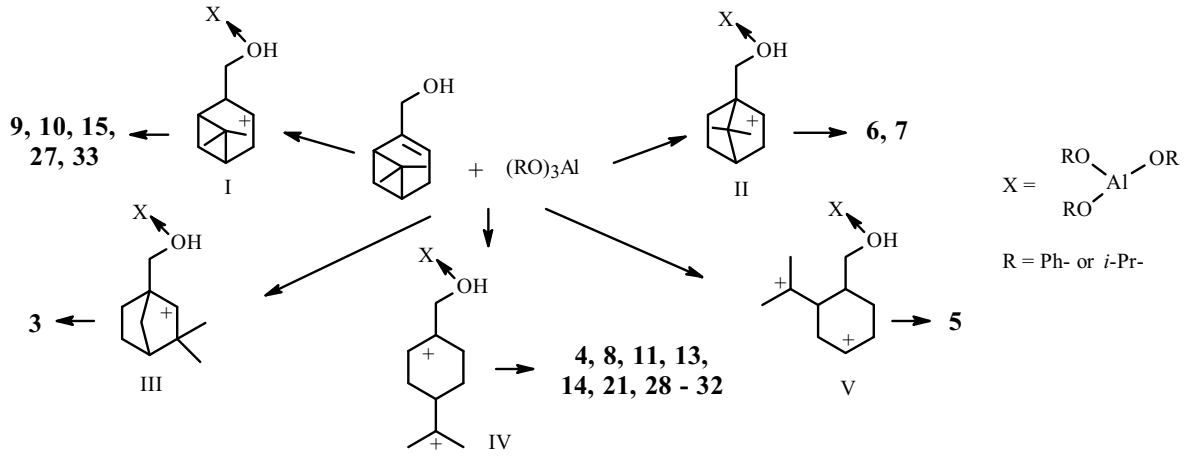
Scheme 1

The use of organoaluminum catalysts for the alkylation has its own pecularities. Certain studies showed that the reaction of terpenes with phenols involving such catalysts occurred in aluminum. It was assumed during the alkylation of phenol by myrtenol that the terpene alcohol O atom first coordinated to the Al atom of the catalyst. Then, the terpene underwent isomerization (in certain instances) and was bonded to phenol (Scheme 2).

TABLE 1. Alkylation of Phenol by Myrtenol in the Presence of $(i\text{-PrO})_3Al$

T, °C	Myrtenol conversion, %	Mass part of reaction products, %								
		phenol derivatives with one terpene substituent				phenol derivatives with two terpene substituents			8	9
		1	2	3	4	5	6	7		
PhOH–myrtenol–$(i\text{-PrO})_3Al$, 1:1:1										
120	96	11	12	9	–	–	–	7	–	61
140	98	–	2	39	–	–	20	–	15	24
160	95	–	–	15	–	17		9	37	33
PhOH–myrtenol–$(i\text{-PrO})_3Al$, 1:1:0.1										
160*	60	–	–	–	2	37		–	25	36

1, ethers; 2, cyclic ethers; 3, *ortho*-substituted phenols; 4, *para*-substituted phenols; 5, O–C-substituted phenols (chromans); 6, O–C-substituted phenols; 7, C–C-substituted phenols; 8, myrtenol derivatives; 9, unidentified products.
*Reaction continued for 8 h; reaction did not go at 120 and 140°C.



Scheme 2

Compounds **3**–**8**, **11**, **13**, **14**, **21**, and **28**-**32** are examples of isomerization of the myrtenol substituent. One of the two terpene substituents in **17** and **19** isomerized. Phenol derivatives **9**, **10**, **15**, **27**, and **33** had a myrtenyl substituent.

Tables 1 and 2 present the experimental results. Table 1 shows the products of phenol alkylation by myrtenol in the presence of aluminum isopropoxide.

The influence of temperature and amount of catalyst on the product yields could be found by analyzing the data in Table 1. In particular, the alkylation did not proceed selectively with equimolar amounts of $(i\text{-PrO})_3Al$, phenol, and myrtenol at 120°C. A difficultly separated product mixture was observed. The major fractions were O-substituted phenol derivatives such as ether **9** and the mixture of chromans **4** and **5** in 11 and 12% yields, respectively. Furthermore, *ortho*-terpenophenol **14** and disubstituted terpenophenol **20** (9 and 7%, respectively) were formed under these same conditions in an approximately equal amount. The formation of monoalkylated *ortho*-terpenophenols was significant (39%) at 140°C. The structure of the terpene substituent in **11**, **13**, and **14** had the *para*-menthane structure. The reaction mixture contained a significant (20%) amount of **19**, a phenol derivative substituted at the O atom and the C atom in the *ortho*-position of the aromatic ring.

Practically the same (26%) amount of disubstituted terpenophenols was formed at 160°C. However, a greater variety of structures was formed. These included **17**, **18**, and **22**. The total content of monoalkylated terpenophenols **14** and **15** was 15% under these conditions. Carrying out the reaction with catalytic amounts of $(i\text{-PrO})_3Al$ gave disubstituted phenol derivatives **17** and **18** (overall yield 37%). Table 2 presents results for the alkylation of phenol by myrtenol in the presence of aluminum phenoxide.

TABLE 2. Alkylation of Aluminum Phenoxide by Myrtenol

T, °C	Myrtenol conversion, %	Mass part of reaction products, %							
		phenol derivatives with one terpene substituent				5	6	7	8
		1	2	3	4				
				$(PhO)_3Al$–myrtenol, 1:1					
120	97	–	18	23	–	–	37	–	22
140	98	–	50	17	–	–	33	–	
160	96	1	12	–	–	2	15	13	57
				PhOH–myrtenol–$(PhO)_3Al$, 1:1:0.1					
160*	50	5	–	9	4	–	–	18	64

1, ethers; 2, chromans; 3, *ortho*-substituted phenols; 4, *para*-substituted phenols; 5, dialkylated phenols; 6, diphenols; 7, myrtenol derivatives; 8, unidentified products.
*Reaction continued for 8 h; reaction did not go at 120 and 140°C.

The alkylation of aluminum phenoxide by myrtenol at 120 and 140°C occurred with formation of chromans, *ortho*-monosubstituted phenols, and diphenols. The chroman content increased from 18 to 50% upon increasing the temperature from 120 to 140°C whereas that of *ortho*-monosubstituted phenols decreased from 23 to 17%. Diphenols were formed in approximately equal amounts, 37 and 33%, respectively, under these temperature conditions. Increasing the temperature further to 160°C produced a large amount of polymeric products and resins. Chromans (12%), diphenols (15%), and insignificant amounts of ethers and disubstituted phenols (1 and 2%, respectively) were isolated under these conditions. Compound **6** was formed regardless of the reaction temperature. Its maximum content (34% of total reaction products) was found at 140°C whereas it was obtained in 11 and 10% at 120 and 160°C, respectively. Derivative **6** with a bornyl moiety was the dominant chroman for the reaction at 160°C. The content of **3** was only 2%. Phenol derivatives with the chroman structure **7** were obtained in 7% yield at 120°C; chroman **8**, 16% at 140°C. Monoalkylated *orto*-substituted phenols included two basic structures. Compound **12** was formed at 120°C (20% of total amount of reaction products); **16**, at 140°C (17%).

A distinguishing feature of the alkylation of $(PhO)_3Al$ by myrtenol was the presence in the reaction products of compounds with two aromatic cores (**28–33**). Heating to 120°C gave mainly phenol derivative **29** (21.6%). Increasing the temperature further did not enhance the selective formation of any product.

Phenol reacted with myrtenol in the presence of a catalytic amount of $(PhO)_3Al$ at temperatures of at least 160°C for 8 h. The myrtenol conversion was 50%. The products included ether **9**, 5%; *ortho*-substituted phenol **15**, 9%; and *para*-substituted phenol **10**, 4%. Polymerization products were also present.

Myrtenol derivatives myrtanol (**24**), myrtenal (**23**), myrtenol ether (**27**), and α-pinene (**25**) and limonene (**26**) were formed in addition to the alkylation products via the reaction of phenol with myrtenol in the presence of organoaluminum catalysts $(i\text{-PrO})_3Al$ and $(PhO)_3Al$. The presence of myrtanol (**24**) in the reaction products was explained by a Meerwein–Ponndorf–Verley reduction [12] that occurred in the presence of aluminum isopropoxide. Alkylation of phenol by myrtenol using equimolar amounts of $(i\text{-PrO})_3Al$ at 140°C formed 15% myrtanol and at 160°C, 37% myrtanol of the total amount of reaction products. Carrying out the reaction with a catalytic amount produced 19% myrtanol. Myranol was observed in the products of the reaction occurring in the presence of $(PhO)_3Al$ (160°C, reagent method, 13% of total amount of reaction products). Myrtenal (**23**) was formed by the reaction with a catalytic amount of $(i\text{-PrO})_3Al$ (6%) and $(PhO)_3Al$ (13%). Another myrtenol derivative, ether **27**, which was obtained in 5% yield as a result of intermolecular dehydration of the alcohols [13], was identified in the products of phenol alkylation in the presence of $(PhO)_3Al$.

A comparison of the action of $(PhO)_3Al$ and $(i\text{-PrO})_3Al$ found that both catalysts were primarily *ortho*-orienting. The optimum temperature range for phenol alkylation by myrtenol was 120–140°C. Selective alkylation occurred with a reagent amount of the organoaluminum compound. The main products in the presence of $(i\text{-PrO})_3Al$ were *ortho*-substituted phenols, among which **11** dominated. The chroman fraction was large with **6** predominating in the presence of $(PhO)_3Al$.

Other features were evident for each of the alkoxides. First, diphenols were formed if $(PhO)_3Al$ was used. Derivatives **28**–**31** had the chroman structure with a second aromatic ring bonded to the terpene. Terpenophenols similar to **32** [14] were prepared by reacting an excess of phenol with unsaturated terpenes such as γ-terpinene, 3-carene, sabinene, limonene, and

α-pinene on Amberlite ion-exchange resin. In this instance, two phenols in the *para*-position relative to the phenol hydroxyl were added to the terpene. *Ortho*-substituted derivatives were formed in the presence of $(PhO)_3Al$.

Second, phenol was disubstituted by terpenes in the presence of $(i\text{-PrO})_3Al$ with compounds of structures **17**–**19** dominating. The reaction of myrtenol and phenol in the presence of $(i\text{-PrO})_3Al$ was accompanied by reduction of myrtenol to myrtanol as a side reaction.

EXPERIMENTAL

IR spectra were recorded in thin layers and KBr pellets on a Shimadzu IR Prestige 21 IR-Fourier spectrometer; PMR and ^{13}C NMR spectra, in $CDCl_3$ on a Bruker Avance 300 (operating frequency 300 and 75 MHz, respectively) using $CHCl_3$ resonances (δ_H 7.26 ppm, δ_C 76.90 ppm) as internal standards. Resonances were assigned using ^{13}C NMR spectra recorded in JMOD mode and 2D NMR spectroscopic methods. The purity of the starting materials was monitored and reaction products were analyzed by GC on a Shimadzu GC-2010AF chromatograph using an HP-1 capillary column (60 m × 0.25 mm × 0.25 μm; 100–240°C temperature regime; heating rate 6°C/min), a flame-ionization detector, and He carrier gas. The course of reactions was monitored by TLC on Sorbfil plates. Compounds were detected using an alcohol solution of vanillin and heating to 100–150°C. Silica gel 60 (70–230 μm) was used for column chromatography.

Alkylation of Aluminum Phenoxide by Myrtenol. A two-necked 100-mL flask equipped with a thermometer and reflux condenser was charged with phenol (3.73 g, 39.6 mmol), heated to 160°C, treated in portions with Al (chips, 0.36 g, 13.2 mmol), and held at the temperature until the Al dissolved completely. The mixture was cooled to room temperature, treated with myrtenol (2.0 g, 13.2 mmol), and held at the set temperature for 3 h. The course of the reaction was followed using TLC (solvent system hexane:Et_2O, 9:1, detection by alcoholic vanillin/H_2SO_4). When the reaction was finished the mixture was transferred to a separatory funnel, treated with HCl solution (5 mL, 0.05 N), and extracted with Et_2O (2 × 15 mL). The Et_2O extract was worked up with aqueous NaOH (5%, 2 × 5 mL), washed with H_2O and saturated NaCl solution, and dried over anhydrous $MgSO_4$. The solvent was removed. The products were separated by adsorption column chromatography over a column (30 × 0.8 cm) of Silica gel 60 (70–230 μm) with elution by petroleum ether:Et_2O with increasing (from 0 to 4%) fraction of Et_2O. The reagents were loaded simultaneously if $(i\text{-PrO})_3Al$ was used. The reaction mixture was worked up and the reaction products were separated using the aforementioned methods.

Alkylation of Phenol by Myrtenol in the Presence of $(PhO)_3Al$ or $(i\text{-PrO})_3Al$. A two-necked 100-mL flask equipped with a thermometer and reflux condenser was charged with phenol (0.56 g, 6.0 mmol), heated to 160°C, and treated in small portions with aluminum chips (0.016 g, 0.6 mmol). After the Al was completely dissolved in the phenol, the solution was cooled to 40°C and treated with myrtenol (1 g, 6 mmol). The reagents were loaded simultaneously if $(i\text{-PrO})_3Al$ (10% of starting phenol) was used. The reaction was carried out maintaining the temperature at 160°C until myrtenol was fully converted (GC and TLC monitoring). When the reaction was finished, the mixture was cooled, diluted with Et_2O, treated with HCl solution (10%) to decompose the catalyst, and washed with saturated NaOH solution and water until neutral. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed. The products were separated by adsorption column chromatography over a column (30 × 0.8 cm) of SiO_2 (100–200 mesh) with elution by petroleum ether:Et_2O with increasing (from 0 to 4%) fraction of Et_2O.

2-*tert*-Butyl-3-ethyl-3-propylchroman (3) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 160°C (1.4% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 1.02 (3H, s, CH_3-9), 1.11 (3H, s, CH_3-8), 1.32 (2H, m, H-7), 1.53 (1H, m, H-1), 1.74 (2H, m, H-6), 1.86 (2H, m, H-5), 3.15 (2H, s, H-10), 3.54 (1H, s, H-3), 6.82-7.16 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 20.03 (C-9), 24.35 (C-6), 26.11 (C-8), 26.33 (C-5), 34.76 (C-7), 39.56 (C-10), 41.41 (C-2), 46.01 (C-4), 49.46 (C-1), 87.31 (C-3), 117.13 (C-13), 119.74 (C-15), 122.74 (C-11), 127.14 (C-14), 127.62 (C-16), 157.57 (C-12).

1-Isopropyl-2,4,4a,9-tetrahydro-3*H*-xanthene (4) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 120°C (7.4% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.99 (3H, d, J = 6.8, CH_3-10), 1.03 (3H, d, J = 6.8, CH_3-9), 1.51 (2H, m, H-5), 1.61 (2H, m, H-4), 3.00 (1H, m, H-8), 3.18 (2H, s, H-7), 4.46 (1H, m, H-3), 6.75-7.35 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 21.17 (C-10), 23.40 (C-4), 25.30 (C-6), 27.59 (C-8), 28.05 (C-7), 29.51 (C-4), 79.92 (C-3), 114.95 (C-13), 120.15 (C-15), 126.94 (C-11), 127.77 (C-14), 135.43 (C-2), 144.09 (C-1), 155.81 (C-12).

11-Isopropyl-12-methyl-8-oxatricyclo[7.3.1.0*2,7*]trideca-2(7),3,5,11-tetraene (5) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 120°C (4.8% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.85 (3H, d, J = 6.8, CH_3-9), 0.90 (3H, d, J = 6.8, CH_3-10), 1.39 (2H, m, H-5), 1.50 (3H, s, CH_3-7), 2.44 (1H, m, H-8), 2.77 (2H, m, H-3), 3.00 (1H, m, H-6), 4.76 (1H, m, H-4), 6.92-7.22 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 15.14 (C-7), 20.60 (C-10), 20.60 (C-9), 27.03 (C-8), 29.20 (C-5), 34.99 (C-3), 39.77 (C-6), 82.59 (C-4), 114.76 (C-13), 119.76 (C-15), 127.18 (C-14), 128.89 (C-16), 132.02 (C-11), 134.34 (C-1), 136.57 (C-2), 153.00 (C-12).

3-*tert*-Butyl-2-ethyl-3-propylchroman (6) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 120°C (11.0% yield) and at 160°C (9.8% yield) and in the presence of $(i\text{-PrO})_3Al$ at 140°C (14.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.92 (3H, s, CH_3-8), 0.94 (3H, s, CH_3-9), 1.61 (2H, m, H-3), 1.76 (1H, m, H-4), 1.83 (2H, m, H-3), 2.11 (2H, m, H-5), 2.72 (2H, d, J = 14.3, H-10), 3.97 (1H, m, H-6), 6.77-7.10 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 19.77 (C-8), 20.47 (C-9), 24.20 (C-3), 25.67 (C-2), 33.95 (C-10), 38.48 (C-5), 44.76 (C-4), 45.11 (C-7), 46.89 (C-1), 81.11 (C-6), 116.63 (C-13), 120.13 (C-15), 122.01 (C-11), 126.75 (C-14), 129.39 (C-16), 156.80 (C-11).

3-*tert*-Butyl-3-methyl-2,4-diethylchroman (7) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 120°C (6.8% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.85 (3H, s, CH_3-10), 1.00 (3H, s, CH_3-9), 1.03 (3H, s, CH_3-8), 1.58 (2H, m, H-3), 1.67 (1H, m, H-4), 2.46 (2H, m, H-5), 2.90 (1H, m, H-6), 4.57 (1H, m, H-2), 6.85–7.14 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 12.28 (C-10), 18.75 (C-8), 19.57 (C-9), 36.05 (C-3), 38.93 (C-4), 39.51 (C-5), 41.96 (C-6), 42.78 (C-7), 49.11 (C-1), 80.25 (C-2), 116.39 (C-16), 119.91 (C-14), 126.75 (C-12), 127.24 (C-13), 129.99 (C-15), 153.57 (C-11).

1-Isopropyl-4-methyl-1,2,3,4-tetrahydrodibenzofuran (8) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 140°C (15.5% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.91 (3H, d, J = 6.64, CH_3-10), 0.94 (3H, d, J = 6.64, CH_3-9), 1.47 (3H, d, J = 6.92, CH_3-7), 1.69 (2H, m, H-6), 2.14 (2H, m, H-5), 2.39 (1H, m, H-8), 2.85 (1H, m, H-1), 3.10 (1H, m, H-4), 7.23–7.61 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 18.67 (C-7), 20.15 (C-10), 20.45 (C-9), 23.05 (C-5), 28.23 (C-1), 29.70 (C-8), 31.88 (C-4), 40.64 (C-6), 110.97 (C-13), 118.19 (C-3), 119.74 (C-16), 121.88 (C-15), 122.62 (C-14), 128.38 (C-11), 155.22 (C-2), 156.35 (C-12).

6,6-Dimethyl-2-phenoxymethylbicyclo[3.1.1]hept-2-ene (9) was prepared by alkylation using the catalytic method in the presence of $(PhO)_3Al$ at 160°C (5.3% yield) and the reagent method in the presence of $(i\text{-PrO})_3Al$ at 120°C (10.9% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.92 (3H, s, CH_3-8), 1.37 (3H, s, CH_3-9), 1.27 (2H, m, H-7), 2.19 (1H, m, H-5), 2.27 (1H, m, H-1), 2.47 (2H, m, H-4), 4.45 (2H, s, H-10), 5.67 (1H, m, H-3), 6.96-7.01 (3H, m, H-13-15), 7.30–7.35 (2H, m, H-12, 16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 21.10 (C-8), 26.24 (C-9), 31.32 (C-7), 31.58 (C-4), 38.13 (C-6), 40.95 (C-5), 43.33 (C-1), 70.63 (C-10), 114.93 (C-12, 16), 120.13 (C-3), 120.59 (C-14), 129.31 (C-13, 15), 144.07 (C-2), 159.04 (C-11).

4-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylethyl)phenol (10) was prepared by alkylation using the catalytic method in the presence of $(PhO)_3Al$ at 160°C (4.0% yield), the reagent method in the presence of $(i\text{-PrO})_3Al$ at 140°C (5.0% yield), and the catalytic method in the presence of $(i\text{-PrO})_3Al$ at 160°C (1.5% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.74 (3H, s, CH_3-9), 1.21 (3H, s, CH_3-8), 1.96 (2H, t, J = 2.8, H-4), 2.05 (1H, m, H-5), 2.30 (2H, m, H-7), 2.32 (1H, m, H-1), 3.20 (2H, s, H-10), 5.21 (1H, m, H-3), 6.61–7.03 (4H, m, H-12, 13, 15, 16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 20.01 (C-9), 26.24 (C-8), 31.37 (C-4), 31.82 (C-7), 38.23 (C-6), 40.71 (C-5), 42.61 (C-10), 45.44 (C-1), 114.93 (C-13, 15), 117.36 (C-3), 130.28 (C-12, 16), 134.01 (C-11), 147.05 (C-2), 155.50 (C-14).

2-[1-(4-Hydroxymethylcyclohexyl)-1-methylethyl]phenol (11) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 140°C (24.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.83 (2H, m, H-3), 0.87 (2H, m, H-5), 0.90 (2H, m, H-2), 0.92 (2H, m, H-6), 1.28 (3H, s, CH_3-10), 1.30 (3H, s, CH_3-9), 1.69 (1H, m, H-1), 1.89 (1H, m, H-4), 3.23 (2H, m, H-7), 5.09 (1H, s, $CH_2O\underline{H}$), 6.76–7.25 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 22.61 (C-10), 22.66 (C-9), 24.33 (C-2, 6), 25.88 (C-3, 5), 33.58 (C-1), 35.65 (C-8), 49.72 (C-4), 66.05 (C-7), 115.10 (C-13), 120.37 (C-15), 126.41 (C-14), 127.00 (C-16), 134.54 (C-11), 152.45 (C-12).

2-(2-Hydroxymethyl-6,6-dimethylbicyclo[3.1.1]hept-3-yl)phenol (12) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 120°C (19.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.90 (3H, s, CH_3-8), 1.25 (3H, s, CH_3-9), 1.95 (2H, m, H-7), 2.16 (2H, m, H-4), 2.33 (1H, m, H-2), 2.50 (1H, m, H-1), 2.54 (1H, m, H-5), 2.94 (1H, m, H-3), 3.49 (2H, d, J = 11.72, H-10), 6.83–7.16 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 20.19 (C-8), 23.45 (C-7), 26.65 (C-9), 37.51 (C-3), 37.75 (C-5), 39.18 (C-6), 39.98 (C-2), 42.14 (C-1), 66.77 (C-10), 115.08 (C-13), 119.78 (C-15), 127.10 (C-16), 127.83 (C-14), 131.18 (C-11), 151.76 (C-12).

2-(4-Isopropenyl-1-methylcyclohex-3-enyl)phenol (13) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 140°C (7.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.83 (3H, m, CH_3-9), 0.88 (3H, m, CH_3-10), 1.53 (2H, m, H-6), 1.58 (2H, m, H-5), 1.65 (1H, m, H-8), 1.68 (3H, s, CH_3-7), 1.99 (1H, m, H-4), 5.43 (1H, m, H-3), 5.48 (1H, m, H-2), 7.03–7.12 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 19.70 (C-9), 20.15 (C-10), 27.83 (C-5), 28.47 (C-7), 32.00 (C-8), 37.98 (C-6), 41.14 (C-4), 43.23 (C-1), 115.06 (C-13), 122.05 (C-15), 127.41 (C-16), 128.28 (C-14), 129.18 (C-2), 132.86 (C-11), 137.34 (C-3), 153.91 (C-12).

2-(4-Isopropenylcyclohex-1-enylmethyl)phenol (14) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 120°C (8.6% yield), at 140°C (2.0% yield), and at 160°C (6.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.53 (2H, m, H-5), 1.78 (3H, s, CH_3-7), 2.01 (1H, m, H-4), 2.20 (2H, m, H-6), 2.24 (2H, m, H-3), 3.39 (2H, s, H-10), 4.47 (2H, d, J = 1.5, H-9), 5.70 (1H, m, H-2), 6.84–7.22 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 21.09 (C-7), 27.63 (C-5), 28.53 (C-6), 29.20 (C-3), 37.74 (C-10), 40.72 (C-4), 108.84 (C-9), 115.08 (C-13), 117.22 (C-15), 122.21 (C-2), 124.86 (C-11), 127.18 (C-14), 130.12 (C-16), 136.57 (C-1), 149.64 (C-8), 153.97 (C-12).

2-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylethyl)phenol (15) was prepared by alkylation using the catalytic method in the presence of $(PhO)_3Al$ at 160°C (9.3% yield) and the reagent method in the presence of $(i\text{-PrO})_3Al$ at 140°C (2.0% yield) and at 160°C (9.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.85 (3H, s, CH_3-9), 1.21 (2H, m, H-7), 1.28 (3H, s, CH_3-8), 2.09 (2H, m, H-4), 2.14 (1H, m, H-5), 2.37 (1H, t, J = 5.6, H-1), 3.40 (2H, s, H-10), 5.47 (1H, t, J = 2.9, H-3), 6.84-7.20 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 20.82 (C-9), 26.25 (C-8), 31.32 (C-4), 31.49 (C-7), 38.01 (C-6), 39.03 (C-10), 40.63 (C-5), 45.37 (C-1), 116.02 (C-13), 118.68 (C-15), 120.56 (C-3), 126.54 (C-11), 127.98 (C-14), 131.01 (C-16), 147.05 (C-2), 155.07 (C-12).

2-(2,6,6-Trimethylbicyclo[3.1.1]hept-3-yl)phenol (16) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 120°C (4.3% yield) and at 140°C (17.3% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.88 (3H, s, CH_3-8), 0.91 (3H, m, CH_3-10), 1.21 (3H, s, CH_3-9), 1.76 (2H, m, H-7), 1.91 (2H, m, H-4), 2.14 (2H, m, H-2), 2.36 (1H, m, H-1), 2.51 (1H, m, H-5), 2.53 (1H, m, H-3), 6.77–7.12 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 19.82 (C-8), 21.66 (C-10), 23.28 (C-7), 24.25 (C-4), 26.77 (C-9), 31.59 (C-2), 35.07 (C-5), 36.22 (C-6), 41.04 (C-3), 49.21 (C-1), 115.18 (C-13), 120.05 (C-15), 126.77 (C-14), 130.74 (C-16), 132.48 (C-11), 152.75 (C-12).

4-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylethyl)-9-isopropyl-8,9,10,10a-tetrahydro-6*H*-benzo[*c*]chromene (17) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 160°C (6.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.84 (3H, s, CH_3-9), 1.33 (6H, s, CH_3-9′, 10′), 1.42 (3H, s, CH_3-8), 1.76 (2H, m, H-3′), 1.95 (1H, m, CH-8′), 2.08 (2H, m, H-5′), 2.18 (2H, m, H-4), 2.20 (1H, m, H-4′), 2.40 (2H, m, H-7), 2.42 (1H, m, H-1), 2.52 (1H, m, H-5), 3.20 (2H, s, H-10), 3.32 (1H, m, H-6′), 4.51 (2H, s, H-7′), 5.26 (1H, m, H-3), 5.72 (1H, m, H-2′), 6.83–7.31 (3H, m, H-14-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 20.92 (C-10′), 20.94 (C-9′), 22.97 (C-9), 26.06 (C-8), 26.74 (C-3′), 26.93 (C-8′), 31.25 (C-5′), 31.39 (C-4), 36.96 (C-7), 37.85 (C-6), 38.05 (C-6′), 40.18 (C-4′), 43.16 (C-5), 44.77 (C-10), 51.23 (C-1), 70.47 (C-7′), 114.75 (C-13), 116.74 (C-15), 120.41 (C-2′), 120.73 (C-2), 122.24 (C-14), 126.54 (C-11), 128.64 (C-16), 143.90 (C-1′), 146.41 (C-2), 154.48 (C-12).

3-(2-((6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)methoxy)benzyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (18) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 160°C (6.0% yield) and the catalytic method in the presence of $(i\text{-PrO})_3Al$ at 160°C (12.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.82 (3H, s, CH_3-9), 0.83 (3H, s, CH_3-9′), 1.39 (3H, s, CH_3-8), 1.40 (3H, s, CH_3-8′), 1.98 (2H, m, H-5, 5′), 2.10 (2H, m, H-4′), 2.13 (1H, m, H-1), 2.26 (2H, m, H-7′), 2.31 (1H, m, H-1′), 2.32 (2H, m, H-4), 2.38 (2H, m, H-7), 3.88 (2H, s, H-10′), 4.48 (2H, s, H-10), 5.56 (1H, m, H-3′), 5.70 (1H, m, H-3), 6.81–7.37 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 20.89 (C-8, 8′), 26.57 (C-9), 26.63 (C-9′), 31.11 (C-7), 31.27 (C-4′), 31.59 (C-7′), 31.78 (C-4), 35.19 (C-6), 37.82 (C-6′), 40.30 (C-5), 41.11 (C-5′), 44.53 (C-10′), 51.30 (C-1′), 72.39 (C-10), 114.72 (C-16), 119.40 (C-3), 119.92 (C-14), 120.37 (C-3′), 127.59 (C-15), 129.10 (C-13), 130.52 (C-12), 145.45 (C-2′), 145.54 (C-2), 157.56 (C-11).

3-[2-(4-Isopropenylcyclohex-1-enylmethyl)phenoxy]-2,6,6-trimethylbicyclo[3.1.1]heptane (19) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 140°C (20.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.89 (3H, d, J = 9.3, CH_3-10), 0.93 (3H, s, CH_3-9), 1.33 (3H, s, CH_3-8), 1.86 (3H, s, CH_3-10′), 1.87 (2H, m, H-5′), 1.92 (1H, m, H-1), 1.98 (1H, m, H-2), 2.00 (1H, m, H-4′), 2.02 (2H, m, H-4), 2.04 (2H, m, H-7), 2.09 (2H, m, H-6′), 2.25 (2H, m, H-3′), 3.12 (2H, s, H-7′), 3.48 (1H, m, H-3), 4.85 (2H, s, H-9′), 5.19 (1H, m, H-2), 6.93–7.18 (4H, m, H-13-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 14.07 (C-10), 21.93 (C-10′), 22.28 (C-9), 27.65 (C-8), 28.05 (C-7), 28.68 (C-5′), 33.90 (C-6′), 36.15 (C-3′), 36.85 (C-4), 37.23 (C-7′), 39.21 (C-6), 39.63 (C-2), 42.09 (C-4′), 43.97 (C-5), 45.73 (C-1), 80.25 (C-3), 108.96 (C-9′), 109.51 (C-16), 119.85 (C-14), 120.14 (C-2′), 127.95 (C-15), 128.02 (C-13), 130.75 (C-12), 132.15 (C-1′), 150.32 (C-8′), 157.11 (C-11).

4-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylethyl)-2-(2,6,6-trimethylbicyclo[3.1.1]hept-3-yl)phenol (20) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 120°C (8.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.79 (3H, s, CH_3-9′), 0.92 (3H, s, CH_3-9), 1.06 (3H, d, J = 7.3, CH_3-10), 1.28 (3H, s, CH_3-8′), 1.31 (3H, s, CH_3-8), 1.75 (2H, m, H-4), 1.79 (2H, m, H-4′), 1.81 (1H, m, H-2), 2.01 (2H, m, H-7′), 2.03 (1H, m, H-5′), 2.08 (1H, m, H-1′), 2.10 (1H, m, H-1), 2.27 (2H, m, H-7), 2.33 (1H, m, H-5), 2.37 (1H, m, H-3), 3.24 (2H, s, H-10′), 5.26 (1H, m, H-3′), 6.77-7.13 (3H, m, H-13, 14, 16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 19.84 (C-9), 20.29 (C-82), 21.61 (C-10), 26.25 (C-9′), 26.40 (C-8), 27.74 (C-7), 29.73 (C-4), 29.88 (C-4′), 31.38 (C-7′), 31.83 (C-2), 36.67 (C-6), 37.89 (C-6′), 40.73 (C-3), 41.09 (C-5), 41.34 (C-10′), 42.64 (C-5′), 45.46 (C-1), 46.21 (C-1′), 114.97 (C-13), 117.36 (C-3′), 129.87 (C-14), 130.27 (C-16), 131.42 (C-15), 131.67 (C-11), 147.72 (C-2′), 153.76 (C-12).

2,4-*bis*-[1-Methyl-1-(4-methylcyclohexyl)ethyl]phenol (21) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 160°C (2.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.88 (3H, m, CH_3-7), 0.90 (3H, m, CH_3-7′), 1.05 (3H, s, CH_3-9′), 1.08 (3H, s, CH_3-10′), 1.25 (2H, m, H-1, 1′), 1.27–1.30 (16H, m, H-2, 3, 5, 6, 2′, 3′, 5′, 6′), 1.39 (3H, s, CH_3-9), 1.42 (3H, s, CH_3-10), 1.52–1.58 (2H, m, H-4, 4′), 7.19–7.62 (3H, m, H-13, 14, 16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 18.67 (C-7), 20.13 (C-7′), 23.05 (C-9, 10), 28.23 (C-9′, 10′), 29.72 (C-3, 3′, 5, 5′), 30.08 (C-2, 2′, 6, 6′), 31.95 (C-1, 1′), 37.12 (C-8′), 37.43 (C-8), 40.64 (C-4, 4′), 119.73 (C-13), 121.86 (C-16), 122.61 (C-14), 132.87 (C-11), 140.67 (C-15), 150.29 (C-12).

2-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylethyl)-6-(1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)phenol (22) was prepared by alkylation using the reagent method in the presence of $(i\text{-PrO})_3Al$ at 160°C (9.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.79 (3H, s, CH_3-9), 0.85 (3H, s, CH_3-10′), 1.07 (3H, s, CH_3-9′), 1.09 (3H, s, CH_3-8′), 1.20 (3H, s, CH_3-8), 1.23 (2H, m, H-3′), 1.41 (2H, m, H-2′), 1.62 (2H, m, H-4), 1.66 (1H, m, H-4′), 1.78 (1H,

m, H-5), 2.07 (2H, m, H-5′), 2.20 (1H, m, H-1), 2.28 (2H, m, H-7), 3.41 (1H, m, H-6′), 3.90 (2H, s, H-10), 5.38 (1H, m, H-3), 6.62–7.15 (3H, m, H-14-16).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 11.40 (C-10′), 20.13 (C-9′), 21.08 (C-9), 22.60 (C-8′), 26.11 (C-8), 29.68 (C-3′), 31.12 (C-4), 31.33 (C-7), 31.79 (C-2′), 32.86 (C-5′), 37.64 (C-6), 40.99 (C-10), 42.25 (C-4′), 43.48 (C-5), 45.40 (C-1), 46.01 (C-1′), 49.34 (C-7′), 52.31 (C-6′), 115.32 (C-15), 120.43 (C-3), 125.83 (C-11), 129.35 (C-14), 129.56 (C-16), 130.14 (C-13), 147.14 (C-2), 155.85 (C-12).

The spectral properties of **23–26** agreed with those published earlier [15, 16].

2,2′-Oxy–*bis*-(methylene)-*bis*-(6,6-dimethylbicyclo[3.1.1]hept-2-ene) (27) was prepared by alkylation using the catalytic method in the presence of $(PhO)_3Al$ at 160°C (5.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.87 (6H, s, CH_3-8, 8′), 1.34 (6H, s, CH_3-9, 9′), 2.17 (2H, m, H-1, 1′), 2.19 (2H, m, H-5, 5′), 2.24 (4H, m, H-4, 4′), 2.41 (4H, m, H-7, 7′), 3.83 (4H, s, H-10, 10′), 5.26 (2H, m, H-3, 3′).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 21.08 (C-8, 8′), 29.98 (C-9, 9′), 31.46 (C-4, 4′), 31.54 (C-7, 7′), 38.00 (C-6, 6′), 39.85 (C-1, 1′), 43.47 (C-5, 5′), 72.57 (C-10, 10′), 119.41 (C-3, 3′), 145.63 (C-2, 2′).

2-(12-Isopropyl-8-oxatricyclo[7.3.1.0*2,7*]trideca-2(7),3,5-trien-9-ylmethyl)phenol (28) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 140°C (1.4% yield) and at 160°C (2.3% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.97 (3H, d, J = 6.6, CH_3-9), 1.08 (3H, d, J = 6.6, CH_3-10), 1.26 (2H, m, H-5), 1.37 (1H, m, H-8), 1.62 (1H, m, H-4), 1.85 (2H, m, H-6), 2.32 (1H, m, H-3), 2.81 (2H, dd, J = 14.8, H-7), 3.06 (2H, m, H-2), 6.84–7.16 (8H, m, H-13-16, 13′-16′).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 19.51 (C-5), 19.70 (C-9), 21.20 (C-10), 26.23 (C-8), 28.15 (C-2), 33.89 (C-6), 34.13 (C-3), 44.43 (C-7), 48.97 (C-4), 79.99 (C-1), 114.92 (C-13), 117.43 (C-13′), 120.05 (C-15), 120.47 (C-15′), 123.08 (C-11′), 126.65 (C-11), 127.50 (C-16), 128.35 (C-14), 128.61 (C-14′), 132.51 (C-16′), 152.95 (C-12′), 154.75 (C-12).

2-(9-Isopropyl-8-oxatricyclo[7.3.1.0*2,7*]trideca-2(7),3,5-trien-12-ylmethyl)phenol (29) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 120°C (21.6% yield), at 140°C (16.0% yield), and at 160°C (0.6% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.11 (3H, d, J = 6.9, CH_3-9), 1.13 (3H, d, J = 6.9, CH_3-10), 1.61 (2H, m, H-5), 1.69 (2H, m, H-6), 1.82 (1H, m, H-8), 1.95 (1H, m, H-1), 2.24 (2H, m, H-3), 2.90 (2H, m, H-7), 3.03 (1H, m, H-2), 6.83–7.19 (8H, m, H-13-16, 13′-16′).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 17.08 (C-9), 17.25 (C-10), 21.58 (C-3), 25.00 (C-5), 30.04 (C-6), 31.85 (C-7), 36.63 (C-8), 37.74 (C-2), 40.91 (C-1), 79.42 (C-4), 115.06 (C-13′), 115.24 (C-13), 118.88 (C-15′), 120.10 (C-15), 127.15 (C-14), 127.32 (C-14′), 127.79 (C-16′), 128.11 (C-11′), 128.29 (C-16), 130.39 (C-11), 154.24 (C-12′), 156.81 (C-12).

2-[2-(9-Methyl-8-oxatricyclo[7.3.1.0*2,7*]trideca-2,4,6-trien-12-ylmethyl)propyl]phenol (30) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 140°C (16.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 1.04 (3H, m, CH_3-9), 1.33 (2H, m, H-3), 1.69 (3H, s, CH_3-7), 1.87 (2H, m, H-2), 1.89 (1H, m, H-4), 2.12 (1H, m, H-8), 2.37 (2H, m, H-6), 2.88 (2H, m, H-10), 2.93 (1H, m, H-5), 6.80–7.19 (8H, m, H-13-16, 13′-16′).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 17.02 (C-9), 21.52 (C-3), 24.53 (C-2), 29.95 (C-7), 30.96 (C-6), 31.81 (C-10), 36.62 (C-5), 37.70 (C-8), 40.84 (C-4), 79.27 (C-1), 114.91 (C-13), 115.05 (C-13′), 118.82 (C-15), 120.84 (C-15′), 126.63 (C-16′), 127.24 (C-14), 127.53 (C-11′), 127.74 (C-11), 127.98 (C-16), 130.96 (C-14′), 153.68 (C-12), 156.77 (C-12′).

2-[1-Methyl-1-(12-methyl-8-oxatricyclo[7.3.1.0*2,7*]trideca-2(7),3,5,-trien-9-yl)ethyl]phenol (31) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 120°C (4.0% yield) and at 160°C (2.3% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.93 (3H, m, CH_3-7), 1.42 (3H, s, CH_3-10), 1.44 (3H, s, CH_3-9), 1.68 (2H, m, H-6), 1.76 (1H, m, H-1), 2.03 (2H, m, H-5), 2.92 (2H, m, H-3), 2.97 (1H, m, H-2), 6.7–7.19 (8H, m, H-13-16, 13′-16′).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 17.05 (C-7), 23.99 (C-9, 10), 24.04 (C-6), 24.45 (C-3), 33.37 (C-5), 36.00 (C-1), 37.90 (C-2), 42.71 (C-8), 87.05 (C-4), 115.79 (C-16), 116.62 (C-13′), 119.73 (C-15′), 120.91 (C-14), 126.74 (C-13), 126.86 (C-16′), 127.78 (C-12), 128.53 (C-15), 135.74 (C-11′), 154.01 (C-12′), 158.68 (C-11).

2-(2-(3-(2-Hydroxyphenyl)-4-methylcyclohexyl)propan-2-yl)phenol (32) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 120°C (10.7% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 0.93 (3H, m, CH_3-7), 1.19 (2H, m, H-6), 1.29 (3H, s, CH_3-10), 1.32 (3H, s, CH_3-9), 1.39 (2H, m, H-5), 1.51 (1H, m, H-1), 1.60 (2H, m, H-3), 1.76 (1H, m, H-4), 2.93 (1H, m, H-2), 6.7–7.19 (8H, m, H-13-16, 13′-16′).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 17.19 (C-7), 24.25 (C-10), 26.24 (C-9), 29.95 (C-5), 31.83 (C-6), 34.76 (C-1), 36.64 (C-3), 40.86 (C-8), 42.73 (C-4), 47.91 (C-2), 115.07 (C-13), 115.30 (C-13′), 120.03 (C-15), 120.43 (C-15′), 126.88 (C-14), 127.10 (C-14′), 127.73 (C-16), 128.57 (C-16′), 130.98 (C-11), 135.74 (C-11′), 153.83 (C-12), 154.01 (C-12′).

2-(6,6-Dimethyl-3-phenoxybicyclo[3.1.1]hept-2-ylmethyl)phenol (33) was prepared by alkylation using the reagent method in the presence of $(PhO)_3Al$ at 160°C (4.0% yield).

PMR spectrum (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.85 (3H, s, CH_3-9), 1.28 (3H, s, CH_3-8), 1.80 (2H, m, H-4), 1.82 (2H, m, H-7), 2.10 (1H, m, H-5), 2.18 (1H, m, H-2), 2.48 (1H, m, H-1), 2.93 (2H, dd, J = 3.8, 8.5, H-10), 4.71 (1H, m, H-3), 6.80–7.32 (9H, m, H-13-16, 12′-16′).

^{13}C NMR spectrum (75 MHz, $CDCl_3$, δ, ppm): 20.05 (C-9), 26.83 (C-8), 27.77 (C-4), 29.96 (C-7), 36.26 (C-10), 36.46 (C-6), 41.07 (C-5), 45.89 (C-1), 82.58 (C-3), 115.22 (C-12, 12′), 115.47 (C-13), 120.08 (C-15), 120.88 (C-14′), 127.00 (C-11, 16), 127.45 (C-13′, 15′), 129.47 (C-16′), 152.19 (C-12), 159.07 (C-11′).

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