# Alkylation of Phenols by Caryophyllene on Acid Aluminosilicate Catalysts

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The reactions of the natural sesquiterpene caryophyllene with phenols on various solid acid catalysts gave the corresponding terpenylphenols and phenyl terpenyl ethers with essentially caryolane structures. The selectivity of the process and yield of product can be raised by varying the catalyst and solvent.

**Introduction.** – Caryophyllene (**1**) is one of the most widespread and accessible sesquiterpenes. Owing to its structure with a strained (*E*)-substituted C=C bond in the nine-membered ring and *trans*-condensation of cyclononene with the cyclobutane fragment, **1** is a most fascinating object of investigation among polyenes with medium-sized rings. The rearrangements of **1** and related compounds were widely discussed in the literature. However, we have not found *Friedel-Crafts* alkylations by **1** [1][2]. The early works showed the use of an 'organized medium' (clays, zeolites) to provide not only better ecological characteristics of already well-known processes involving natural substrates, but also, owing to the special features of the latter, conformational mobility and polyfunctionality, give opportunity to realize inordinate transformations, and consequently a wider outlook for the use of 'renewable raw materials' in fine organic synthesis [3]. Present work shows that using zeolites and clay as 'organized medium' allows us to synthesize new products with high yields and selectivities. Moreover, the reactions do not proceed without catalysts or in the presence of AcOH.

**Results and Discussion.** – We have performed alkylations of various Me- and OH-substituted phenols (phenol (**2**), *o*-cresol (**3**), 3,5-dimethylphenol (**4**), 2,6-dimethylphenol (**5**), pyrocatechin (**6**), resorcin (**7**), hydroquinone (**8**), and eugenol (**9**) by diene **1**, forming terpenylphenols and phenyl terpenyl ethers with predominantly caryolane structures (*Scheme 1*). Interest in these products is motivated to some extent by the finding that analogous compounds isolated from *Magnolia ovobata* [4] affect neuron differentiation and chemotaxis and can act as neuron-growth and choline acetyltransferase activity promoters. The compound with a caryolane framework exhibits the greatest activity. Previously, for reactions of the natural terpene camphene, we succeeded in selecting solvents promoting either phenol or ether formation [5]. It appeared that the tendencies found for these reactions may occasionally be extended to reactions of sesquiterpene **1**. Thus, $CH_2Cl_2$ as a solvent promotes formation of terpenylphenols (**B**-type products), whereas terpenyl phenyl ethers (**A**-type products) are formed in $CH_2Cl_2$/benzene 1:1 (*v*/*v*). In both cases, the alicyclic fragment has a caryolane structure. The only exception is the reaction of phenol **3** in $CH_2Cl_2$, forming an unusual (**C**-type) product. The data of the reaction are summarized in *Table 1*.

*Scheme 1*

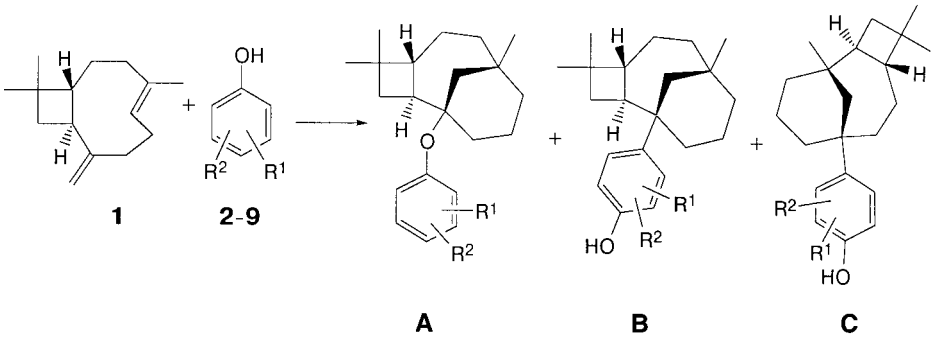
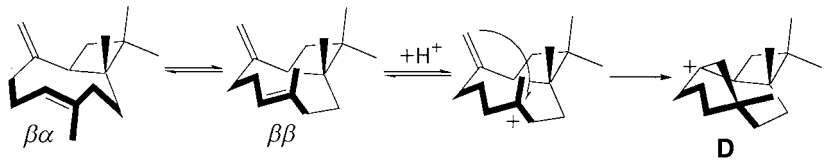



Table 1. *Experimental Conditions*

| Caryo-phyllene [mg] | Phenol [mg] | Solvent [ml] | Catalyst [mg] | Product, type of product, mass [mg] | Yield [%] | $[\alpha]_{580}^{20}$, $c$ [g/100 ml] | $M^+$, Elemental composition | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Found | Calc. |
| 455 | **2**, 205 | $CH_2Cl_2$, 5 | HB-2, 500 | **11**, **B**, 182 | 28 | +29.2, 2.3 | $C_{21}H_{30}O$, 298.22965 | $C_{21}H_{30}O$, 298.22965 |
| 509 | **2**, 228 | $CH_2Cl_2$/hexane, 1:1 (*v*/*v*), 10 | HB-2, 500 | **12**, **A**, 162<br>**11**, **B**, 1.5 | 23 | +42.6, 8.9 | $C_{21}H_{30}O$, 298.22974 | $C_{21}H_{30}O$, 298.22965 |
| 1387 | **3**, 724 | $CH_2Cl_2$, 20 | HB-2, 1500 | **13**, **A**, 175 | 8 | +22.4, 4.6 | $C_{22}H_{32}O$, 312.24473 | $C_{22}H_{32}O$, 312.24530 |
| | | | | **14**, **B**, 325 | 16 | +27.9, 4.9 | $C_{22}H_{32}O$, 312.24504 | $C_{22}H_{32}O$, 312.24530 |
| | | | | **15**, **C**, 120 | 6 | −8.4, 5.0 | $C_{22}H_{32}O$, 312.24497 | $C_{22}H_{32}O$, 312.24530 |
| 474 | **3**, 242 | $CH_2Cl_2$/benzene 1:1 (*v*/*v*), 10 | HB-2, 500 | **13**, **A**, 78 | 11 | | | |
| 449 | **3**, 228 | $CH_2Cl_2$, 6 | K-10, 2000 | **14**, **B**, 148 | 23 | | | |
| 441 | **3**, 233 | $CH_2Cl_2$, 6 | ZSM-12, 500 | **14**, **B**, 252 | 37 | | | |
| 441 | **4**, 244 | $CH_2Cl_2$, 10 | HB-2, 500 | **16**, **A**, 211 | 33 | +23.5, 5.8 | $C_{23}H_{34}O$, 326.25924 | $C_{23}H_{34}O$, 326.26095 |
| 410 | **4**, 227 | $CH_2Cl_2$/benzene 1:1 (*v*/*v*), 10 | HB-2, 500 | **16**, **A**, 97 | 12 | | | |
| 464 | **4**, 260 | $CH_2Cl_2$, 6 | K-10, 2000 | **16**, **A**, 122 | 11 | | | |
| 431 | **4**, 255 | $CH_2Cl_2$, 6 | ZSM-12, 500 | **16**, **A**, 115 | 14 | | | |
| 498 | **5**, 255 | $CH_2Cl_2$, 8 | HB-2, 500 | **17**, **B**, 122 | 18 | +23.8, 4.3 | $C_{23}H_{34}O$, 326.26085 | $C_{23}H_{34}O$, 326.26095 |
| 386 | **6**, 196 | $CH_2Cl_2$, 15 | HB-2, 500 | **18**, **A**, 174 | 31 | +22.4, 2.4 | $C_{21}H_{30}O_2$, 314.22416 | $C_{21}H_{30}O_2$, 314.22457 |
| | | | | **19**, **B**, 78 | 14 | +31.0, 2.0 | $C_{21}H_{30}O_2$, 314.22447 | $C_{21}H_{30}O_2$, 314.22457 |
| 218 | **7**, 118 | $CH_2Cl_2$, 10 | HB-2, 150 | **20**, **B**, 193 | 57 | +33.8, 2.5 | $C_{21}H_{30}O_2$, 314.22447 | $C_{21}H_{30}O_2$, 314.22457 |
| 455 | **8**, 199 | $CH_2Cl_2$, 15 | HB-2, 500 | **21**, **A**, 39 | 4 | +22.4, 0.7 | $C_{21}H_{30}O_2$, 314.22447 | $C_{21}H_{30}O_2$, 314.22457 |
| 313 | **9**, 248 | $CH_2Cl_2$, 6 | HB-2, 500 | **22**, **A**, 34 | 6 | +2, 2.0 | $C_{25}H_{36}O_2$, 368.27173 | $C_{25}H_{36}O_2$, 368.27151 |

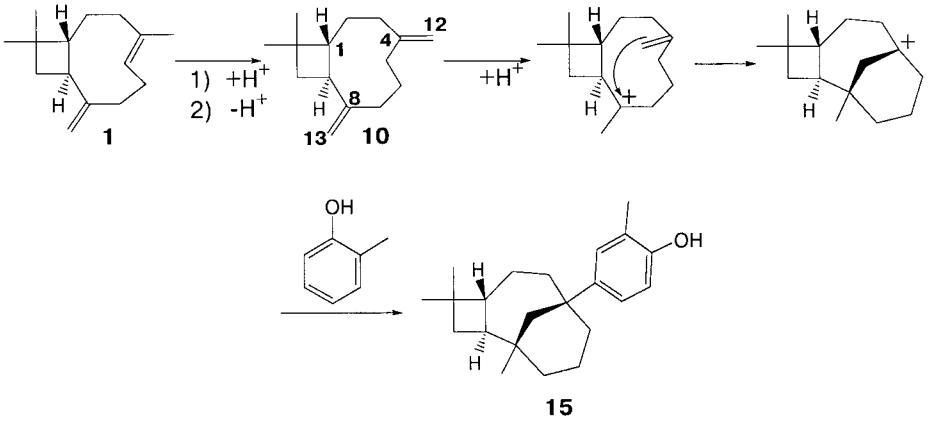
The products with a caryolane structure are formed probably as a result of a cationoid rearrangement leading to cation **D**, which is trapped by the aromatic reagent [1] (*Scheme 2*).

*Scheme 2*




Formation of the **C**-type product suggests that the reaction mechanism is different, involving the initial formation of the dimethylidene derivative **10** of caryophyllene, in which the cyclization starts with protonation of the C(8)=C(13) but not C(4)=C(12) bond, leading to a nucleophilic attack at C(4) but not at C(8) of the alicyclic framework (*Scheme 3*). Few references to formation of such products may be cited, among which it is worthwhile to note [6].

*Scheme 3*




We have established that diene **1** does not react at room temperature with benzene and $PhCH_2CH_2OH$; the reagents (*cf.* [7][8]) as well as caryophyllene on beta-zeolite and in $CH_2Cl_2$ remain unchanged. On the other hand, adduct formation always leads to a great variety of caryophyllene isomers (GC/MS data), the key isomer being clovene. Therefore, it is assumed that *i*) formation of carbocations from caryophyllene involves phenol, but the alkylation does not proceed in the absence of a catalyst; *ii*) the carbocations undergo rearrangements leading to various products, which correspond to the reacting conformers of caryophyllene. Notably, in homogeneous media, the carbocations formed from different conformers do not undergo mutual transformations [9]. This circumstance indicates that, under conditions of heterogeneous catalysis, alteration of the activation barriers of the possible transformations leads to new reactions, not observed in homogeneous reaction conditions.

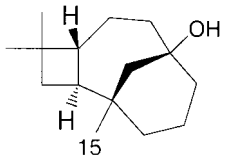
The reactions of phenols **3** and **4** were used to study the promoting effect of various solid catalyts (zeolites ZSM-5 and ZSM-12, clay K-10). The zeolite ZSM-5 proved to be

inactive as a catalyst; the reagents remained unchanged. On the wide-pore zeolite ZSM-12 and montmorillonite K-10, the products are the same as on $\beta$-zeolite, but the **C**-type product **15** is not formed at all. In the case of phenol **3**, using ZSM-12 and K-10 leads to high yields and high selectivity of reactions, which were not observed for phenol **4**. In the case of phenol **7**, we considered the effects of the temperature regime, solvent, application technique, reagent, and reagent/catalyst ratios on the reaction (*Table 2*). When the reaction is carried out with an excess of sesquiterpene **1**, the yield increases from 57 to 63% (based on phenol); in the case of excess phenol, the yield was 43% (based on diene **1**). For this reaction, the standard conditions are evidently close to optimal.

Table 2. *Optimization of Reactions Conditions for Resorcin Interaction with Caryophyllene*

| Caryo-phyllene [mg] | Resorcin [mg] | Solvent $CH_2Cl_2$, [ml] | HB-2, [mg] | Caryo-phyllene/ resorcin | Catalyst/ reagents (mass) | Conditions | Product [mg] | Yield [%] |
|---|---|---|---|---|---|---|---|---|
| 218 | 118 | 10 | 150 | 1 : 1 | 1 : 2 | 20 h at 25° | 193 | 57 |
| 253 | 68 | 10 | 150 | 2 : 1 | 1 : 2 | 20 h at 25° | 122 | 63 |
| 227 | 61 | 3 | 150 | 2 : 1 | 1 : 2 | 20 h at 25° | 97 | 55 |
| 236 | 63 | 0 | 150 | 2 : 1 | 1 : 2 | 20 h at 25° | 0 | 0 |
| 365 | 98 | 15 | 150 | 2 : 1 | 1 : 3 | 120 h at −22° | 168 | 60 |
| 373 | 101 | addition in $Et_2O$, evaporation | 150 | 2 : 1 | 1 : 3 | 48 h at 25° | 0 | 0 |
| 371 | 100 | in 300 ml $Et_2O$ | 150 | 2 : 1 | 1 : 3 | 48 h at 25° | 0 | 0 |
| 694 | 202 | 6 | 100 | 2 : 1 | 1 : 9 | 4 h at 0°, 17 h at 25°, 2 h at 40° | 257 | 45 |
| 370 | 100 | 15 | 150 | 2 : 1 | 1 : 3 | 30 min at −22°, 20 h at 25° | 126 | 44 |
| 609 | 160 | 15 | 150 | 2 : 1 | 1 : 4 | 30 min at −22°, addition of 2 equiv. **1**, 20 h at 25° | 91 | 20 |
| 371 | 100 | 5 | 150 | 2 : 1 | 1 : 3 | 72 h at −22°, 3 h at 25° | 94 | 33 |
| 374 | 101 | 2 | 150 | 2 : 1 | 1 : 3 | 72 h at −22°, 3 h at 25° | 66 | 23 |
| 494 | 533 | 23 | 500 | 1 : 2 | 1 : 2 | 20 h at 25° | 319 | 42 |

An analysis of the $^1$H- and $^{13}$C-NMR spectra of compound **15** and their comparison with the corresponding spectra of **14** and with the spectra of caryolanol and compound **23** reported in [6] have shown that the framework and the substituents in the aromatic ring did not change but the Me(15) substituent exchanged places with the aryl group. The attachment of the Me group to the C(1) atom and of the Ph residue to the C(8) atom is confirmed by the LRJMD spectra (1D $^{13}$C,$^1$H correlations on long-range constants [10]). Thus, selective pulse saturation of the Me group at 0.87 ppm (Me(15)) led to the following signals in the LRJMD spectrum: 32.41 (*s*), 37.4 (*d*), 37.58 (*t*), and 46.67 (*t*) ppm. This set of signals is characteristic of compound **15**. When the $^1$H-NMR signals of H−C(2) (2.37 ppm) and H−C(11) (1.12 ppm) were suppressed separately, the LRJMD spectrum contained not only the signals of **15** and **14**, but also a *quaduplet* at 27.69 ppm, assigned to the Me group at C(1). Note that the chemical shift of this group is close to that reported in [6] for **23** ($\delta$(Me(15)) 26.80 ppm).



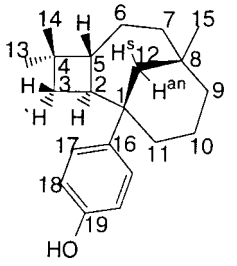

**23**

The upfield shift of the $H-C(3)$ signal by more than 1 ppm in compounds **11**, **14**, **17**, and **19** compared to those in **12**, **13**, **16**, **21**, and **22** is explained by the screening effect of the aromatic ring. For **20**, the diamagnetic shift of the signal of $H-C(3)$ is slightly smaller (*ca.* 0.3 ppm) than that of the compounds mentioned above. This is probably due to some steric hindrance created by the OH group, which is *ortho* to the substituted position, leading to rotation of the aryl residue in such a way that the H-atom at C(3) moves farther away from the center of the screening cone of the aromatic ring.

Thus, we have shown that the reactions of natural sesquiterpene **1** with phenols on various solid acid catalysts give the corresponding terpenylphenols and phenyl terpenyl ethers with essentially caryolane structures. The selectivity of the process and yield of product may be raised by varying the catalyst and solvent.

## Experimental Part

*General*. Reagents and products were analyzed by GLC with a flame-ionization detector, column temp. of 60–250°, and He as the carrier. Chromatograph '3700' was equipped with a glass cap. column. 17000 × 25 mm, phase VS-30. Products were separated over $SiO_2$ (40–100 μ, eluent containing from 1–10% of $Et_2O$ in hexane). K-10 Clay was obtained from *Fluka* (No. 69866). The catalyst was calcined for 3 h at 120° just before use. β-Zeolite was obtained as described in [12], $SiO_2/Al_2O_3$ *ca.* 40, $d \approx 8$ Å. It was calcined for 2 h at 500° before use. 2 H-ZSM-12 zeolite was obtained as described in [13], $SiO_2/Al_2O_3$ *ca.* 200, 5.7 × 6.2 Å; it was calcined for 2 h at 500° before use. Specific rotation was determined with spectrometer *Polamat A* in $CHCl_3$. $^1H$- and $^{13}C$-NMR spectra were recorded with *Bruker AM-400* ($^1H$: 400.13 MHz, $^{13}C$: 100.61 MHz) in $CCl_4/CDCl_3$ 1:1 (*v*/*v*) or $CCl_4/(CD_3)_2CO$ *ca.* 4:1 (*v*/*v*). $CDCl_3$ and $(CD_3)_2CO$ were used as internal standards ($\delta$(H) 7.24, $\delta$(C) 76.90 ppm) and ($\delta$(H) 2.04, $\delta$(C) 29.80 ppm), resp. The structure of the products was established by analyzing the geminal, vicinal, and long-range spin-spin coupling constants of protons in the $^1H,^1H$ double-resonance spectra and the $^{13}C$-NMR spectra. Signals in $^{13}C$-NMR spectra were assigned with selective and off-resonance proton irradiation and by means of differential spectra modulated with far spin-spin interaction $^{13}C,^1H$ (LRJMD experimental conditions were optimized for constant $J$(C,H) equal to 10 Hz). In some cases, the signals of the arom. C-atoms were assigned by considering data on the additive effect of substituents in the aromatic ring; the shift parameters were taken from [11]. For all of the new compounds, 2D $^{13}C,^1H$ heteronuclear correlation (2D-COSY) spectra were recorded (with the direct constant $^1J$(C,H) 134 Hz). The $^{13}C$-NMR data are given in *Tables 3* and *4*. Elemental composition was determined by the high-resolution mass spectrometry with *Finnigan 8200*.




**11**

*Standard Procedure.* A soln. of reagents in a solvent is added dropwise with stirring to a suspension of a solid catalyst in a solvent. The mixture is allowed to stay while stirring, then filtered off on a porous glass filter, washed with $Et_2O$, evaporated on a rotary evaporator, and kept for 20 min in vacuum (10 torr) at 60°. The particular experimental conditions are given in *Tables 1* and *2*.

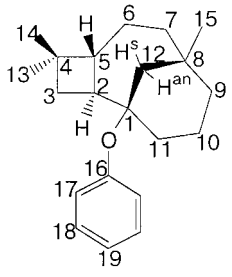
*(1*R*,2*S*,5*R*,8*S*)-4-(4,4,8-Trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-1-yl)phenol* (**11**): $^1$H-NMR: 0.51 (*dd*, *J*(3,3′) = 10, *J*(3,2) = 10, H−C(8)); 0.78 (*s*, Me(14)); 0.93 (*s*, Me(15)); 0.94 (*s*, Me(13)); 1.08 (*d*, *J*(12an,12s) = 13, $H_{an}$−C(12)); 1.09 (*m*, $H_a$−C(9)); 1.17 (*ddd*, *J*(7,7′) = 14, *J*(7,6) = 7, *J*(7,6′) = 4, H−C(1)); 1.26 (*m*, $H_a$−C(11)); 1.32 (*dd*, *J* = 10, *J*(3,2) = 8, 1 H−C(3)); 1.39, 1.54 (2*m*, 2 H−C(6)); 1.48 (*dm*, *J*(9e,9a) = 13, $H_2$−C(9)); 1.62 (*m*, H−C(5), 1 H−C(10)); 1.69 (*ddd*, *J* = 14, 9.5, 4, 1 H−C(7)); 1.93–2.04 (*m*, 1 H−C(10), $H_a$−C(11)); 2.10 (*ddd*, *J* = 13, *J*(12s,9e) = 2.5, *J*(12s,11e) = 2.5, $H_s$−C(12)); 2.38 (*ddd*, *J*(2,5) = 12, *J* = 10, 8, H−C(2)); 6.64 (*d*, *J*(18,17) = 9, 2 H−C(18)); 6.96 (*d*, *J* = 9, 2 H−C(17)); 7.45 (*s*, OH). $^{13}$C-NMR: see *Table 3*. MS: 298 (14, $M^+$), 255 (4), 199 (5), 187 (100), 134 (7), 107 (26), 95 (6), 81 (7), 69 (5), 55 (8), 41 (10).

*(1*R*,2*S*,5*R*,8*S*)-4,4,8-Trimethyl-1-phenoxytricyclo[6.3.1.0$^{2,5}$]dodecane* (**12**): $^1$H-NMR: 0.93 (*s*, Me(15)); 1.02 (*m*, 1 H−C(9)); 1.03 (*s*, Me(14)); 1.05 (*s*, Me(13)); 1.21, 1.60 (2*m*, 2 H−C(7)); 1.22 (*d*, *J*(12an,12s) = 13, $H_{an}$−C(12)); 1.35–1.46 (*m*, 1 H−C(6), 1 H−C(8), 1 H−C(11)); 1.54 (*m*, 1 H−C(6)); 1.67, 1.79 (2*m*, 2 H−C(10)); 1.69 (*dd*, *J*(3,3) = 10, *J*(3,2) = 8, 1 H−C(3)); 1.75 (*dd*, *J* = 10, *J*(3,2) = 10, 1 H−C(3)); 1.93 (*ddd*, *J* = 13, 3, 2,5, $H_s$−C(12)); 1.97 (*m*, 1 H−C(11)); 2.01 (*m*, 1 H−C(5)); 2.40 (*ddd*, *J*(2,5) = 12, *J* = 10, 8 H−C(2));

Table 3. *$^{13}$C-NMR Data for Compounds* **11**–**16** (chemical shifts in ppm)

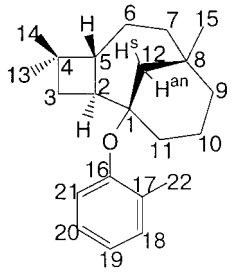
| C-Atom | **11**[a]) | **12**[a]) | **13**[b]) | **14**[b]) | **15**[b]) | **16**[b]) |
|---|---|---|---|---|---|---|
| C(1) | 39.88 (*s*) | 80.11 (*s*) | 80.40 (*s*) | 39.70 (*s*) | 32.41 (*s*) | 79.64 (*s*) |
| C(2) | 40.72 (*d*) | 41.93 (*d*) | 42.38 (*d*) | 40.56 (*d*) | 37.47 (*d*) | 41.58 (*d*) |
| C(3) | 39.15 (*t*) | 37.86 (*t*) | 38.14 (*t*) | 39.05 (*t*) | 35.95 (*t*) | 37.63 (*t*) |
| C(4) | 34.28 (*s*) | 34.77 (*s*) | 34.53 (*s*) | 34.06 (*s*) | 34.87 (*s*) | 34.58 (*s*) |
| C(5) | 46.18 (*d*) | 45.76 (*d*) | 45.77 (*d*) | 46.12 (*d*) | 44.92 (*d*) | 45.40 (*d*) |
| C(6) | 22.91 (*t*) | 22.88 (*t*) | 22.91 (*t*) | 22.80 (*t*) | 21.84 (*t*) | 22.56 (*t*) |
| C(7) | 37.88 (*t*) | 38.03 (*t*) | 38.06 (*t*) | 37.79 (*t*) | 37.67 (*t*) | 37.68 (*t*) |
| C(8) | 34.28 (*s*) | 35.01 (*s*) | 34.77 (*s*) | 34.09 (*s*) | 40.12 (*s*) | 34.80 (*s*) |
| C(9) | 38.38 (*t*) | 36.97 (*t*) | 36.66 (*t*) | 38.10 (*t*) | 37.28 (*t*) | 36.81 (*t*) |
| C(10) | 20.24 (*t*) | 21.08 (*t*) | 20.90 (*t*) | 20.02 (*t*) | 19.75 (*t*) | 20.89 (*t*) |
| C(11) | 37.90 (*t*) | 35.36 (*t*) | 35.38 (*t*) | 37.88 (*t*) | 37.58 (*t*) | 35.14 (*t*) |
| C(12) | 45.32 (*t*) | 47.54 (*t*) | 47.76 (*t*) | 45.02 (*t*) | 46.67 (*t*) | 47.34 (*t*) |
| C(13) | 21.20 (*q*) | 21.22 (*q*) | 21.08 (*q*) | 20.99 (*q*) | 21.06 (*q*) | 21.09 (*q*) |
| C(14) | 30.72 (*q*) | 30.70 (*q*) | 30.52 (*q*) | 30.52 (*q*) | 30.88 (*q*) | 30.50 (*q*) |
| C(15) | 34.80 (*q*) | 33.75 (*q*) | 33.66 (*q*) | 34.68 (*q*) | 27.69 (*q*) | 33.49 (*q*) |
| C(16) | 140.05 (*s*) | 155.86 (*s*) | 154.12 (*s*) | 141.64 (*s*) | 146.10 (*s*) | 155.49 (*s*) |
| C(17) | 126.88 (*d*) | 121.98 (*d*) | 129.94 (*s*) | 128.68 (*d*) | 127.72 (*d*) | 119.74 (*d*) |
| C(18) | 114.64 (*d*) | 128.65 (*d*) | 130.58 (*d*) | 122.43 (*s*) | 122.68 (*s*) | 137.51 (*s*) |
| C(19) | 154.82 (*s*) | 121.55 (*d*) | 120.87 (*d*) | 151.09 (*s*) | 151.16 (*s*) | 123.26 (*d*) |
| C(20) | | | 125.47 (*d*) | 114.09 (*d*) | 114.27 (*d*) | 21.48 (*q*) |
| C(21) | | | 119.78 (*d*) | 124.52 (*d*) | 123.50 (*d*) | |
| C(22) | | | 17.48 (*q*) | 16.21 (*q*) | 16.19 (*q*) | |

[a]) Solvent $CCl_4/(CD_3)_2CO$. [b]) Solvent $CCl_4/CDCl_3$.



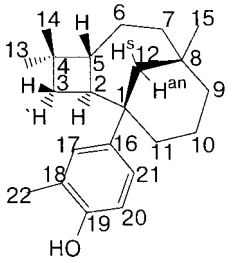

**12**

6.79 (*dd*, *J*(17,18) = 8.5, *J*(17,19) = 1, 2 H–C(17)); 6.87 (*tt*, *J*(19,18) = 7, *J* = 1, H–C(19)); 7.13 (*dd*, *J* = 8.5, 7, 2 H–C(18)). $^{13}$C-NMR: see *Table 3*. MS: 298 (59, $M^+$), 205 (66), 187 (100, 161 (26), 149 (55), 135 (42), 123 (49), 109 (58), 107 (44), 95 (71), 81 (71), 69 (54), 55 (38), 41 (32).



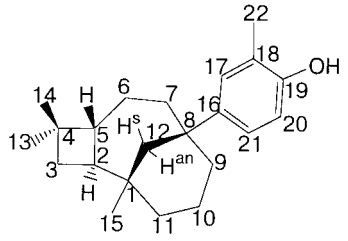

**13**

*(1*R*,2*S*,5*R*,8*S*)-4,4,8-Trimethyl-1-(2-methylphenoxy)tricyclo[6.3.1.0$^{2,5}$]dodecane* (**13**): $^1$H-NMR: 1.02 (*s*, Me(15)); 1.10 (*s*, Me(14)); 1.12 (*s*, Me(13)); 1.13 (*m*, 1 H–C(9)); 1.29, 1.67 (2*m*, 2 H–C(7)); 1.43 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.37–1.53 (*m*, 1 H–C(6), 1 H–C(9), H–C(11)); 1.62 (*m*, 1 H–C(6)); 1.75, 1.84 (2*m*, 2 H–C(10)); 1.81 (*dd*, *J*(3,3) = 10, *J*(3,2) = 8, 1 H–C(3)); 1.85 (*dd*, *J* = 10, *J*(3,2) = 10, 1 H–C(2)); 2.04–2.15 (*m*, H–C(5), 1 H–C(9), 1 H–C(11)); 2.28 (*s*, Me(22)); 2.46 (*ddd*, *J*(2,5) = 12, *J* = 10, 8, H–C(2)); 6.80 (*dd*, *J*(21,20) = 8, *J*(21,19) = 1.2, H–C(21)); 6.84 (*td*, *J* = 8, 1.2, H–C(19)); 7.02 (*td*, *J* = 8, *J*(20,18) = 1.5, H–C(20)); 7.12 (br. *d*, *J* = 8, H–C(18)). $^{13}$C-NMR: see *Table 3*. MS: 312 (34, $M^+$), 205 (100), 161 (14), 149 (76), 135 (53), 123 (66), 121 (45), 109 (69), 95 (80), 81 (78), 69 (55), 67 (34), 55 (40), 41 (41).



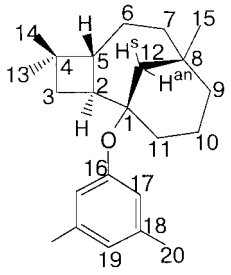

**14**

*(1*R*,2*S*,5*R*,8*S*)-2-Methyl-4-(4,4,8-trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-1-yl)phenol* (**14**): $^1$H-NMR: 0.56 (*dd*, *J*(3,3′) = 10, *J*(3,2) = 10, 1 H–C(3)); 0.85 (*s*, Me(14)); 0.99 (*s*, Me(15)); 1.00 (*s*, Me(13)); 1.14 (*ddd*, *J*(9a,9e) = 13, *J*(9a,10a) = 13, *J*(9a,10e) = 4.5, $H_a$–C(9)), 1.15 (*d*, 1 H–C(7), *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.23 (*ddd*, *J*(7,7) = 14, *J*(7,6) = 7, 1 H–C(7)); 1.32 (*ddd*, *J*(11a,11e) = 13, *J*(11a,10a) = 13, *J*(11a,10e) = 5, $H_a$–C(11)); 1.39 (*dd*, *J* = 10, *J*(3,2) = 8, 1 H–C(3)); 1.45 (*m*, 1 H–C(6)); 1.54 (br. *d*, *J* = 13, $H_e$–C(9)); 1.57 (*m*, 1 H–C(6)); 1.66 (*m*, H–C(5)); 1.67 (*m*, $H_e$–C(10)); 1.73 (*ddd*, *J* = 14, *J*(7,6) = 9, *J*(7,6) = 4, 1 H–C(7)); 2.00–2.09 (*m*, $H_a$–C(10), $H_e$–C(14)); 2.14 (*ddd*, *J* = 13, *J*(12s,9e) = 2.5, *J*(12s,11e) = 2.5, $H_s$–C(12)); 2.27 (*s*, Me(22)); 2.43 (*ddd*, *J*(2,5) = 12, *J* = 10, 8 H–C(2)); 5.10 (br. *s*, OH); 6.65 (*d*, *J* = 8, H–C(20)); 6.91 (*dd*, *J* = 8, 2 H–C(2)); 6.96 (*d*, *J* = 2, H–C(17)). $^{13}$C-NMR: see *Table 3*. MS: 312 (29, $M^+$), 202 (16), 201 (100), 148 (7), 121 (21), 95 (6), 81 (7), 55 (6), 41 (9).



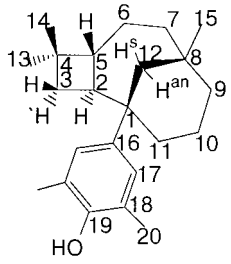

**15**

*(1S,2S,5R,8R)-2-Methyl-4-(1,4,4-trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-8-yl)phenol* (**15**). $^1$H-NMR: 0.87 (*s*, Me(15)); 1.04 (*s*, Me(14)); 1.047 (*s*, Me(13)); 1.053 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.12, 1.46 (2*m*, 2 H–C(11)); 1.38 (*dd*, *J*(3,3) = 10, *J*(3,2) = 10, H–C(3)); 1.38, 1.55 (2*m*, 2 H–C(6)); 1.42, 1.98 (2*m*, 2 H–C(9)); 1.46, 1.94 (2*m*, 2 H–C(7)); 1.54 (*dd*, *J* = 10, *J*(3,2) = 8, 1 H–C(3)); 1.68, 2.07 (2*m*, 2 H–C(10)); 1.87 (*m*, H–C(5)); 2.04 (*dm*, *J* = 13, $H_s$–C(12)); 2.26 (*s*, Me(22)); 2.37 (*ddd*, *J*(2,5) = 12, *J* = 10, 8 H–C(2)); 4.90 (br. *s*, OH); 6.62 (*d*, *J* = 8, H–C(20)); 7.05 (*dd*, *J* = 8, 2, H–C(21)); 7.10 (*d*, *J* = 2, H–C(17)). $^1$C-NMR: see *Table 3*. MS: 312 (24, $M^+$), 202 (17), 201 (100), 148 (8), 121 (18), 108 (20), 46 (21), 45 (36), 31 (71).




**16**

*(1R,2S,5R,8S)-1-(3,5-Dimethylphenoxy)-4,4,8-trimethyltricyclo[6.3.1.0$^{2,5}$]dodecane* (**16**): $^1$H-NMR: 0.97 (*s*, Me(15)); 1.07 (*m*, $H_a$–C(9)); 1.08 (*s*, Me(14)); 1.09 (*s*, Me(13)); 1.24 (*m*, 1 H–C(7)); 1.25 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.38–1.49 (*m*, 1 H–C(6), $H_e$–C(9), $H_a$–C(11)); 1.58 (*m*, 1 H–C(6)); 1.62 (*m*, 1 H–C(7)); 1.72 (*dd*, *J*(3,3) = 10, *J*(3,2) = 8, 1 H–C(3)); 1.73, 1.82 (2*m*, 2 H–C(10)); 1.81 (*dd*, *J* = 10, *J*(3,2) = 10, 1 H–C(3)); 1.94 (*ddd*, *J* = 13, *J*(12s,9e) = 2.5, *J*(12s,11e) = 2.5, $H_s$–C(12)); 1.98 (*m*, 1 $H_e$–C(11)); 2.05 (*ddd*, *J*(5,2) = 12, *J*(5,6) = 7.5, *J*(5,6) = 6.5, H–C(5)); 2.30 (*s*, 2 Me(20)); 2.42 (*ddd*, *J* = 12, 10, 8, H–C(2)); 6.64 (br. *s*, 2 H–C(17)); 6.57 (br. *s*, 1 H–C(19)). $^{13}$C-NMR: see *Table 3*. MS: 326 (44, $M^+$), 279 (6), 205 (53), 204 (37), 189 (56), 161 (27), 149 (74), 135 (52), 123 (60), 122 (100), 109 (52), 95 (63), 81 (63), 69 (54), 55 (42), 41 (42).




**17**

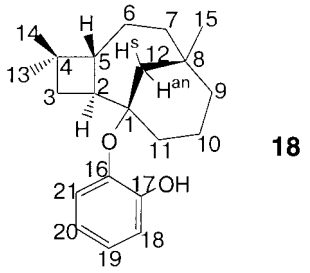
*(1R,2S,5R,8S)-2,6-Dimethyl-4-(4,4,8-trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-1-yl)phenol* (**17**): $^1$H-NMR: 0.55 (*dd*, *J*(3,3) = 10, *J*(3,2) = 10, 1 H–C(3); 0.83 (*s*, Me(14)); 0.97 (*s*, Me(15)); 0.98 (*s*, Me(13)); 1.12 (*m*, 1 $H_a$–C(8)); 1.13 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.21 (*ddd*, *J*(7,7) = 14, *J* = 7.5, 4, H–C(7)); 1.30 (*ddd*, *J*(11a,11e) = 13, *J*(11a,10a) = 13, *J*(11a,10e) = 5, $H_a$–C(11)); 1.38 (*dd*, *J* = 10, *J*(3,2) = 8, 1 H–C(3)); 1.42 (*m*, 1 H–C(6)); 1.52 (*dm*, *J*(9e,9a) = 13, $H_e$–C(9)); 1.54–1.70 (*m*, 1 H–C(6), H–C(5), $H_a$–C(10)); 1.71 (*m*, 1 H–C(7)); 2.02 (*m*, $H_a$–C(10)); 2.04 (br. *d*, *J* = 13, $H_e$–C(11)); 2.13 (*ddd*, *J* = 13, *J*(12s,9e) = 2.5, *J*(12s,11e) = 2.5, $H_s$–C(12)); 2.26 (*s*, 2 Me(20)); 2.41 (*ddd*, *J*(2,5) = 12, *J* = 10, 8, H–C(2)); 4.46 (br. *s*, OH); 6.84 (br. *s*, 2 H–C(17)); $^{13}$C-NMR: see *Table 4*. MS: 326 (31, $M^+$), 215 (100), 135 (19), 122 (45), 107 (39), 85 (26), 83 (42), 43 (16).

*(1R,2S,5R,8S)-2-(4,4,8-Trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-1-yloxy)phenol* (**18**): $^1$H-NMR: 0.93 (*s*, Me(15)); 1.03 (*s*, Me(14)); 1.04 (*m*, 1 $H_a$–C(9)); 1.04 (*s*, Me(13)); 1.20, 1.58 (2*m*, 2 H–C(7)); 1.30 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.29–1.46 (*m*, $H_a$–C(11), 1 H–C(6), $H_e$–C(9)); 1.54 (*m*, 1 H–C(6)); 1.68, 1.78 (2*m*, 2 H–C(10)); 1.73 (*dd*, *J*(3,3) = 10, *J*(3,2) = 8, 1 H–C(3)); 1.77 (*dd*, *J* = 10, *J*(3,2) = 10, 1 H–C(3)) (*AB* system); 1.91 (*dm*, *J*(11e,11a) = 13, $H_e$–C(11)); 2.00 (*ddd*, *J* = 13, *J*(12s,11e) = 3, *J*(12s,9e) = 2, $H_s$–C(12)); 2.03 (*m*, H–C(5)); 2.42 (*ddd*, *J*(2,5) = 12, *J* = 10, 8, H–C(2)); 5.88 (br. *s*, OH); 6.59 (*m*, 1 arom. H); 6.73–6.79 (*m*, 3 arom. H). $^{13}$C-NMR: see *Table 4*. MS: 314 (17, $M^+$), 205 (92), 163 (12), 149 (74), 135 (52), 123 (73), 109 (82), 95 (90), 81 (100), 69 (70), 55 (39), 41 (43).

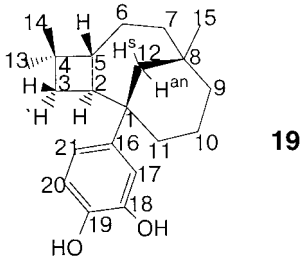
Table 4. *$^{13}$C-NMR Data for Compounds* **17**–**22** (chemical shifts in ppm)

| C-Atom | **17**[b]) | **18**[b]) | **19**[a]) | **20**[a]) | **21**[a]) | **22**[a]) |
|---|---|---|---|---|---|---|
| C(1) | 39.53 (*s*) | 82.08 (*s*) | 39.94 (*s*) | 40.00 (*s*) | 79.30 (*s*) | 80.92 (*s*) |
| C(2) | 40.64 (*d*) | 41.51 (*d*) | 40.76 (*d*) | 41.85 (*d*) | 40.65 (*d*) | 40.81 (*d*) |
| C(3) | 38.97 (*t*) | 37.47 (*t*) | 39.13 (*t*) | 40.17 (*t*) | 36.39 (*t*) | 36.36 (*t*) |
| C(4) | 33.92 (*s*) | 34.97 (*s*) | 34.22 (*s*) | 33.45 (*s*) | 34.97 (*s*) | 34.91 (*s*) |
| C(5) | 46.08 (*d*) | 45.82 (*d*) | 46.17 (*d*) | 46.75 (*d*) | 45.21 (*d*) | 44.98 (*d*) |
| C(6) | 22.73 (*t*) | 22.69 (*t*) | 22.95 (*t*) | 23.88 (*t*) | 22.26 (*t*) | 22.21 (*t*) |
| C(7) | 37.73 (*t*) | 37.77 (*t*) | 37.94 (*t*) | 39.17 (*t*) | 37.33 (*t*) | 37.30 (*t*) |
| C(8) | 33.99 (*s*) | 35.23 (*s*) | 34.30 (*s*) | 34.53 (*s*) | 35.23 (*s*) | 35.16 (*s*) |
| C(9) | 38.00 (*t*) | 37.02 (*t*) | 38.37 (*t*) | 38.32 (*t*) | 37.61 (*t*) | 37.51 (*t*) |
| C(10) | 19.94 (*t*) | 21.10 (*t*) | 20.24 (*t*) | 20.44 (*t*) | 21.25 (*t*) | 21.25 (*t*) |
| C(11) | 37.88 (*t*) | 34.91 (*t*) | 37.83 (*t*) | 36.00 (*t*) | 34.69 (*t*) | 34.55 (*t*) |
| C(12) | 44.92 (*t*) | 47.52 (*t*) | 45.27 (*t*) | 45.76 (*t*) | 46.81 (*t*) | 46.06 (*t*) |
| C(13) | 20.80 (*q*) | 21.10 (*q*) | 21.22 (*q*) | 21.38 (*q*) | 21.25 (*q*) | 21.32 (*q*) |
| C(14) | 30.32 (*q*) | 30.71 (*q*) | 30.71 (*q*) | 30.66 (*q*) | 30.79 (*q*) | 30.85 (*q*) |
| C(15) | 34.57 (*q*) | 33.68 (*q*) | 34.81 (*q*) | 35.48 (*q*) | 33.71 (*q*) | 33.70 (*q*) |
| C(16) | 141.25 (*s*) | 149.60 (*s*) | 141.45 (*s*) | 126.53 (*s*) | 152.74 (*s*) | 153.76 (*s*) |
| C(17) | 126.21 (*d*) | 142.31 (*s*) | 113.46[c]) (*d*) | 156.31[c]) (*s*) | 115.24 (*d*) | 143.56 (*s*) |
| C(18) | 121.57 (*s*) | 118.96 (*d*) | 143.99[d]) (*s*) | 103.71 (*d*) | 124.35 (*d*) | 113.79 (*d*) |
| C(19) | 149.42 (*s*) | 121.01[c]) (*d*) | 142.03[d]) (*s*) | 155.53[c]) (*s*) | 147.85 (*s*) | 134.40 (*s*) |
| C(20) | 16.13 (*q*) | 122.92[c]) (*d*) | 114.24[c]) (*d*) | 106.00 (*d*) | | 120.47 (*d*) |
| C(21) | | 114.93 (*d*) | 117.42 (*d*) | 127.09 (*d*) | 124.50 (*d*) | |
| C(22) | | | | | | 56.04 (*q*) |
| C(23) | | | | | | 40.17 (*t*) |
| C(24) | | | | | | 137.77 (*d*) |
| C(25) | | | | | | 115.74 (*t*) |

[a]) Solvent $CCl_4/(CD_3)_2CO$; [b]) Solvent $CCl_4/CDCl_3$; [c])[d]) The values of the chemical shifts denoted with the same letter may be exchanged within the column.

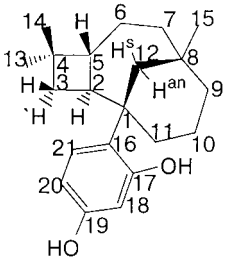



**18**



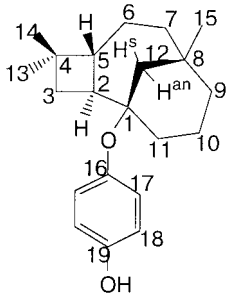

**19**

*(1*R*,2*S*,5*R*,8*S*)-4-(4,4,8-Trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-1-yl)benzene-1,2-diol* (**19**): $^1$H-NMR: 0.54 (*dd*, *J*(3,3) = 10, *J*(3,2) = 10, 1 H–C(3)); 0.78 (*s*); 0.91 (*s*); 0.93 (*s*); 1.05 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.07 (*m*, $H_a$–C(9)); 1.15 (*ddd*, *J*(7,7) = 14, *J*(7,6) = 7, *J*(7,6) = 4, 1 H–C(7)); 1.26 (*ddd*, *J*(11a,11e) = 13, *J*(11a,10a) = 13, *J*(11a,10e) = 5, $H_a$–C(11)); 1.32 (*dd*, *J* = 10, *J*(3,2) = 8, 1 H–C(3)); 1.36 (*m*, 1 H); 1.46 (*dm*, *J*(9e,9a) = 13, $H_a$–C(9)); 1.52 (*m*, 1 H–C(6)); 1.55–1.65 (*m*, H–C(5), $H_a$–C(10)); 1.67 (*ddd*, *J* = 14, *J*(7,6) = 9, *J*(7,6) = 4, 1 H–C(7)); 1.95 (*m*, $H_e$–C(10), $H_e$–C(11)); 2.05 (*ddd*, *J* = 13, *J*(12s,9e) = 2.5, *J*(12s,11e) = 2.5, $H_s$–C(12)); 2.34 (*ddd*, *J*(2,5) = 12, *J* = 10, 8, H–C(2)); 6.48 (*dd*, *J*(21,20) = 8, *J*(21,17) = 2.2, H–C(21)); 6.62 (*d*, *J* = 8, H–C(20)); 6.62 (*d*, *J* = 2.2, H–C(17)); 6.65, 6.89 (2 br. *s*, 2 OH). $^{13}$C-NMR: see *Table 4*. MS: 314 (37, $M^+$), 203 (100), 150 (7), 123 (20), 95 (6), 81 (6), 55 (6), 41 (7).



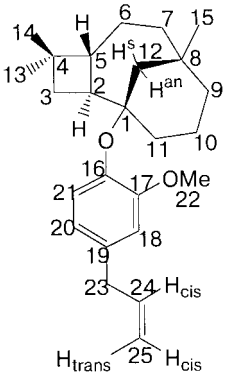

**20**

*(1*R*,2*S*,5*R*,8*S*)-4-(4,4,8-Trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-1-yl)benzene-1,3-diol* (**20**): $^1$H-NMR: 0.77 (*s*, Me(14)); 0.86 (*dd*, *J*(3,3) = 10, *J*(3,2) = 10, 1 H–C(3)); 0.91 (*s*, Me(15)); 1.08 (*m*, $H_a$–C(9)); 1.11 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.14 (*m*, 1 H–C(7)); 1.47 (*m*, $H_e$–C(9)); 1.64 (*dd*, *J* = 10, *J*(3,2) = 8, 1 H–C(3)); 1.90 (*dm*, *J*(10e,10a) = 13, $H_e$–C(10)); 2.12 (br. *d*, *J* = 13, $H_s$–C(12)); 2.40 (*ddd*, *J*(2,5) = 12, *J* = 10, 8, H–C(2)); 6.11 (*d*, *J*(18,20) = 2.2, H–C(18)); 6.13 (*dd*, *J*(20,21) = 8, *J* = 2.2, H–C(20)); 6.86 (*d*, *J* = 8, H–C(21)); 6.98, 7.11 (2 br. *s*, 2 OH). $^{13}$C-NMR: see *Table 4*. MS: 314 (25, $M^+$), 203 (100), 149 (9), 123 (35), 81 (8), 41 (10).




**21**

*(1*R*,2*S*,5*R*,8*S*)-4-(4,4,8-Trimethyltricyclo[6.3.1.0$^{2,5}$]dodec-1-yloxy)phenol* (**21**): $^1$H-NMR: 0.86 (*s*, Me(15)); 0.93 (*m*, 1 H–C(9)); 1.02 (*s*, Me(13), Me(14)); 1.04 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.13 (*m*, 1 H–C(7)); 1.24–1.40 (*m*, 1 H–C(6), 1 H–C(9), 1 H–C(11)); 1.45–1.68 (*m*, 1 H–C(6), 1 H–C(7), 1 H–C(10), 1 H–C(11); 1.59 (*dd*, *J*(3,3) = 10, *J*(3,2) = 8, 1 H–C(3)); 1.75 (*ddd*, *J* = 13, 2.5, 2.5, $H_s$–C(12)); 1.76 (*m*, 1 H–C(10)); 1.79 (*dd*, *J* = 10, *J*(3,2) = 1 H–C(3)); 1.97 (*ddd*, *J*(5,2) = 12, *J*(5,6) = 7.5, *J*(5,6) = 7.5), H–C(5)); 2.35 (*ddd*, *J* = 12, 10, 8, H–C(2)); 6.57, 6.60 (*AB*, 2 *d*, *J* = 9, 2 H–C(17), 2 H–C(18)); 7.44 (br. *s*, OH). $^{13}$C-NMR: see *Table 4*. MS: 314 (20, $M^+$), 205 (30), 189 (11), 161 (13), 149 (30), 135 (21), 123 (29), 110 (100), 95 (36), 81 (40), 69 (28) 55 (23), 41 (23).




**22**

*(1*R*,2*S*,5*R*,8*S*)-1-(4-Allyl-2-methoxyphenoxy)-4,4,8-trimethyltricyclo[6.3.1.0$^{2,5}$]dodecane* (**22**): $^1$H-NMR: 0.87 (*s*, Me(15)); 0.95 (*ddd*, *J*(9a,9e) = 13.5, *J*(9a,10a) = 12, *J*(9a,10e) = 5, $H_a$–C(9)); 1.03 (*s*, Me(13)); 1.05 (*s*,

Me(14)); 1.09 (*d*, *J*(12an,12s) = 13, $H_{an}$–C(12)); 1.13, 1.55 (2*m*, 2 H–C(7)); 1.28–1.42 (*m*, $H_e$–C(9), 1 H–C(6), $H_a$–C(11)); 1.51 (*m*, 1 H–C(6)); 1.62 (*dd*, *J*(3,3) = 10, *J*(3,2) = 8, 1 H–C(3)); 1.62, 1.75 (2 *m*, 2 H–C(10)); 1.73 (*m*, 1 $H_e$–C(11)); 1.84 (*ddd*, *J* = 13, *J*(12s,9e) = 2.5, *J*(12s,11e) = 2.5, $H_s$–C(12)); 1.90 (*dd*, *J* = 10, *J*(3,2) = 10, 1 H–C(3)); 2.06 (*ddd*, *J*(5,2) = 12, *J*(5,6) = 7, *J*(5,6) = 7, H–C(5)); 2.35 (*ddd*, *J* = 12, 10, 8, H–C(2)); 3.28 (*ddd*, *J*(23,24) = 6.5, *J*(23,25*trans*) = 2, *J*(23,25*cis*) = 1.2, 2 H–C(22)); 3.76 (*s*, MeO); 5.01 (*ddt*, *J*(25*cis*,24) = 10, *J*(25*cis*,25*trans*) = 2, *J* = 1.2, $H_{cis}$–C(25)); 5.04 (*ddt*, *J*(25*trans*,24) = 17, *J* = 2, 2, $H_{trans}$–C(25)); 5.91 (*ddt*, *J* = 17, 10, 6.5 , H–C(24)); 6.54 (*dd*, *J*(20,21) = 8, *J*(20,18) = 2, H–C(20)); 6.60 (*d*, *J* = 2, H–C(18)); 6.68 (*d*, *J* = 8, H–C(21)). $^{13}$C-NMR: see *Table 4*. MS: 368 (9, $M^+$), 205 (9), 164 (100), 149 (15), 123 (12), 109 (12), 95 (15), 81 (16), 69 (13), 55 (9), 41 (10).

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