



# A general, ring closure metathesis based enantiospecific approach to polyfunctional eudesmane, eremophilane and agarofuran sesquiterpenoids

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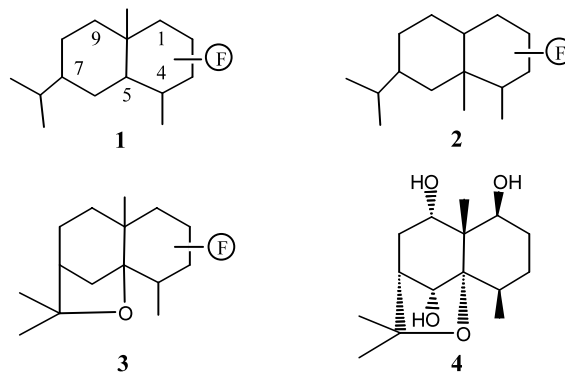
**Abstract**—An enantiospecific and stereo- and functional group diversity oriented approach to eudesmane, eremophilane and agarofuran sesquiterpenoids from (–)-carvone has been devised. RCM has been employed as the key reaction to generate the highly functionalized eudesmane framework. Further elaboration of the eudesmane framework to agarofurans and biogenetic-type rearrangement to eremophilanes is outlined.

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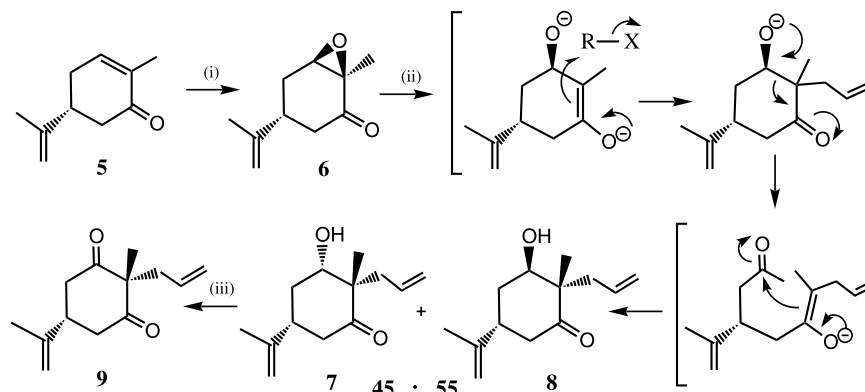
Eudesmane **1** and eremophilane **2** sesquiterpenoid skeleta based on the bicyclic decalin framework are fairly widespread in nature and occur in different stereochemical and functionalization patterns.<sup>1</sup> Eremophilane **2** represents the earliest known example of an irregular isoprenoid in nature and in a classical proposal, Robinson in 1939<sup>2</sup> invoked a carbonium ion-mediated methyl migration in eudesmane **1** to explain their biogenesis which was subsequently confirmed through both in vivo and in vitro experiments.<sup>3</sup> Another interesting sub-class of natural products derived from eudesmanes are agarofurans **3** whose polyoxygenated derivatives, e.g. celorbicol **4** are of wide occurrence, particularly in the *Celastraceae* family and many of them have been found to exhibit broad ranging biological activity profiles.<sup>4,5</sup> Not surprisingly, eudesmanes, eremophilanes and particularly agarofurans continue to evoke a great deal of synthetic interest and many interesting strategies have been devised to access these families of sesquiterpenoids.<sup>1,6</sup> In particular, extensive synthetic studies have been directed towards the polyhydroxylated agarofurans in view of their biological potential and the challenge associated with the generation of the network of hydroxyl functionalities.<sup>6</sup> Herein, we describe a new, general, enantiospecific synthetic approach towards eudesmanes from (–)-carvone **5** employing a ring closing metathesis (RCM) reaction<sup>7</sup> as the key step and their further elaboration towards

polyfunctional agarofurans as well as biogenetic-type rearrangement to the eremophilane framework.

The  $\alpha,\beta$ -epoxyketone **6**,<sup>8</sup> readily obtained from (–)-carvone **5**, on reductive allylation under dissolving metal conditions charted an interesting course and epimeric hydroxy-ketones **7** and **8** (45:55), sharing identical stereochemistry at the newly generated quaternary center were realized (Scheme 1).<sup>9</sup> The epimeric nature of the hydroxy-ketones followed from their oxidation to the same dione **9** and their formation involving an eventful fragmentation-realdolization process is depicted in Scheme 1. It is worth noting that the allyl group in **7** and **8** is *cis* with respect to the isopropenyl group, a situation conducive to accessing eudesmane based natural products which occur predominantly with the angular methyl group and the isopropyl group in a *trans* arrangement.



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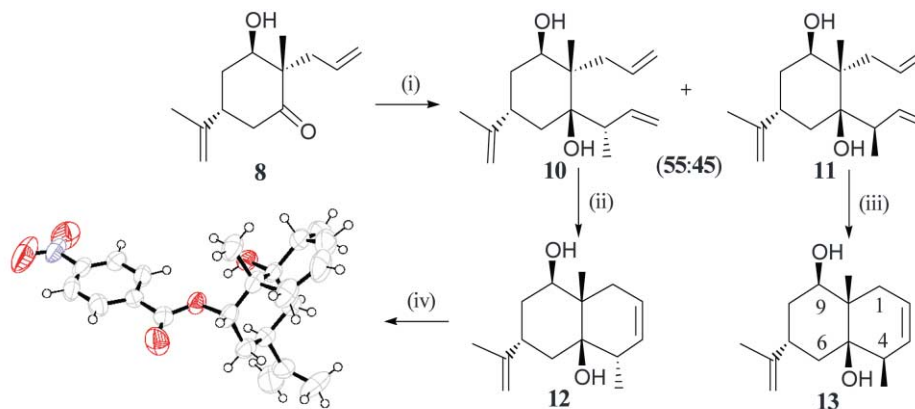
**Scheme 1.** Reagents and conditions: (i) 30%  $\text{H}_2\text{O}_2$ , 6N NaOH, MeOH,  $0^\circ\text{C}$ , 92%; (ii) Li, liq.  $\text{NH}_3$ ,  $\text{CH}_2=\text{CHCH}_2\text{Br}$ ,  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ , 60%; (iii) PCC, DCM, 88%.

Addition of the Grignard reagent derived from 3-chloro-1-butene to the major  $\beta$ -hydroxy-ketone **8** in the presence of Ce(III) furnished two diastereomeric addition products **10** and **11** (55:45) (Scheme 2). Interestingly, the Grignard reagent addition to the carbonyl group of **8** was  $\alpha$ -face selective to furnish **10** and **11** with the two allyl side arms in *cis* disposition. Both **10** and **11** were now set for the RCM reaction to generate the eudesmane framework. Indeed, exposure of **10** and **11** to Grubbs' catalyst [benzylidene-bis(tricyclohexylphosphine)-dichlororuthenium] resulted in smooth and efficient conversion to bicycles **12** and **13**, respectively (Scheme 2)<sup>9</sup> and their stereostructures were secured through the X-ray crystal structure determination of the PNB-derivative of **12**.<sup>10</sup> Thus, in a short sequence from carvone **5**, highly functionalized eudesmanes **12** and **13** could be accessed, paving the way for further transformations.

Polyfunctional dihydroxyeudesmane **13** was well-poised for further elaboration to the eremophilane ring system **2**. The monobenzoate **14** derived from **13** was smoothly and regioselectively dehydrated to the bicyclic triene **15** (Scheme 3).<sup>9</sup> The exocyclic double bond in **15** could be regioselectively hydrated through oxymercuration to

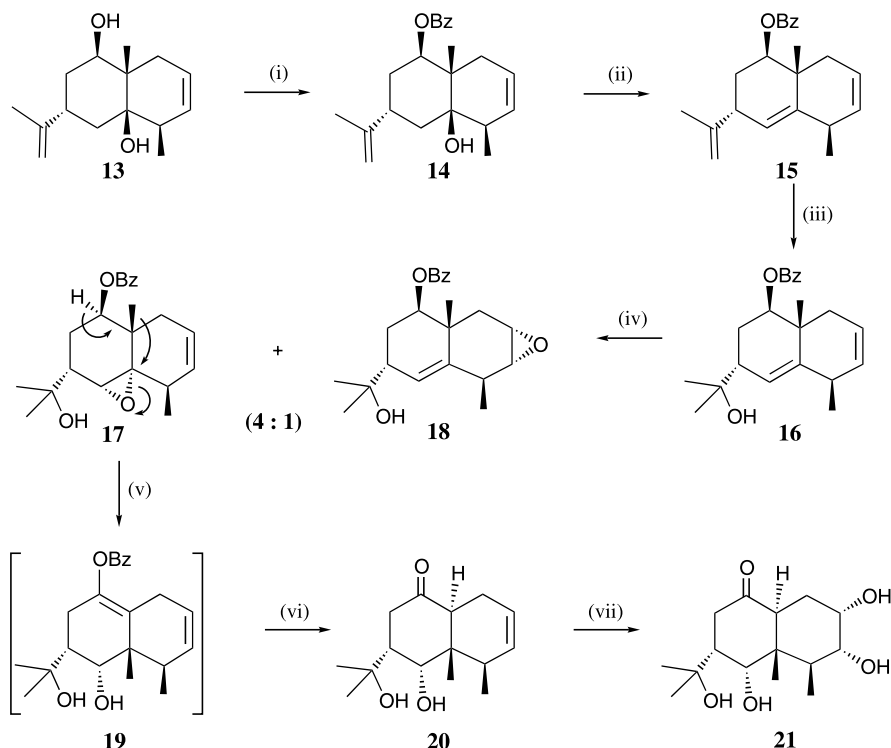
furnish the tertiary alcohol **16**.<sup>9</sup> Further epoxidation of **16** was stereoselective but exhibited only 4:1 regioselectivity and a 4:1 mixture of  $\alpha$ -epoxides **17** and **18** was obtained (Scheme 3). Exposure of the major epoxide **17** to  $\text{BF}_3$ -etherate and hydrolysis of the intermediate enolbenzoate **19**, formed through sequential methyl and hydrogen migrations, resulted in the eremophilane keto-diol **20** in good yield (Scheme 3).<sup>9</sup> The olefinic moiety in **20** was further hydroxylated with  $\text{OsO}_4$  to furnish polyfunctional eremophilane **21** whose stereostructure was secured through single crystal X-ray structure determination.<sup>10</sup>

As per our plan, dihydroxyeudesmane derivative **13** appeared to be serviceable for elaboration to the agarofuran framework **3**, particularly because the C4  $\beta$ -methyl stereochemistry present in it is widespread among natural products of this class. However, in the biologically more important agarofurans, the C9 hydroxyl group is usually  $\alpha$ -oriented, see celorbicol **4**. Our first effort therefore was to carry out a Mitsunobu type reaction on **13** to invert the C9 hydroxy group stereochemistry but these efforts were not successful. Consequently, **13** was oxidised to ketone **22** (X-ray crystal structure)<sup>10</sup> and its reduction with sodium boro-



**ORTEP diagram of the PNB derivative of 12**

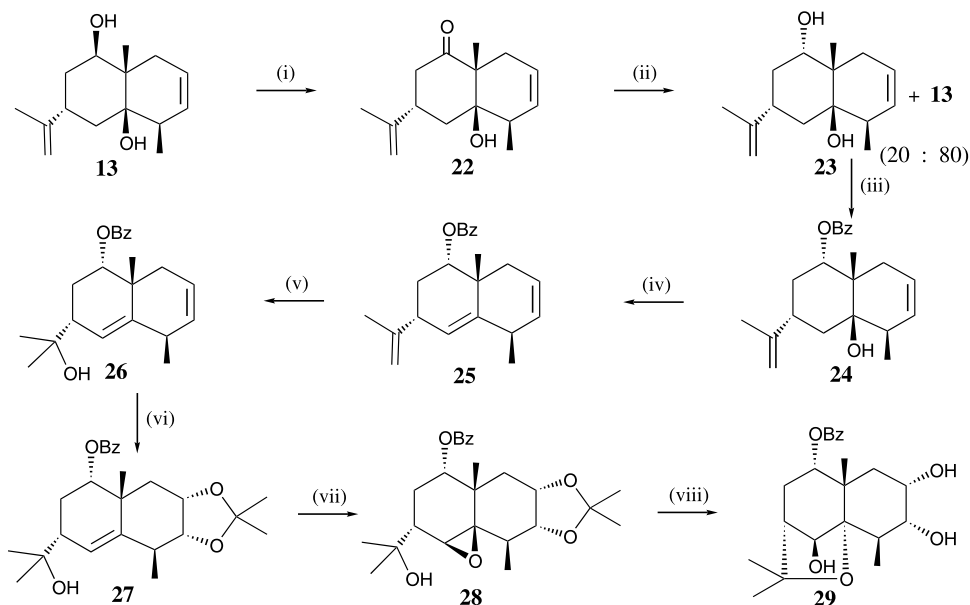
**Scheme 2.** Reagents and conditions: (i)  $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{MgCl}$ , anhyd.  $\text{CeCl}_3$ , THF,  $-78^\circ\text{C}$ , 95%; (ii) Grubbs' cat. (7 mol%),  $\text{C}_6\text{H}_6$ ,  $85^\circ\text{C}$ , 89%; (iii) Grubbs' cat. (5 mol%),  $\text{C}_6\text{H}_6$ ,  $85^\circ\text{C}$ , 95%; (iv) *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$ ,  $\text{Et}_3\text{N}$ , DCM, rt, 90%.



**Scheme 3.** Reagents and conditions: (i)  $\text{C}_6\text{H}_5\text{COCl}$ ,  $\text{Et}_3\text{N}$ , DMAP, DCM, rt, 90%; (ii)  $\text{SOCl}_2$ , pyridine,  $-35^\circ\text{C}$ , 85%; (iii)  $\text{Hg}(\text{OAc})_2$ , cat.  $\text{AcOH}$ ,  $\text{THF}:\text{H}_2\text{O}$ , rt, 75%; (iv)  $m\text{CPBA}$ ,  $\text{NaHCO}_3$ , DCM, 83%; (v)  $\text{BF}_3\cdot\text{Et}_2\text{O}$ , DCM,  $0^\circ\text{C}$ , 80%; (vi)  $\text{K}_2\text{CO}_3$ , MeOH, rt, 95%; (vii)  $\text{OsO}_4$ , NMMO,  $\text{CH}_3\text{COCH}_3:\text{H}_2\text{O}$ , rt, 92%.

hydride led to a readily separable 4:1 mixture of **13** and the epimeric diol **23**. Although the stereoselectivity in this reaction to access desired **23** was not satisfactory, **13** could be recycled via **22** to build reasonable quantities of **23** (Scheme 4).<sup>9</sup> Monobenzoate **24** derived from

**23** was dehydrated to furnish triene **25** regioselectively (Scheme 4). Oxymercuration of **25** was regioselective at the terminal olefinic moiety and readily led to the tertiary alcohol **26**.<sup>9</sup> Catalytic  $\text{OsO}_4$ -mediated dihydroxylation in **26** was stereoselective and acetonide protec-



**Scheme 4.** Reagents and conditions: (i) PCC, DCM, rt, 78%; (ii)  $\text{NaBH}_4$ , MeOH,  $0^\circ\text{C}$ , 90%; (iii)  $\text{C}_6\text{H}_5\text{COCl}$ ,  $\text{Et}_3\text{N}$ , DMAP, DCM, rt, 87%; (iv)  $\text{SOCl}_2$ , pyridine,  $-35^\circ\text{C}$ , 80%; (v)  $\text{Hg}(\text{OAc})_2$ , cat.  $\text{AcOH}$ ,  $\text{THF}:\text{H}_2\text{O}$ , rt, 70%; (vi) (a)  $\text{OsO}_4$ , NMMO,  $\text{CH}_3\text{COCH}_3:\text{H}_2\text{O}$ , rt, 95%; (b)  $\text{CH}_3\text{COCH}_3$ , Amberlyst, rt, 81%; (vii)  $m\text{CPBA}$ ,  $\text{NaHCO}_3$ , DCM, 90%; (viii) TMSOTf, DCM,  $0^\circ\text{C}$ , 55%.

tion led to the polyfunctional **27** (Scheme 4). As the  $\alpha$ -face of **27** was sterically shielded, epoxidation of **27** was stereoselective and furnished exclusively the  $\beta$ -epoxide **28**. Brief exposure of **28** to TMSOTf led to the contemplated tetrahydrofuran formation through epoxide opening and capture by the tertiary hydroxyl group to lead to agarofuran derivative **29**. The complete stereostructure of **29** was confirmed through its X-ray crystal structure determination.<sup>10</sup> Access to the agarofuran **29** with secured stereochemistry at eight stereogenic centers and five oxygen functionalities, particularly with C6 and C9 hydroxyl groups, makes our approach amenable to adaptation for the synthesis of many natural products of this family.

In summary, we have outlined a new approach to assemble rapidly, strategically functionalized eudesmanes from (–)-carvone employing RCM as the key step. Further transformations involving functional group amplification and rearrangements provide entry into polyoxyfunctionalized eremophilanes and agarofurans.

### Acknowledgements

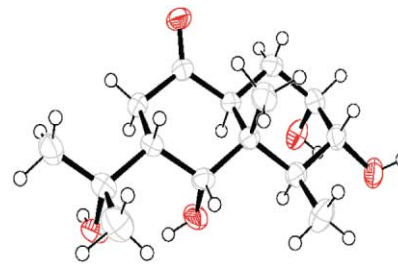
We thank JNCASR for the financial support. One of us (R.S.K.) thanks CSIR for the award of a research fellowship.

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- All new compounds reported here were duly characterized on the basis of spectroscopic data (IR, <sup>1</sup>H and <sup>13</sup>C NMR) and elemental analyses. Data for **29**: mp 213–214°C; [ $\alpha$ ]<sub>D</sub> = –11.1 (c 0.45, CHCl<sub>3</sub>); IR (cm<sup>–1</sup>) 3438, 1711; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 5.10 (d, *J* = 7.5 Hz, 1H), 4.70 (br s, 1H), 4.30 (d, *J* = 9.9 Hz, 1H), 3.91 (br s, -OH), 3.69 (d, *J* = 9.6 Hz, 1H), 2.71 (ddd, *J* = 16.5, 7.5, 4.2 Hz, 1H), 2.46–2.43 (br m, -OH), 2.36–2.20 (m, 2H), 1.99–1.93 (m, 2H), 1.79 (br s, -OH), 1.48 (s, 6H), 1.32 (s, 3H), 1.31 (d, *J* = 7.8 Hz, 3H), 1.17 (dd, *J* = 12.9, 4.5 Hz, 1H); <sup>13</sup>C NMR (75 MHz)  $\delta$  166.1, 132.9, 130.4, 129.7, 128.5, 83.5, 79.7, 76.9, 75.9, 75.8, 65.9, 47.8, 46.9, 45.4, 35.8, 30.6, 25.5, 25.3, 25.1, 14.9; HRMS calcd for 413.1940 (M+Na). Found: 413.1945. **28**: [ $\alpha$ ]<sub>D</sub> = –19.0 (c 1.0, CHCl<sub>3</sub>); IR (cm<sup>–1</sup>) 3452, 1718, 1273; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.96 (dd, *J* = 11.7, 3.6 Hz, 1H), 4.51–4.44 (m, 1H), 4.18–4.16 (m, 1H), 3.13 (s, 1H), 2.19–1.92 (m, 4H), 1.77–1.73 (m, 2H), 1.52 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H), 1.22 (d, *J* = 7.8 Hz, 3H), 1.15 (s, 3H); <sup>13</sup>C NMR (75 MHz)  $\delta$  165.9, 133.1, 130.2, 129.6, 128.4, 107.9, 79.5, 75.9, 72.1, 71.3, 65.4, 64.2, 44.8, 38.8, 37.6, 32.3, 28.5, 26.2, 26.1, 24.0, 19.8, 16.0; HRMS calcd for 453.2253 (M+Na). Found 453.2291. **26**: mp 146.5–147.5°C; [ $\alpha$ ]<sub>D</sub> = –4.1 (c 1.2, CHCl<sub>3</sub>); IR (cm<sup>–1</sup>) 3351, 1715, 1273; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 5.66 (s, 2H), 5.64 (s, 1H), 5.22 (dd, *J* = 12.3, 3.6 Hz, 1H), 2.97 (d, *J* = 6.9 Hz, 1H), 2.43–2.38 (m, 2H), 2.18 (dd, *J* = 4.5, 3.6 Hz, 1H), 2.02–1.98 (m, 1H), 1.51 (q, *J* = 12 Hz, 1H), 1.25 (d, *J* = 7.5 Hz, 3H), 1.24 (s, 3H), 1.23 (s, 3H), 1.17 (s, 3H); <sup>13</sup>C NMR (75 MHz)  $\delta$  166.4, 146.1, 132.9, 132.2, 130.6, 129.5, 128.4, 123.8, 122.2, 79.3, 72.4, 46.0, 39.7, 38.9, 34.9, 27.9, 27.1, 25.9, 24.8, 21.4; HRMS calcd for 363.1936 (M+Na), Found 363.1970. **21**: mp 189–191°C; [ $\alpha$ ]<sub>D</sub> = –42.8 (c 1.05, MeOH); IR (cm<sup>–1</sup>) 3413, 1696, 1025; <sup>1</sup>H NMR (300 MHz, MeOH-*d*<sub>4</sub>)  $\delta$  4.06 (s, 1H), 3.87 (d, *J* = 2.7 Hz, 1H), 3.25–3.17 (m, 2H), 2.67 (t, *J* = 13.5 Hz, 1H), 2.34–2.19 (m, 2H), 1.87–1.81 (m, 2H), 1.51 (dt, *J* = 13.5, 2.4 Hz, 1H), 1.32 (s, 3H), 1.12 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.54 (s, 3H); <sup>13</sup>C NMR (75 MHz)  $\delta$  216.7, 74.2, 73.7, 72.0, 69.7, 47.5, 46.6, 44.9, 38.1, 35.7, 28.8, 28.4, 27.6, 14.0, 10.5; HRMS calcd for 309.1678 (M+Na). Found 309.1692. **17**: [ $\alpha$ ]<sub>D</sub> = –62.5 (c 1.2, CHCl<sub>3</sub>); IR (cm<sup>–1</sup>) 3479, 1717, 1275; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, *J* = 6.9 Hz, 2H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 5.67–5.62 (br s, 2H), 5.24 (dd, *J* = 12, 4.5 Hz, 1H), 3.31 (d, *J* = 3 Hz, 1H), 2.29–1.96 (m, 3H), 1.91–1.87 (m, 2H), 1.79–1.67 (m, 1H),

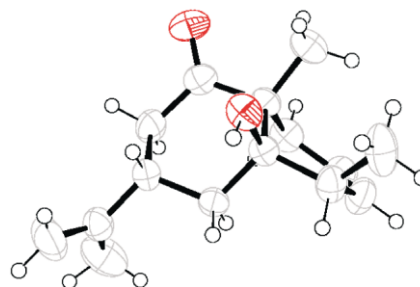
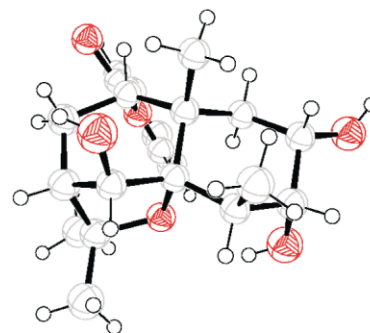
1.43 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H), 1.24 (d,  $J=7.8$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  165.9, 132.9, 130.6, 129.5, 128.4, 123.4, 76.6, 74.2, 66.3, 58.9, 41.8, 39.0, 35.9, 34.2, 27.9, 27.7, 23.7, 18.5, 16.5; HRMS calcd for 379.1885 (M+Na). Found 379.1907. **16**:  $[\alpha]_{\text{D}}=-33.1$  ( $c=1.0$ ,  $\text{CHCl}_3$ ); IR ( $\text{cm}^{-1}$ ) 3489, 1715, 1275;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J=7.5$  Hz, 2H), 7.56 (d,  $J=6.6$  Hz, 1H), 7.45 (t,  $J=6.6$  Hz, 2H), 5.66 (s, 1H), 5.60 (s, 2H), 5.16 (t,  $J=6.9$  Hz, 1H), 2.96 (d,  $J=6.3$  Hz, 1H), 2.38 (br s, 1H), 2.17–2.12 (m, 1H), 1.99–1.95 (m, 3H), 1.31 (s, 6H), 1.27 (s, 3H), 1.25 (d,  $J=7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  166.3, 145.8, 132.8, 131.5, 129.5, 128.4, 122.8, 121.7, 78.0, 73.3, 44.8, 37.8, 37.6, 37.0, 27.9, 27.6, 25.6, 24.2, 21.0; HRMS calcd for 363.1936 (M+Na). Found 363.1956. **13**:  $[\alpha]_{\text{D}}=-66.2$  ( $c=0.8$ ,  $\text{CHCl}_3$ ); IR ( $\text{cm}^{-1}$ ) 3321, 1455;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.63–5.60 (m, 1H), 5.48–5.46 (m, 1H), 4.73 (s, 2H), 3.59–3.55 (m, 1H), 3.14–3.07 (br s, -OH), 2.75–2.72 (m, 1H), 2.18–2.12 (m, 2H), 1.81–1.63 (m, 4H), 1.74 (s, 3H), 1.46 (dd,  $J=8.7, 3.3$  Hz, 1H), 1.21 (s, 3H), 1.15 (d,  $J=7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  149.2, 131.4, 121.0, 109.0, 78.5, 75.7, 43.5, 42.2, 39.3, 35.5, 34.0, 33.9, 21.1, 21.0, 16.0; HRMS calcd for 259.1674 (M+Na). Found 259.1695. **12**:  $[\alpha]_{\text{D}}=+75.9$  ( $c=0.83$ ,  $\text{CHCl}_3$ ); IR ( $\text{cm}^{-1}$ ) 3343, 1455;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.47 (br s, 1H), 5.36 (d,  $J=9.9$  Hz, 1H), 4.74 (s, 2H), 3.63 (br s, 1H), 3.09 (d,  $J=6.6$  Hz, 1H), 2.97 (s, 1H), 2.68–2.65 (m, 1H), 2.45 (m, 1H), 2.18 (d,  $J=17.7$  Hz, 1H), 1.84–1.81 (m, 2H), 1.75 (s, 3H), 1.31–1.23 (m, 1H), 1.16 (s, 3H), 0.99 (d,  $J=7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  149.5, 130.6, 122.8, 109.1, 77.4, 76.1, 39.2, 38.5, 36.1, 33.9, 33.5, 31.9, 20.9, 18.8, 13.2; HRMS calcd for 259.1674 (M+Na). Found 259.1683.

10. X-Ray crystal structure determination: X-ray data were collected at 293 K on a SMART CCD-BRUKER diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda=0.7107$  Å). Structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on  $F^2$  using SHELXL-97. The non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. **Compound PNB derivative of 12**:  $\text{C}_{22}\text{H}_{27}\text{O}_5\text{N}$ , MW=385.45, crystal system: monoclinic, space group:  $P2(1)$ , cell parameters:  $a=8.265$  (2),  $b=13.123$  (3),  $c=18.829$  (5) Å,  $\beta=94.113$  (5),  $V=2037.09$  (6) Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{calcd}}=1.257$  g cm<sup>-3</sup>,  $F(000)=824.0$ ,  $\mu=0.09$  mm<sup>-1</sup>. Total number of l.s. parameters=721,  $R_1=0.0576$  for 6673,  $F_o>4\sigma(F_o)$  and 0.0797 for all 8820 data.  $WR_2=0.1213$ , GOF=1.123. Restrained GOF=1.123 for all data. There are two molecules in an asymmetric unit. An ORTEP diagram with only one molecule is shown in Scheme 2. (CCDC 214302). **Compound 21**:  $\text{C}_{15}\text{H}_{26}\text{O}_5$ , MW=286.37, colorless crystal, Crystal system: monoclinic, space group:  $P2(1)$ , cell parameters:  $a=7.6151$  (6),  $b=12.361$  (1),  $c=16.356$  (1) Å,  $V=1539.76$  Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{calcd}}=1.235$  g cm<sup>-3</sup>,  $F(000)=624.0$ ,  $\mu=0.09$  mm<sup>-1</sup>. Total number of l.s. parameters=285,  $R_1=0.0385$  for 2927,  $F_o>4\sigma(F_o)$  and 0.0417 for all 53125 data.  $WR_2=0.0925$ , GOF=1.086. Restrained GOF=1.086 for all data (CCDC 214303).

ORTEP diagram of **21**

**Compound 22**:  $\text{C}_{15}\text{H}_{22}\text{O}_2$ , MW=234.34, colorless crystal, crystal system: monoclinic, space group:  $P2(1)$ , cell parameters:  $a=10.305$  (2),  $b=10.916$  (2),  $c=12.805$  (3) Å,  $\beta=108.436$  (4),  $V=1366.75$  (6) Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{calcd}}=1.139$  g cm<sup>-3</sup>,  $F(000)=512.0$ ,  $\mu=0.07$  mm<sup>-1</sup>. Total number of l.s. parameters=315,  $R_1=0.0565$  for 4301,  $F_o>4\sigma(F_o)$  and 0.0739 for all 5368 data.  $WR_2=0.1254$ , GOF=1.106, restrained GOF=1.106 for all data. There are two molecules in an asymmetric unit. (CCDC 214304).

**Compound 29**:  $\text{C}_{22}\text{H}_{30}\text{O}_6$ , MW=390.48, crystal system: monoclinic, space group:  $P2(1)$ , cell parameters:  $a=8.198$  (2),  $b=15.354$  (4),  $c=16.138$  (4) Å,  $\beta=94.364$  (5),  $V=2025.55$  Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{calcd}}=1.28$  g cm<sup>-3</sup>,  $F(000)=840.0$ ,  $\mu=0.09$  mm<sup>-1</sup>. Total number of l.s. parameters=239,  $R_1=0.0897$  for 5614,  $F_o>4\sigma(F_o)$  and 0.1226 for all 7976 data.  $wR_2=0.2182$ , GOF=1.025, Restrained GOF=1.025 for all data. There are two molecules in an asymmetric unit. (CCDC 214305).

ORTEP diagram of **22**ORTEP diagram of **29**