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Journal of Organometallic Chemistry 690 (2005) 847–856
Journal of Organometallic Chemistry
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Selective functionalization of crown ethers via arene chromium tricarbonyl complexes

Abir Ben Hadj Amor [a], Siden Top [b,*], Faouzi Meganem [a], Gérard Jaouen [b,*]

[a] *Laboratoire de Synthèse Organique, Faculté des Sciences de Bizerte, 7021 Jarzouna, Bizerte Tunisie*
[b] *Laboratoire de Chimie et Biochimie des Complexes Moléculaires, Ecole Nationale Supérieure de Chimie de Paris, UMR C.N.R.S. 7576, 11, Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*

Received 16 June 2004; accepted 10 September 2004
Available online 19 November 2004

Abstract

The crown ethers dibenzo-16-crown-4 and dibenzo-18-crown-5 and a diaryl polyether were complexed by the chromium tricarbonyl group for the purpose of selective functionalization. This complexation did indeed permit exclusive functionalization of the complexed ring. CHO and CH_2OH functionalities were introduced *ortho* to the ether group. It was noted that the nature of the two ether chains had a strong influence on the regioselectivity of the functionalization, which occurred preferentially on the side with the polyether chain. Photochemical decomplexation produced functionalized organic crown ethers.

Keywords: Crown ether; Chromium tricarbonyl; Polyether; Aldehyde; Alcohol; Arene activation

1. Introduction

The chemistry of crown ethers has been considerably developed since Pedersen's studies were first published [1]. In particular, the organometallic crown ethers have already been the subject of study, principally with the aim of using the organometallic entity as an analytical probe in electrochemistry. For this reason the organometallic crown ethers are chiefly known in the form of ferrocene derivatives [2]. Other organometallic crown ethers have been reported with complexes of an Fe–Mo cluster [3], ruthenium [4], cymantrene [5], cobaltocene [5], platinum [6], or arene chromium tricarbonyl [4,6a].

Here, we present a new way of exploiting the properties of organometallics in the crown ether series. The concept may be outlined as follows. One of the reasons for the current interest in the chemistry of crown ethers, which selectively complex cations, is that they may be capable of selective coupling with biological species (peptides, proteins) [8] and even with solid supports [9]. This is made possible by the selective addition of a functional group to a crown ether, which is not initially capable of coupling in this way.

Crown ethers containing 4 or 5 oxygen atoms are known to complex Li^+ and K^+ cations, respectively [1a,10]. We thought that crown ethers **1** and **2** would be good candidates for the application of the concept of selective functionalization of one of the arenes by temporary activation due to the $Cr(CO)_3$ moiety.

The approach is based on ideas that we introduced in the 1970s [11] and which have since been extended [12], although curiously not in the context of selective activation of crown ethers. The CHO and CH_2OH functionalities were chosen for attachment to the arene. These functionalities can of course be used to establish a bond between the crown ether and a selected substrate. The

* Corresponding authors. Tel.: +33 144 27 6699; fax: +33 143 26 0061 (S. Top), Tel.: +33 143 26 9555; fax: +33 143 26 0061 (G. Jaouen).
E-mail addresses: siden@ext.jussieu.fr (S. Top), gerard-jaouen@enscp.jussieu.fr (G. Jaouen).

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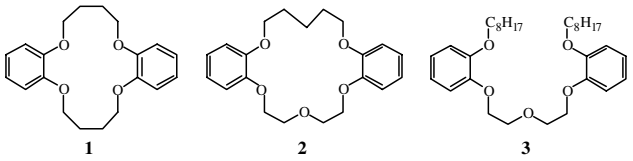
doi:10.1016/j.jorganchem.2004.09.090



work was also extended to a polyether, **3**, considered as an open chain, to complete the study. In addition, we show that the nature of the substituents on the complexed arene ring plays an important part in regioselectivity when new substituents are introduced.

2. Results and discussion

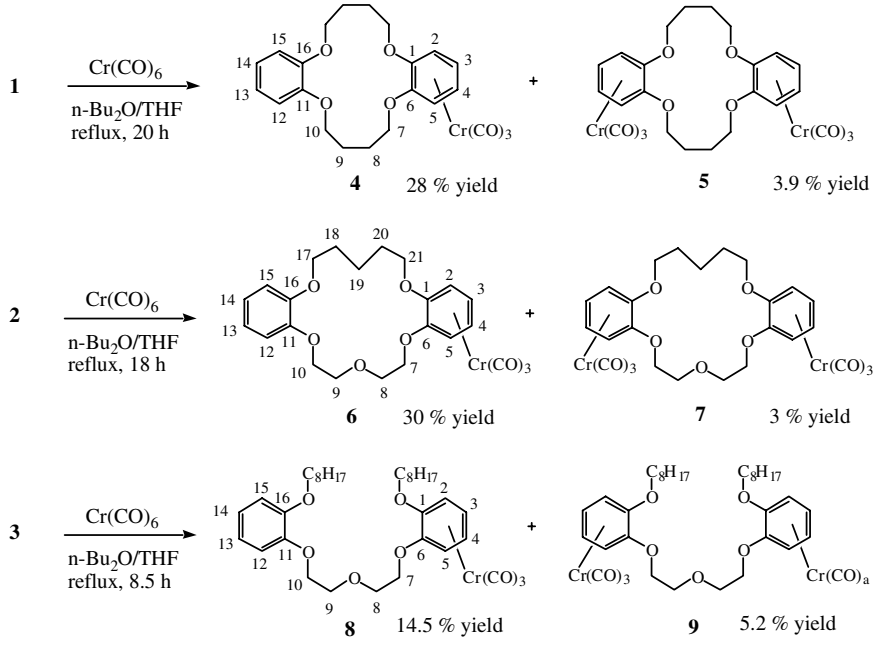
Access to functionalized crown ethers involves three reaction steps: complexation, the functionalization itself, and decomplexation. Several methods have been described for the complexation of an arene by a chromium tricarbonyl group to obtain a variety of complexes. As far as crown ethers are concerned, a method has been published [7a] which consists of heating a mixture of the crown ether and chromium hexacarbonyl under reflux in THF/2,2,4-trimethylpentane while irradiating the mixture with a UV lamp. However, the characteristics of the lamp were not given. This complexation method was tested on compounds **1**, **2** and **3** but without irradiation. After 8 hours of heating, no noticeable quantities of complexed products were produced. There are several other complexation methods given in the literature, such as heating with chromium hexacarbonyl in a mixture of THF/dibutyl ether [13] or use of the reagents $Cr(CO)_3(NH_3)_3$ [14], $Cr(CO)_3(MeCN)_3$ [15], or (naphthalene)$Cr(CO)_3$ [16]. We first chose to use the classic method which involves heating the arene with chromium hexacarbonyl in the THF/dibutyl ether mixture in an apparatus described by Toma [16a].

The crown ethers **1**, **2** and **3** were thus heated with chromium hexacarbonyl in dibutyl ether containing 10% THF (Scheme 1) [13]. This was expected to give a mixture of the monocomplexed and the dicomplexed compound.

After 20 h heating, the monocomplexed compound **4** was produced in 28% yield and the dicomplexed compound **5** in 3.9% yield. With the ether **2**, the monocomplexed compound **6** was obtained in 30% yield and the dicomplexed compound **7** in 3% yield. Compound **3** gave only 14.5% of the monocomplexed **8** and 5.2% of the dicomplexed compound **9**. The X-ray structures of the mono chromium complex **4** and the dichromium complex **7** have been submitted for publication [17,18].

Using this complexation route, yields of the desired complexes remain mediocre. These unsatisfactory results led us to test the reagent $Cr(CO)_3(NH_3)_3$ in an attempt to achieve an acceptable yield level [14]. The crown ether and $Cr(CO)_3(NH_3)_3$ were heated under reflux in dioxane for 2 h. In this case, the yield for the ether **2** was similar to the previous result, but the yield of complex **8** was much improved at a level of 36.7%, and the dicomplexed compound **9** was not found in any noticeable quantity, facilitating recovery of **8**.

It is clear that the crown ethers do not lend themselves particularly well to the complexation reaction with the $Cr(CO)_6$. It is likely that the chromiumtricarbonyl group



Scheme 1.

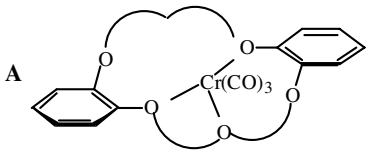


Fig. 1.

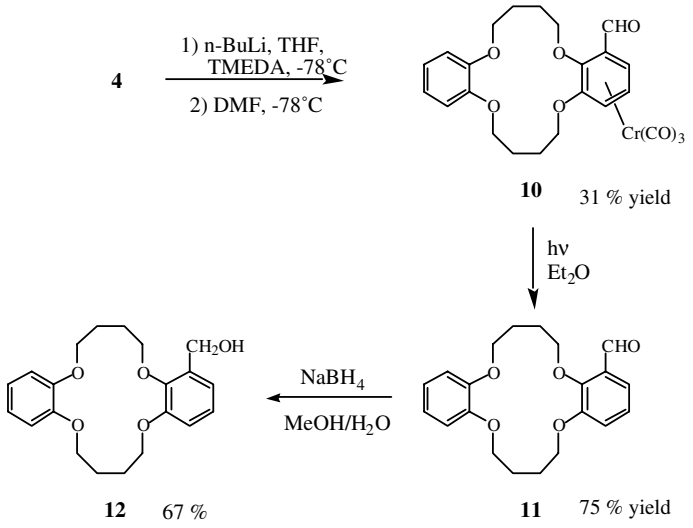
binds first to oxygen atoms of the ether functionality. In this case, we may posit the formation of several intermediates of which one is the A isomer (Fig. 1). This intermediate would have to possess a certain degree of stability which, owing to the complexation by oxygen of the chromium tricarbonyl group, would disfavor the direct attachment of the chromium tricarbonyl moiety onto the arene ring for steric reason. This hypothesis is strengthened by the rapid formation of a yellow compound, the characteristic colour of a chromium complex, when the crown ether was heated with $Cr(CO)_3(NH_3)_3$. This intermediate progressively disappeared as heating continued, to be replaced by the final complex.

Functionalization of the complexes by addition of the formyl group occurs via the generation of an organolithium compound under the action of *n*-BuLi, followed by addition of DMF or dry ice. It has been shown that addition of TMEDA to the solution containing the organolithium improves the yield of the functionalized product [12]. The organolithium compound of complex **4** is thus generated by addition of *n*-BuLi at −78 °C in the presence of TMEDA. The addition of DMF to the formed organolithium compound derivative generates the complexed aldehyde **10** (Scheme 2).

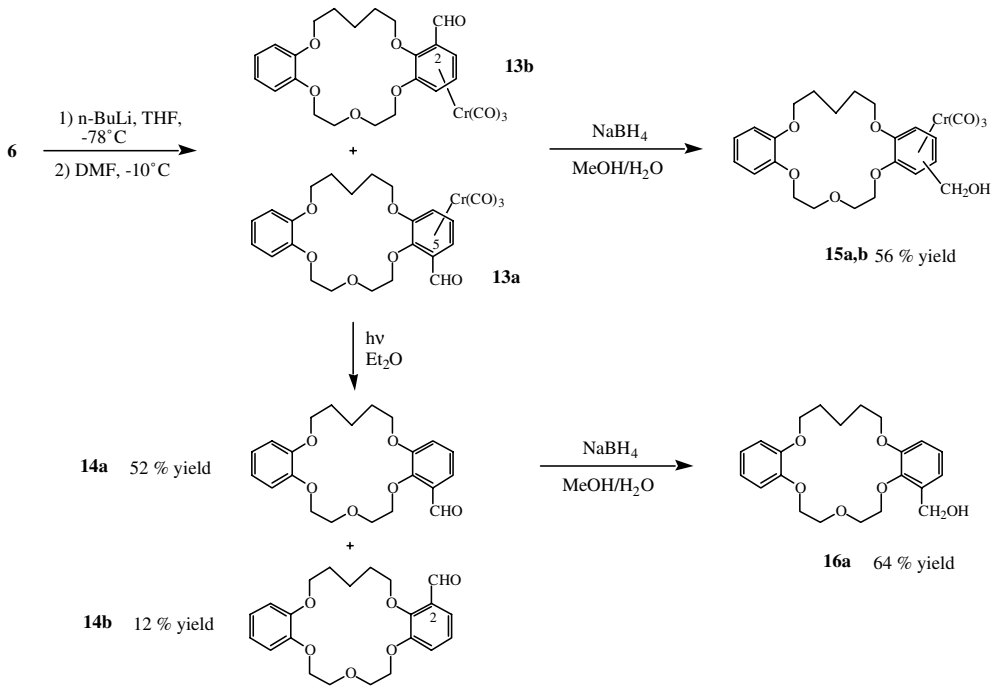
Normally functionalization occurs at the ortho position relative to the ether functionality [19]. This substitution position is confirmed by the NMR spectrum which shows two doublets and a triplet for the protons of the complexed ring. The complexation thus permits selective activation of one of the arene rings.

To obtain the purely organic functionalized crown ether requires only decomplexation of compound **10** by exposing it to sunlight in an ethereal solution, as described in the literature [20]. The aldehyde **11** was obtained in this manner in 75% yield. Furthermore, the addition of $NaBH_4$ to the solution of the aldehyde **11** rapidly gave the alcohol **12** in 67% yield. The same reactions were carried out on the complexed crown ether **6**. Scheme 3 summarizes the reactions employed and the yields obtained.

In the case of the crown ether **6**, the two chains linking the two arene rings are not identical. Consequently, substitution at position 2 does not give the same compound as that in position 5. In theory a mixture of two isomers, **13a** and **13b**, is formed, and a mixture of these two isomers was indeed obtained with an overall yield of 40% after addition of DMF to the organolithium precursor. The NMR spectrum clearly shows the mixture of the two isomers, but with strong selectivity, in a ratio of 80/20. The pure isomer **13a** was isolated by fractional crystallization and identified by 2D NMR. It is clear that the high level of selectivity between **13a** and **13b** is due to the nature of the two ether chains. In the case of the more abundant isomer **13a**, functionalization occurs ortho to the $OCH_2CH_2OCH_2$-CH_2O chain, while **13b** is functionalized ortho to the $OCH_2CH_2CH_2CH_2CH_2O$ chain. Clearly the ether functionality in the middle of the chain is responsible for the observed selectivity. It is in fact well known that an ether or amine functionality in a carbon chain stabilizes the lithium substitution in the ortho position [19g,21]. Consequently, the most abundant species in the substitution reaction may be described by the intermediate **B** (Fig. 2)



Scheme 2.



Scheme 3.

with the lithium further stabilized by complexation by the oxygen in the middle of the carbon chain.

The ethereal solution of the mixture of **13a** and **13b** was exposed to sunlight to induce decomplexation. In this case it was possible to separate the non-complexed aldehydes **14a** and **14b** with yields of 52% and 12%, respectively. Reduction of the mixture of **13a** and **13b** with $NaBH_4$ gave the alcohol complexes **15a** and **15b**. Reduction of **14a** with $NaBH_4$ gave the alcohol **16a**.

Scheme 4 summarizes the reactions carried out on the complexed polyether **8**.

In the case of complex **8**, the addition of TMEDA to the organolithium solution gave increased yields of the complexed aldehydes. The aldehydes **17a** and **17b** were obtained in yields of 59% and 3%, respectively, compared to 28% and 6% when TMEDA was not present. The ratio of the two isomers was 82/18. The more abundant isomer **17a** was unambiguously identified, by 2D NMR, NOESY, HMBC and HMQC on the non-complexed aldehyde **19** and the alcohol **20**, as the compound substituted at position 5. Exposure of the ethereal solution of **17a** to sunlight produced the non-complexed aldehyde **18a** in 53% yield. Reduction of **17a** by $NaBH_4$ gave the alcohol **19**. 2D NMR spectra of **19** show a correlation between H-2 and the OCH_2 protons of the C_8H_{17} chain on the one hand, and between the CH_2OH protons and the OCH_2CH_2O protons on the other hand. It is interesting to note that the two CH_2OH protons and the two OCH_2 protons at position 8 are non-equivalent, proving that the CHO group must be at position 5. The high selectivity at position 5 relative to that of position 2 confirms the hypothesis stated above. In fact the ether chain has a stabilizing effect on the organolithium precursor at position 5 while the C_8H_{17} alkyl chain does not produce this effect. Exposure of the ethereal solution of **19** to sunlight gave the non-complexed alcohol **20** in 87.5% yield.

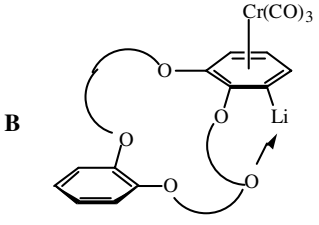
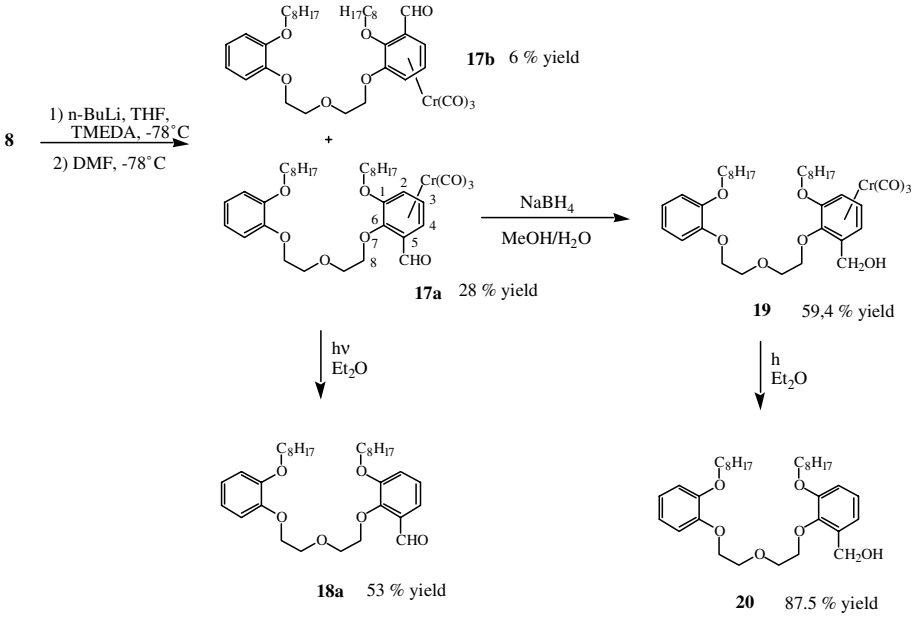


Fig. 2.

3. Conclusion

This work has shown that complexation of one of the two aromatic rings of the crown ethers dibenzo-16-crown-4 and dibenzo-18-crown-5, plus a diaryl polyether, by the chromium tricarbonyl group permits exclusive and selective functionalization of the complexed ring, which is activated for directed lithiation at the position adjacent to the OR groups. The nature of the two ether chains plays a large part in regioselective control of the functionalization, which occurs preferentially on the side where the polyether chain is located. This approach may be useful not only for the selective functionalization of crown ethers but also for their detection, thanks to the $Cr(CO)_3$ group which can act as a very sensitive infra-red probe [22]. Further



Scheme 4.

studies will be undertaken to further explore these possibilities.

4. Experimental

4.1. General data

Starting materials were synthesized using standard Schlenk technique under an argon atmosphere. Anhydrous THF and di-*n*-butyl ether were distilled from sodium/benzophenone. Thin layer chromatography was performed on silica gel 60 GF254. FT-IR spectra were recorded on a BOMEM Michelson-100 spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on Bruker 200 or 400 MHz spectrometers. Mass spectrometry was performed on a Nermag R 10-10C spectrometer. Melting points were measured with a Kofler device and DSC apparatus. Elemental analyses were performed by the Regional Microanalysis Department of Université Pierre et Marie Curie.

4.2. Synthesis of complexes *4* and *5*

Crown ether **1** (1.641 g, 5 mmol) and chromium hexacarbonyl (2.200 g, 10 mmol) were placed in a 250 mL flask equipped with a condenser. *n*-dibutyl ether (150 mL) and THF (15 mL) were added into the flask. The mixture was then heated at reflux for 20 h. The yellow solution obtained was allowed to cool to room temperature and then was put in a refrigerator in order to precipitate the unreacted chromium hexacarbonyl. After filtration and evaporation of solvent, the yellow oil obtained (2.030 g) was chromatographed on a silica gel column using diethyl ether:petroleum ether 2:1 as eluent. The mono-complexed compound, **4**, was first eluted, 0.648 g (28% yield). Recrystallization from diethyl ether/pentane furnished yellow crystals, m.p. 112 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.89 (m, 4H, non-complexed aromatic ring), 5.30 and 5.05 (m, m, 2H, 2H, complexed aromatic ring), 4.04 (m, 8H, OCH_2), 2.04 (m, 8H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 233.9 (CO), 149.8 (C11, C16, non-complexed aromatic ring), 133.5 (C1, C6, complexed aromatic ring), 121.5 and 114.9 (C12–C15, non-complexed aromatic ring), 87.4 and 81.5 (C2–C5, complexed aromatic ring), 72.1 and 69.4 (OCH_2), 26.7 and 26.5 (CH_2). IR (KBr, cm^{-1}): ν_{CO} = 1944, 1858. MS (DCI) 482 $[M + NH_4]^+$, 465 $[M + H]^+$, 380 $[M - 3CO]^+$, 346. Anal. Calc. for $C_{23}H_{24}O_7Cr$: C, 59.48; H, 5.21. Found: C, 59.56; H, 5.34%. After isolation of the mono-complexed compound, the eluent was switched to diethyl ether:petroleum ether 3:1. The di-complexed compound, **5**, was then isolated (0.119 g, 3.9% yield). Recrystallization from diethyl ether/pentane furnished yellow crystals, m.p. 212 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.27 and 5.04 (m, m, 4H, 4H, complexed aromatic ring), 4.00 (m, 8H, OCH_2), 2.04 (m, 8H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8 (C1, C6, C11, and C16, complexed aromatic ring), 86.9, and 80.1 (C2–C5, C12–C15, complexed aromatic ring), 71.2 (OCH_2), 26.1 (CH_2). IR (KBr, cm^{-1}): ν_{CO} = 1946, 1847. MS (DCI) 618 $[M + NH_4]^+$, 601 $[M + H]^+$, 482 $[M - 3COCr]^+$, 465$[M + H - 6CO - Cr]^+$, 346$[M + NH_4 - 6CO - 2Cr]^+$. Anal. Calc. for $C_{26}H_{24}$ Cr_2O_{10}: C, 52.05; H, 4.03. Found: C, 51.96; H, 4.15%.

4.3. Synthesis of complexes **6** and **7**

The complexation procedure is identical to that of **1**. Crown ether **2** (1.790 g, 5 mmol), chromium hexacarbonyl (2.200 g, 10 mmol), di-*n*-butyl ether (150 mL) and THF (15mL) were combined in a flask equiped with a condensor. The mixture was heated at reflux for 18 h. After filtration and evaporation of solvent, the yellow oil obtained (2.30 g), was chromatographed on silica gel column using diethyl ether:petroleum ether 2:1 as eluent. The mono-complexed compound, **6**, was first eluted, 0.751 g (30% yield). Recrystallization from diethyl ether/pentane furnished yellow crystals, m.p. 142 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.86 (s, 4H, non-complexed aromatic ring), 5.32 and 5.23 (dd, dd, 1H, 1H, J = 6.4 Hz and J = 1.2 Hz, H2 and H5), 5.09 and 4.97 (t, t, 1H, 1H, J = 6.4 Hz and J = 1.2 Hz, H3 and H4), 4.01 (m, 12H, OCH_2), 1.90 (m, 6H, –CH_2). ^{13}C NMR (100 MHz, DMSO): δ 233.8 (CO), 149.2 and 148.4 (non-complexed aromatic ring), 133.6 and 131.7 (complexed aromatic ring), 121.3, 120.5, 113.5, and 112.3 (non-complexed aromatic ring), 88.1, 86.3, 81.4, 78.2 (complexed aromatic ring), 71.0, 70.2, 69.6, 68.7, and 68.0 (OCH_2), 29.5, 29.2, 23.8 (CH_2). IR (KBr, cm^{-1}): ν_{CO} = 1951, 1855. MS (DCI) 512 $[M + NH_4]^+$, 376 $[M + NH_4 - 3CO - Cr]^+$. Anal. Calc. for $C_{24}H_{26}O_8Cr$: C, 58.29; H, 5.29. Found: C, 58.04; H, 5.50%. After isolation of mono-complexed compound, the eluent was switched to diethyl ether:petroleum ether 3:1. The di-complexed compound, **7**, was then isolated (0.100 g, 3.1% yield). Recrystallization from diethyl ether/pentane furnished yellow crystals, m.p. 234 °C. ^{1}H NMR (400 MHz, DMSO): δ 5.88 and 5.86 (d, d, 2H, 2H, aromatic ring), 5.42 and 5.35 (t, t, 2H, 2H, aromatic ring), 4.12, 4.00, 3.85, 3.73 (m, m, m, 12H, OCH_2), 1.72 (m, 6H, CH_2). ^{13}C NMR (100 MHz, DMSO): δ 133.7 and 132. 5 (aromatic ring), 89.7, 88.7, 82.2, and 80.8 (aromatic ring), 69.6, and 68.6 (OCH_2), 28.5 (2 CH_2), 23.2 (CH_2). IR (KBr, cm^{-1}): ν_{CO} = 1954, 1866. MS (DCI) 648 $[M + NH_4]^+$, 512 $[M + NH_4 - 3CO - Cr]^+$, 376 $[M + NH_4 - 6CO - 2Cr]^+$. Anal. Calc. for $C_{27}H_{24}O_{11}Cr_2$: C, 51.42; H, 4.15. Found: C, 51.52; H, 4.27%.

4.4. Synthesis of complexes **8** and **9**

The complexation procedure is identical to that of **1**, using ether **3** (2.570 g, 5 mmol), chromium hexacarbonyl (2.200 g, 10 mmol), di-*n*-butyl ether (150 mL) and THF (15 mL). The mixture was heated at reflux for 8.5 h. After filtration and evaporation of solvent, the yellow oil obtained (1.15 g), was chromatographed on a silica gel column using diethyl ether:petroleum ether 2:1 as eluent. The mono-complexed compound, **8**, was first eluted, 0.471 g (yellow oil, 14.5% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.90 (m, 4H, non-complexed aromatic ring), 5.42, 5.23, 5.07, and 4.96 (d, d, t, t, 1H, 1H, 1H, 1H, complexed aromatic ring), 4.18 (t, OCH_2, 2H), 4.11 (t, 2H, OCH_2), 3.90 (m, 8H, OCH_2), 1.77, 1.44, and 1.28 (m, s, s, 4H, 4H 16H, –CH_2), 0.88 (m, 6H, 2 CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 233.8 (CO), 149.6 and 148.8 (non-complexed aromatic ring), 133.8 and 132.3 (complexed aromatic ring), 121.9, 121.0, 115.3, and 113.9 (non-complexed aromatic ring), 88.01, 86.7, 82.1, 79.1 (complexed aromatic ring), 71.6, 70.8, 70.2, 69.9, and 69.2 (OCH_2), 31.9-22.7 (CH_2), 14.2 (CH_3). IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1960, 1877. MS (DCI) 668 $[M + NH_4]^+$, 566 $[M + H - 3CO]^+$, 532 $[M + NH_4 - 3CO - Cr]^+$. Anal. Calc. for $C_{35}H_{50}O_8Cr$: C, 64.53; H, 7.74. Found: C, 64.45; H, 7.86%. After isolation of the mono-complexed compound, the eluent was switched to diethyl ether:petroleum ether 4:1. The di-complexed compound, **9**, was then isolated as a yellow oil (0.204 g, 5.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42, 5.24, 5.09, and 5.00 (m, m,m, m, 8H, aromatic ring), 4.20–4.38 (m, 12H, OCH_2), 1.78, 1.44, 1.28 (m, m, m, 4H, 4H, 16H, CH_2), 0.88 (m, 4H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8 and 132.2 (C1, C6, aromatic ring), 88.1, 86.8, 82.2, and 79.0 (C2, C3, C4, and C5, aromatic ring), 71.6, 70.8, 69.8 (OCH_2), 31.8, 29.3, 29.1, 25.9, 22.7 (CH_2), 14.2 (CH_3). IR (KBr, cm^{-1}): ν_{CO} = 1961, 1877. MS (electrospray) 809.4 $[M + Na]^+$. MS (EI) 618 $[M - 6CO]^+$, 566 $[M - 6CO - Cr]^+$, 514 $[M - 6CO - 2Cr]^+$,. Anal. Calc. for $C_{38}H_{50}O_{11}Cr_2$: C, 58.01; H, 6.85. Found: C, 58.63; H, 6.61%.

4.5. Synthesis of aldehyde **10**

Complex **4** (0.464 g, 1 mmol) was dissolved in THF (20 mL). The solution was cooled to −78 °C. Then 0.40 mL of *n*-BuLi solution (1 mmol, 2.56 M in hexane) was added dropwise. After 2 h stirring, the temperature was raised to −10 °C, and 0.155 mL of DMF was added. Stirring was continued for 15 min, and the mixture was poured into a diluted HCl aqueous solution. The compound was extracted with 100 mL of CH_2Cl_2. After filtration and evaporation of solvent, the orange oil obtained (0.534 g) was chromatographed on a silica gel column by using diethyl ether:petroleum ether 2:1 as eluent. The aldehyde **10** was isolated as an orange oil (0.153 g, 31% yield). Recrystallization from diethyl ether/pentane furnished orange crystals, m.p. 52 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.10 (s, 1H, CHO), 6.89 (m, 4H, non-complexed aromatic ring), 5.66 (d, 1 H, J = 6.6 Hz, complexed aromatic ring), 5.48 (d, 1 H, J = 5.5 Hz, complexed aromatic ring), 5.12 (t, 1H, J = 5.9 Hz, complexed aromatic ring), 4.65, 4.40, 4.05, 3.84 (m, m, m, m, 8H, OCH_2), 2.04 (m, 8H, CH_2). IR (KBr, cm^{-1}): ν_{CO} = 1966, 1888, $\nu_{C=O}$ = 1683. MS

(DCI) 510 $[M + NH_4]^+$, 493 $[M + H]^+$, 374 $[M + NH_4 - 3CO - Cr]^+$, 357 $[M + H - 3CO - Cr]^+$. Anal. Calc. for $C_{24}H_{24}O_8Cr$: C, 58.53; H, 4.91. Found: C, 59.02; H, 5.49%.

4.6. Synthesis of aldehyde **11**

Aldehyde complex **10** (0.050 g, 0.10 mmol) was dissolved in 20 mL diethyl ether. The solution was exposed to sunlight for 2 h. The colourless solution was then filtered on silica gel pad to give 0.040 g of a solid after evaporation of the solvent. The crude product was purified by TLC using diethyl ether:pentane 1:1 as eluent. Aldehyde **11** was obtained as a colourless solid (0.027 g, 75.0% yield, m.p. 99 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.40 (s, 1H, CHO), 7.32 (dd, 1 H, $J = 6.6$ Hz and 2.8 Hz, H4), 7.03 (m, 2 H, H2 and H3), 6.83 (m, 4H, non-substituted ring), 4.27 (t, 2 H, CH_2O), 3.99 (m, 6 H, CH_2O), 2.04 (m, 8 H, CH_2-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7 (CHO), 152.9 and 152.6 (C1, C6), 149.7 and 149.5 (C11, C16), 129.9 (C5), 123.7, 121.5, 118.9 and 114.7 (C2, C3, C4, C12, C13, C14, C15), 75.7 (C7), 69.4 (C8), 69.0 (C9), 68.5 (C10, C17, C20), 27.9, 26.9, 26.0 and 25.3 (C8, C9, C18 and C19). IR (KBr, cm^{-1}): $\nu_{C=O} = 1684$. MS (ES) 379 $[M + Na]^+$. Anal. Calc. for $C_{21}H_{24}O_5$: C, 70.76; H, 6.78. Found: C, 70.58; H, 6.97%.

4.7. Synthesis of alcohol **12**

Aldehyde **11** (0.090 g, 0.25 mmol) was dissolved in 10 mL of ethanol. A solution of $NaBH_4$ (0.125 g) in 2 mL of water was added to the first solution. After stirring for 30 min, the mixture was poured in 10 mL of a 10% HCl solution. The product was extracted with diethyl ether. The organic layer was washed with 20 mL of water. After drying on $MgSO_4$, filtration, and solvent removal, 0.070 g of crude product was obtained as a solid. Crystallization in CH_2Cl_2:hexane gave 0.060 mg of alcohol **13** (67% yield, m.p. 87 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.91–6.74 (m, 7H, aromatic ring), 4.63 (d, 2 H, $J = 5.1$ Hz, CH_2OH), 4.16 and 4.00 (t, m, 2 H, 6 H, CH_2O), 1.98 (m, 8 H, CH_2-CH_2). MS (EI) 381 $[M + Na]^+$. Anal. Calc. for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.28; H, 7.38%.

4.8. Synthesis of aldehyde ***13a*** and ***13b***

The procedure is identical to that for **10**, using complex **6** (0.99 g, 2 mmol), THF (30 mL), *n*-BuLi solution (0.80 mL, 2 mmol), and DMF (0.31 mL, 4 mmol). After work-up, the orange oil obtained (1.70 g) was chromatographed on a silica gel column using diethyl ether:petroleum ether 2:1 as eluent. The aldehyde **13a,b** was isolated as an orange oil (0.400 g, 40% yield). The NMR spectrum showed a mixture of two isomers in 80:20 proportion. ^{1}H NMR (200 MHz, $CDCl_3$) of major isomer: δ 10.12 (s, 1H, CHO), 6.87 (m, 4H, non-complexed aromatic ring), 5.58 (d, 1 H, $J = 6.4$ Hz, complexed aromatic ring), 5.42 (d, 1 H, $J = 6.5$ Hz, complexed aromatic ring), 5.20 (t, 1H, $J = 6.5$ Hz, complexed aromatic ring), 4.55, 4.30, 4.15 and 4.03 (4 m, OCH_2), 1.87 (m, 6 H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 231.5 (CO), 187.5 (CHO), 149.9 and 148.4 (C11, C16), 132.8 and 132.2 (C1, C6), 121.2, 120.7, 113.6, and 112.4 (C12, C13, C14, and C15), 92.6, 87.3, 84.9, 78.8 (C2, C3, C4, C5), 70.4, 69.8, 69.2, 67.8 (C7, C8, C9, C10, C17, C21), 29.5, 29.2 and 23.8 ($CH_2CH_2CH_2$). IR (KBr, cm^{-1}): $\nu_{CO} = 1967$, 1885, $\nu_{C=O} = 1684$. MS (DCI) 540 $[M + NH_4]^+$, 523 $[M + H]^+$, 404 $[M + NH_4 - 3CO - Cr]^+$, 387 $[M + H - 3CO - Cr]^+$, 376 $[M + H - 4CO - Cr]^+$. Anal. Calc. for $C_{25}H_{26}O_9Cr$: C, 57.42; H, 5.01. Found: C, 57.65; H, 5.26%.

4.9. Synthesis of aldehydes ***14a*** and ***14b***

The aldehyde complex **13** (0.052 g, 0.1 mmol) was dissolved in 10 mL of diethyl ether. The solution was exposed to sunlight for 2 h. The colourless solution was then filtered on a silica gel pad to give 0.035 g of a solid after evaporation of the solvent. The crude product was purified by TLC using CH_2Cl_2:$CHCl_3$ 2:3 as eluent. Aldehyde **14a**, the major isomer, was obtained as a colourless solid (0.020 g, 52.0% yield, mp 119 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.49 (s, 1H, CHO), 7.38 (dd, 1 H, $J = 5.6$ Hz and 3.8 Hz, substituted ring), 7.10 (d, 1 H, $J = 3.8$ Hz, substituted ring), 7.09 (d, 1 H, $J = 5.6$ Hz, substituted ring), 6.87 (m, 4 H, non-substituted ring), 4.37 (t, 2 H, $J = 3.7$ Hz, CH_2O), 4.17 (m, 2 H, CH_2O), 4.00 (m, 8 H, 4 CH_2O), 1.90 (m, 6 H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5 (CHO), 152.4 (C1), 151.5 (C6), 148.9 (C16), 148.3 (C11), 129.9 (C5), 124.0 (C3), 121.1, and 120.7 (C13, C14), 118.7 (C4), 118.1 (C2), 112.7, and 112.3 (C12 and C15), 73.7 (C7), 70.7 (C8), 69.6 (C9), 69.3 (C10), 68.4 (C21), 67.9 (C17), 29.6 and 29.5 (C18 and C20), 24.0 (C19). IR (KBr, cm^{-1}): $\nu_{C=O} = 1684$. MS (EI) 386 $[M^{+\cdot}]$. Anal. Calc. for $C_{22}H_{26}O_6$: C, 68.39; H, 6.73. Found: C, 68.30; H, 6.91%. 0.005 g of aldehyde **14b**, the minor isomer, was also isolated (12% yield, mp 96 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.37 (s, 1H, CHO), 7.34 (m, 1 H, substituted ring), 7.02 (m, 2 H, substituted ring), 6.84 6.87 (m, 4 H, non-substituted ring), 4.16–3.90 (m, 12 H, CH_2O), 1.81 (m, 6 H, $CH_2CH_2CH_2$). IR (KBr, cm^{-1}): $\nu_{C=O} = 1686$. MS (ES) 411 $[M + Na]^+$, 406 $[M + NH_4]^+$. Anal. Calc. for $C_{22}H_{26}O_6$: C, 68.39; H, 6.73. Found: C, 69.31; H, 7.22%.

4.10. Synthesis of alcohol *15a* and *15b*

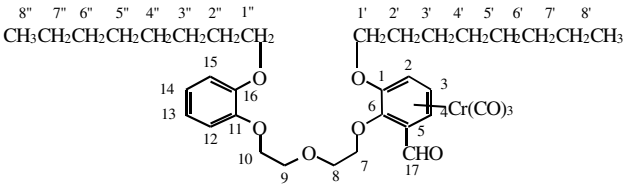
The aldehyde complexes **13a** and **13b** (0.150 g, 0.3 mmol) were dissolved in 20 mL ethanol. A solution of $NaBH_4$ (0.20 g) in 1 mL water was added to the first solution. The mixture immediately turned yellow. After stirring for 30 min, the mixture was poured into 10 mL of water. The product was extracted with diethyl ether. The organic layer was washed with 20 mL water. After drying on $MgSO_4$, filtration and solvent removal, the product was purified by TLC using diethyl ether:pentane 3:1 as eluent. Alcohols **15a,b** were obtained as an yellow solid (0.090 g, 56% yield, m.p. 139 °C). Major isomer : ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.86 (m, 4H, non-substituted ring), 5.38 (t, 1 H, $J = 6.5$ Hz, substituted ring), 5.05 (d, 1 H, $J = 6.8$ Hz, substituted ring), 4.96 (d, 1 H, $J = 6.1$ Hz, substituted ring), 4.80 and 4.42 (dd, dd, 1H, 1H,, $J = 14.3$ Hz and $J = 4.8$ Hz, CH_2OH), 4.59 (t, 1H, OH), 4.38 and 4.01 (m, m, 2H, 10 H, CH_2O), 2.03 (m, 6 H, $CH_2CH_2CH_2$). IR (KBr, cm^{-1}): ν_{OH} 3416, ν_{CO} = 1955, 1874. MS (EI) 388 $[M - 3CO - Cr]^+$. Anal. Calc. for $C_{25}H_{28}O_9Cr$: C, 57.25; H, 5.38. Found: C, 57.22; H, 5.58%.

4.11. Synthesis of alcohol *16a*

The aldehyde **14a** (0.040 g, 0.1 mmol) was dissolved in 10 mL ethanol. A solution of $NaBH_4$ (0.050 g) in 1 mL water was added to the first solution. The mixture turned yellow immediately. After stirring for 30 min, the mixture was poured into 10 mL water. The product was extracted with diethyl ether. The organic layer was washed with 20 mL of water. After drying on $MgSO_4$, filtration and solvent removal, 0.030 g of the alcohol **16a** was obtained as a colourless solid. A crystallization in CH_2Cl_2:hexane gave colourless crystals, 0.025 g, 64% yield, m.p. 205 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.80 (m, 7H, aromatic ring), 4.60, 4.32, 4.09 and 3.98 (d, m, m, m, 15 H, CH_2O, CH_2OH and OH), 1.80 (m, 6 H, $CH_2CH_2CH_2$). IR (KBr, cm^{-1}): ν_{OH} 3435. MS (EI) 388 $[M]^+$. Anal. Calc. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27. Found: C, 67.77; H, 7.58%.

4.12. Synthesis of aldehyde *17a* and *17b*

The procedure is identical to that of **10** using complex **8** (0.700 g, 1.07 mmol), THF (10 mL), *n*-BuLi 2.5 M solution (0.48 mL, 1.2 mmol), and DMF (0.5 mL). After a work-up, the orange oil obtained (1.07 g), was chromatographed on silica gel plates (TLC) by using diethyl ether:petroleum ether 1:1 as eluent. Two aldehyde complexes were isolated. The major aldehyde **17a** was first isolated as an orange oil (0.211 g, 28% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.13 (s, 1H, CHO), 6.90 (m, 4H, non-complexed aromatic ring), 5.58 (dd, 1 H, $J = 6.5$ and 1.0 Hz, complexed aromatic ring), 5.42 (dd, 1 H, $J = 6.5$ and 1.0 Hz, complexed aromatic ring), 5.11 (t, 1H, $J = 6.5$ Hz, complexed aromatic ring), 4.37, 4.13 and 3.90 (m, m, m, 2 H, 4 H, and 6 H, OCH_2), 1.79, and 1.28 (m, m, 4 H, and 24 H, 6 CH_2), 0.88 (m, 6H, 2 CH_3). ^{13}C NMR (100 MHz, DMSO): δ 231.4 (CO), 187.8 (CHO), 149.5 and 148.6 (C11, C16), 134.1 and 132.5 (C1, C6), 121.9, 121.0, 113.8, and 113.9 (C12, C13, C14, and C15), 91.8, 86.7, 85.3, 79.6, 75.6 (C2, C3, C4, C5, and C7), 70.9, 70.5, 69.9, 69.3, and 69.0 (C8, C9, C10, C1′, C1″), 31.9–22.7 (C2′–C7′ and C2″–C7″), 14.2 and 14.0 (C8′ and C8″). IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1976, 1902, $\nu_{C=O}$ = 1679. MS (DCI) 713 $[M + NH_3 + NH_4]^+$, 696 $[M + NH_4]^+$, 679 $[M + H]^+$, 560 $[M + NH_4 - 3CO - Cr]^+$, 543 $[M + H - 3CO - Cr]^+$, 532 $[M + NH_4 - 4CO - Cr]^+$. Anal. Calc. for $C_{36}H_{50}O_9Cr$: C, 63.70; H, 7.42. Found: C, 63.11; H, 7.72%. The minor aldehyde **17b** was eluted after **17a** and isolated as an orange oil (0.049 g, 6% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.04 (s, 1H, CHO), 6.92 (m, 4H, non-complexed aromatic ring), 5.67 (dd, 1 H, $J = 6.5$ and 1.1 Hz, complexed aromatic ring), 5.59 (dd, 1 H, $J = 6.5$ and 1.1 Hz, complexed aromatic ring), 5.07 (t, 1H, $J = 6.5$ Hz, complexed aromatic ring), 4.20, and 3.90 (m, m, 4 H, and 8 H, OCH_2), 1.77, and 1.27 (m, m, 4 H, and 24 H, 6 CH_2), 0.88 (m, 6H, 2 CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 231.3 (CO), 187.1 (CHO), 149.5 and 148.6 (C11, C16), 122.7, 122.1, 121.1, 120.9, 115.2, and 113.8 (C1, C6, C12, C13, C14, and C15), 91.3, 86.5, 86.0, 81.8, 74.4 (C2, C3, C4, C5, and C7), 71.2, 70.2, 69.7, 69.4, and 69.0 (C8, C9, C10, C1′, C1″), 31.3–22.7 (C2′–C7′ and C2″–C7″), 14.2 (C8′ and C8″). IR (CH_2Cl_2, cm^{-1}): ν_{CO} = 1977, 1907, $\nu_{C=O}$ = 1684. MS (ES) 701 $[M + Na]^+$, 565 $[M + Na - 3CO - Cr]^+$. Anal. Calc. for $C_{36}H_{50}O_9Cr$: C, 63.70; H, 7.42. Found: C, 63.44; H, 7.67%.



4.13. Synthesis of aldehyde *18a*

Aldehyde complex **17a** (0.090 g, 0.13 mmol) was dissolved in 10 mL of diethyl ether. The solution was exposed to sunlight for 30 min. The colourless solution was then filtered on a silica gel pad to give 0.062 g of oil after evaporation of the solvent. The crude product was purified by TLC using diethyl ether:petroleum ether 1:2 as eluent. The aldehyde **18a** was obtained as a

colourless oil (0.038 g, 53.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.52 (s, 1H, CHO), 7.40 (dd, 1 H, $J = 7.1$ and 2.1 Hz, H4), 7.10 (m, 2 H, H2 and H3), 6.90 (m, 4H, non-substituted ring), 4.36 (m, 2 H, H7), 4.15 (t, 2 H, $J = 3.6$ Hz, H10), 4.00 (t, 2 H, $J = 6.5$ Hz, H1′), 3.96 (t, 2 H, $J = 6.7$ Hz, H1″), 3.90 (m, 4 H, H8 and H9), 1.81 (m, 4 H, H2′ and H2″), 1.30 (m, 4 H, H3′ and H3″), 1.27 (m, 16 H, H4′–H7′ and H4″–H7″), 0.88 (m, 6H, H8′ and H8″). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0 (CHO), 152.4 and 151.6 (C1, C6), 149.5 and 148.7 (C11, C16), 130.2 (C5), 124.0 (C4), 121.8, 121.0, 118.9, 118.8, 115.1, and 113.8 (C2, C3, C12, C13, C14, and C15), 73.2, 70.7, 69.8, 69.2, 69.1, and 34.2 (C1′, C1″, C7, C8, C9, C10), 31.9 (C6′, C6″), 29.4, 29.4, 29.3 (C2′, C2″, C4′, C4″, C5′, C5″, C6′, C6″), 26.2, 26.1 (C3′, C3″), 22.7 (C7′, C7″), 14.1 (C8′, C8″). IR (CH_2Cl_2, cm^{-1}): $\nu_{C=O} = 1684$. MS (EI) 542 $[M]^+$, 514 $[M + CO]^+$. Anal. Calc. for $C_{33}H_{50}O_6$: C, 73.03; H, 9.39. Found: C, 72.52; H, 9.78%.

4.14. Synthesis of alcohol **19**

The aldehyde complex **17a** (0.160 g, 0.23 mmol) was dissolved in 3 mL of ethanol. A solution of $NaBH_4$ (0.038 g, 1 mmol) in 1 mL water was added to the first solution. The mixture turned yellow immediately. After stirring for 15 min, the mixture was poured into 30 mL water. The product was extracted with diethyl ether (2×30 mL). The organic layer was washed with 20 mL water. After drying on $MgSO_4$, filtration and solvent removal, the product was purified by TLC using diethyl ether:petroleum ether 1:1 as eluent. Alcohol **19** was obtained as a yellow oil (0.093 g, 59.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (m, 4H, H12, H13, H14, H15), 5.27 (t, 1 H, $J = 6.5$ Hz, H3), 5.08 (dd, 1 H, $J = 6.6$ Hz and $J = 0.9$ Hz, H2), 4.94 (dd, 1 H, $J = 6.2$ Hz and $J = .9$ Hz, H4), 4.82 and 4.30 (dd, dd, 1H, 1H,, $J = 12.9$ Hz and $J = 5.9$ Hz, H17, CH_2OH), 4.30 and 4.20 (m, m, 1H, 1H, H7), 4.20 (m, 2 H, H10), 4.00 (t, 4 H, $J = 6.7$ Hz, H1′ and H1″), 3.93 (m, 4 H, H8 and H9), 1.80 (m, 4 H, H2′ and H2″), 1.44 (m, 4 H, H3′ and H3″), 1.30 (m, 16 H, H4′–H7′ and H4″–H7″), 0.88 (m, 6H, H8′ and H8″). ^{13}C NMR (100 MHz, $CDCl_3$): δ 233.4 (CO), 149.3 (C16), 148.5 (C11), 136.9 (C1), 128.0 (C1), 122.0, 121.1, 115.1, 114.0 (C12, C13, C14, and C15), 109.1 (C5), 90.9 (C3), 85.4 (C4), 76.4 (C7), 75.2 (C2), 70.6, 69.9 and 69.7 (C1′, C8, C9), 69.2 (C1″), 69.0 (C10), 60.8 (C17), 31.9 and 31.8 (C6′, C6″), 29.4, 29.3, 29.2, and 29.0 (C2′, C2″, C4′, C4″, C5′, C5″), 26.0, 25.9 (C3′, C3″), 22.7 (C7′, C7″), 14.2 (C8′, C8″). IR (CH_2Cl_2, cm^{-1}): $\nu_{OH} = 3459$, $\nu_{CO} = 1962$, 1881. MS (ES) 703 $[M + Na]^+$, 567 $[M + Na - 3CO - Cr]^+$. Anal. Calc. for $C_{36}H_{52}O_9Cr$: C, 63.51; H, 7.70. Found: C, 63.05; H, 8.15%.

4.15. Synthesis of alcohol **20**

Alcohol complex **19** (0.060 g, 0.09 mmol) was dissolved in 5 mL of diethyl ether. The solution was exposed to sunlight for 30 min. The colourless solution was then filtered on a silica gel pad to give 0.042 g of **20** as an oil after evaporation of the solvent (87.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (m, 7 H, arene ring), 4.55 (d, 2 H, $J = 6.3$ Hz, CH_2OH), 4.25 (m, 2 H, H7), (t, 2 H, $J = 5.2$ Hz, H10), 3.87 (m, 9 H, H1′, H1″, H8, H9, OH), 1.73 (m, 4 H, H2′ and H2″), 1.21 (m, 20 H, H3′-H7′ and H3″–H7″), 0.81 (m, 6H, H8′ and H8″). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.7 (C1), 149.4 (C16), 148.5 (C11), 146.5 (C4), 135.1 (C5), 123.6, 121.8, 121.5, 121.0, 115.2, 113.9, 113.2 (C2, C3, C4, C12, C13, C14, and C15), 72.1, 71.2, 69.7, 69.1, 68.6, and 65.8 (C1′, C1″, C7, C8, C9, C10), 61.8 (CH_2OH), 31.8, 29.3, 26.1, 26.0, 22.6 (C2′–C7′ and C2″–C7″), 15.2 and 14.1 (C8′, C8″). IR (CH_2Cl_2, cm^{-1}): $\nu_{CO} = 1592$. MS (EI) 544 $[M]^+$, 527 $[M - OH]^+$. Anal. Calc. for $C_{33}H_{52}O_6$: C, 72.76; H, 9.62. Found: C, 72.53; H, 9.83%.

Acknowledgements

Financial support from the Ministère de la Recherche, the Centre National de la Recherche Scientifique and the Tunisian Ministère de l'enseignement supérieur et de la recherche scientifique are gratefully acknowledged. We thank B. McGlinchey for translating the manuscript.

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