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# Nicholas Reactions in the Construction of Cyclohepta[de]naphthalenes and Cyclohepta[de]naphthalenones. The Total Synthesis of Microstegiol

RAFIQ TAJ

*University of Windsor*

James R. Green

*University of Windsor*

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# Nicholas reactions in the construction of cyclohepta[*de*]naphthalenes and cyclohepta[*de*]naphthalenones. Preparation of the microstegiol ring system

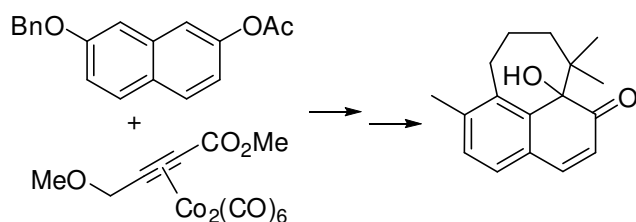
*Rafiq A. Taj and James R. Green\**

Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, N9B 3P4, Canada

jgreen@uwindsor.ca

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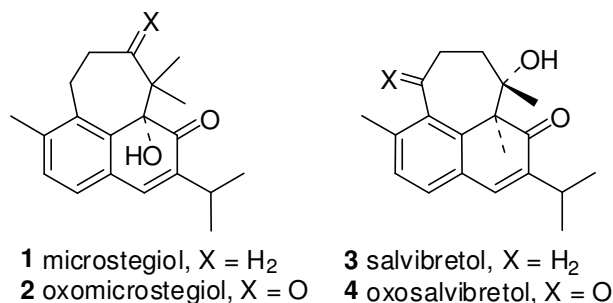


The application of the Nicholas reaction chemistry of 2,7-dioxygenated naphthalenes towards the synthesis of cyclohepta[*de*]naphthalenes, particularly the rearranged abietane ring system of microstegiol, is presented. The substitution profile of Nicholas monosubstitution (predominantly C-1) and disubstitution reactions (predominantly 1,6-) on 2,7-dioxygenated naphthalenes is reported. Application of a 1,8-dicondensation product and selected C-1 monocondensation products to the construction of

cyclohepta[de]naphthalenes by way of ring closing metathesis and intramolecular Friedel-Crafts reactions, respectively, are described. Deprotection of the C-7 oxygen function to the corresponding naphthol allows tautomerization to cyclohepta[de]naphthalene-1-ones upon seven membered ring closure in most cases, and replacement of the C-2 oxygen function in the naphthalene by a methyl group ultimately allows the synthesis of model compound **38**, lacking only the isopropyl group of microstegiol.

## Introduction

The cyclohepta[de]naphthalenes comprise a class of seven membered ring compounds that has received significant attention for decades. Much of the early work centered around the pleiadienes and acepleiadylenes and stemmed from interest in their electronic structure. More recently, several rearranged abietanes containing the cyclohepta[de]naphthalene nucleus, including microstegiol (**1**),<sup>1</sup> oxomicrostegiol (**2**),<sup>2</sup> salvibretol (**3**),<sup>1c</sup> and oxosalvibretol (**4**),<sup>1c,1m</sup> have been isolated from roots of a number of plants of the genus *Salvia*. These plants have often been seen used as folk remedies, and their crude extracts have demonstrated antibacterial, anticancer, and insect antifeedant activities.<sup>1h,1k,3</sup> Microstegiol itself has been demonstrated to have antileukemic activity and modest antibacterial activity.<sup>1a,1k,1m,1n</sup>



Despite the recent upsurge in interest in the natural product literature, none of the rearranged abietanes **1-4** have been the subject of synthetic activity. The carbon framework of the cyclohepta[de]naphthalenes themselves have normally been prepared by sequential Friedel-Crafts acylations of succinic anhydride or some variation of that approach,<sup>4</sup> although scattered reports of access to this ring system by 2+2 cycloaddition/ring expansion reactions of cyclopenta[de]naphthalenes,<sup>5</sup>

malonate intramolecular alkylation processes,<sup>6</sup> reductive carbonyl coupling reactions,<sup>7</sup> and *o*-xylylene Diels-Alder cycloadditions<sup>8</sup> have been published.<sup>9</sup>

Our group has a long-standing interest in the synthesis of seven-membered ring compounds,<sup>10</sup> based in part on the ability of alkynedicobalt complexes and the Nicholas reaction chemistry<sup>11</sup> of their derived propargyldicobalt cations to allow umpolung bond constructions from reactions of  $\alpha$ -carbonyl cation equivalents with electron rich arenes or other nucleophiles.<sup>12,13,14,15</sup> Given the recent interest in **1-4** and the relative paucity of methods for the synthesis of cyclohepta[*de*]naphthalenes, we considered it of importance to study the applicability of these cations to this ring system, with a particular attention to the tautomerized naphthol (cyclohepta[*de*]naphthalene-1-one) framework of microstegiol (**1**). Given its structural characteristics, we consider the issues of a) the fundamental substitution characteristics in Nicholas reactions on 2,7-disubstituted naphthalenes, b) seven membered ring construction derived from Nicholas reaction adducts, c) tautomerization to the keto- form of the 7- (or 2-) hydroxynaphthalenes, and d) regioselection in the constructed cycloheptane to be significant for the methodology. This work describes in complete form our developments in these directions.<sup>16</sup>

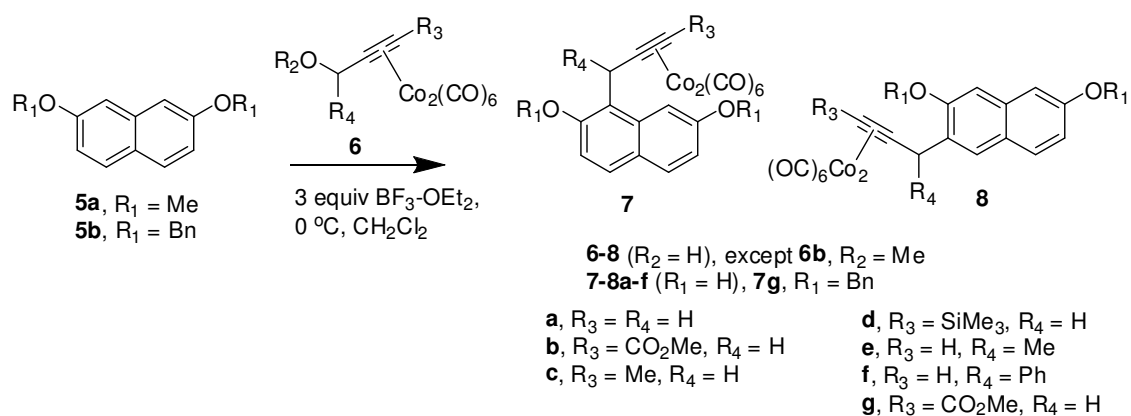
## Results and Discussion

We believed it necessary to develop a comprehensive understanding of the pattern of reactivity of propargyldicobalt cations with naphthalene-2,7-diol derivatives. To this end we chose 2,7-dimethoxynaphthalene (**5a**) as a reference molecule and studied the Lewis acid mediated Nicholas reactions of a number of substituted propargyl alcohol- or propargyl ether  $\text{Co}_2(\text{CO})_6$  complexes (**6a-f**).

**Monocondensation.** The condensation reactions of **6** with 2,7-dimethoxynaphthalene (**5a**) occurred to variable levels of conversion in the presence of stoichiometric amounts of  $\text{BF}_3\text{-OEt}_2$ , but readily to complete conversion in the presence of 3 equiv of  $\text{BF}_3\text{-OEt}_2$  (Table 1). With approximately equimolar amounts of **6a-f** (1.1 equiv) relative to **5a**, monocondensation products (**7,8**) were formed in most cases without significant contamination from the products of dialkylation. Nicholas reaction precursors (**6a-d**) bearing no substitution at the propargylic site cleanly afforded C-1 substitution in good yields, regardless of whether the remote site of the alkyne bore no substitution (**7a**, 93%), or substitution by an

electron withdrawing group (**7b**, 76%), an alkyl group (**7c**, 84%) or a silyl group (**7d**, 97%). Substitution at the propargylic site by a methyl group (**6e**) still allowed C-1 substitution to occur (**7e**, 66%), but phenyl substitution at the propargyl site (**6f**) resulted in condensation to give C-3 substitution product (**8f**, 51%) as the sole isolable one. Use of 2,7-dibenzoyloxysubstituted **5b** gave an analogous reaction with ester substituted complex **6b**, with the exception of giving a small amount of 1,8-dicondensation product **9g** (13%) in addition to the C-1 monocondensation product **7g** (71%).

**Table 1.** Monocondensation reactions of **6a-f** with **5a-b**.

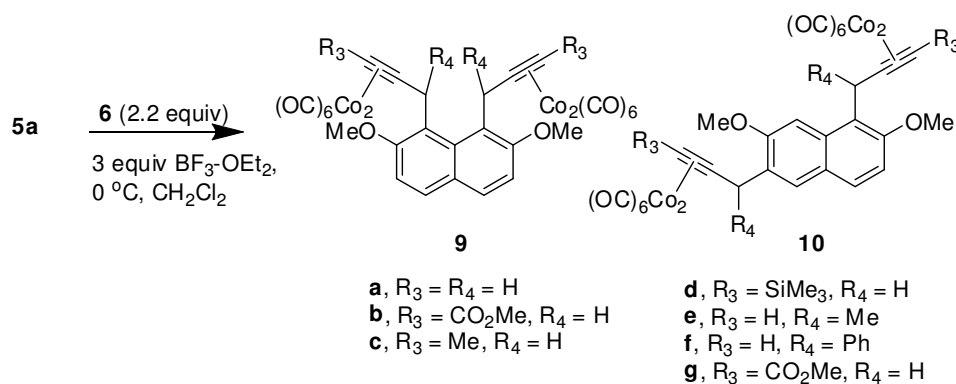


Entry	<b>5</b>	<b>6</b>	<b>7</b> (yield, %)	<b>8</b> (yield, %)
1	<b>5a</b>	<b>6a</b>	<b>7a</b> (93)	
2	<b>5a</b>	<b>6b</b>	<b>7b</b> (88)	
3	<b>5a</b>	<b>6c</b>	<b>7c</b> (84)	
4	<b>5a</b>	<b>6d</b>	<b>7d</b> (97)	
5	<b>5a</b>	<b>6e</b>	<b>7e</b> (66)	
6	<b>5a</b>	<b>6f</b>	-	<b>8f</b> (51)
7	<b>5b</b>	<b>6b</b>	<b>7g</b> (71) <sup>a</sup>	

<sup>a</sup> In addition, 13% of **9g** was isolated.

**Dicondensation.** Increasing the amount of propargyl alcohol/ether-  $\text{Co}_2(\text{CO})_6$  complex **6a-e** to slightly over two equivalents enabled, in most cases, ready conversion of 2,7-dimethoxynaphthalene (**5a**) to disubstituted products (**9-10**) (Table 2). In these cases, a competition existed between the formation of 1,8-disubstitution products (**9**) and 1,6-disubstitution products (**10**), which depended upon the structure of the Nicholas reaction precursor complex **6**. In the case of unsubstituted **6a**, 1,8-disubstitution predominated, although not to the exclusion of 1,6-disubstitution (**9a**, 63%, **10a**, 9%). This tendency toward 1,8-disubstitution was increased in the case of remote electron withdrawing group substituted **6b**, as **9b** (86%) was formed to the exclusion of any 1,6-disubstitution product. Conversely, substitution at the remote end of the alkyne complex with either methyl (**6c**) or trimethylsilyl (**6d**) groups resulted in the second substitution occurring at C-6, giving 1,6-disubstitution products **10c** (86%) and **10d** (40%); in the case of **6d**, the second substitution was incomplete, despite allowing the reaction to warm to rt, and a significant amount of **7d** (59%) was also isolated.

**Table 2.** Dicondensation reactions of **6** with **5a**.

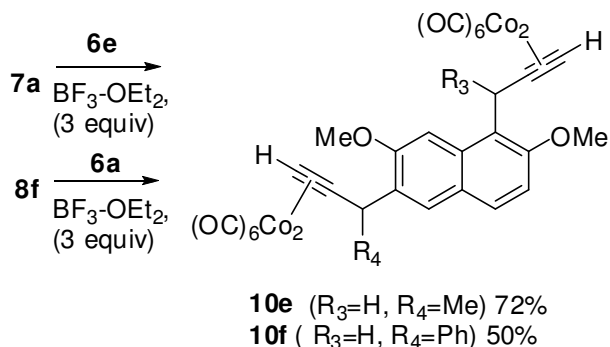


Entry	<b>5a</b>	<b>6</b>	<b>9</b> (yield, %)	<b>10</b> (yield, %)
1	<b>5a</b>	<b>6a</b>	<b>9a</b> (63)	<b>10a</b> (9)
2	<b>5a</b>	<b>6b</b>	<b>9b</b> (86)	-
3	<b>5a</b>	<b>6c</b>	-	<b>10c</b> (86)
4	<b>5a</b>	<b>6d</b>	-	<b>10d</b> (40) <sup>a</sup>

<sup>a</sup> In addition, 59% of **7d** was isolated.

In addition, two of the monocondensation products were taken and subjected to a second Nicholas reaction (Scheme 1). C-1 substitution product **7a** was subjected to  $\text{BF}_3\text{-OEt}_2$  mediated reaction with butyn-2-ol complex **6e**, giving **10e** in 72% yield. C-3 substituted **8f**, under analogous conditions with unsubstituted **6a**, afforded **10f** (50% yield).

**SCHEME 1.** Mixed dicondensation products.

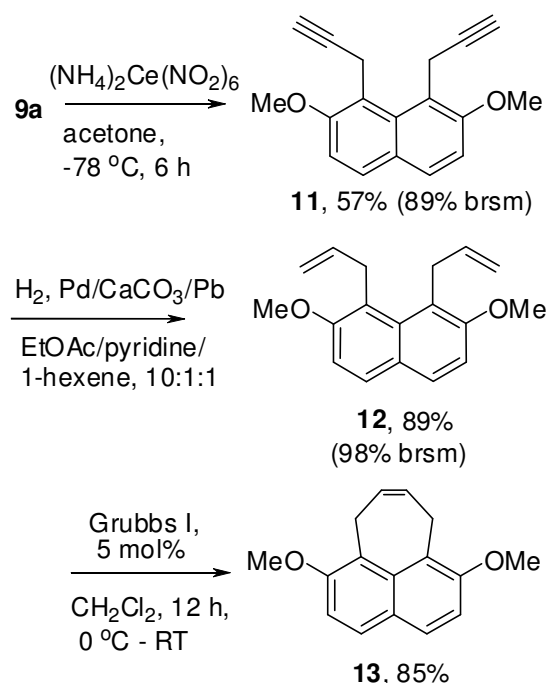


The pattern of Nicholas reaction reactivity of 2,7-dimethoxynaphthalene is therefore relatively consistent. Propargyldicobalt cations which are unsubstituted or substituted with electron withdrawing groups undergo C-1 monosubstitution and C-1, C-8 disubstitution. If the cation possesses an alkynyl substituent that is not electron withdrawing, monosubstitution is at C-1, while the second substitution occurs at C-6. Substitution of **5** with groups at the propargylic site allow C-1 monosubstitution if the group is of moderate size, while a group of sufficient size at this site ultimately forces the initial Nicholas reaction to occur at C-3. The dichotomy in disubstitution is reminiscent of that of nitration and chlorination (1,8-) versus dibromination (1,6-) of 2,7-dimethoxynaphthalene,<sup>17</sup> including the element of the most electrophilic reagents being directed toward the 1,8- positions.

**Application Towards Cyclohepta[de]naphthalene Synthesis.** Given an understanding of the substitution patterns of 2,7-dioxygenated naphthalenes towards propargyldicobalt cations, three different approaches to construction of the cyclohepta[de]naphthalene ring system were envisaged. Use of dicondensation product **9a** was the most readily apparent precursor, as it was one of the few cases in which the naphthalene 1,8-disubstitution pattern incorporated within the cyclohepta[de]naphthalene

predominated; consequently its use in the preparation of the cyclohepta[*de*]naphthalene system was pursued (Scheme 2). Decomplexation of **9a** could be accomplished with  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  under carefully controlled, low temperature conditions, giving **11** (57% yield, 89% by recovered starting material (brsm)). Other common reagents for decomplexation ( $\text{Me}_3\text{NO}$ ,  $\text{I}_2$ ) gave poorer yields of **11** or none at all. Semi-hydrogenation of **11** in the presence of the Lindlar catalyst then afforded diene **12**<sup>18</sup> (89% yield, 98% brsm). Finally, ring closing metathesis (RCM) employing Grubbs 1 catalyst (5 mol%) gave dihydrocyclohepta[*de*]naphthalene **13** (85% yield). While this work was in progress, the Kotha and Chattopadhyay groups demonstrated the accessibility of the corresponding acetates by RCM.<sup>19</sup>

**SCHEME 2.** Cyclohepta[*de*]naphthalenes by RCM.

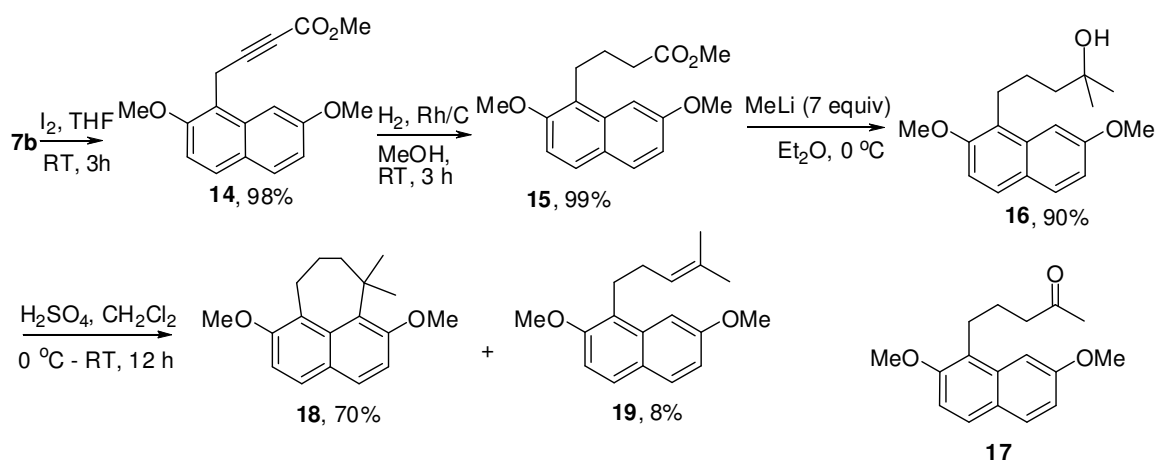


Using this dipropargylation-RCM approach to cycloheptanaphthalenes, however, afforded only limited possibilities for creating unsymmetrical substitution patterns regioselectively on both the naphthalene and cycloheptene portions of **13**, due to the incompatibility of propargyl substitution in **6** with 1,8- disubstitution on **5**. Consequently, the applicability of monocondensation product **7b** toward cyclohepta[*de*]naphthalene construction was explored (Scheme 3). Decomplexation of the organic unit from the  $\text{Co}_2(\text{CO})_6$  residue of **7b** was readily accomplished by treatment of iodine in THF, giving **14** in excellent yield (98%). While hydrogenation of **14** over Pd/C was sluggish, reduction of the triple bond



to the alkanolate (**15**) was straightforward in the presence of H<sub>2</sub> and Rh/C (99% yield). Addition of excess MeLi (7 equiv) to **15** resulted in attack on the ester function to give tertiary alcohol **16** in high yield (90% yield) provided a significant excess of MeLi was employed; more modest excesses (i.e., 3 equiv) resulted in noticeable amounts of ketone **17** being isolated in addition to **16**. Subjecting tertiary alcohol **16** to H<sub>2</sub>SO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> induced its conversion to 7,7-dimethyltetrahydrocyclohepta[*de*]naphthalene **18** (70% yield), contaminated with a small amount of elimination product **19** (8% yield).

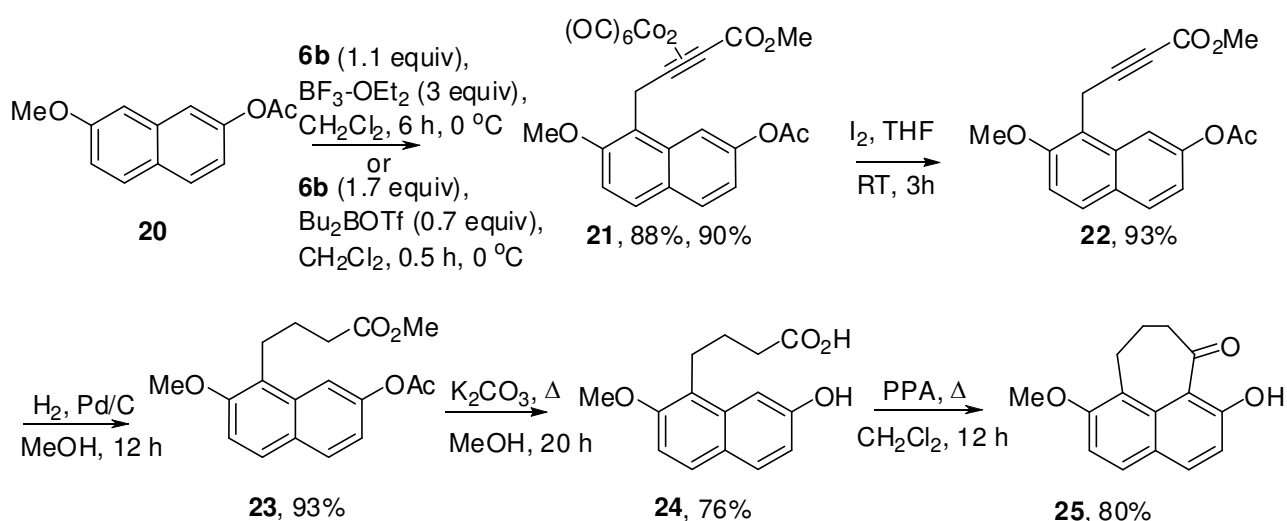
**SCHEME 3.** Ring closure by Friedel-Crafts alkylation.



As all the naturally occurring cyclohepta[*de*]naphthalenes exist as dehydrotetralones, and since the matter of selective deprotection of the methoxy groups of **18** is non trivial, related approaches to these ring systems were made on phenolic acetate **20**.<sup>20</sup> The Nicholas reaction of **20** with **6b** in the presence of BF<sub>3</sub>-OEt<sub>2</sub> occurred somewhat sluggishly (relative to 2,7-dimethoxybenzene), but ultimately afforded the product of  $\alpha$ -carbonyl cation substitution ortho- to the methoxy function (**21**) in excellent yield (88%) (Scheme 4). Bu<sub>2</sub>BOTf has often proved more effective in generating  $\alpha$ -carbonyl cation based Nicholas reactions, and accordingly, this Lewis acid enabled the same transformation to occur more rapidly, even in substoichiometric amounts, ultimately giving **21** in similar yields (90%).<sup>21</sup> Alkyne decomplexation with I<sub>2</sub> in THF occurred readily to give alkyne **22** (93%), and Pd/C catalyzed hydrogenation of the alkyne afforded alkanolate **23** in excellent yield (93%).

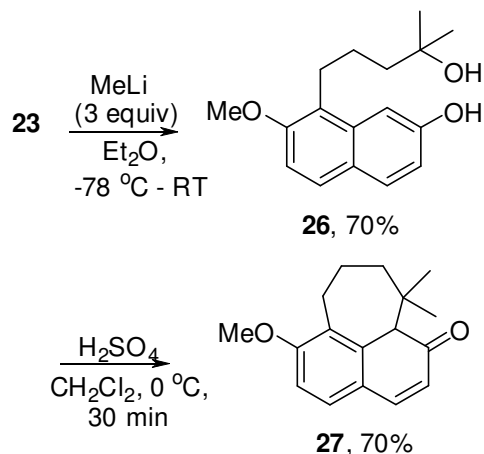
From alkanooate **23**, the synthesis of cyclohepta[*de*]naphthalene systems diverged in two ways. Given the oxygenated cycloheptane unit present within salvibretol, access to a ketone function in the seven membered ring was desired. Consequently, saponification of **23** was accomplished, albeit slowly, by  $K_2CO_3$  in MeOH at reflux, giving **24** (70% yield). After experimentation with several sets of acidic conditions, it was found that exposure to polyphosphoric acid (PPA) ( $CH_2Cl_2$ , reflux) gradually converted **24** to **25** (80% yield). Compound **25** was found to exist entirely as the phenolic tautomer, the conjugation of the aromatic system to the ketone no doubt being in part responsible; the existence of 1-hydroxy-7,12-pleiadenedione and related compounds in their naphthol tautomer provides additional precedent for this observation.<sup>22</sup>

**SCHEME 4.** Ring closure by Friedel-Crafts acylation.



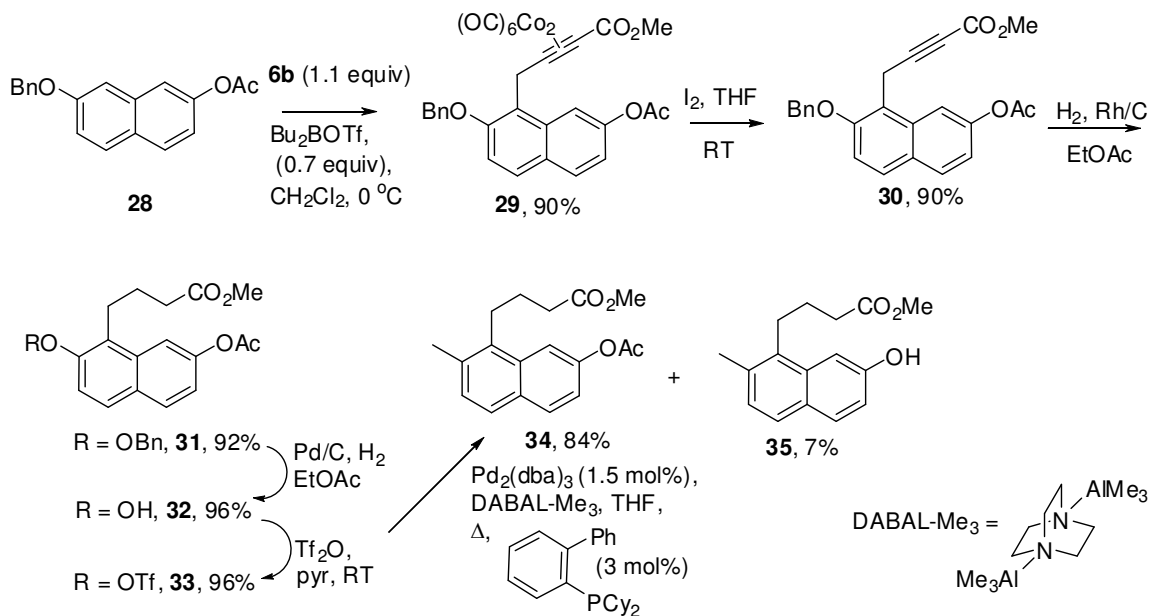
In contrast to **25**, PM5 and DFT (B88-PW91 functional, dzvp basis set) calculations suggest that without the ketone function in the cycloheptane unit, the 1-hydroxycyclohepta[*de*]naphthalene – cyclohepta[*de*]naphthalen-1(7H)-one equilibrium strongly favors the latter tautomer. As a result, **23** was subjected to reaction with excess MeLi, to give tertiary alcohol **26** (70% yield) (Scheme 5). Subsequent addition of one drop of  $H_2SO_4$  to a  $CH_2Cl_2$  solution of this phenol at  $0 \text{ }^\circ\text{C}$  induced rapid closure of the seven membered ring, producing **27** (70% yield) exclusively as its keto tautomer. This angle strain-directed tautomerization demonstrates the viability of the approach for preparing the rearranged abietane framework of microstegiol.

**SCHEME 5.** Cyclohepta[*de*]naphthalenone synthesis by cyclization-tautomerization.



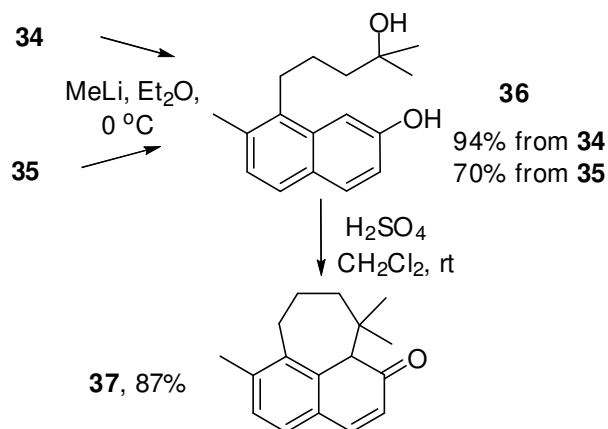
**Methyl Group Incorporation.** In the naturally occurring cyclohepta[*de*]naphthalenes, there resides a C-6 methyl function (C-2 in the source naphthalene) as opposed to an oxygen based one. As a strongly electron donating function is required for viable Nicholas reaction/ -carbonyl cation chemistry on the naphthalene nucleus, its ultimate replacement by methyl is necessary. To that end, we chose benzyl/acetyl protected **28**, prepared from 7-benzyloxy-2-naphthol, as a starting point for further studies (Scheme 6). Compound **28** underwent reaction with **6b** only sluggishly in the presence of  $\text{BF}_3\text{-OEt}_2$  (24h, 0 °C, 45% yield of **29**, 66% brsm), but gave **29** promptly and in excellent yield in the presence of  $\text{Bu}_2\text{BOTf}$  (1.5 h, 0 °C, 90% yield). Following uneventful decomplexation with  $\text{I}_2$  (**30**, 90% yield), hydrogenation under Rh/C catalysis reduced the triple bond without affecting the benzyl protecting group (**31**, 92% yield); subsequent treatment of **31** with  $\text{H}_2$  and Pd/C then gave phenolic acetate **32** in excellent yield (96%). Attempts at using  $\text{H}_2$  with Pd/C on **30** to effect a one pot conversion to **32** resulted in less clean reaction mixtures, which did contain some **32**. Compound **32** was converted readily into its triflate (**33**, 96%) in the presence of  $\text{Tf}_2\text{O}$ /pyridine, which was subjected to methylation. After some experimentation, it was found that  $\text{Pd}_2(\text{dba})_3$  catalyzed reaction of **33** with the DABCO- $(\text{AlMe}_3)_2$  complex (DABAL- $\text{Me}_3$ )<sup>23</sup> gave efficient methyl group incorporation, resulting in the formation of both **34** (84%) and a small amount of deacetylated **35** (7%).

**SCHEME 6.** C-2 methyl group incorporation.

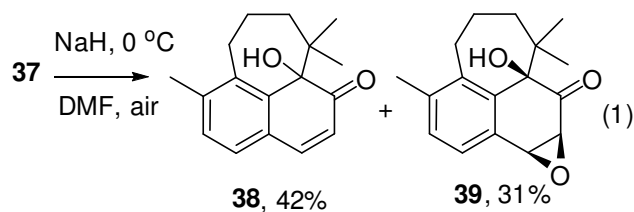


Each of these methylnaphthalenes could be converted into naphthol-tertiary alcohol **36** by reaction with excess MeLi (Scheme 7). In the case **34**, **36** was obtained in 94% yield; in the case of **35**, **36** could be isolated in 70% yield. Subjecting **36** in CH<sub>2</sub>Cl<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> then resulted in rapid conversion to cyclohepta[de]naphthalenone **37** in excellent yield (87%).

**SCHEME 7.** Preparation of cyclohepta[de]naphthalenone **37**.



The incorporation of an -hydroxy function relative to the ketone was briefly explored (eq 1). Exposure of a solution of **37** in DMF to NaH in air<sup>24</sup> gave resulted in the disappearance of **37** and the formation of 2 compounds; -hydroxy ketone **38** (42%), and the relatively unstable -hydroxylated epoxide **39** (31%).



In summary, a systematic study of the applicability of Nicholas reaction based  $\alpha$ -carbonyl cation chemistry on 2,7-dioxygenated naphthalenes has demonstrated a preference for C-1 over C-3 monosubstitution in all but the most sterically hindered cases, and with a preference for C-1/C-6 disubstitution, except in the least sterically hindered or most electron deficient cases. While the 1,8-dipropargylated case may be converted to cyclohepta[*de*]naphthalenes by way of RCM, the C-1  $\alpha$ -carbonyl cation adducts may be converted to the cyclohepta[*de*]naphthalenes by a cyclization based on Friedel-Crafts acylation or alkylation; in the latter case this allows tautomerization of the naphthol to cyclohepta[*de*]naphthalen-1-one. Replacement of the C-2 oxygen function of the naphthalene by a methyl group after Nicholas reaction allows formation of the framework of microstegiol, including the  $\alpha$ -hydroxy function. Future work will be targeted towards an early introduction of an isopropyl function, and ultimately the synthesis of microstegiol itself.

**Acknowledgements.** The authors are grateful to NSERC (Canada), the Canada Foundation for Innovation (CFI), and the Ontario Innovation Trust (OIT) for support of this research.

**Supporting Information Available.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Experimental Section.

The General Experimental Methods follow a previous report from our laboratory.<sup>12a</sup> Starting materials **5b**,<sup>25</sup> **6a**,<sup>26</sup> **6b**,<sup>27</sup> **6c**,<sup>28</sup> **6d**,<sup>29</sup> **6e**,<sup>30</sup> **6f**<sup>29</sup> and **20**<sup>31</sup> were prepared by a literature procedures.

**Hexacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-1-(prop-2-ynyl)naphthalene)]dicobalt (7a).** **Method 1:** To a solution of 2,7-dimethoxynaphthalene **5a** (0.050 g, 0.27 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was added propargyl alcohol complex **6a** (0.100 g, 0.292 mmol).  $\text{BF}_3\text{-OEt}_2$  (101  $\mu\text{L}$ , 0.797 mmol) was added dropwise at 0° C. After 3h of continuous stirring,  $\text{NH}_4\text{Cl}_{(\text{aq})}$  was added and the mixture was subjected to a conventional

extractive workup (CH<sub>2</sub>Cl<sub>2</sub>). The residue was subjected to flash chromatography (50:1 petroleum ether: Et<sub>2</sub>O) to give **7a** (0.127 g, 93%): IR (KBr)  $\nu_{\max}$  3003, 2960, 2090, 2055 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.71 (d, J = 8.9, 1H), 7.70 (d, J = 8.9, 1H), 7.22 (d, J = 2.4, 1H), 7.10 (d, J = 8.9, 1H), 7.04 (dd, J = 8.9, 2.4, 1H), 5.95 (s, 1H), 4.60 (s, 2H), 3.97 (s, 3H), 3.94 (s, 3H); <sup>13</sup>C NMR 199.9, 158.4, 154.7, 133.9, 130.2, 128.6, 124.6, 120.1, 116.1, 109.7, 101.6, 96.1, 73.5, 55.4, 55.1, 29.5; MS 484 (M<sup>+</sup>-CO), 456 (M<sup>+</sup>-2CO), 428 (M<sup>+</sup>-3CO), 372 (M<sup>+</sup>-5CO); HRMS m/e for C<sub>21</sub>H<sub>14</sub>Co<sub>2</sub>O<sub>8</sub> calcd (M<sup>+</sup>-2CO) 455.9454, found 455.9441.

**Hexacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene)]dicobalt (7b):**

Subjecting **5a** (0.210 g, 1.12 mmol), **6a** (0.508 g, 1.23 mmol) and BF<sub>3</sub>-OEt<sub>2</sub> (425  $\mu$ L, 3.35 mmol) to Method 1 gave product **7b** (0.560 g, 88% yield) following flash chromatography (5:1 petroleum ether: Et<sub>2</sub>O) as red brown solid: IR (KBr)  $\nu_{\max}$  3003, 2951, 2097, 2063, 2028, 1708; <sup>1</sup>H NMR 7.72 (d, J = 8.9, 1H), 7.68 (d, J = 8.9, 1H), 7.18 (d, J = 2.3, 1H), 7.10 (d, J = 8.9, 1H), 7.02 (dd, J = 8.9, 2.3, 1H), 4.64 (s, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 3.53 (s, 3H); <sup>13</sup>C NMR 198.4, 170.7, 158.5, 154.7, 133.9, 130.2, 128.8, 124.4, 119.1, 116.2, 109.4, 101.1, 99.4, 79.3, 55.2, 54.9, 52.4, 29.1; MS m/e 570 (M<sup>+</sup>), 542 (M<sup>+</sup>-1CO), 514 (M<sup>+</sup>-2CO), 486 (M<sup>+</sup>-3CO), 458 (M<sup>+</sup>-4CO), 430 (M<sup>+</sup>-5CO), 402 (M<sup>+</sup>-6CO); HRMS m/e for C<sub>23</sub>H<sub>16</sub>Co<sub>2</sub>O<sub>10</sub> calcd (M<sup>+</sup>-CO) 541.9458, found 541.9455.

**Hexacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-1-(but-2-ynyl)naphthalene)]dicobalt (7c):**

Subjecting **5a** (0.0960 g, 0.511 mmol), **6c** (0.200 g, 0.562 mmol) and BF<sub>3</sub>-OEt<sub>2</sub> (196  $\mu$ L, 1.55 mmol) to Method 1 gave product **7c** (0.225 g, 84% yield) following flash chromatography (100:1 petroleum ether: Et<sub>2</sub>O) as red brown solid: IR (KBr)  $\nu_{\max}$  2941, 2086, 2044, 2015, 1629 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.73 (d, J = 9.0, 1H), 7.71 (d, J = 9.0, 1H), 7.26 (d, J = 2.2, 1H), 7.12 (d, J = 8.9, 1H), 7.03 (dd, J = 8.9, 2.2, 1H), 4.61 (s, 2H), 3.98 (s, 3H), 3.96 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C NMR 200.1, 158.4, 154.7, 133.8, 130.2, 128.5, 124.5, 119.6, 116.1, 109.5, 101.6, 98.1, 94.2, 55.3, 55.0, 29.5, 21.0; MS m/e 442 (M<sup>+</sup>-3CO), 414 (M<sup>+</sup>-4CO), 386 (M<sup>+</sup>-5CO), 358 (M<sup>+</sup>-6CO); HRMS m/e for C<sub>22</sub>H<sub>16</sub>Co<sub>2</sub>O<sub>8</sub> calcd (M<sup>+</sup>-CO) 497.9560, found 497.9583.

**Hexacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-1-(3-trimethylsilylprop-2-ynyl)naphthalene)]dicobalt (7d):**

Subjecting **5a** (0.0433 g, 0.230 mmol), **6d** (0.1092 g, 0.264 mmol) and BF<sub>3</sub>-OEt<sub>2</sub> (87  $\mu$ L, 0.69 mmol) to

Method 1 gave product **7d** (0.1308 g, 97% yield) following flash chromatography (50:1 petroleum ether: Et<sub>2</sub>O) as red brown solid: IR (KBr)  $\nu_{\max}$  2959, 2083, 2042, 2013, 1629 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.73 (d, J = 8.8, 1H), 7.72 (d, J = 8.8, 1H), 7.26 (d, J = 2.3, 1H), 7.12 (d, J = 8.9, 1H), 7.05 (dd, J = 8.9, 2.3, 1H), 4.72 (br s, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 0.06 (s, 9H); <sup>13</sup>C NMR 200.6, 158.7, 154.8, 134.0, 130.3, 128.7, 124.8, 120.0, 115.8, 110.6, 109.8, 102.5, 79.3, 55.3, 55.2, 30.6, 0.3; MS m/e 556 (M<sup>+</sup>-CO), 528 (M<sup>+</sup>-2CO), 500 (M<sup>+</sup>-3CO), 444 (M<sup>+</sup>-5CO); HRMS for C<sub>24</sub>H<sub>22</sub>Co<sub>2</sub>O<sub>8</sub>Si calcd. (M<sup>+</sup>-3CO) 499.9900, found 499.9898.

**Hexacarbonyl[μ- 4-(2,7-dibenzyloxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene)]dicobalt (7g)** and **Dodecacarbonyl[μ- 4-(2,7-dibenzyloxy-1,8-di(3-carbomethoxyprop-2-ynyl)naphthalene)]tetracobalt (9g)**: Subjecting 2,7-dibenzyloxynaphthalene (**5b**) (0.754 g, 2.21 mmol), **6b** (1.009g, 2.437 mmol) and BF<sub>3</sub>-OEt<sub>2</sub> (842 μL, 6.64 mmol) to Method 1 gave, in order of elution, **7g** (1.133g, 71% yield), and **9g** (0.3210 g, 13% yield), following flash chromatography (5:1 petroleum ether: Et<sub>2</sub>O) as red brown solid. (**7g**): IR (KBr)  $\nu_{\max}$  3039, 2957, 2098, 2031, 1706 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.81 (dd, J = 8.9, 2.4, 2H), 7.66 (d, J = 7.1, 2H), 7.62 (d, J = 7.1, 2H), 7.45-7.59 (m, 7H), 7.28 (dd, J = 8.7, 1.9, 1H), 7.26 (d, J = 8.8, 1H), 5.39 (s, 2H), 5.33 (s, 2H), 4.81 (br s, 2H), 3.56 (s, 3H); <sup>13</sup>C NMR 198.3, 170.5, 157.7, 154.1, 137.0, 134.0, 130.2, 128.8, 128.5, 127.9, 127.6, 127.4, 124.8, 120.0, 116.5, 111.5, 103.1, 99.0, 79.6, 70.7, 69.6, 52.4, 29.5; MS m/e 610 (M<sup>+</sup>-4CO), 554 (M<sup>+</sup>-6CO); HRMS for C<sub>35</sub>H<sub>24</sub>Co<sub>2</sub>O<sub>10</sub> calcd. (M<sup>+</sup>-6CO) 554.0339, found 554.0354.

(**9g**): IR (KBr)  $\nu_{\max}$  2951, 2097, 2063, 2030, 1709 cm<sup>-1</sup>; 7.67 (d, J = 8.9, 2H), 7.51 (d, J = 7.3, 4H), 7.40 (apparent t, J = 7.3, 4H), 7.33 (t, J = 7.1, 2H), 7.16 (d, J = 8.9, 2H), 5.35 (d, J = 16.7, 2H), 5.30 (1/2 ABquartet, J = 12.2, 2H), 5.22 (1/2 ABquartet, J = 12.2, 2H), 4.82 (d, J = 16.6, 2H), 3.36 (s, 6H); <sup>13</sup>C NMR 198.2, 170.4, 155.6, 137.0, 132.2, 130.8, 128.5, 127.9, 127.2, 126.8, 121.4, 112.0, 99.6, 80.2, 71.0, 52.3, 31.0; MS m/e ; Anal. Calc. For C<sub>46</sub>H<sub>28</sub>Co<sub>4</sub>O<sub>18</sub>: C, 50.02; H, 2.56. Found C, 49.87, H, 2.52.

**Hexacarbonyl[μ- 4-(2,7-dimethoxy-1-(1-methylprop-2-ynyl)naphthalene)]dicobalt (7e)**: Subjecting **5a** (0.0498 g, 0.264 mmol), **6e** (0.0880g, 0.247mmol) and BF<sub>3</sub>-OEt<sub>2</sub> (105 μL, 0.829 mmol) to Method 1 gave product **7e** (0.0920 g, 66% yield) following flash chromatography (40:1 petroleum ether:

Et<sub>2</sub>O) as red brown solid: IR (KBr)  $\nu_{\max}$  3039, 2957, 2098, 2031, 1706 cm<sup>-1</sup>; <sup>1</sup>H NMR (58:42 mixture of rotamers) 7.66-7.70 (m, 2H, both), 7.60 (d, J = 2.3, 1H minor), 7.35 (d, J = 1.9, 1H major), 7.10 (d, J = 8.9, 1H, minor), 7.08 (d, J = 8.8, 1H, major), 7.03 (dd, J = 8.8, 2.3, 1H, major), 7.02 (dd, J = 8.9, 1.9, 1H minor), 6.09 (s, 1H, both), 5.65 (q, J = 7.5, 1H, minor), 5.04 (q, J = 6.9, 1H, major), 3.99 (s, 3H, minor), 3.97 (s, 3H, major), 3.96 (s, 3H, minor), 3.93 (s, 3H, major), 1.89 (d, J = 6.9, 3H, major), 1.88 (d, J = 7.5, 3H, minor); <sup>13</sup>C NMR 200.3, 199.9, 158.7, 157.1, 156.3, 154.1, 133.5, 133.3, 130.6, 130.4, 128.9, 128.8, 125.4, 124.9, 124.7, 124.4, 116.1, 115.5, 111.0, 110.3, 104.6, 102.4, 101.8, 101.0, 74.1, 72.6, 56.1, 55.3, 55.2, 55.0, 37.7, 35.3, 22.4, 21.5; MS m/e 498 (M<sup>+</sup>-CO), 470 (M<sup>+</sup>-2CO), 442 (M<sup>+</sup>-3CO), 414 (M<sup>+</sup>-4CO), 386 (M<sup>+</sup>-5CO); HRMS m/e for C<sub>22</sub>H<sub>16</sub>Co<sub>2</sub>O<sub>8</sub> calc. (M<sup>+</sup>-2CO) 469.9611, found 469.9608.

**Hexacarbonyl[μ- 4-(2,7-dimethoxy-3-(1-phenylprop-2-ynyl)naphthalene)]dicobalt (8f):**

Subjecting **5a** (0.0560 g, 0.298 mmol), **6f** (0.1500g, 0.3588 mmol) and BF<sub>3</sub>-OEt<sub>2</sub> (113 μL, 0.892 mmol) to Method 1 gave product **8f** (0.0900g, 51% yield) following flash chromatography (10:1 petroleum ether: Et<sub>2</sub>O), as red brown solid; (**8f**) IR (KBr)  $\nu_{\max}$  2922, 2089, 2050, 2014, 1632 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.78 (s, 1H), 7.62 (d, J = 8.9, 1H), 7.48 (d, J = 7.3, 2H), 7.26 (m, 2H), 7.18 (t, J = 7.3, 1H), 7.02 (obscured d, J = 2.5, 1H), 7.01 (s, 1H), 6.98 (dd, J = 8.9, 2.5, 1H), 6.46 (s, 1H), 6.01 (s, 1H), 3.93 (s, 3H), 3.89 (s, 3H); <sup>13</sup>C NMR 199.5, 158.1, 155.5, 144.2, 134.9, 131.4, 129.1, 128.4, 127.9, 126.9, 123.8, 116.2, 105.0, 104.8, 100.5, 74.1, 55.4, 55.2, 48.7; MS m/e 532 (M<sup>+</sup>-2CO), 476 (M<sup>+</sup>-4CO), 448 (M<sup>+</sup>-5CO), 420 (M<sup>+</sup>-6CO); HRMS m/e for C<sub>27</sub>H<sub>18</sub>Co<sub>2</sub>O<sub>8</sub> calcd. (M<sup>+</sup>- 4CO) 475.9869, found 475.9853.

**Dodecacarbonyl[μ- 4-(2,7-dimethoxy-1,8-di(prop-2-ynyl)naphthalene)]tetracobalt (9a) and**

**Dodecacarbonyl[μ- 4-(2,7-dimethoxy-1,6-di(prop-2-ynyl)naphthalene)]tetracobalt (10a). Method**

**2.:** To a solution of 2,7-dimethoxynaphthalene **5a** (0.100 g, 0.531 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added propargyl alcohol complex **6a** (0.393 g, 1.149 mmol), followed by the dropwise addition of BF<sub>3</sub>-OEt<sub>2</sub> (202 μL, 1.59 mmol) at 0° C. After 3h of continuous stirring, NH<sub>4</sub>Cl<sub>(aq)</sub> was added and the mixture was subjected to a conventional extractive workup. The residue was subjected purified by flash chromatography (10:1 petroleum ether: Et<sub>2</sub>O) to give, in order of elution, **10a** (0.040 g, 9% yield), and **9a** (0.280g, 63% yield); (**9a**): IR (KBr)  $\nu_{\max}$  2917, 2090, 2051, 2021 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.70 (d, J = 8.9,



2H), 7.12 (d, J = 8.9, 2H), 5.83 (s, 2H), 5.22 (d, J = 16.4, 2H), 4.50 (d, J = 16.4, 2H), 3.99 (s, 6H);  $^{13}\text{C}$  NMR 199.6, 156.1, 131.9, 130.7, 126.5, 121.3, 110.1, 97.5, 73.8, 55.9, 30.6; MS m/e 808 ( $\text{M}^+ - 1\text{CO}$ ), 780 ( $\text{M}^+ - 2\text{CO}$ ), 752 ( $\text{M}^+ - 3\text{CO}$ ), 724 ( $\text{M}^+ - 4\text{CO}$ ), 696 ( $\text{M}^+ - 5\text{CO}$ ), 668 ( $\text{M}^+ - 6\text{CO}$ ), 640 ( $\text{M}^+ - 7\text{CO}$ ), 612 ( $\text{M}^+ - 8\text{CO}$ ); HRMS m/e for  $\text{C}_{30}\text{H}_{16}\text{Co}_4\text{O}_{14}$  calcd. ( $\text{M}^+ - \text{CO}$ ) 807.7917, found 807.7904.

**(10a)**: IR (KBr)  $\text{max}$  2922, 2091, 2048, 2016  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 7.67 (d, J = 8.5, 1H), 7.57 (s, 1H), 7.19 (s, 1H), 7.08 (d, J = 8.5, 1H), 6.05 (s, 1H), 5.86 (s, 1H), 4.59 (s, 2H), 4.26 (s, 2H), 3.97 (s, 3H), 3.96 (s, 3H);  $^{13}\text{C}$  199.8, 156.5, 154.4, 133.2, 130.4, 128.2, 127.8, 124.4, 120.0, 110.0, 100.9, 97.9, 96.1, 73.8, 73.4, 55.5, 54.7, 39.3, 29.7; MS m/e 640 ( $\text{M}^+ - 6\text{CO}$ ), 612 ( $\text{M}^+ - 7\text{CO}$ ), 584 ( $\text{M}^+ - 8\text{CO}$ ), 500 ( $\text{M}^+ - 12\text{CO}$ ); HRMS m/e for  $\text{C}_{30}\text{H}_{16}\text{Co}_4\text{O}_{14}$  calcd. ( $\text{M}^+ - 7\text{CO}$ ) 639.8224, found 639.8223.

**Dodecacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-1,8-di(3-carbomethoxyprop-2-ynyl)naphthalene)]tetracobalt (9b)**: Subjecting a solution of 2,7-dimethoxynaphthalene **5a** (0.0258 g, 0.137 mmol), propargyl ether complex **6b** (0.1314 g, 0.317 mmol) and  $\text{BF}_3\text{-OEt}_2$  (115  $\mu\text{L}$ , 0.91 mmol) to Method 2 gave **9b** (0.1117 g, 86%) following g flash chromatography (5:1 petroleum ether:  $\text{Et}_2\text{O}$ ) as red brown solid: IR (KBr)  $\text{max}$  3004, 2950, 2097, 2067, 1710  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 7.71 (d, J = 9.0, 2H), 7.10 (d, J = 9.0, 2H), 5.19 (d, J = 16.5, 2H), 4.69 (d, J = 16.5, 2H), 3.94 (s, 6H), 3.46 (s, 6H);  $^{13}\text{C}$  NMR 198.2, 170.5, 156.0, 132.0, 130.9, 126.3, 120.2, 109.7, 99.8, 80.2, 55.6, 52.3, 30.8; MS m/e 896 ( $\text{M}^+ - 2\text{CO}$ ), 840 ( $\text{M}^+ - 4\text{CO}$ ), 784 ( $\text{M}^+ - 6\text{CO}$ ), 728 ( $\text{M}^+ - 8\text{CO}$ ), 700 ( $\text{M}^+ - 9\text{CO}$ ); Anal. for  $\text{C}_{34}\text{H}_{20}\text{Co}_4\text{O}_{18}$ : calcd. C, 42.88; H, 2.12. Found: C, 43.12, H, 2.10.

**Dodecacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-1,6-di(but-2-ynyl)naphthalene)]tetracobalt (10c)**. Subjecting **5a** (0.1000 g, 0.5314 mmol), **6c** (0.400g, 1.123 mmol) and  $\text{BF}_3\text{-OEt}_2$  (202  $\mu\text{L}$ , 1.59 mmol) to Method 2 to give product **10c** (0.3950g, 86% yield) following flash chromatography (100:1 petroleum ether:  $\text{Et}_2\text{O}$ ) as red brown solid: IR (KBr)  $\text{max}$  2949, 2085, 2000, 1631  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 7.71 (d, J = 8.9, 1H), 7.60 (s, 1H), 7.27 (s, 1H), 7.13 (d, J = 8.9, 1H), 4.62 (s, 2H), 4.30 (s, 2H), 4.01 (s, 3H), 3.98 (s, 3H), 2.55 (s, 3H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR 200.1, 156.6, 154.6, 133.3, 130.4, 128.3, 127.4, 124.4, 119.6, 109.8, 100.7, 99.3, 98.2, 94.3, 55.3, 54.7, 34.8, 29.7, 21.0, 20.4; MS m/e 808 ( $\text{M}^+ - 2\text{CO}$ ), 780 ( $\text{M}^+ - 3\text{CO}$ ),

724 ( $M^+ - 5CO$ ), 640 ( $M^+ - 8CO$ ), 612 ( $M^+ - 9CO$ ); HRMS  $m/e$  for  $C_{32}H_{20}Co_4O_{14}$ , calcd ( $M^+ - 3CO$ ) 779.8334, found 779.8342.

**Dodecacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-1,6-di(3-trimethylsilylprop-2-ynyl)naphthalene)]tetracobalt (10d):** Subjecting **5a** (0.050 g, 0.266 mmol), **6d** (0.242 g, 0.585 mmol) and  $BF_3 \cdot OEt_2$  (118  $\mu L$ , 0.931 mmol) to Method 2, with the exception that the reaction mixture was additionally warmed to room temperature for 5 h. Flash chromatography (50:1 petroleum ether:  $Et_2O$ ) gave, in order of elution, **10d** (0.105 g, 40% yield) as a red-brown solid, and **7d** (0.091 g, 59%); **(10d)**: IR (KBr)  $\nu_{max}$  2960, 2089, 2050, 2023, 1632  $cm^{-1}$ ;  $^1H$  NMR 7.70 (d,  $J = 8.9$ , 1H), 7.61 (s, 1H), 7.21 (s, 1H), 7.12 (d,  $J = 8.9$ , 1H), 4.70 (br s, 2H), 4.38 (s, 2H), 3.97 (s, 3H), 3.94 (s, 3H), 0.25 (s, 9H), 0.12 (s, 9H);  $^{13}C$  NMR 200.3, 156.6, 154.9, 133.4, 131.1, 128.3, 127.6, 124.5, 119.9, 112.7, 110.6, 110.0, 100.7, 79.4, 79.2, 55.3, 54.6, 34.9, 30.7, 0.5, 0.4; MS  $m/e$  952 ( $M^+ - CO$ ), 924 ( $M^+ - 2CO$ ), 896 ( $M^+ - 3CO$ ), 840 ( $M^+ - 5CO$ ), 784 ( $M^+ - 7CO$ ); HRMS (electrospray, neg ion)  $m/e$  for  $C_{36}H_{32}Co_4O_{14}Si_2$  calcd ( $M - H^+$ ) 978.8580; found 978.8584.

**Dodecacarbonyl[ $\mu$ - 4-(6-(but-3-yn-2-yl)-2,7-dimethoxy-1-(prop-2-ynyl)naphthalene)]tetracobalt (10e):** Subjecting **7a** (0.0300 g, 0.0585 mmol), **6e** (0.0330 g, 0.0926 mmol) and  $BF_3 \cdot OEt_2$  (25  $\mu L$ , 0.20 mmol) to Method 1 to give product **10e** (0.0360 g, 72% yield) following flash chromatography (100:1 petroleum ether:  $Et_2O$ ) as red brown solid; **(10e)**: IR (KBr)  $\nu_{max}$  2935, 2089, 2050, 2018, 1627  $cm^{-1}$ ;  $^1H$  NMR 7.69 (d,  $J = 8.9$ , 1H), 7.63 (s, 1H), 7.22 (s, 1H), 7.09 (d,  $J = 8.9$ , 1H), 6.02 (s, 1H), 5.90 (s, 1H), 4.80 (q,  $J = 7.1$ , 1H), 4.66 (1/2 ABquartet,  $J = 15.2$ , 1H), 4.57 (1/2 ABquartet,  $J = 15.3$ , 1H), 4.01 (s, 3H), 3.97 (s, 3H), 1.77 (d,  $J = 7.1$ , 3H);  $^{13}C$  NMR 199.9, 156.1, 154.5, 133.0, 132.8, 128.5, 126.8, 124.4, 119.9, 110.0, 105.4, 101.0, 96.2, 74.1, 73.5, 55.5, 54.9, 35.3, 30.0, 22.1; MS  $m/e$  822 ( $M^+ - CO$ ), 794 ( $M^+ - 2CO$ ), 766 ( $M^+ - 3CO$ ), 738 ( $M^+ - 4CO$ ), 710 ( $M^+ - 5CO$ ), 682 ( $M^+ - 6CO$ ), 654 ( $M^+ - 7CO$ ), 626 ( $M^+ - 8CO$ ), 598 ( $M^+ - 9CO$ ); HRMS  $m/e$  for  $C_{31}H_{18}Co_4O_{14}$  calcd. ( $M^+ - 4CO$ ) 737.8228, found 737.8201.

**Dodecacarbonyl[ $\mu$ - 4-(2,7-dimethoxy-6-(1-phenylprop-2-ynyl)-1-(prop-2-ynyl)naphthalene)]tetracobalt (10f):** Subjecting **8f** (0.0372 g, 0.0632 mmol), **6a** (0.0238 g, 0.0695 mmol) and  $BF_3 \cdot OEt_2$  (24  $\mu L$ , 0.19 mmol) to Method 1 to give product **10f** (0.0380 g, 65% yield) following flash

chromatography (10:1 petroleum ether: Et<sub>2</sub>O) as red brown solid; (**10f**) IR (KBr)  $\nu_{\max}$  2929, 2089, 2049, 2018, 1629 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.80 (s, 1H), 7.66 (d, J = 9.0, 1H), 7.51 (d, J = 7.6, 2H), 7.27-7.31 (apparent t, J = 7.6, 2H), 7.21 (t, J = 7.4, 1H), 7.17 (d, J = 1.0, 1H), 7.07 (d, J = 9.0, 1H), 6.46 (s, 1H), 6.05 (s, 1H), 5.88 (s, 1H), 4.60 (1/2 AB quartet, J = 15.4, 1H), 4.52 (1/2 ABquartet, J = 15.4, 1H), 3.97 (s, 3H), 3.95 (s, 3H); <sup>13</sup>C NMR 199.4, 155.7, 154.5, 144.0, 132.8, 131.4, 128.9, 128.6, 128.4, 126.9, 124.2, 119.8, 110.0, 101.1, 100.4, 96.0, 74.0, 73.5, 55.4, 55.2, 48.5, 29.6; MS m/e 884 (M<sup>+</sup>-CO), 856 (M<sup>+</sup>-2CO), 828 (M<sup>+</sup>-3CO), 800 (M<sup>+</sup>-4CO); HRMS for C<sub>36</sub>H<sub>20</sub>Co<sub>4</sub>O<sub>14</sub>, calcd. (M<sup>+</sup>-4CO) 799.8384, found 799.8414.

**2,7-Dimethoxy-1,8-di(prop-2-ynyl)naphthalene (11)**: To a solution of **9a** (0.0970 g, 0.116 mmol) in acetone (30 mL) with silica gel (0.600 g) was added ceric ammonium nitrate (0.360 g) at -78°C. The reaction was stirred for 4 h, followed by the addition of H<sub>2</sub>O and filtration through Celite®. After a conventional aqueous workup, the mixture was filtered through Celite® and concentrated under reduced pressure. Preparative TLC (10:1 petroleum ether : Et<sub>2</sub>O) afforded, in order of elution, **9a** (0.0350 g, 36% recovery), and **11** (0.0175 g, 57%, 89% based on recovered starting material); (**11**): mp 144-145 °C; IR (KBr)  $\nu_{\max}$  3291, 2932, 2107, 1618 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.72 (d, J = 9.0, 2H), 7.18 (d, J = 9.0, 2H), 4.31 (d, J = 2.6, 4H), 4.03 (s, 6H), 2.16 (t, J = 2.6, 2H); <sup>13</sup>C NMR 156.7, 133.5, 130.1, 126.2, 117.3, 111.0, 84.7, 69.1, 56.9, 17.3; MS m/e 264 (M<sup>+</sup>); HRMS m/e for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>, calcd (M<sup>+</sup>) 264.1150, found 264.1153.

**1,8-Diallyl-2,7-dimethoxynaphthalene (12)**: To a solution of **11** (.0200 g, 0.0758 mmol) in 20 mL mixture of ethyl acetate: 1-hexene: pyridine (10:1:1), Lindlar catalyst added (5 mole %) at room temperature. The reaction was stirred under an H<sub>2</sub> atmosphere for 3 h. The reaction mixture was filtered through Celite®, and the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (5:1 petroleum ether : Et<sub>2</sub>O) to give, in order of elution, **12** (0.0180 g, 0.0671 mmol, 89 % yield, 98 % based on recovered starting material), and **11** (0.0018 g); (**12**): mp 93-94 °C; lit.<sup>18</sup> 189.4-194 °C; IR (KBr)  $\nu_{\max}$  3077, 2934, 1614 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.72 (d, J = 8.9, 2H), 7.18 (d, J = 8.9, 2H), 6.22 (m, 2H), 5.09 (dd J= 10.3, 1.9, 2H), 4.84 (dd, J= 17.3, 1.9, 2H), 3.93 (s, 6H), 3.91 (br s, 4H); <sup>13</sup>C NMR 155.7, 139.0, 134.9, 129.4, 126.3, 120.4, 114.5, 111.0, 56.8, 30.9; MS m/e 268 (M<sup>+</sup>); HRMS m/e for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub> calcd (M<sup>+</sup>) 268.1463, found 268.1466.

**(Z)-1,6-Dimethoxy-7,10-dihydrocyclohepta[de]naphthalene (13):** To a solution of **12** (0.0170 g, 0.0634 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), was added Grubbs' 1 Catalyst (0.0027 g, 5 mole %) at room temperature. After 6 h, the mixture was filtered through Celite<sup>®</sup>. The filtrate was concentrated under reduced pressure and the crude product was purified by preparative TLC (100:1 petroleum ether: Et<sub>2</sub>O) to give **13** (0.0130 g, 0.0541 mmol, 85%): mp 95-96 °C; IR (KBr)  $\nu_{\max}$  1628; <sup>1</sup>H NMR 7.58 (d, J = 9.0, 2H), 7.10 (d, J = 9.0, 2H), 6.19 (m, 2H), 4.02 (d, J = 5.6, 4H), 3.92 (s, 6H); <sup>13</sup>C NMR 154.0, 134.8, 130.9, 128.3, 126.8, 120.2, 112.0, 57.3, 24.3; MS m/e 240 (M<sup>+</sup>), HRMS m/e for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub> calcd (M<sup>+</sup>) 240.1150, found 240.1150.

**2,7-Dimethoxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene (14): Method 3.** To a solution of **7b** (0.446 g, 0.782 mmol) in THF (50 mL) at room temperature, an excess of iodine (I<sub>2</sub>) was added. The solution was stirred for 3h. Following the addition of aqueous sodium bisulfate, and the mixture subjected to a conventional extractive workup (Et<sub>2</sub>O). Purification by preparative TLC (1:1 petroleum ether: Et<sub>2</sub>O) gave **14** (0.218 g, 98 % yield): mp 80-81 °C; IR (KBr)  $\nu_{\max}$  2956, 2233, 1712, 1628; <sup>1</sup>H NMR 7.72 (d, J = 9.0, 1H), 7.69 (d, J = 8.9, 1H), 7.22 (d, J = 2.4, 1H), 7.11 (d, J = 9.0, 1H), 7.05 (dd, J = 8.9, 2.4, 1H), 4.11 (s, 2H), 3.97 (s, 3H), 3.96 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR 158.4, 154.6, 154.0, 133.7, 129.9, 128.9, 124.3, 116.1, 113.6, 110.1, 101.2, 87.7, 71.9, 56.1, 55.0, 52.2, 14.5; MS m/e 284 (M<sup>+</sup>); Anal. for C<sub>17</sub>H<sub>16</sub>O<sub>4</sub> Calcd. C, 71.82; H, 5.67. Found: C, 71.72; H, 5.47.

**2,7-Dimethoxy-1-(3-carbomethoxypropyl)naphthalene (15):** To a solution of **14** (0.210 g, 0.739 mmol) in MeOH (20 mL) under H<sub>2</sub>, Rh/C (excess) at room temperature. The solution was stirred for 6h with monitoring by TLC. The suspension was filtered and the solvent was removed under reduced pressure. Preparative TLC (2:1 petroleum ether: Et<sub>2</sub>O) to give **15** (0.211 g, 99% yield): bp 170-175 °C (0.5 torr); IR (KBr)  $\nu_{\max}$  2954, 1740, 1628; <sup>1</sup>H NMR 7.69 (d, J = 8.9, 1H), 7.66 (d, J = 8.9, 1H), 7.32 (d, J = 2.0, 1H), 7.12 (d, J = 8.9, 1H), 7.03 (dd, J = 8.9, 2.0, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.70 (s, 3H), 3.11 (t, J = 7.6, 2H), 2.44 (t, J = 7.1, 2H), 2.00 (m, 2H); <sup>13</sup>C NMR 174.1, 158.2, 155.0, 134.3, 129.9, 127.4, 124.7, 121.4, 115.7, 110.5, 101.9, 56.1, 55.1, 51.2, 33.5, 24.4, 24.2; MS m/e 288 (M<sup>+</sup>); HRMS m/e for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub> calcd (M<sup>+</sup>) 288.1362, found 288.1360.

**1-(4-Hydroxy-4-methylpentyl)-2,7-dimethoxynaphthalene (16):** To a solution of **15** (0.114 g, 0.396 mmol) in Et<sub>2</sub>O (10 mL) at 0 °C, MeLi (1.9 mL, 1.5 M, 2.9 mmol) was added. The solution was stirred for 3h, at which time aqueous NH<sub>4</sub>Cl was added and a conventional extractive workup (Et<sub>2</sub>O) performed. The volatiles were removed under reduced pressure. Purification by preparative TLC (1:1 petroleum ether: Et<sub>2</sub>O) gave **15** (0.103 g, 0.356 mmol, 90 % yield): mp 45-46 °C; IR (KBr)  $\nu_{\max}$  3422 br, 2966, 1627 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.70 (d, J = 8.9, 1H), 7.66 (d, J = 8.9, 1H), 7.24 (d, J = 2.3, 1H), 7.13 (d, J = 8.9, 1H), 7.03 (dd, J = 8.9, 2.3, 1H), 3.952 (s, 3H), 3.945 (s, 3H), 3.07 (t, J = 7.6, 2H), 1.74 (m, 2H), 1.69 (m, 2H) 1.38 (br s, 1H), 1.23 (s, 6H); <sup>13</sup>C NMR 158.0, 154.8, 134.1, 130.0, 127.1, 124.8, 122.6, 115.5, 110.8, 102.0, 70.9, 56.3, 55.1, 43.8, 29.1, 25.4, 24.4; MS m/e 288 (M<sup>+</sup>); HRMS m/e for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub> calcd (M<sup>+</sup>) 288.1725, found 288.1713.

**1,6-Dimethoxy-7,7-dimethyl-7,8,9,10-tetrahydrocyclohepta[de]naphthalene (18) and 2,7-Dimethoxy-1-(4-methylpent-3-enyl)naphthalene (19):** To a solution of **16** (0.0750 g, 0.260 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10mL), one drop of H<sub>2</sub>SO<sub>4</sub> was added. The solution was refluxed for 24h. Water was added and a conventional extractive workup performed (CH<sub>2</sub>Cl<sub>2</sub>). Purification by preparative TLC (4:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) gave, in order of elution, **18** (0.0490 g, 70% yield) and **19** (0.0056 g, 8% yield) as a mixture. **18**, mp 101 °C. IR (KBr)  $\nu_{\max}$  2929, 1612; <sup>1</sup>H NMR 7.54 (d, J = 8.9, 1H), 7.52 (d, J = 8.8, 1H), 7.09 (d, J = 8.9, 1H), 7.06 (d, J = 8.8, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.00 (br m, 2H), 1.95 (m, 2H), 1.69 (m, 2H), 1.52 (s, 6H); <sup>13</sup>C NMR 158.8, 154.5, 137.6, 131.7, 127.3, 126.9, 125.4, 122.9, 112.1, 111.6, 57.4, 56.0, 41.1, 39.4, 25.5, 22.1; MS m/e 270 (M<sup>+</sup>); HRMS m/e for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub> calcd (M<sup>+</sup>) 270.1620, found 270.1614.

**(19):** 55-56 °C; <sup>1</sup>H NMR 7.69 (d, J = 9.4, 1H), 7.66 (d, J = 9.4, 1H), 7.25 (d, J = 2.1, 1H), 7.13 (d, J = 8.7, 1H), 7.02 (dd, J = 8.7, 2.1, 1H), 5.36 (7, J = 7.2, 1h), 3.95 (s, 6H), 3.05 (m, 2H), 2.31 (m, 2H), 1.73 (s, 3H), 1.61 (s, 3H); <sup>13</sup>C NMR 158.1, 155.0, 134.2, 131.8, 130.0, 127.2, 124.8, 124.6, 122.7, 115.7, 110.9, 102.0, 56.5, 55.2, 28.2, 25.7, 25.5, 17.6; HRMS m/e for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub> calcd (M<sup>+</sup>) 270.1620, found 270.1606.

**Hexacarbonyl[ $\mu$ - 4-(7-acetoxy-2-methoxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene)]dicobalt**

**(21)**: Subjecting **20** (0.249 g, 1.152 mmol), **6b** (0.525 g, 1.27 mmol) and  $\text{BF}_3\text{-OEt}_2$  (440  $\mu\text{L}$ , 3.5 mmol) to Method 1 afforded **21** (0.609 g, 1.018 mmol, 88% yield) following flash chromatographic purification (2:1 petroleum ether:  $\text{Et}_2\text{O}$ ), as a viscous red-brown oil: IR (KBr)  $\nu_{\text{max}}$  3004, 2952, 2099, 2063, 2029, 1765, 1709;  $^1\text{H NMR}$  7.82 (d,  $J = 9.0$ , 1H), 7.81 (d,  $J = 8.8$ , 1H), 7.62 (d,  $J = 2.2$ , 1H), 7.25 (d,  $J = 9.0$ , 1H), 7.11 (dd,  $J = 8.8, 2.2$ , 1H), 4.60 (s, 2H), 3.95 (s, 3H), 3.76 (s, 3H), 2.33 (s, 3H);  $^{13}\text{C NMR}$  198.3, 170.7, 169.6, 155.0, 149.5, 133.4, 130.0, 129.0, 127.0, 120.2, 118.8, 114.3, 112.0, 98.7, 94.1, 55.4, 52.7, 28.4, 21.0; MS  $m/e$  542( $\text{M}^+ - 2\text{CO}$ ), 514( $\text{M}^+ - 3\text{CO}$ ), 486 ( $\text{M}^+ - 4\text{CO}$ ), 458( $\text{M}^+ - 5\text{CO}$ ), 430( $\text{M}^+ - 6\text{CO}$ ); HRMS  $m/e$  for  $\text{C}_{24}\text{H}_{16}\text{Co}_2\text{O}_{11}$  calcd ( $\text{M}^+ - 3\text{CO}$ ) 513.9509, found 513.9511.

**7-Acetoxy-2-methoxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene (22)**: Subjecting **21** (0.284 g, 0.475 mmol) to Method 3, followed by recrystallization from  $\text{Et}_2\text{O}$  afforded **22** (0.138 g, 93% yield): mp 132-133  $^\circ\text{C}$ ; IR (KBr)  $\nu_{\text{max}}$  2917, 2234, 1761, 1712;  $^1\text{H NMR}$  7.80 (d,  $J = 8.9$ , 1H), 7.78 (d,  $J = 8.9$ , 1H), 7.61 (d,  $J = 1.9$ , 1H), 7.23 (d,  $J = 8.9$ , 1H), 7.14 (dd,  $J = 8.9, 1.9$ , 1H), 4.07 (s, 2H), 3.96 (s, 3H), 3.70 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C NMR}$  169.4, 154.7, 154.0, 149.5, 133.1, 129.9, 129.2, 126.9, 118.8, 114.8, 113.7, 112.7, 87.4, 72.0, 56.3, 52.3, 21.0, 14.6; MS  $m/e$  312 ( $\text{M}^+$ ); HRMS  $m/e$  for  $\text{C}_{18}\text{H}_{16}\text{O}_5$  calcd ( $\text{M}^+$ ) 312.0998, found 312.0991.

**7-Acetoxy-1-(3-carbomethoxypropyl)-2-methoxynaphthalene (23)**: To a solution of **22** (0.157 g, 0.503 mmol) in MeOH (15 mL) under  $\text{H}_2$  was added Pd/C (excess). The solution was stirred for 6 h, following which the suspension was filtered and the filtrate concentrated under reduced pressure. Preparative TLC (1:1 petroleum ether:  $\text{Et}_2\text{O}$ ) gave **23** (0.148 g, 93% yield) as white solid: mp 125  $^\circ\text{C}$ ; IR (KBr)  $\nu_{\text{max}}$  3067, 2950, 1759, 1734;  $^1\text{H NMR}$  7.79 (d,  $J = 8.8$ , 1H), 7.72 (d,  $J = 9.0$ , 1H), 7.65 (d,  $J = 2.0$ , 1H), 7.22 (d,  $J = 9.0$ , 1H), 7.11 (dd,  $J = 8.8, 2.0$ , 1H), 3.92 (s, 3H), 3.68 (s, 3H), 3.09 (t,  $J = 7.5$ , 2H), 2.42 (t,  $J = 7.5$ , 2H), 2.37 (s, 3H), 1.98 (m, 2H);  $^{13}\text{C NMR}$  173.9, 169.5, 154.9, 149.1, 133.6, 129.9, 127.6, 127.1, 122.3, 118.4, 114.0, 112.7, 56.1, 51.2, 33.5, 24.7, 24.0, 21.1; MS  $m/e$  316 ( $\text{M}^+$ ); HRMS  $m/e$  for  $\text{C}_{18}\text{H}_{20}\text{O}_5$  calcd ( $\text{M}^+$ ) 316.1311, found 316.1316.

**1-(3-Carboxypropyl)-7-hydroxy-2-methoxynaphthalene (24):** To a solution of **23** (0.117 g, 0.370 mmol) in methanol (20 mL) was added an excess of sodium hydroxide. Following heating to reflux for 18h, the mixture was acidified (3 M HCl) and a conventional extractive workup performed (Et<sub>2</sub>O). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> afforded product **24** (0.0730 g, 73 % yield): mp 164-165 °C; IR (KBr)  $\nu_{\text{max}}$  3385 br, 2924, 1703, 1626; <sup>1</sup>H NMR (acetone-d<sub>6</sub>) 7.63 (d, J = 8.8, 1H), 7.62 (d, J = 9.0, 1H), 7.28 (br s, 1H), 7.11 (d, J = 9.0, 1H), 6.93 (dd, J = 8.8, 2.1, 1H), 3.87 (s, 3H), 2.99 (t, J = 7.7, 2H), 2.35 (m, 2H), 1.85 (m, 2H); <sup>13</sup>C NMR (acetone-d<sub>6</sub>) 174.5, 156.0, 155.1, 134.8, 130.2, 127.7, 124.5, 120.7, 115.7, 110.3, 104.8, 55.8, 33.3, 24.8, 24.1; MS m/e 260 (M<sup>+</sup>); HRMS m/e for C<sub>15</sub>H<sub>16</sub>O<sub>4</sub> calcd (M<sup>+</sup>) 260.1049, found 260.1045.

**6-Hydroxy-1-methoxy-9,10-dihydrocyclohepta[de]naphthalen-7(8H)-one (25):** A solution of polyphosphoric acid (PPA, ca. 0.1 g, excess) and **24** (0.100 g, 0.385 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), was heated to reflux for 36 h. Water was added and the mixture subjected to a conventional extractive workup (CH<sub>2</sub>Cl<sub>2</sub>). Preparative TLC (2:1 petroleum ether: Et<sub>2</sub>O) gave **25** (0.075 g, 80 % yield); mp 90 °C; IR (KBr)  $\nu_{\text{max}}$  3009, 2970, 1616 cm<sup>-1</sup>; <sup>1</sup>H NMR 12.73 (s, 1H), 7.71 (d, J = 8.9, 1H), 7.63 (d, J = 8.8, 1H), 7.12 (d, J = 8.8, 1H), 6.93 (d, J = 8.9, 1H), 3.95 (s, 3H), 3.01 (t, J = 7.1, 2H), 2.71 (t, J = 7.4, 2H), 2.39 (m, 2H); <sup>13</sup>C NMR 207.4, 162.5, 157.3, 136.2, 135.7, 128.6, 123.2, 122.4, 116.5, 115.2, 110.3, 56.2, 42.3, 29.5, 25.4; MS m/e 242 (M<sup>+</sup>); HRMS for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub> calcd (M<sup>+</sup>) 242.0943, found 242.0931.

**7-Hydroxy-1-(4-hydroxy-4-methylpentyl)-2-methoxynaphthalene (26):** To a solution of **23** (0.1030 g, 0.3259mmol) in Et<sub>2</sub>O at 0°C was added MeLi (0.76 mL, 1.1 mmol, 1.5 M in Et<sub>2</sub>O). After 4h of stirring, aqueous NH<sub>4</sub>Cl was added. A conventional workup and preparative TLC (1:1 petroleum ether: Et<sub>2</sub>O) gave **26** (0.0625 g, 70% yield): mp 140 °C; IR (KBr)  $\nu_{\text{max}}$  3358, 2967 cm<sup>-1</sup>; <sup>1</sup>H NMR 8.10 (br s, 1H), 7.65 (d, J = 8.8, 1H), 7.61 (d, J = 8.9, 1H), 7.33 (d, J = 2.2, 1H), 7.08 (d, J = 8.9, 1H), 7.01 (dd, J = 8.8, 2.2, 1 H), 3.91 (s, 3H), 2.95 (br t, J = 7.0, 2H), 2.60 (br s, 1H), 1.65 (m, 4H), 1.21 (s, 6H); <sup>13</sup>C NMR 154.6, 154.5, 134.4, 130.3, 127.3, 124.5, 122.1, 115.6, 110.7, 105.3, 72.0, 56.4, 43.5, 29.0, 25.4, 24.3; MS m/e 274 (M<sup>+</sup>); HRMS m/e for C<sub>17</sub>H<sub>22</sub>O<sub>3</sub> calcd 274.1569, found 274.1574.

**6-Methoxy-10,10-dimethyl-8,9,10,10a-tetrahydrocyclohepta[de]naphthalen-1(7H)-one (27):** To a solution of **26** (0.0625 g, 0.228 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10mL), one drop of H<sub>2</sub>SO<sub>4</sub> was added at 0°C. After stirring for 0.5 h, a conventional extractive workup (CH<sub>2</sub>Cl<sub>2</sub>) followed by preparative TLC (10:1 petroleum ether:Et<sub>2</sub>O) afforded **27** (0.0410 g, 70% yield): mp 85-87 °C; IR (KBr) <sub>max</sub> 2934, 1653, 1615 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.29 (d, J = 9.7, 1H), 7.13 (d, J = 8.4, 1H), 6.79 (d, J = 8.4, 1H), 5.97 (d, J = 9.7, 1H), 3.84 (s, 3H), 3.63 (s, 1H), 3.36 (m, 1H), 2.42 (m, 1H), 1.84 (m, 1H), 1.51 (m, 1H), 1.38 (m, 1H), 1.27 (m, 1H), 1.17 (s, 3H), 0.66 (s, 3H); <sup>13</sup>C NMR 203.2, 157.7, 145.5, 140.8, 129.4, 127.9, 124.4, 123.5, 108.9, 58.3, 55.7, 43.2, 37.0, 27.5, 24.3, 21.5, 20.2; MS m/e 256 (M<sup>+</sup>); HRMS m/e for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub> calcd 256.1463, found 256.1457.

**2-Acetoxy-7-benzyloxynaphthalene (28):** To a solution of 7-benzyloxy-2-naphthol (2.000 g, 7.991 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) were added Et<sub>3</sub>N (2 mL, excess) and acetic anhydride (2 mL, excess). After stirring for 1h, the mixture was subjected to a conventional extractive workup. Recrystallization from Et<sub>2</sub>O afforded **28** (2.1958g, 94% yield) as a white crystalline solid: mp 121 °C; IR (KBr) <sub>max</sub> 2938, 1751 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.78 (d, J = 8.9, 1H), 7.76 (d, J = 8.9, 1H), 7.49 (d, J = 7.4, 2H), 7.45 (d, J = 2.2, 1H), 7.42 (apparent t, J = 7.5, 2H), 7.36 (t, J = 7.5, 1H), 7.22 (dd, J = 8.8, 2.2, 1H), 7.19 (d, J = 2.2, 1H), 7.10 (dd, J = 9.0, 2.2, 1H), 5.19 (s, 2H), 2.36 (s, 3H); <sup>13</sup>C 169.5, 157.3, 149.0, 136.7, 135.0, 129.3, 129.1, 128.6, 128.0, 127.5, 127.0, 118.8, 118.7, 117.5, 107.1, 70.0, 21.1; MS m/e 292 (M<sup>+</sup>); HRMS for C<sub>19</sub>H<sub>16</sub>O<sub>3</sub> calcd 292.1099, found 292.1097.

**Hexacarbonyl[μ- 4-(7-acetoxy-2-benzyloxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene)]dicobalt (29):** To a solution of **28** (0.2000 g, 0.6849 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added **6b** (0.3120 g, 0.7534 mmol) and Bu<sub>2</sub>BOTf (479 μL, 0.479 mmol) was added dropwise at 0° C. After 1h of continuous stirring, NH<sub>4</sub>Cl<sub>(aq)</sub> was added and the mixture was subjected to a conventional extractive workup. The residue was purified by flash chromatography (2:1 petroleum ether: Et<sub>2</sub>O) to give **29** (0.4150 g, 90% yield) as a red-brown solid: IR (KBr) <sub>max</sub> 2953, 2113, 2063, 2031, 1765, 1708 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.80 (d, J = 8.8, 1H), 7.78 (d, J = 9.0, 1H), 7.65 (d, J = 2.1, 1H), 7.46 (d, J = 7.2, 2H), 7.39 (apparent t, J = 7.2, 2H), 7.33 (t, J = 7.2, 1H), 7.31 (d, J = 9.0, 1H), 7.14 (dd, J = 8.8, 2.1, 1H), 5.28



(s, 2H), 4.68 (br s, 2H), 3.64 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  198.2, 170.5, 169.5, 154.2, 149.5, 136.8, 133.5, 130.1, 128.9, 128.6, 128.0, 127.34, 127.25, 121.0, 119.0, 114.6, 113.9, 98.3, 78.8, 70.9, 52.6, 28.9, 21.0; MS m/e 618 ( $\text{M}^+ - 2\text{CO}$ ), 590 ( $\text{M}^+ - 3\text{CO}$ ), 506 ( $\text{M}^+ - 6\text{CO}$ ); HRMS m/e for  $\text{C}_{30}\text{H}_{20}\text{Co}_2\text{O}_{11}$  calcd ( $\text{M}^+ - 2\text{CO}$ ) 617.9771, found 617.9773.

**7-Acetoxy-2-benzyloxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene (30):** Subjecting **29** (0.3630 g, 0.5385 mmol) to Method 3 gave the crude reaction product, which upon recrystallization from methanol gave **30** (0.1880g, 90 % yield): mp 144 °C; IR (KBr)  $_{\text{max}}$  2956, 2234, 1761, 1712  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 7.79 (d, J = 8.8, 1H), 7.75 (d, J = 9.0, 1H), 7.67 (d, J = 1.5, 1H), 7.49 (d, J = 7.5, 2H), 7.43 (apparent t, J = 7.5, 2H), 7.36 (t, J = 7.5, 1H), 7.26 (d, J = 9.0, 1H), 7.17 (dd, J = 8.8, 1.5, 1H), 5.25 (s, 2H), 4.13 (s, 2H), 3.72 (s, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  169.5, 154.14, 154.09, 149.6, 136.8, 133.3, 130.1, 129.3, 128.6, 128.1, 127.3, 119.2, 116.0, 114.4, 114.1, 87.4, 72.3, 71.4, 52.4, 21.2, 15.1 ; MS m/e 388 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{24}\text{H}_{20}\text{O}_5$  calcd. 388.1311, found 388.1298.

**7-Acetoxy-2-benzyloxy-1-(3-carbomethoxypropyl)naphthalene (31):** To a solution of **30** (0.2000 g, 0.5154 mmol) in ethyl acetate (20 mL) under  $\text{H}_2$  was added Rh/C (excess) at room temperature. The solution was stirred for 18h with monitoring by TLC. The suspension was filtered and the solvent was removed under reduced pressure. Preparative TLC (2:1 petroleum ether:  $\text{Et}_2\text{O}$ ) to give **31** (0.1880 g, 93% yield): bp 180-185 °C (0.15 torr); IR (KBr)  $_{\text{max}}$  2956, 1763, 1731  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 7.81 (d, J = 8.8, 1H), 7.73 (d, J = 2.1, 1H), 7.72 (d, J = 8.9, 1H), 7.50 (d, J = 7.4, 2H), 7.44 (apparent t, J = 7.4, 2H), 7.37 (t, J = 7.4, 1H), 7.29 (d, J = 8.9, 1H), 7.16 (dd, J = 8.8, 2.1, 1H), 5.22 (s, 2H), 3.64 (s, 3H), 3.20 (t, J = 7.7, 2H), 2.46 (t, J = 7.4, 2H), 2.40 (s, 3H), 2.05 (m, 2H);  $^{13}\text{C}$  173.8, 169.5, 154.0, 149.0, 137.2, 133.6, 129.8, 128.4, 127.7, 127.5, 127.3, 127.0, 123.0, 118.6, 114.2, 114.1, 70.9, 51.2, 33.6, 24.7, 24.3, 21.0; MS m/e 392 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{24}\text{H}_{24}\text{O}_5$  calcd. 392.1624, found 392.1610.

**7-Acetoxy-1-(3-carbomethoxypropyl)-2-hydroxynaphthalene (32):** To a solution of **31** (0.1900 g, 0.4846 mmol) in ethyl acetate (20 mL) under  $\text{H}_2$ , Pd/C (excess) at room temperature. The solution was stirred for 4h with monitoring by TLC. The suspension was filtered and the solvent was removed under

reduced pressure. Preparative TLC (1:1 petroleum ether: Et<sub>2</sub>O) afforded **32** (0.1400 g, 96% yield), mp 80-81 °C: IR (KBr)  $\nu_{\max}$  3425 br, 2952, 1759, 1733 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.75 (d, J = 8.8, 1H), 7.572 (d, J = 8.8, 1H), 7.565 (d, J = 2.3, 1H), 7.25 (br, 1H), 7.073 (d, J = 8.8, 1H), 7.069 (dd, J = 8.8, 2.3, 1H), 3.74 (s, 3H), 3.02 (t, J = 7.8, 2H), 2.43 (t, J = 6.8, 2H), 2.38 (s, 3H), 1.96 (m, 2H); <sup>13</sup>C 175.6, 170.0, 152.5, 149.0, 133.7, 130.0, 127.7, 127.1, 118.3, 118.2, 117.7, 113.7, 51.9, 32.6, 24.3, 23.8, 21.2; Ms m/e 302 (M<sup>+</sup>); HRMS m/e for C<sub>17</sub>H<sub>18</sub>O<sub>5</sub> calcd. 302.1154, found 302.1141.

**7-Acetoxy-1-(3-carbomethoxypropyl)-2-(trifluoromethylsulfonyloxy)naphthalene (33):** To a solution of **32** (0.1700 g, 0.5629 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20mL), pyridine (136 μL, 1.69mmol) and Tf<sub>2</sub>O (105 μL, 0.625 mmol), were added sequentially. The reaction mixture was stirred for 0.5 h. Following a conventional extractive workup (CH<sub>2</sub>Cl<sub>2</sub>), preparative TLC (1:1 petroleum ether: Et<sub>2</sub>O) afforded **33** (0.2347 g, 96% yield) as a viscous oil: IR (KBr)  $\nu_{\max}$  2955, 1765, 1738 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.91 (d, J = 8.9, 1H), 7.86 (d, J = 2.1, 1H), 7.80 (d, J = 9.1, 1H), 7.37 (d, J = 9.1, 1H), 7.35 (dd, J = 8.9, 2.1, 1H), 3.72 (s, 3H), 3.17 (m, 2H), 2.48 (t, J = 7.3, 2H), 2.40 (s, 3H), 2.03 (m, 2H); <sup>13</sup>C 173.4, 169.4, 149.8, 145.5, 133.2, 130.7, 130.3, 129.8, 128.8, 122.2, 119.1, 118.5 (q, J<sub>CF</sub> = 319.8), 115.9, 51.6, 33.4, 25.6, 24.8, 21.1; MS m/e 434 (M<sup>+</sup>); HRMS m/e for C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>O<sub>7</sub>S calcd. 434.0647, found 434.0641.

**7-Acetoxy-1-(3-carbomethoxypropyl)-2-methylnaphthalene (34) and 1-(3-Carbomethoxypropyl)-7-hydroxy-2-methylnaphthalene (35):** To a solution of Pd<sub>2</sub>(dba)<sub>3</sub> (0.0058 g, 0.0063 mmol) and (2-biphenyl)dicyclohexylphosphine (0.0045 g, 0.013 mmol) in anhydrous THF (20 mL), DABAL-Me<sub>3</sub> (0.0987 g, 0.385 mmol in THF) and **33** (0.1860 g, 0.4281mmol, in THF (2 mL)) were added sequentially. After 0.5 h of stirring, dilute HCl (1M) was added. After conventional extractive workup (Et<sub>2</sub>O), the residue was subjected to preparative TLC, which afforded, in order of elution (1:1 petroleum ether: Et<sub>2</sub>O), **34** (0.1080 g, 84% yield), and **35** (0.0080 g, 7% yield); (**34**) mp 48 °C; (KBr)  $\nu_{\max}$  2951, 1769, 1736 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.81 (d, J = 9.0, 1H), 7.73 (d, J = 2.0, 1H), 7.63 (d, J = 8.5, 1H), 7.29 (d, J = 8.5, 1H), 7.19 (dd, J = 9.0, 2.0, 1H), 3.72 (s, 3H), 3.06 (m, 2H), 2.51 (s, 3H), 2.50 (t, J = 7.0, 2H), 2.39 (s, 3H), 1.96 (m, 2H); <sup>13</sup>C 173.8, 169.8, 148.6, 134.5, 133.9, 132.6, 130.6, 129.9, 129.0, 126.1, 119.7,

114.6, 51.5, 33.9, 28.0, 24.8, 21.2, 20.1; MS m/e 300 ( $M^+$ ); HRMS m/e for  $C_{18}H_{20}O_4$  calcd. 300.1362, found 300.1351.

**(35):** (KBr)  $\nu_{\max}$  3395 br. 2953, 1736  $cm^{-1}$ ;  $^1H$  NMR 7.70 (d,  $J = 9.0$ , 1H), 7.56 (d,  $J = 8.5$ , 1H), 7.44 (d,  $J = 2.3$ , 1H), 7.14 (d,  $J = 9.0$ , 1H), 7.08 (dd,  $J = 8.5$ , 2.3, 1H), 3.76 (s, 3H), 3.01 (m, 2H), 2.52 (t,  $J = 7.0$ , 2H), 2.47 (s, 3H), 1.95 (m, 2H);  $^{13}C$  174.4, 153.9, 133.6, 133.5, 133.1, 130.4, 127.9, 126.8, 126.1, 116.4, 105.9, 51.7, 33.9, 28.2, 24.5, 20.1; MS m/e 258 ( $M^+$ ); HRMS m/e for  $C_{16}H_{18}O_3$  calcd. 258.1256, found 258.1259.

**7-Hydroxy-1-(4-hydroxy-4-methylpentyl)-2-methylnaphthalene (36):** To a solution of **34** (0.0380 g, 0.127 mmol) in  $Et_2O$  at  $0^\circ C$ , MeLi (0.59 mL, 1.5 M in  $Et_2O$ , 0.89 mmol) was added. After 4h of stirring, aqueous  $NH_4Cl$  was added. After a conventional extractive workup ( $Et_2O$ ), preparative TLC (1:1 petroleum ether:  $Et_2O$ ) gave product **36** (0.0306 g, 94% yield): mp 145-146  $^\circ C$ ; IR (KBr)  $\nu_{\max}$  3312 (br), 2968, 1635  $cm^{-1}$ ;  $^1H$  NMR ( $DMSO-d_6$ ) 9.57 (s, 1H), 7.67 (d,  $J = 8.8$ , 1H), 7.51 (d,  $J = 8.3$ , 1H), 7.25 (d,  $J = 2.1$ , 1H), 7.07 (d,  $J = 8.3$ , 1H), 6.99 (dd,  $J = 8.8$ , 2.1, 1H), 4.09 (s, 1H), 2.87 (m, 2H), 2.41 (s, 3H), 1.57 (m, 4H), 1.08 (s, 6H);  $^{13}C$  ( $DMSO$ ) 155.4, 133.7, 133.3, 132.4, 129.8, 126.8, 125.8, 125.5, 116.9, 105.1, 68.7, 44.0, 29.3, 28.8, 24.3, 19.8; MS m/e 258 ( $M^+$ ); HRMS for  $C_{17}H_{22}O_2$  calcd. ( $M^+$ ) 258.1620, found 258.1620.

**6,10,10-Trimethyl-8,9,10,10a-tetrahydrocyclohepta[de]naphthalen-1(7H)-one (37):** To a solution of **36** (0.0260 g, 0.101 mmol) in  $CH_2Cl_2$  (10mL),  $H_2SO_4$  (1 drop) was added and the solution was stirred for 4h. A conventional extractive workup ( $CH_2Cl_2$ ) followed by preparative TLC (1:4 hexanes:  $CH_2Cl_2$ ) afforded product **37** (0.0210 g, 87% yield): mp 73-74  $^\circ C$ ; IR (KBr)  $\nu_{\max}$  2955, 1654  $cm^{-1}$ ;  $^1H$  NMR 7.33 (d,  $J = 9.8$ , 1H), 7.11 (1/2 AB quartet,  $J = 7.7$ , 1H), 7.08 (1/2 Abquartet,  $J = 7.7$ , 1H), 6.05 (d,  $J = 9.8$ , 1H), 3.66 (s, 1H), 2.99 (m, 1H), 2.70 (m, 1H), 2.36 (s, 3H), 1.90 (m, 1H), 1.55 (m, 1H), 1.32 (m, 1H), 1.21 (s, 3H), 1.19 (m, 1H), 0.67 (s, 3H);  $^{13}C$  203.6, 145.7, 138.9, 136.9, 128.9, 128.1, 126.6, 125.9, 58.2, 42.3, 37.4, 29.7, 26.8, 25.6, 24.9, 20.4, 19.9; MS m/e 240 ( $M^+$ ); HRMS m/e for  $C_{17}H_{20}O$  calcd. 240.1514, found 240.1518.

**10a-Hydroxy-6,10,10-trimethyl-8,9,10,10a-tetrahydrocyclohepta[de]naphthalen-1(7H)-one (38)**

**and (2R\*,3R\*,10aS\*)- 10a-Hydroxy-6,10,10-trimethyl-8,9,10,10a-tetrahydrocyclohepta[de]naphthalen-1(7H)-one 2,3-oxide (39):** To a solution of **37** (0.0200 g, 0.0833 mmol) in dry DMF (3mL), NaH (0.0024 g, 0.10 mmol) was added. After stirring of reaction mixture for 3h in open air, the reaction was subjected to a conventional extractive workup (Et<sub>2</sub>O). Preparative TLC (1:1 hexanes : CH<sub>2</sub>Cl<sub>2</sub>) gave, in order of elution, **38** (0.0090 g, 42% yield), and **39** (0.0070 g, 31% yield);

**(38):** mp 102 °C; IR (KBr)  $\nu_{\max}$  3450, 2959, 1657 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.29 (d, J = 9.8, 1H), 7.10 (d, J = 7.6, 1H), 6.95 (d, J = 7.6, 1H), 6.20 (d, J = 9.8, 1H), 4.40 (s, 1H), 3.64 (m, 1H), 2.79 (m, 1H), 2.34 (s, 3H), 2.33 (m, 1H), 1.83 (m, 1H), 1.45 (m, 1H), 1.29 (m, 1H), 0.82 (s, 6H); <sup>13</sup>C 205.6, 148.0, 143.5, 140.4, 138.8, 130.2, 128.8, 127.3, 123.1, 84.4, 42.4, 39.0, 27.9, 26.8, 23.2, 22.0, 21.5; MS m/e 256 (M<sup>+</sup>); HRMS m/e for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub> calcd. 256.1463, found 256.1473.

**(39):** mp 110-111 °C IR (KBr)  $\nu_{\max}$  3456, 2924, 1698 cm<sup>-1</sup>; <sup>1</sup>H NMR 7.15 (1/2 AB quartet, J = 7.7, 1H), 7.11 (1/2 AB quartet, J = 7.7, 1H), 4.37 (s, 1H), 4.21 (d, J = 4.2, 1H), 3.95 (d, J = 4.2, 1H), 3.46 (dd, J = 14.3, 14.3, 1H), 2.87 (dd, J = 14.3, 5.9, 1H), 2.49 (m, 1H), 2.35 (s, 3H), 1.78 (m, 1H), 1.58 (m, 1H), 1.26 (m, 1H), 1.03 (s, 3H), 0.84 (s, 3H); <sup>13</sup>C 212.1, 143.9, 139.3, 138.3, 130.2, 127.5, 127.2, 85.2, 59.5, 54.4, 43.7, 39.5, 28.7, 27.8, 25.7, 23.4, 21.7; MS m/e 272 (M<sup>+</sup>); HRMS m/e for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub> calcd. 272.1412, found 272.1404. <sup>1</sup>H NOESY spectral studies showing cross peaks between the 0.84 ppm (methyl) and 4.37 ppm (hydroxy) resonances, along with cross peaks between 1.03 ppm (methyl) and both the 3.95 ppm and 4.21 ppm (epoxide CH) resonances support a *cis*- relationship between the OH and epoxy functions.

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