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

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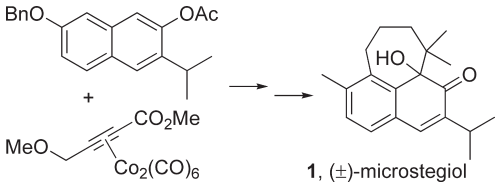
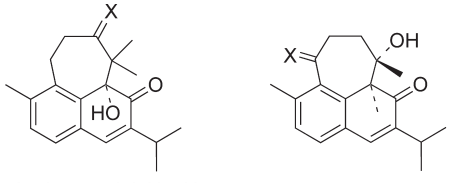


The application of the Nicholas reaction chemistry of 2,7-dioxygenated naphthalenes in the synthesis of cyclohepta[*de*]napthalenes and in the synthesis of (±)-microstegiol (**1**) is presented. The substitution profile of Nicholas monosubstitution (predominantly C-1) and disubstitution reactions (predominantly 1,6-) on 2,7-dioxygenated napthalenes 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, is 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 (±)-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**),[1] oxomicrostegiol (**2**),[2] salvibretol (**3**),[1c] and oxosalvibretol (**4**),[1c,m] have been isolated from roots of a number of plants of the genus *Salvia*. These plants have often seen use as folk remedies, and their crude extracts have demonstrated antibacterial, anticancer, and insect antifeedant activities.[1h,k,3] Microstegiol itself has been demonstrated to have antileukemic activity and modest antibacterial activity.[1a,k,m,n]



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

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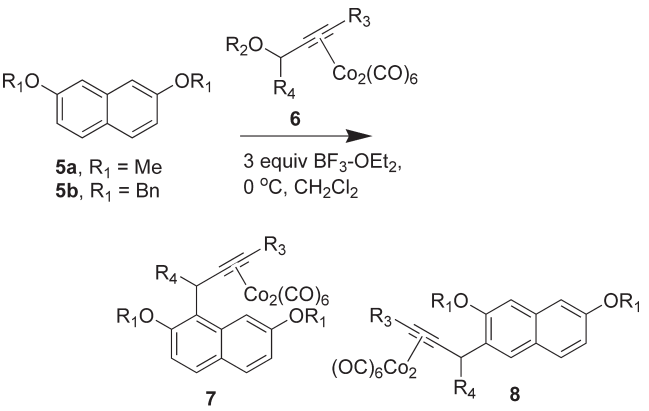
cyclohepta[*de*]naphthalenes themselves has normally been prepared by sequential Friedel−Crafts acylations of succinic anhydride or some variation of that approach,[4] although scattered reports of access to this ring system by 2 + 2 cycloaddition/ring expansion reactions of cyclopenta[*de*]naphthalenes,[5] malonate intramolecular alkylation processes,[6] reductive carbonyl coupling reactions,[7] and *o*-xylylene Diels−Alder cycloadditions[8] have been published.[9]

Our group has a long-standing interest in the synthesis of seven-membered-ring compounds,[10] based in part on the ability of alkynedicobalt complexes and the Nicholas reaction chemistry[11] of their derived propargyldicobalt cations to allow umpolung bond constructions from reactions of γ-carbonyl cation equivalents with electron-rich arenes, enol derivatives, allylmetalloids, or other nucleophiles.[12−17] Given the recent interest in **1**−**4**, the absence of synthetic work on these compounds, and the relative paucity of methods for the synthesis of cyclohepta[*de*]naphthalenes in general, we considered it of importance to study the applicability of propargyldicobalt cation chemistry to this ring system, with particular attention to microstegiol (**1**). Given structural characteristics of **1**, 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, culminating in the synthesis of (±)-microstegiol (**1**).[18]

TABLE 1. Monocondensation Reactions of 6a−f with 5a,b



6 (R_2 = H), except **6b**, R_2 = Me
7a-e, 8f (R_1 = Me), **7g**, R_1 = Bn

a, $R_3 = R_4$ = H
b, R_3 = CO_2Me, R_4 = H
c, R_3 = Me, R_4 = H
d, R_3 = $SiMe_3$, R_4 = H
e, R_3 = H, R_4 = Me
f, R_3 = H, R_4 = Ph
g, R_3 = CO_2Me, R_4 = H

entry	5	6	7 (yield, %)	8 (yield, %)
1	**5a**	**6a**	**7a** (93)	
2	**5a**	**6b**	**7b** (88)	
3	**5a**	**6c**	**7c** (84)	
4	**5a**	**6d**	**7d** (97)	
5	**5a**	**6e**	**7e** (66)	
6	**5a**	**6f**		**8f** (51)
7	**5b**	**6b**	**7g** (71)[a]	

[a]In addition, 13% of **9g** was isolated.

Results and Discussion

To develop a comprehensive understanding of the pattern of reactivity of propargyldicobalt cations with naphthalene-2,7-diol derivatives, 2,7-dimethoxynaphthalene (**5a**) was chosen as a reference molecule, and its Lewis acid-mediated Nicholas reactions of a number of substituted propargyl alcohol− or propargyl ether−$Co_2(CO)_6$ complexes were studied (**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 BF_3−OEt_2, but readily to complete conversion in the presence of 3 equiv of BF_3−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

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(13) For γ-carbonyl cation equivalents by way of cationic allyl iron complexes, see: (a) Green, J. R.; Carroll, M. K. *Tetrahedron Lett.* **1991**, *32*, 1141–1144. (b) Zhou, T.; Green, J. R. *Tetrahedron Lett.* **1993**, *34*, 4497–4500. (c) Charlton, M. A.; Green, J. R. *Can. J. Chem.* **1997**, *75*, 965–974. (d) Enders, D.; Jandeleit, B.; Von Berg, S. *Synlett* **1997**, 421–431. and references citd therein. (e) Enders, D.; Jandeleit, B.; von Berg, S.; Raabe, G.; Runsink, J. *Organometallics* **2001**, *20*, 4312–4332.

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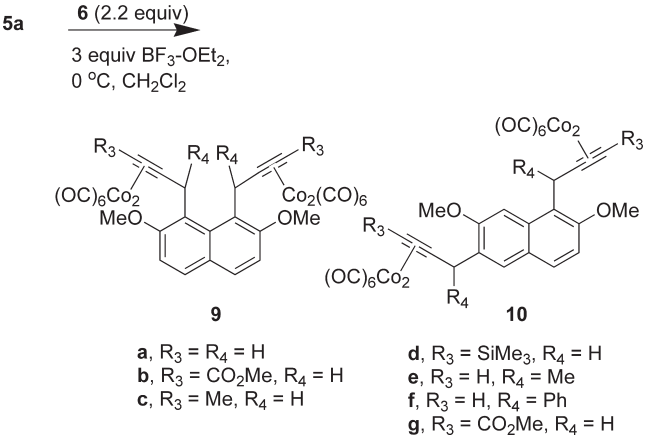
(18) For a preliminary report of this work, see: Taj, R.; Abhayawardhana, A.; Green, J. R. *Synlett* **2009**, 292–296.

TABLE 2. Dicondensation Reactions of 6 with 5a



entry	5a	6	9 (yield, %)	10 (yield, %)
1	**5a**	**6a**	**9a** (63)	**10a** (9)
2	**5a**	**6b**	**9b** (86)	
3	**5a**	**6c**		**10c** (86)
4	**5a**	**6d**		**10d** (40)[a]

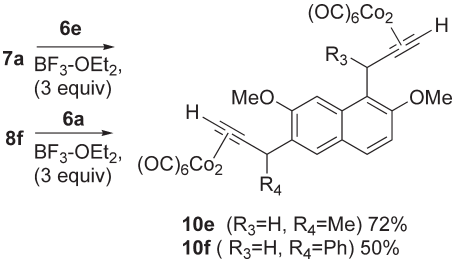
[a]In addition, 59% of **7d** was isolated.

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-dibenzyloxy-substituted **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%).

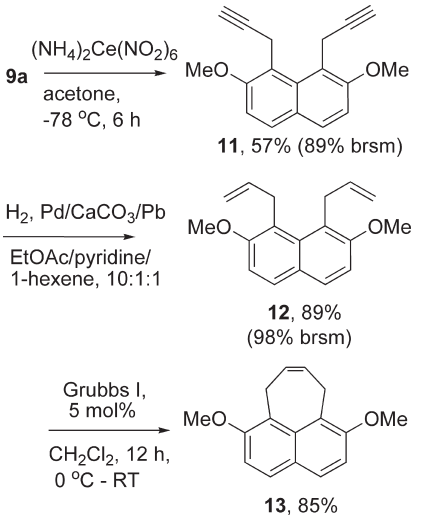
Dicondensation. Increasing the amount of propargyl alcohol/ether−$Co_2(CO)_6$ complex **6a**−**e** to slightly over 2 equiv enabled, in most cases, ready conversion of 2,7-dimethoxynaphthalene (**5a**) to disubstituted products (**9**−**10**) (Table 2). In these cases, a competition existed between the formation of 1,8-disubstitution products (**9**) and 1,6-disubtitution 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.

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 BF_3−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



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



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 substitutent that is not electron withdrawing, monosubstitution is at C-1, while the second substitution occurs at C-6. Substitution of **6** with groups at the propargylic site allows 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 dinitration and chlorination (1,8-) versus dibromination (1,6-) of 2,7-dimethoxynaphthalene,[19] including the element of the most electrophilic reagents being directed toward the 1,8-positions.

Application toward Cyclohepta[*de*]naphthalene Synthesis. Given an understanding of the substitution patterns of 2,7-dioxygenated naphthalenes toward 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).

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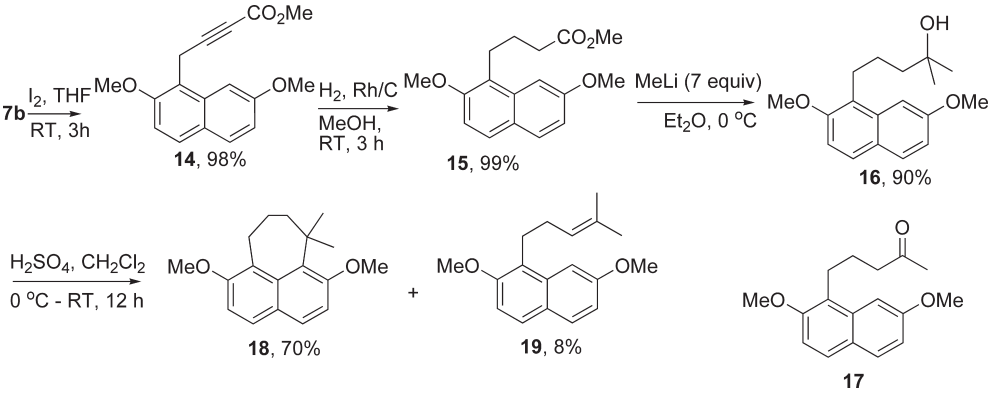
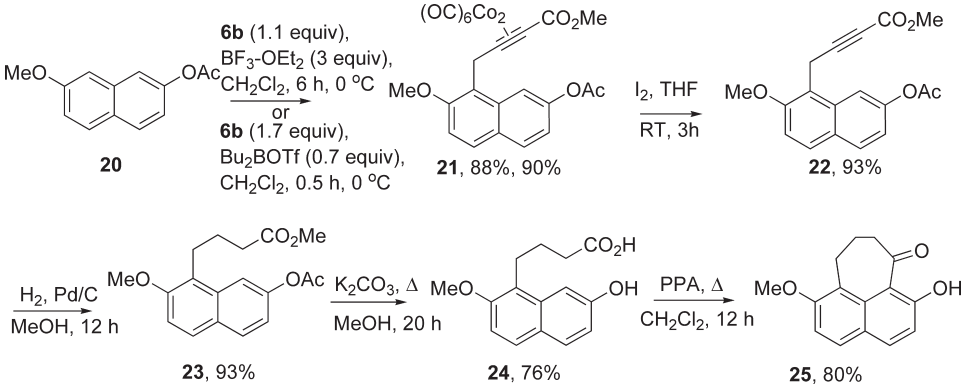
SCHEME 3. Ring Closure by Friedel−Crafts Alkylation



SCHEME 4. Ring Closure by Friedel−Crafts Acylation



Decomplexation of **9a** could be accomplished with $(NH_4)_2Ce(NO_3)_6$ under carefully controlled, low-temperature conditions, giving **11** (57% yield, 89% by recovered starting material (brsm)). Other common reagents for decomplexation (Me_3NO, I_2) gave poorer yields of **11** or none at all. Semihydrogenation of **11** in the presence of the Lindlar catalyst then afforded diene **12**[20] (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.[21]

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 $Co_2(CO)_6$ 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 alkanoate (**15**) was straightforward in the presence of H_2 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_2SO_4 in CH_2Cl_2 induced its conversion to 7,7-dimethyltetrahydrocyclohepta[*de*]naphthalene **18** (70% yield), contaminated with a small amount of elimination product **19** (8% yield).

As all the naturally occurring cyclohepta[*de*]napthalenes exist as dehydrotetralones, and since the matter of selective deprotection of the methoxy groups of **18** is not trivial, related approaches to these ring systems were made on phenolic acetate **20**.[22] The Nicholas reaction of **20** with **6b** in the presence of BF_3-OEt_2 occurred somewhat sluggishly (relative to 2,7-dimethoxynaphthalene), but ultimately afforded the product of γ-carbonyl cation substitution ortho to the methoxy function (**21**) in excellent yield (88%) (Scheme 4). Bu_2BOTf has often proved more effective in generating γ-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%).[23] Alkyne decomplexation with I_2 in THF occurred readily to give alkynoate **22** (93%), and Pd/C catalyzed hydrogenation of the alkyne afforded alkanoate **23** in excellent yield (93%).

From alkanoate **23**, the synthesis of cyclohepta[*de*]naphthalene systems diverged in two ways. Given the oxygenated

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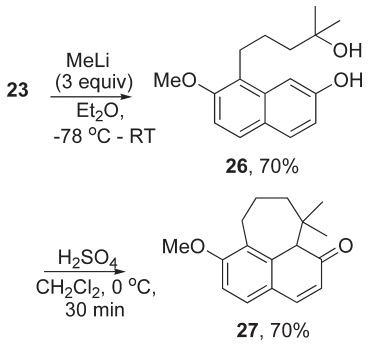
(23) The superiority of Bu_2BOTf over BF_3-OEt_2 in Nicholas reactions for substrates possessing Lewis basic groups has been observed in our group previously: (a) Green, J. R. *Chem. Commun.* **1998**, 1751–1752. (b) Green, J. R.; Tjeng, A. A. *J. Org. Chem.* **2009**, *74*, 7411–7416.

SCHEME 5. Cyclohepta[*de*]napthalenone Synthesis by Cyclization−Tautomerization



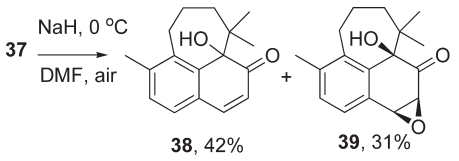
cycloheptane unit present within salvibretol, access to a ketone function in the seven-membered ring was desired. Consequently, saponification of **23** was accomplished, albeit slowly, by K_2CO_3 in MeOH at reflux, giving **24** (76% yield). After experimentation with several sets of acidic conditions, 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.[24]

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(7*H*)-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 °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.

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/γ-carbonyl cation chemistry on the naphthalene nucleus, the use of a C-2/C-7 oxygen-based function followed by 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 BF_3-OEt_2 (24 h, 0 °C, 45% yield of **29**, 66% brsm), but gave **29** promptly and in excellent yield in the presence of Bu_2-BOTf (1.5 h, 0 °C, 90% yield). Following uneventful decomplexation with 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 H_2 and Pd/C then gave phenolic acetate **32** in excellent yield (96%). Attempts at using 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 Tf_2O/pyridine, which was subjected to methylation. After some experimentation, it was found that $Pd_2(dba)_3$/Cy-JohnPhos-catalyzed reaction of **33** with the DABCO-$(AlMe_3)_2$ complex (DABAL-Me_3)[25] gave efficient methyl group incorporation, resulting in the formation of both **34** (84%) and a small amount of deacetylated **35** (7%).

Each of these methylnaphthalenes could be converted into naphthol-tertiary alcohol **36** by reaction with excess MeLi (Scheme 7). In the case of **34**, **36** was obtained in 94% yield; in the case of **35**, **36** could be isolated in 70% yield. Subjecting **36** in CH_2Cl_2 to H_2SO_4 then resulted in rapid conversion to cyclohepta[*de*]naphthalenone **37** in excellent yield (87%).

The incorporation of an α-hydroxy function relative to the ketone was briefly explored (eq 1). Exposure of a solution of **37** in DMF to NaH in air[26] resulted in the disappearance of **37** and the formation of two compounds: α-hydroxy ketone **38** (42%), and the relatively unstable α-hydroxylated epoxide **39** (31%).



(1)

Synthesis of Microstegiol. With model studies for cyclohepta-[de]naphthalene-1-one preparation, C-6 methyl group incorporation, and α-hydroxylation completed, the synthesis of microstegiol could now be undertaken. 7-Benzyloxy-3-bromo-2-naphthol (**40**) was chosen as the foundation compound for this synthesis. Compound **40** has been prepared by the method of the Diederich group from 2,7-naphthalenediol,[27] by way of dibromination/monodebromination to give **41**, selective methoxymethyl ether formation (**42**), conventional benzylation (**43**), and MOM ether deprotection (Scheme 8). Incorporation of the C-3 isopropyl group was preceded by naphthol acetylation under standard conditions, giving **44** (96% yield).[28] Suzuki−Miyaura coupling of **44** with isopropenylboronic acid pinacol ester gave **45** cleanly (80% yield), and reduction of the alkene function by hydrogenation over Rh/C afforded **46** (92% yield) (Scheme 2).

With the two arene rings of the naphthalene now possessing distinctly different levels of activation toward electrophilic substitution, the critical Nicholas reaction of γ-carbonyl cation equivalent **6b** was attempted. In the presence of an excess amount of BF_3-OEt_2 (3 equiv), compounds **46** and **6b** gradually underwent reaction at 0 °C, and **47** was formed in excellent yield (89%) (Scheme 9). In accordance with the majority of cases in our methodological study,[19] polyalkylation was not a detectable side reaction for this process.

(24) (a) Rieche, A.; Fruhwald, E. *Chem. Ber.* **1931**, *64B*, 1603–1606. (b) Moghaddam, F. M.; Porkaleh, H.; Zali-Boeini, H. *Lett. Org. Chem.* **2006**, *3*, 123–127.

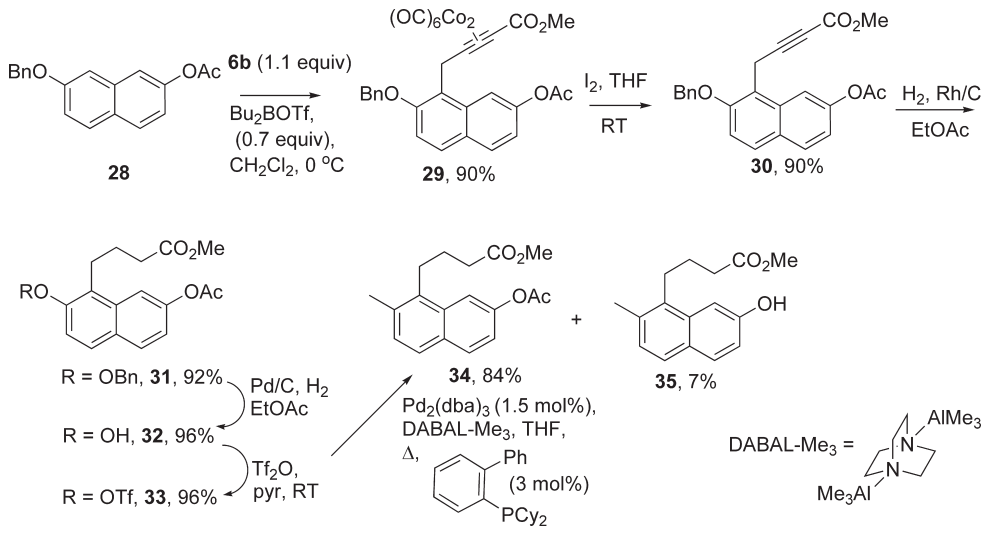
(25) (a) Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2232–2234. *Angew. Chem.* **2005**, *117*, 2272−2274; (b) Cooper, T.; Novak, A.; Humphreys, L. D.; Walker, M. D.; Woodward, S. *Adv. Synth. Catal.* **2006**, *348*, 686–690.

(26) Ishikawa, T.; Hino, K.; Yoneda, T.; Murota, M.; Yamaguchi, K.; Watanabe, T. *J. Org. Chem.* **1999**, *64*, 5691–5695.

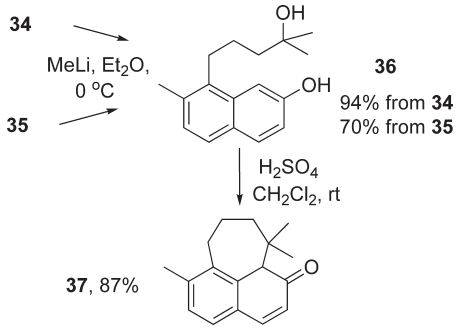
(27) Bähr, A.; Droz, A. S.; Püntener, M.; Neidlein, U.; Anderson, S.; Seiler, P.; Diederich, F. *Helv. Chem. Acta* **1998**, *81*, 1931–1963.

(28) Attempts to subject **41** to initial acetylation, in order to give an expedited route to **44**, were not selective for protection of the C-2 alcohol.

SCHEME 6. C-2 Methyl Group Incorporation



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

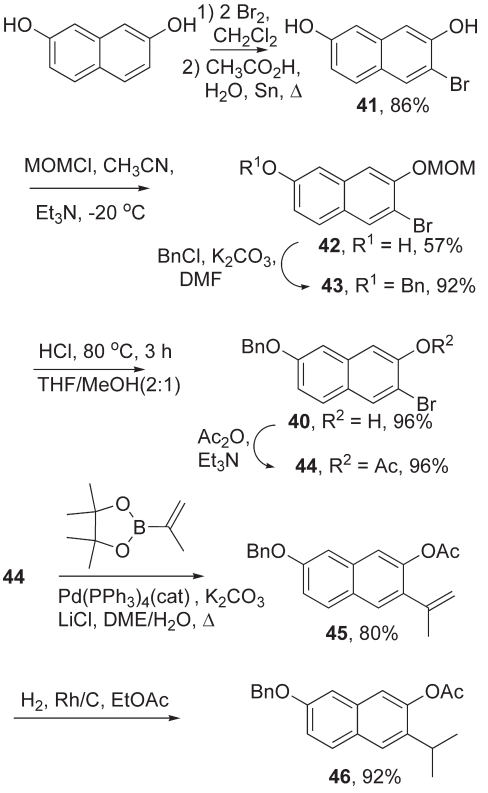


Decomplexation of **47** was straightforward in the presence of I_2/THF (**48**, 87% yield). With the four-carbon unit incorporated, replacement of the benzyloxy function with a methyl group was facilitated by the observation that in the presence of H_2 and Pd/C, alkyne reduction was accompanied by hydrogenolytic removal of the benzyl ether, giving **49** in 84% yield. The naphthol function of **49** was then readily converted into its triflate in the presence of Tf_2O and pyridine, with **50** being obtained in 83% yield. Cross coupling of the methyl organometallic was accomplished by the palladium-catalyzed reaction with DABAL-Me_3,[23] providing **51** in excellent (91%) yield (Scheme 10).

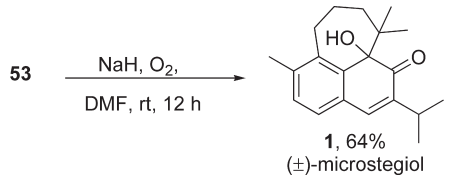
Formation of the tautomerized cyclohepta[*de*]naphthol was pursued following the methodology developed for **23** (Scheme 10). The ester function of **51** was cleanly converted into 3° alcohol **52** in the presence of excess MeLi (**52**, 92% yield). In a manner analogous to our model compound (**26**), a CH_2Cl_2 solution of **52**, when exposed to 1 drop of H_2SO_4, underwent ring closure in conjunction with tautomerization of the naphthol function to a cyclohexenone, giving **53** (81% yield).

Incorporation of the alcohol function α to the keto function remained the sole requirement for the synthesis of microstegiol. Fortunately, the addition of NaH to a DMF solution of **53**, with exposure to an oxygen atmosphere, resulted in the clean formation of (±)-microstegiol **1** (64% yield) (eq 2). The synthetic

SCHEME 8. Differentially Protected C-3 Isopropyl-2,7-naphthalenediol Preparation



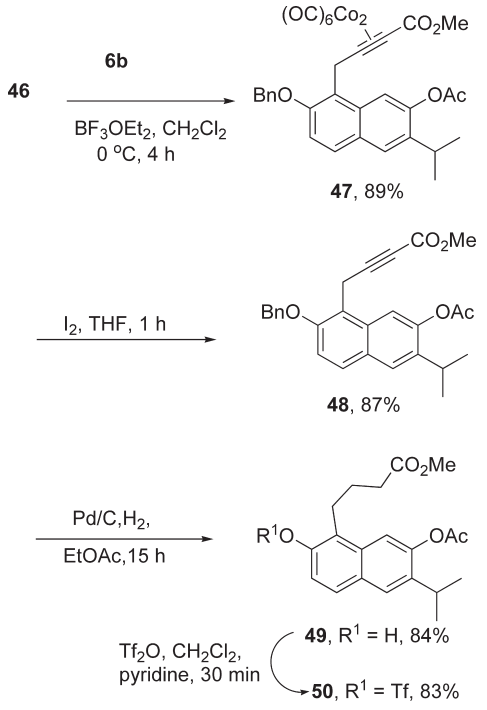
material was spectroscopically identical with that isolated from *Salvia microstegia*.[1a]



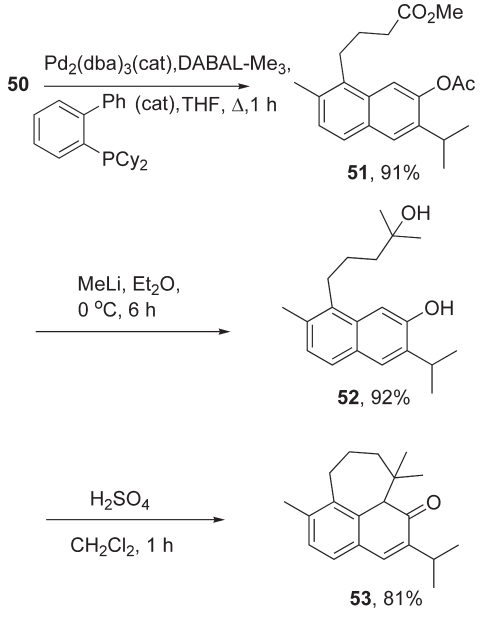
(2)

In summary, a systematic study of Nicholas reaction-based γ-carbonyl cation chemistry on 2,7-dioxygenated naphthalenes

SCHEME 9. Nicholas Reaction of 46 and Triflate Incorporation



SCHEME 10. Methyl Incorporation and Cycloheptane Formation



has established the pattern of monosubstitution and disubstitution reactions. With use of selected condensation products, three different methods for generation of the cyclohepta[*de*]naphthalene ring system have been developed. Selective C-3 functionalization and replacement of the C-7 oxygen-based function by a methyl group has allowed the synthesis of (±)-microstegiol (**1**) in 15 steps and 7.2% overall yield from 2,7-dihydroxynaphthalene.

Experimental Section

General Methods. All reaction solvents were used after passage through a solvent purification system. Commercial BF_3-OEt_2 was distilled and stored under nitrogen. All reactions were conducted under a nitrogen atmosphere unless otherwise noted. Flash chromatography was performed as described by Still using silica gel 60 (230−400 mesh).[29] Compounds **5b**,[30] **6a**,[31] **6b**,[32] **6c**,[33] **6d**,[34] **6e**,[35] **6f**,[31] and **20**[22] were prepared by literature procedures and are >95% pure as determined by ^{1}H and ^{13}C NMR spectroscopy. All new compounds are >95% pure as determined by ^{1}H and ^{13}C NMR spectroscopy. NMR spectra were run at 500 or 300 MHz for ^{1}H and 125 or 75 MHz for ^{13}C in $CDCl_3$; chemical shifts are given in ppm and coupling constants (*J*) are given in Hz. High-resolution mass spectra were run by time-of-flight mass spectroscopy, in EI mode, at 70 eV.

Hexacarbonyl[μ-η^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 CH_2Cl_2 (15 mL) was added propargyl alcohol complex **6a** (0.100 g, 0.292 mmol). BF_3-OEt_2 (101 μL, 0.797 mmol) was added dropwise at 0 °C. After 3 h of continuous stirring, $NH_4Cl_{(aq)}$ was added and the mixture was subjected to a conventional extractive workup (CH_2Cl_2). The residue was subjected to flash chromatography (50:1 petroleum ether:Et_2O) to give **7a** (0.127 g, 93%) as a red brown solid: IR (KBr) υ_{max} 3003, 2960, 2090, 2055 cm^{-1}; ^{1}H NMR δ 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); ^{13}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^+ − CO), 456 (M^+ − 2CO), 428 (M^+ − 3CO), 372 (M^+ − 5CO); HRMS *m*/*e* for $C_{21}H_{14}Co_2O_8$ calcd (M^+ − 2CO) 455.9454, found 455.9441.

Hexacarbonyl[μ-η^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_3-OEt_2 (425 μL, 3.35 mmol) to Method 1 gave product **7b** (0.560 g,, 88% yield) following flash chromatography (5:1 petroleum ether:Et_2O) as red brown solid: IR (KBr) υ_{max} 3003, 2951, 2097, 2063, 2028, 1708; ^{1}H NMR δ 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); ^{13}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^+), 542 (M^+ − 1CO), 514 (M^+ − 2CO), 486 (M^+ − 3CO), 458 (M^+ − 4CO), 430 (M^+ − 5CO), 402 (M^+ − 6CO); HRMS *m*/*e* for $C_{23}H_{16}Co_2O_{10}$ calcd (M^+ − CO) 541.9458, found 541.9455.

Hexacarbonyl[μ-η^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_3-OEt_2 (196 μL, 1.55 mmol) to Method 1 gave product **7c** (0.225 g, 84% yield) following flash chromatography (100:1 petroleum ether:Et_2O) as red brown solid: IR (KBr) υ_{max} 2941, 2086, 2044, 2015, 1629 cm^{-1}; ^{1}H NMR δ 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); ^{13}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^+ − 3CO), 414 (M^+ − 4CO), 386 (M^+ − 5CO), 358 (M^+ − 6CO); HRMS *m*/*e* for $C_{22}H_{16}Co_2O_8$ calcd (M^+ − CO) 497.9560, found 497.9583.

Hexacarbonyl[μ-η^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_3-OEt_2 (87 μL,

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(31) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *Organometallics* **1990**, *9*, 2972–2984.
(32) Tjeng, A. A.; Green, J. R. *J. Org. Chem.* **2009**, *74*, 7411–7416.
(33) (a) Vessieres, A.; Jaouen, G.; Gruselle, M.; Rossignol, J. L.; Savignac, M.; Top, S.; Greenfield, S. *J. Steroid Biochem.* **1988**, *30*, 301–305. (b) Lang, H.; Köhler, K.; Emmerich, C. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 923–930.
(34) Kuhn, O.; Rau, D.; Mayr, H. *J. Am. Chem. Soc.* **1998**, *120*, 900–907.
(35) Connor, R. E.; Nicholas, K. M. *J. Am. Chem. Soc.* **1987**, *109*, 5749–5759.

0.69 mmol) to Method 1 gave product **7d** (0.1308 g, 97% yield) following flash chromatography (50:1 petroleum ether:Et_2O) as red brown solid: IR (KBr) υ_{max} 2959, 2083, 2042, 2013, 1629 cm^{-1}; ^1H NMR δ 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); ^{13}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^+-CO), 528 (M^+-2CO), 500 (M^+-3CO), 444 (M^+-5CO); HRMS for $C_{24}H_{22}Co_2O_8Si$ calcd (M^+-3CO) 499.9900, found 499.9898.

Hexacarbonyl[μ-η^4-(2,7-dibenzyloxy-1-(3-carbomethoxyprop-2-ynyl)naphthalene)]dicobalt (7g) and Dodecacarbonyl[μ-η^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** (1.009 g, 2.437 mmol), and BF_3-OEt_2 (842 μL, 6.64 mmol) to Method 1 gave, in order of elution, **7g** (1.133 g, 71% yield) as a red brown solid, and **9g** (0.3210 g, 13% yield), following flash chromatography (5:1 petroleum ether:Et_2O) as red brown viscous oil. **7g**: IR (KBr) υ_{max} 3039, 2957, 2098, 2031, 1706 cm^{-1}; ^1H NMR δ 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); ^{13}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^+ − 4CO), 554 (M^+ − 6CO); HRMS for $C_{35}H_{24}Co_2O_{10}$ calcd (M^+ − 6CO) 554.0339, found 554.0354. **9g**: IR (KBr) υ_{max} 2951, 2097, 2063, 2030, 1709 cm^{-1}; 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); ^{13}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. Anal. Calcd for $C_{46}H_{28}Co_4O_{18}$: C, 50.02; H, 2.56. Found: C, 49.87, H, 2.52.

Hexacarbonyl[μ-η^4-(2,7-dimethoxy-1-(1-methylprop-2-ynyl)-naphthalene)]dicobalt (7e). Subjecting **5a** (0.0498 g, 0.264 mmol), **6e** (0.0880 g, 0.247 mmol), and BF_3-OEt_2 (105 μL, 0.829 mmol) to Method 1 gave product **7e** (0.0920 g, 66% yield) following flash chromatography (40:1 petroleum ether:Et_2O) as red brown solid: IR (KBr) υ_{max} 3039, 2957, 2098, 2031, 1706 cm^{-1}; ^1H NMR (58:42 mixture of rotamers) δ 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); ^{13}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^+ − CO), 470 (M^+ − 2CO), 442 (M^+ − 3CO), 414 (M^+ − 4CO), 386 (M^+ − 5CO); HRMS m/e for $C_{22}H_{16}Co_2O_8$ calcd (M^+ − 2CO) 469.9611, found 469.9608.

Hexacarbonyl[μ-η^4-(2,7-dimethoxy-3-(1-phenylprop-2-ynyl)-naphthalene)]dicobalt (8f). Subjecting **5a** (0.0560 g, 0.298 mmol), **6f** (0.1500 g, 0.3588 mmol), and BF_3-OEt_2 (113 μL, 0.892 mmol) to Method 1 gave product **8f** (0.0900 g, 51% yield) following flash chromatography (10:1 petroleum ether:Et_2O), as red brown solid: IR (KBr) υ_{max} 2922, 2089, 2050, 2014, 1632 cm^{-1}; ^1H NMR δ 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); ^{13}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^+ − 2CO), 476 (M^+ − 4CO), 448 (M^+ − 5CO), 420 (M^+ − 6CO); HRMS m/e for $C_{27}H_{18}Co_2O_8$ calcd (M^+ − 4CO) 475.9869, found 475.9853.

Dodecacarbonyl[μ-η^4-(2,7-dimethoxy-1,8-di(prop-2-ynyl)naphthalene)]tetracobalt (9a) and Dodecacarbonyl[μ-η^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_2Cl_2 (10 mL) was added propargyl alcohol complex **6a** (0.393 g, 1.149 mmol), followed by the dropwise addition of BF_3-OEt_2 (202 μL, 1.59 mmol) at 0 °C. After 3 h of continuous stirring, $NH_4Cl_{(aq)}$ was added and the mixture was subjected to a conventional extractive workup. The residue was purified by flash chromatography (10:1 petroleum ether:Et_2O) to give, in order of elution, **10a** (0.040 g, 9% yield) and **9a** (0.280 g, 63% yield) as red brown solids. **9a**: IR (KBr) υ_{max} 2917, 2090, 2051, 2021 cm^{-1}; ^1H NMR δ 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}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 (M^+-1CO), 780 (M^+-2CO), 752 (M^+-3CO), 724 (M^+-4CO), 696 (M^+-5CO), 668 (M^+-6CO), 640 (M^+-7CO), 612 (M^+ − 8CO); HRMS m/e for $C_{30}H_{16}Co_4O_{14}$ calcd (M^+ − CO) 807.7917, found 807.7904. **10a**: IR (KBr) υ_{max} 2922, 2091, 2048, 2016 cm^{-1}; ^1H NMR δ 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}C NMR 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 (M^+ − 6CO), 612 (M^+ − 7CO), 584 (M^+-8CO), 500 (M^+-12CO); HRMS m/e for $C_{30}H_{16}Co_4O_{14}$ calcd (M^+ − 7CO) 639.8224, found 639.8223.

Dodecacarbonyl[μ-η^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 BF_3-OEt_2 (115 μL, 0.91 mmol) to Method 2 gave **9b** (0.1117 g, 86%) following flash chromatography (5:1 petroleum ether:Et_2O) as red brown solid: IR (KBr) υ_{max} 3004, 2950, 2097, 2067, 1710 cm^{-1}; ^1H NMR δ 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}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 (M^+ − 2CO), 840 (M^+ − 4CO), 784 (M^+ − 6CO), 728 (M^+ − 8CO), 700 (M^+ − 9CO). Anal. Calcd for $C_{34}H_{20}Co_4O_{18}$: C, 42.88; H, 2.12. Found: C, 43.12; H, 2.10.

Dodecacarbonyl[μ-η^4-(2,7-dimethoxy-1,6-di(but-2-ynyl)naphthalene)]tetracobalt (10c). Subjecting **5a** (0.1000 g, 0.5314 mmol), **6c** (0.400 g,1.123 mmol), and BF_3-OEt_2 (202 μL, 1.59 mmol) to Method 2 gave product **10c** (0.3950 g, 86% yield) following flash chromatography (100:1 petroleum ether:Et_2O) as red brown solid: IR (KBr) υ_{max} 2949, 2085, 2000, 1631 cm^{-1}; ^1H NMR δ 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}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 (M^+ − 2CO), 780 (M^+ − 3CO), 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[μ-η^4-(2,7-dimethoxy-1,6-di(3-trimethylsilyl-prop-2-ynyl)naphthalene)]tetracobalt (10d). Subjecting **5a** (0.050 g, 0.266 mmol), **6d** (0.242 g, 0.585 mmol), and BF_3-OEt_2 (118 μL, 0.931 mmol) to Method 2, with the exception that the reaction mixture was additionally warmed to room temperature for 5 h, with 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) υ_{max} 2960, 2089, 2050, 2023, 1632 cm^{-1}; ^1H NMR δ 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, negative ion) m/e for $C_{36}H_{32}Co_4O_{14}Si_2$ calcd ($M - H^+$) 978.8580, found 978.8584.

Dodecacarbonyl[μ-η^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-OEt_2 (25 μL, 0.20 mmol) to Method 1 gave product **10e** (0.0360 g, 72% yield) following flash chromatography (100:1 petroleum ether:Et_2O) as red brown solid: IR (KBr) υ_{max} 2935, 2089, 2050, 2018, 1627 cm^{-1}; ^1H NMR δ 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 = 15.3, 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[μ-η^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-OEt_2 (24 μL, 0.19 mmol) to Method 1 gave product **10f** (0.0380 g, 65% yield) following flash chromatography (10:1 petroleum ether:Et_2O) as red brown viscous oil: IR (KBr) υ_{max} 2929, 2089, 2049, 2018, 1629 cm^{-1}; ^1H NMR δ 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); ^{13}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 ($M^+ - CO$), 856 ($M^+ - 2CO$), 828 ($M^+ - 3CO$), 800 ($M^+ - 4CO$); HRMS for $C_{36}H_{20}Co_4O_{14}$, calcd ($M^+ - 4CO$) 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_2O 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_2O) 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) υ_{max} 3291, 2932, 2107, 1618 cm^{-1}; ^1H NMR δ 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); ^{13}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^+); HRMS m/e for $C_{18}H_{16}O_2$ calcd (M^+) 264.1150, found 264.1153.

1,8-Diallyl-2,7-dimethoxynaphthalene (12). To a solution of **11** (0.0200 g, 0.0758 mmol) in 20 mL of a mixture of ethyl acetate:1-hexene:pyridine (10:1:1) was added Lindlar catalyst (5 mol %) at room temperature. The reaction was stirred under an H_2 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_2O) 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.[20] mp 189.4−194 °C); IR (KBr) υ_{max} 3077, 2934, 1614 cm^{-1}; ^1H NMR δ 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); ^{13}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^+); HRMS m/e for $C_{18}H_{20}O_2$ calcd (M^+) 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_2Cl_2 (2 mL) was added Grubbs' 1 Catalyst (0.0027 g, 5 mol %) at room temperature. After 6 h, the mixture was filtered through Celite. The filtrate was concentrated under reduced pressure and the crude product was purified by preparative TLC (100:1 petroleum ether:Et_2O) to give **13** (0.0130 g, 0.0541 mmol, 85%): mp 95−96 °C; IR (KBr) υ_{max} 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); ^{13}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^+), HRMS m/e for $C_{16}H_{16}O_2$ calcd (M^+) 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 was added an excess of iodine (I_2). The solution was stirred for 3 h. Following the addition of aqueous sodium bisulfate, the mixture was subjected to a conventional extractive workup (Et_2O). Purification by preparative TLC (1:1 petroleum ether:Et_2O) gave **14** (0.218 g, 98% yield): mp 80−81 °C; IR (KBr) υ_{max} 2956, 2233, 1712, 1628; ^1H NMR δ 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); ^{13}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^+). Anal. Calcd for $C_{17}H_{16}O_4$: 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_2 was added Rh/C (excess) at room temperature. The solution was stirred for 6 h with monitoring by TLC. The suspension was filtered and the solvent was removed under reduced pressure. Preparative TLC (2:1 petroleum ether:Et_2O) to give **15** (0.211 g, 99% yield): bp 170−175 °C (0.5 Torr); IR (KBr) υ_{max} 2954, 1740, 1628; ^1H NMR δ 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); ^{13}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^+); HRMS m/e for $C_{17}H_{20}O_4$ calcd (M^+) 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_2O (10 mL) at 0 °C was added MeLi (1.9 mL, 1.5 M, 2.9 mmol). The solution was stirred for 3 h, at which time aqueous NH_4Cl was added and a conventional extractive workup (Et_2O) performed. The volatiles were removed under reduced pressure. Purification by preparative TLC (1:1 petroleum ether:Et_2O) gave **15** (0.103 g, 0.356 mmol, 90% yield): mp 45−46 °C; IR (KBr) υ_{max} 3422 br, 2966, 1627 cm^{-1}; H NMR δ 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); ^{13}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^+); HRMS m/e for $C_{18}H_{24}O_3$ calcd (M^+) 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_2Cl_2 (10 mL) was added one drop of H_2SO_4. The solution was refluxed for 24 h. Water was added and a conventional extractive workup performed CH_2Cl_2. Purification by preparative TLC (4:1 hexanes:CH_2Cl_2) 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) υ_{max} 2929, 1612; ^1H NMR δ 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); ^{13}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^+); HRMS m/e for $C_{18}H_{22}O_2$ calcd (M^+) 270.1620, found 270.1614. **19**: 55−56 °C; ^1H NMR δ 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 (t, J = 7.2, 1 H), 3.95 (s, 6H), 3.05 (m, 2H), 2.31 (m, 2H), 1.73 (s, 3H), 1.61 (s, 3H); ^{13}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 $C_{18}H_{22}O_2$ calcd (M^+) 270.1620, found 270.1606.

Hexacarbonyl[μ-η^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 $BF_3{-}OEt_2$ (440 μL, 3.5 mmol) to Method 1 afforded **21** (0.609 g, 1.018 mmol, 88% yield), following flash chromatographic purification (2:1 petroleum ether:Et_2O), as a viscous red-brown oil: IR (KBr) υ_{max} 3004, 2952, 2099, 2063, 2029,1765, 1709; ^{1}H NMR δ 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}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 (M^+-2CO), 514 (M^+-3CO), 486 (M^+-4CO), 458 (M^+-5CO), 430 (M^+-6CO); HRMS m/e for $C_{24}H_{16}Co_2O_{11}$ calcd (M^+ − 3CO) 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 Et_2O afforded **22** (0.138 g, 93% yield): mp 132−133 °C; IR (KBr) υ_{max} 2917, 2234, 1761, 1712; ^{1}H NMR δ 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}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 (M^+); HRMS m/e for $C_{18}H_{16}O_5$ calcd (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 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:Et_2O) gave **23** (0.148 g, 93% yield) as colorless solid: mp 125 °C; IR (KBr) υ_{max} 3067, 2950, 1759, 1734; ^{1}H NMR δ 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}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 (M^+); HRMS m/e for $C_{18}H_{20}O_5$ calcd (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 18 h, the mixture was acidified (3 M HCl) and a conventional extractive workup performed (Et_2O). Recrystallization from CH_2Cl_2 afforded product **24** (0.0730 g, 76% yield): mp 164−165 °C; IR (KBr) υ_{max} 3385 br, 2924, 1703, 1626; ^{1}H NMR (acetone-d_6) δ 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); ^{13}C NMR (acetone-d_6) 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^+); HRMS m/e for $C_{15}H_{16}O_4$ calcd (M^+) 260.1049, found 260.1045.

6-Hydroxy-1-methoxy-9,10-dihydrocyclohepta[*de*]naphthalen-7(8*H*)-one (25). A solution of polyphosphoric acid (PPA, ca. 0.1 g, excess) and **24** (0.100 g, 0.385 mmol) in CH_2Cl_2 (20 mL) was heated to reflux for 36 h. Water was added and the mixture was subjected to a conventional extractive workup (CH_2Cl_2). Preparative TLC (2:1 petroleum ether:Et_2O) gave **25** (0.075 g, 80% yield): mp 90 °C; IR (KBr) λ_{max} 3009, 2970, 1616 cm^{-1}; ^{1}H NMR δ 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); ^{13}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^+); HRMS for $C_{15}H_{14}O_3$ calcd (M^+) 242.0943, found 242.0931.

7-Hydroxy-1-(4-hydroxy-4-methylpentyl)-2-methoxynaphthalene (26). To a solution of **23** (0.1030 g, 0.3259 mmol) in Et_2O at 0 °C was added MeLi (0.76 mL, 1.1 mmol, 1.5 M in Et_2O). After 4 h of stirring, aqueous NH_4Cl was added. A conventional workup and preparative TLC (1:1 petroleum ether:Et_2O) gave **26** (0.0625 g, 70% yield): mp 140 °C; IR (KBr) υ_{max} 3358, 2967 cm^{-1}; ^{1}H NMR δ 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); ^{13}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^+); HRMS m/e for $C_{17}H_{22}O_3$ calcd 274.1569, found 274.1574.

6-Methoxy-10,10-dimethyl-8,9,10,10a-tetrahydrocyclohepta-[*de*]naphthalen-1(7*H*)-one (27). To a solution of **26** (0.0625 g, 0.228 mmol) in CH_2Cl_2 (10 mL) was added one drop of H_2SO_4 at 0 °C. After 0.5 h of stirring, a conventional extractive workup (CH_2Cl_2) followed by preparative TLC (10:1 petroleum ether:Et_2O) afforded **27** (0.0410 g, 70% yield): mp 85−87 °C; IR (KBr) υ_{max} 2934, 1653, 1615 cm^{-1}; ^{1}H NMR δ 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); ^{13}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^+); HRMS m/e for $C_{17}H_{20}O_2$ 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_2Cl_2 (50 mL) were added Et_3N (2 mL, excess) and acetic anhydride (2 mL, excess). After 1 h of stirring, the mixture was subjected to a conventional extractive workup. Recrystallization from Et_2O afforded **28** (2.1958 g, 94% yield) as a white crystalline solid: mp 121 °C; IR (KBr) υ_{max} 2938, 1751 cm^{-1}; ^{1}H NMR δ 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); ^{13}C NMR 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^+); HRMS for $C_{19}H_{16}O_3$ calcd 292.1099, found 292.1097.

Hexacarbonyl[μ-η^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_2Cl_2 (10 mL) was added **6b** (0.3120 g, 0.7534 mmol) and Bu_2BOTf (479 μL, 0.479 mmol) was added dropwise at 0 °C. After 1 h of continuous stirring, $NH_4Cl_{(aq)}$ was added and the mixture was subjected to a conventional extractive workup. The residue was purified by flash chromatography (2:1 petroleum ether:Et_2O) to give **29** (0.4150 g, 90% yield) as a red brown solid: IR (KBr) υ_{max} 2953, 2113, 2063, 2031, 1765, 1708 cm^{-1}; ^{1}H NMR δ 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}C NMR 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 (M^+ − 2CO), 590 (M^+ − 3CO), 506 (M^+ − 6CO); HRMS m/e for $C_{30}H_{20}Co_2O_{11}$ calcd (M^+ − 2CO) 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** (0.1880 g, 90% yield): mp 144 °C; IR (KBr) υ_{max} 2956, 2234, 1761, 1712 cm^{-1}; ^{1}H NMR δ 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}C NMR 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 (M^+); HRMS m/e for $C_{24}H_{20}O_5$ 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 H_2 was added Rh/C (excess) at room temperature. The solution was stirred for 18 h with monitoring by TLC. The suspension was filtered and the solvent was removed under reduced pressure. Preparative TLC (2:1 petroleum ether:Et_2O)

gave **31** (0.1880 g, 93% yield): bp 180−185 °C (0.15 Torr); IR (KBr) υ_{max} 2956, 1763, 1731 cm^{-1}; ^1H NMR δ 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}C NMR 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 (M^+); HRMS m/e for $C_{24}H_{24}O_5$ 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 H_2 was added Pd/C (excess) at room temperature. The solution was stirred for 4 h with monitoring by TLC. The suspension was filtered and the solvent was removed under reduced pressure. Preparative TLC (1:1 petroleum ether:Et_2O) afforded **32** (0.1400 g, 96% yield): mp 80−81 °C; IR (KBr) υ_{max} 3425 br, 2952, 1759, 1733 cm^{-1}; ^1H NMR δ 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); ^{13}C NMR 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^+); HRMS m/e for $C_{17}H_{18}O_5$ 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_2Cl_2 (20 mL) were added pyridine (136 μL,1.69 mmol) and Tf_2O (105 μL, 0.625 mmol) sequentially. The reaction mixture was stirred for 0.5 h. Following a coventional extractive workup (CH_2Cl_2), preparative TLC (1:1 petroleum ether:Et_2O) afforded **33** (0.2347 g, 96% yield) as a viscous oil: IR (KBr) υ_{max} 2955, 1765, 1738 cm^{-1}; ^1H NMR δ 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); ^{13}C NMR 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_{CF} = 319.8), 115.9, 51.6, 33.4, 25.6, 24.8, 21.1; MS m/e 434 (M^+); HRMS m/e for $C_{18}H_{17}F_3O_7S$ 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 $Pd_2(dba)_3$ (0.0058 g, 0.0063 mmol) and (2-biphenyl)dicyclohexylphosphine (0.0045 g, 0.013 mmol) in anhydrous THF (20 mL) were added DABAL-Me_3 (0.0987 g, 0.385 mmol in THF) and **33** (0.1860 g, 0.4281 mmol, in THF (2 mL)) sequentially. After 0.5 h of stirring, dilute HCl (1 M) was added. After conventional extractive workup (Et_2O), the residue was subjected to preparative TLC, which afforded, in order of elution (1:1 petroleum ether:Et_2O), **34** (0.1080 g, 84% yield) and **35** (0.0080 g, 7% yield). **34**: colorless crystals, mp 48 °C; (KBr) υ_{max} 2951, 1769, 1736 cm^{-1}; ^1H NMR δ 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); ^{13}C NMR 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**: viscous oil; (KBr) υ_{max} 3395 br, 2953, 1736 cm^{-1}; ^1H NMR δ 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 NMR 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 °C was added MeLi (0.59 mL, 1.5 M in Et_2O, 0.89 mmol). After 4 h 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 °C; IR (KBr) υ_{max} 3312 (br), 2968, 1635 cm^{-1}; ^1H NMR δ (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 NMR (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(7*H*)-one (37). To a solution of **36** (0.0260 g, 0.101 mmol) in CH_2Cl_2 (10 mL) was added H_2SO_4 (1 drop) and the solution was stirred for 4 h. 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 °C; IR (KBr) υ_{max} 2955, 1654 cm^{-1}; ^1H NMR δ 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 NMR 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(7*H*)-one (38) and (2*R,3*R**,10a*S**)-10a-Hydroxy-6,10,10-trimethyl-8,9,10,10a-tetrahydrocyclohepta[*de*]naphthalen-1(7*H*)-one 2,3-Oxide (39).** To a solution of **37** (0.0200 g, 0.0833 mmol) in dry DMF (3 mL) was added NaH (0.0024 g, 0.10 mmol). After the reaction mixture was stirred for 3 h in open air, it was subjected to a conventional extractive workup (Et_2O). Preparative TLC (1:1 hexanes:CH_2Cl_2) gave, in order of elution, **38** (0.0090 g, 42% yield) and **39** (0.0070 g, 31% yield). **38**: mp 102 °C; IR (KBr) υ_{max} 3450, 2959, 1657 cm^{-1}; ^1H NMR δ 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); ^{13}C NMR 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^+); HRMS m/e for $C_{17}H_{20}O_2$ calcd 256.1463, found 256.1473. **39**: mp 110−111 °C IR (KBr) υ_{max} 3456, 2924, 1698 cm^{-1}; ^1H NMR δ 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); ^{13}C NMR 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^+); HRMS m/e for $C_{17}H_{20}O_3$ calcd 272.1412, found 272.1404. ^1H 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 and 4.21 ppm (epoxide CH) resonances support a cis-relationship between the OH and epoxy functions.

3-Bromonaphthalene-2,7-diol (41). 41 was prepared according to the method of Diederich:[36] mp 187−188 °C (lit.[36] mp 191−192 °C). This compound has >95% purity as determined by ^1H and ^{13}C NMR spectroscopy.

6-Bromo-7-(methoxymethoxy)naphthalen-2-ol (42). 42 was prepared according to the method of Diederich:[27] mp 109−110 °C (lit.[27] 107−108 °C). This compound has >95% purity as determined by ^1H and ^{13}C NMR spectroscopy.

6-(Benzyloxy)-2-bromo-3-(methoxymethoxy)naphthalene (43). 43 was prepared according to the method of Diederich:[27] mp 114−115 °C (lit.[27] mp 114−115 °C). This compound has >95% purity as determined by ^1H and ^{13}C NMR spectroscopy.

7-(Benzyloxy)-3-bromonaphthalen-2-ol (40). 40 was prepared according to the method of Diederich:[27] mp 153−154 °C (lit.[27] mp

(36) Martinborough, E.; Denti, T. M.; Castro, P. P.; Wyman, T. B.; Knobler, C. B.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 1037–1066.

153−154 °C). This compound has >95% purity as determined by ^{1}H and ^{13}C NMR spectroscopy.

2-Acetoxy-7-benzyloxy-3-bromonaphthalene (44). To a solution of **44** (1.500 g, 4.573 mmol) in CH_2Cl_2 (50 mL) was added Et_3N (1 mL, excess) and acetic anhydride (1 mL, excess). After 0.5 h, the reaction mixture was concentrated under reduced pressure. Recrystallization from CH_2Cl_2:petroleum ether gave **44** as a colorless crystalline solid (1.624 g, 4.390 mmol, 96%): mp 125−126 °C (CH_2Cl_2−petroleum ether); IR (KBr) υ_{max} 2940, 1773 cm^{-1}; ^{1}H NMR δ 8.03 (s, 1H), 7.65 (d, J = 9.0, 1H), 7.52 (d, J = 7.5, 2H), 7.51 (s, 1H), 7.46 (t, J = 7.5, 2H), 7.41 (t, J = 7.5, 1H), 7.25 (dd, J = 9.0, 2.5, 1H), 7.13 (dd, J = 2.5, 1H), 5.15 (s, 2H), 2.45 (s, 3H); ^{13}C NMR 168.7, 157.3, 145.7, 136.3, 133.8, 131.7, 128.5, 128.3, 128.3, 128.0, 127.9, 127.4, 120.0, 112.0, 106.6, 69.8, 20.7; MS m/e 370 (M^+); HRMS m/e for $C_{19}H_{15}BrO_3$ calcd (M^+) 370.0205, found 370.0193.

2-Acetoxy-7-benzyloxy-3-(prop-1-en-2-yl)naphthalene (45). To a solution of Na_2CO_3 (0.746 g, 5.405 mmol) in degassed water (3 mL) was added a solution of **44** (0.500 g, 1.351 mmol), isopropenylboronic acid pinacol ester (508 μL, 2.70 mmol), [$Pd(PPh_3)_4$] (0.078 g, 0.067 mmol), and LiCl (0.172 g, 4.054 mmol) in DME (20 mL). The resulting solution was stirred for 12 h at 80 °C before it was diluted with water. The crude product was extracted from aqueous phase with Et_2O. The organic extract was dried over $MgSO_4$, the solvent was evaporated to obtain pure product **45** (0.359 g, 1.081 mmol, 80%) as a colorless crystalline solid following flash chromatography (petroleum ether:Et_2O, 5:1): mp 91−92 °C; IR (KBr) υ_{max} 2921, 1762, 1633 cm^{-1}; ^{1}H NMR δ 7.80 (obscured d, J = 8.9, 1H), 7.79 (s, 1H), 7.56 (d, J = 7.3, 2H), 7.51 (s, 1H), 7.49 (apparent t, J = 7.6, 2H), 7.43 (t, J = 7.2, 1H), 7.31 (dd, J = 8.9, 2.5, 1H), 7.23 (dd, J = 2.5, 1H), 5.37 (s, 1H), 5.28 (s, 1H), 5.21 (s, 2H), 2.40 (s, 3H), 2.28 (s, 3H); ^{13}C NMR 169.3, 157.0, 146.5, 141.6, 136.6, 134.0, 133.1, 129.1, 128.4, 127.8, 127.7, 127.3, 127.0, 119.0, 118.6, 115.8, 106.4, 69.8, 23.4, 20.9; MS m/e 332 (M^+); HRMS m/e for $C_{22}H_{20}O_3$ calcd (M^+) 332.1412, found 332.1409.

2-Acetoxy-7-benzyloxy-3-isopropylnaphthalene (46). To a solution of **45** (0.500 g, 1.506 mmol) in ethyl acetate (25 mL) was added Rh/C (0.0050 g). The reaction was stirred for 2 h under an H_2 atmosphere, with monitoring by TLC. The reaction mixture was filtered and the solvents evaporated under reduced pressure to afford a colorless solid, which upon recrystallization (petroleum ether−Et_2O) to give **46** as a colorless crystalline solid (0.463 g, 1.386 mmol, 92% yield): mp 91−92 °C; IR (KBr) υ_{max} 2963, 1759 cm^{-1}; ^{1}H NMR δ 7.79 (d, J = 9.0, 1H), 7.77 (s, 1H), 7.55 (d, J = 7.2, 2H), 7.484 (apparent t, J = 7.3, 2H), 7.476 (s, 1H), 7.41 (t, J = 7.3, 1H), 7.28 (dd, J = 9.0, 2.5, 1H), 7.22 (dd, J = 2.5, 1H), 5.21 (s, 2H), 3.21 (septet, J = 6.9, 1H), 2.45 (s, 3H), 1.41 (d, J = 6.9, 6H); ^{13}C NMR 169.6, 156.6, 147.5, 137.0, 136.7, 133.2, 128.9, 128.5, 127.9, 127.5, 127.4, 125.2, 118.8, 118.4, 106.5, 69.8, 27.7, 23.0, 20.9; MS m/e 334 (M^+); HRMS m/e for $C_{22}H_{22}O_3$ calcd (M^+) 334.1569, found 334.1563.

Hexacarbonyl[μ-η^4-(methyl 4-(7-acetoxy-2-(benzyloxy)-6-isopropylnaphthalen-1-yl)but-2-ynoate)]dicobalt (47). To a solution of **46** (0.600 g, 1.80 mmol) in CH_2Cl_2 (30 mL) was added cobalt complex **6b** (0.818 g, 1.98 mmol) and BF_3−OEt_2 (680 μL, 5.39 mmol) at 0 °C. The mixture was stirred for 4 h under nitrogen and then $NH_4Cl_{(aq)}$ was added. After a conventional workup the volatiles were evaporated under reduced pressure to give reddish brown solid, which was subjected to column chromatography (petroleum ether:Et_2O, 10:1) to give product **47** (1.145 g, 1.599 mmol, 89% yield) as a reddish brown solid: mp 115 °C dec; IR (KBr) υ_{max} 2964, 2095, 2058, 2031, 1759, 1706 cm^{-1}; ^{1}H NMR δ; 7.76 (d, J = 9.0, 1H), 7.72 (s, 1H), 7.62 (s, 1H), 7.48 (d, J = 7.3, 2H), 7.41 (apparent t, J = 7.4, 2H), 7.34 (t, J = 7.3, 1H), 7.30 (d, J = 9.0, 1H), 5.27 (s, 2H), 4.68 (br s, 2H), 3.66 (s, 3H), 3.14 (septet, J = 6.8, 1H), 2.39 (s, 3H), 1.35 (d, J = 6.8, 6H); ^{13}C NMR 198.2, 170.5, 169.6, 153.5, 148.1, 137.4, 136.8, 131.7, 128.5, 128.4, 127.8, 127.8, 127.3, 126.1, 120.5, 115.5, 113.4, 98.4, 78.7, 70.7, 52.5, 28.9, 27.6, 23.02, 22.95, 20.8; MS m/e 716 (M^+); HRMS m/e for $C_{33}H_{26}O_{11}Co_2$ calcd (M^+ − 6CO) 548.0473, found 548.0486.

Methyl 4-(7-Acetoxy-2-(benzyloxy)-6-isopropylnaphthalen-1-yl)but-2-ynoate (48). To a solution of **47** (0.830 g, 1.16 mmol) in THF (50 mL) was added I_2 (excess). After 1 h, aqueous sodium bisulfite was added. After a conventional workup (Et_2O) and removal of volatiles under reduced pressure, the resulting colorless solid was recrystallized from methanol to give **48** as colorless crystals (0.435 g, 1.01 mmol, 87% yield): mp 92−93 °C; IR (KBr) υ_{max} 2962, 2233, 1757, 1712 cm^{-1}; ^{1}H NMR δ 7.74 (d, J = 9.0, 1H), 7.71 (s, 1H), 7.59 (s, 1H), 7.48 (d, J = 7.3, 2H), 7.41 (apparent t, J = 7.4, 2H), 7.34 (t, J = 7.3, 1H), 7.26 (d, J = 9.0, 1H), 5.25 (s, 2H), 4.12 (s, 2H), 3.72 (s, 3H), 3.11 (septet, J = 6.9, 1H), 2.43 (s, 3H), 1.33 (d, J = 6.9, 6H); ^{13}C NMR 169.7, 154.1, 153.4, 148.2, 137.6, 136.8, 131.6, 128.9, 128.6, 128.0, 127.3, 127.2, 126.2, 115.5, 115.1, 114.6, 87.6, 72.2, 71.4, 52.4, 27.7, 23.0, 21.0, 15.0; MS m/e 430 (M^+); HRMS m/e for $C_{27}H_{26}O_5$ calcd (M^+) 430.1780, found 430.1797.

Methyl 4-(7-Acetoxy-2-hydroxy-6-isopropylnaphthalen-1-yl)-butanoate (49). To a solution of **48** (0.530 g, 1.23 mmol) in ethyl acetate (20 mL) was added excess Pd/C. The reaction mixture was stirred for 15 h under an H_2 atmosphere. The mixture was filtered and the volatiles were removed under reduced pressure to give a residue that was further subjected to preparative TLC (petroleum ether:Et_2O, 1:1) to give **49** as a viscous oil (0.356 g, 1.03 mmol, 84%): IR (KBr) υ_{max} 3427 br, 2962, 1756, 1735 cm^{-1}; ^{1}H NMR δ 7.67 (s, 1H), 7.56 (d, J = 8.8, 1H), 7.50 (s, 1H), 7.12 (br s, 1H), 7.05 (d, J = 8.8, 1H), 3.75 (s, 3H), 3.09 (septet, J = 6.8, 1H), 3.00 (t, J = 7.6, 2H), 2.42 (obscured m, 2H), 2.42 (s, 3H), 1.96 (m, 2H), 1.32 (d, J = 6.8, 6H); ^{13}C NMR 175.2, 170.3, 151.5, 147.4, 135.7, 132.0, 127.5, 127.0, 126.0, 118.1, 117.8, 114.7, 77.2, 51.5, 32.7, 27.4, 24.3, 23.7, 22.9, 20.8; MS m/e 344 (M^+); HRMS m/e for $C_{20}H_{24}O_5$ calcd (M^+) 344.1624, found 344.1622.

Methyl 4-(7-Acetoxy-6-isopropyl-2-(trifluoromethylsulfonyloxy)naphthalen-1-yl)butanoate (50). To solution of **49** (0.346 g, 1.01 mmol) in CH_2Cl_2 (20 mL) were added $(F_3CSO_2)_2O$ (204 μL, 1.21 mmol) and pyridine (204 μL, 3.02 mmol) at room temperature. The solution was stirred for 0.5 h. After a conventional extractive workup (CH_2Cl_2), the volatiles were removed under reduced pressure to give a crude product, which was subjected to preparative TLC (petroleum ether:Et_2O, 5:1) to give **50** (0.396 g, 0.832 mmol, 83%) as a viscous oil: IR (KBr) υ_{max} 2967, 1763, 1739 cm^{-1}; ^{1}H NMR δ 7.80 (s, 1H), 7.79 (s, 1H), 7.76 (d, J = 9.1, 1H), 7.34 (d, J = 9.1, 1H), 3.71 (s, 3H), 3.12−3.18 (m, 3H), 2.46 (t, J = 7.1, 2H), 2.44 (s, 3H), 2.03 (m, 2H), 1.33 (d, J = 6.9, 6H); ^{13}C NMR 173.1, 169.2, 148.4, 144.8, 140.8, 131.3, 131.1, 129.2, 128.3, 126.3, 118.7, 118.4 (d, J_{CF} = 319 Hz), 116.9, 51.1, 33.1, 27.7, 25.3, 24.7, 22.5, 20.6; MS m/e 476 (M^+); HRMS m/e for $C_{21}H_{23}F_3O_7S$ calcd (M^+) 476.1117, found 476.1115.

Methyl 4-(7-Acetoxy-6-isopropyl-2-methylnaphthalen-1-yl)butanoate (51). To a solution of **50** (0.390 g, 0.819 mmol) in THF (20 mL) were added $Pd_2(dba)_3$ (0.011 g, 0.012 mmol), dicyclohexyl-(2-phenylphenyl)phosphane (0.0090 g, 0.026 mmol), and DABAL-Me_3 (0.168 g, 0.656 mmol). The reaction mixture was heated to reflux for 1 h, followed by the addition of a dilute HCl solution. After a conventional extractive workup (Et_2O) and evaporation of the volatiles under reduced pressure, the crude product was subjected to preparative TLC (petroleum ether:Et_2O, 5:1) to give **51** (0.255 g, 0.7456 mmol, 91%) as a viscous oil: IR (KBr) υ_{max} 2962, 1760, 1737 cm^{-1}; ^{1}H NMR δ 7.75 (s, 1H), 7.72 (s, 1H), 7.63 (d, J = 8.2, 1H), 7.28 (d, J = 8.2, 1H), 3.74 (s, 3H), 3.16 (septet, J = 6.9, 1H), 3.07 (m, 2H), 2.52 (obscured m, 2H), 2.52 (s, 3H), 2.45 (s, 3H), 1.99 (m, 2H), 1.38 (d, J = 6.9, 6H); ^{13}C NMR 173.6, 169.7, 147.2, 137.9, 134.0, 132.7, 131.0, 130.9, 128.8, 125.9, 125.6, 115.7, 51.3, 33.7, 27.8, 27.6, 24.8, 22.9, 20.9, 19.8; MS m/e 342 (M^+); HRMS m/e for $C_{21}H_{26}O_4$ calcd (M^+) 342.1831, found 342.1824.

8-(4-Hydroxy-4-methylpentyl)-3-isopropyl-7-methylnaphthalen-2-ol (52). To a solution of **51** (0.221 g, 0.646 mmol) in Et_2O (20 mL) was added MeLi (1.5 M in Et_2O, 3.0 mL, 4.5 mmol) at 0 °C. The reaction mixture was stirred for 6 h at which time $NH_4Cl_{(aq)}$ was added. The mixture was subjected to conventional extractive workup (Et_2O). The volatiles were evaporated under reduced pressure to give a crude product, which was subjected to preparative TLC (petroleum ether:Et_2O, 1:1) to give **52** (0.178 g, 0.593 mmol, 92%) as a colorless solid: mp 141−142 °C; IR (KBr) υ_{max} 3348 br, 2963, 1630 cm^{-1}; ^1H NMR δ 7.61 (s, 1H), 7.54 (d, J = 8.3, 1H), 7.39 (br s, 1H), 7.33 (s, 1H), 7.13 (d, J = 8.3, 1H), 3.41 (septet, J = 6.9, 1H), 2.96 (m, 2H), 2.60 (br s, 1H), 2.46 (s, 3H), 1.73 (m, 4H), 1.37 (d, J = 6.9, 6H), 1.25 (s, 6H); ^{13}C NMR 152.8, 135.8, 133.4, 132.0, 131.6, 128.0, 126.4, 125.6, 125.5, 105.8, 72.0, 43.8, 29.3, 29.1, 27.2, 24.4, 22.7, 20.1; MS m/e 300 (M^+); HRMS m/e for $C_{20}H_{28}O_2$ calcd (M^+) 300.2089, found 300.2085.

2-Isopropyl-6,10,10-trimethyl-8,9,10,10a-tetrahydrocyclohepta-[*de*]naphthalen-1(7*H*)-one (53). To a solution of **52** (0.170 g, 0.566 mmol) in CH_2Cl_2 was added one drop of concentrated H_2SO_4 at room temperature. The reaction mixture was stirred for 1 h. After a conventional extractive workup (CH_2Cl_2) and evaporation of the volatiles under reduced pressure, the crude product was subjected to preparative TLC (petroleum ether:Et_2O, 20:1) to give **53** (0.130 g, 0.461 mmol, 81%) as a colorless solid: mp 46−47 °C; IR (KBr) υ_{max} 2958, 1655 cm^{-1}; ^1H NMR δ 7.06 (m, 3H), 3.66 (s, 1H), 3.04 (apparent septet, J = 6.9, 1H), 2.96 (m, 1H), 2.67 (m, 1H), 2.34 (s, 3H), 1.87 (m, 1H), 1.49 (m, 1H), 1.36 (m, 1H), 1.25 (m, 1H), 1.17 (s, 3H), 1.16 (d, J = 6.9, 3H), 1.14 (d, J = 6.9, 3H), 0.62 (s, 3H); ^{13}C NMR 203.0, 143.0, 138.9, 138.6, 138.2, 135.4, 128.9, 128.7, 126.0, 58.3, 43.2, 37.3, 27.3, 26.4, 25.8, 24.3, 22.0, 21.8, 20.4, 20.3; MS m/e 282 (M^+); HRMS m/e for $C_{20}H_{26}O$ calcd (M^+) 282.1984, found 282.1991.

10a-Hydroxy-2-isopropyl-6,10,10-trimethyl-8,9,10,10a-tetrahydrocyclohepta[*de*]naphthalen-1(7*H*)-one ((±)-Microstegiol) (1). To a solution of **53** (0.052 g, 0.18 mmol) in DMF (10 mL) was added NaH (0.0067 g, 0.28 mmol). The reaction mixture was stirred for 12 h under oxygen. After a conventional extractive workup (Et_2O) and evaporation of volatiles under reduced pressure, the crude product was subjected to preparative TLC (petroleum ether:Et_2O, 50:1) to give **1** (0.035 g, 64%) as a colorless solid: mp 57−58 °C (lit.[1a] (enantiomerically pure material) mp 69−70 °C); IR (KBr) υ_{max} 3443, 2962, 1654 cm^{-1}; ^1H NMR δ 7.07 (d, J = 7.5, 1H), 6.97 (s, 1H), 6.91 (d, J = 8.0, 1H), 4.52 (s, 1H), 3.61 (apparent t, J = 13.1, 1H), 3.00 (apparent septet, J = 6.9, 1H), 2.79 (ddd, J = 14.1, 6.4, 2.3, 1H), 2.37 (m, 1H), 2.33 (s, 3H), 1.82 (m, 1H), 1.47 (m, 1H), 1.29 (m, 1H), 1.21 (d, J = 6.0, 3H), 1.16 (d, J = 6.9, 3H), 0.80 (s, 3H), 0.79 (s, 3H); ^{13}C NMR 206.1, 143.3, 141.0, 140.9, 139.3, 137.4, 130.1, 129.0, 126.7, 84.4, 42.9, 39.0, 28.0, 27.0, 26.8, 23.5, 22.1, 21.7; MS m/e 298 (M^+); HRMS m/e for $C_{20}H_{26}O_2$ calcd (M^+) 298.1933, found 298.1940.

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