Cyclopentadienylcobalt-Mediated Intermolecular Cycloaddition of α,ω-Diynes to (Cyclo)alkenes: Synthesis of Linearly Fused Oligocycles and Extension to Enantiomerically Pure (6a*R*,10a*R*)-Dihydroanthracyclinones

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Received 26 March 2010

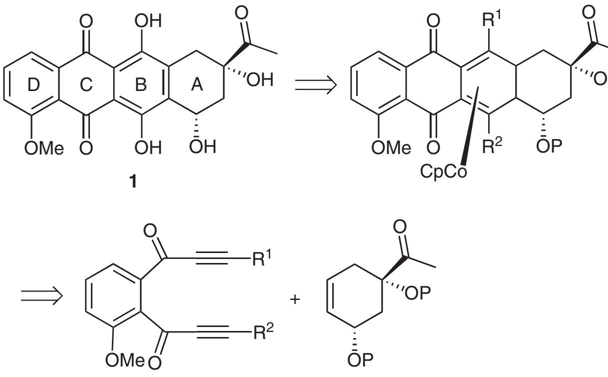
Dedicated to Professor Rolf Huisgen, whose introductory organic 'Experimentalvorlesung' doomed the corresponding author's ambitions as a rock 'n roll musician, on the occasion of his 90th birthday

Abstract: The generality of the [CpCoL$_2$]-mediated [2+2+2] cycloaddition of α,ω-diynes to (cyclo)alkenes has been extended to include linear oligocycles as models for the one-step, A + D → ABCD construction of optically pure, novel 6,10-dihydroanthracyclinones.

Key words: alkenes, alkynes, cycloadditions, polycycles, transition metals

Transition-metal-enabled [2+2+2] cycloadditions of unsaturated functionalities have emerged as a powerful strategy for ring construction in organic synthesis.[1] One of its topological variants is the intermolecular cocyclization of α,ω-diynes with (cyclo)alkenes to give fused cyclohexadienes.[1b,d,g,2] While much progress has been made on this approach, the published work indicates limitations with respect to the choice of diyne, alkene, functionality, selectivity toward the cyclic diene product, and lability of the latter to undergo rearrangements and/or aromatization.[2] We have used CpCoL$_2$ (L = CO or CH$_2$=CH$_2$) to effect cooligomerizations of alkynes with alkenes,[3] but the above option was employed only rarely and always within the context of a specific substrate.[4] This metal system has the advantage of providing the products in complexed, hence protected, form, from which the ligands are readily obtained by mild oxidative decomplexation, and appears to be the hitherto most versatile in functional scope. We report a comprehensive study of such cyclizations, which had as their ultimate goal the regioselective assembly of enantiopure antitumor daunomycinone (**1**) derivatives[5] according to Scheme 1.[6–8]

Table 1 depicts the simplest versions of the key reaction shown in Scheme 1, featuring octa-1,7-diyne (**2**; Figure 1) and various (cyclo)alkenes. The stereochemistry of the metal relative to the newly generated ring junction (*syn* or *anti*) was ascertained by ^{1}H NMR spectroscopy, including 2D techniques, as described at length previously.[1k,3,4] The relative disposition of the norbornane bridges in **9** and **10** was, in addition, secured by comparison with the data for analogous complexes derived by cocyclization of norbornene with diphenylacetylene.[9] While some diastereoselectivity for the *syn* cycloadducts was discerned (the metal emerging on the same side as the newly fused ring), frequently mixtures of both isomers were observed, the result of nearly isoenergetic pathways for *exo* versus *endo* complexation of the alkene in the intermediate cobaltacyclopentadiene and its subsequent insertion, as expected on the basis of DFT computational work.[4a,10] Most relevant to the stated aims in Scheme 1, the functionalized cyclohexenes in the last two entries to Table 1 failed in this chemistry. Switching from CpCo(CO)$_2$ to CpCo(CH$_2$=CH$_2$)$_2$ as a cobalt source, a strategy used to great advantage for other systems,[3,4] was unsuccessful, although cyclohexenone furnished some **15**. The major identifiable side product in all of these reactions was 1,4-bis(5,6,7,8-tetrahydronaphthalen-2-yl)butane, the alkyne cyclotrimerization product of **2**.[1k]



P = protecting group

Scheme 1

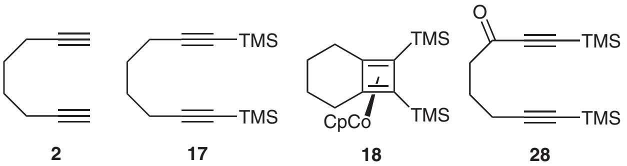


Figure 1 Octa-1,7-diynes **2**, **17**, and **28**, and cyclobutadiene **18**

SYNTHESIS 2010, No. 13, pp 2179–2200
Advanced online publication: 18.05.2010
DOI: 10.1055/s-0029-1220007; Art ID: C01210SS

Table 1 Cocyclization of Octa-1,7-diyne (**2**) with Various Alkenes[a]

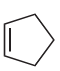
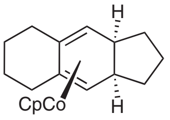
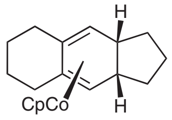
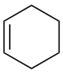
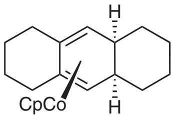
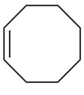
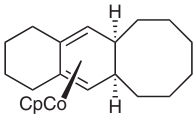
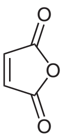
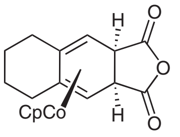
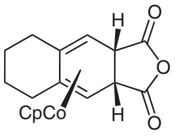
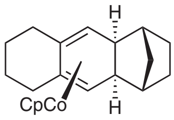
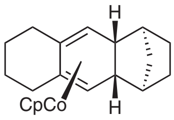
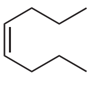
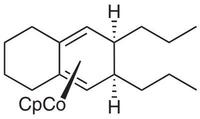
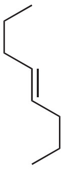
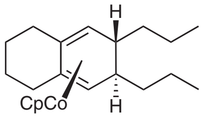
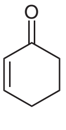
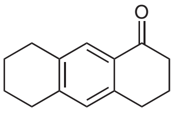
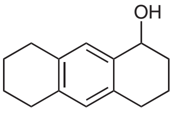
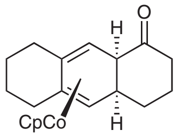
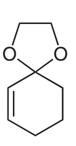
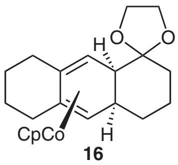
Alkene	Products	Yield (%)
	 **3** 2:1  **4**	28[b]
	 **5**	20
	 **6**	36
	 **7** 3:4  **8**	35
	 **9** 1:1  **10**	29[c]
	 **11**	23
	 **12**	18
	 **13** 1.0:1.2  **14**	37[d]
	 **15**	10[e]
	 **16**	1

Table 1 Cocyclization of Octa-1,7-diyne (**2**) with Various Alkenes[a] (continued)

[a] $CpCo(CO)_2$ (1.0 equiv), alkene (5 equiv), boiling *m*-xylene, *h*ν, 25–72 h.

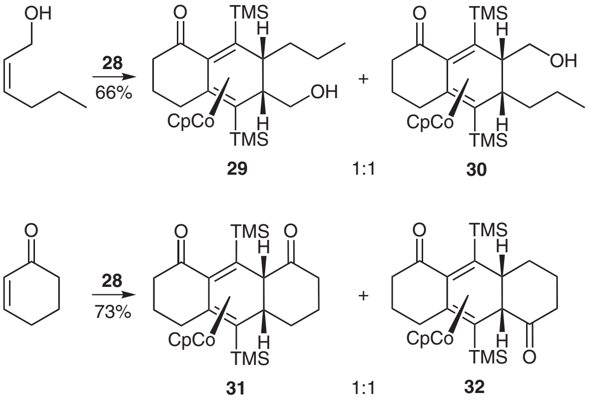
[b] Mixture from which **3** was selectively crystallized (MeOH).

[c] Mixture from which **9** was selectively crystallized (MeOH).

[d] Known compounds: **13**, see ref. 28; **14**, see ref. 29.

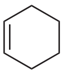
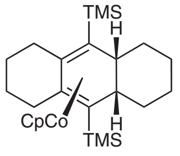
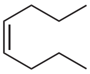
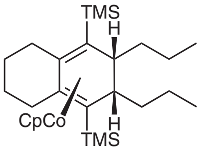
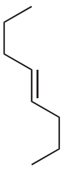
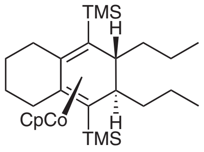
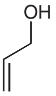
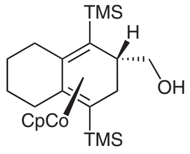
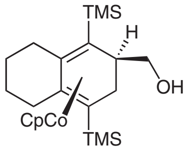
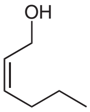
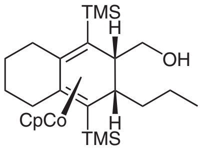
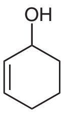
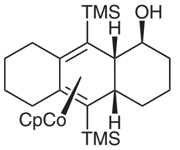
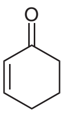
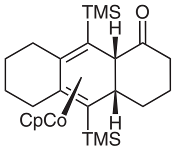
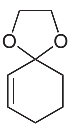
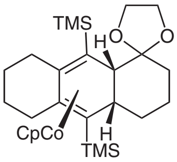
[e] Only product using $CpCo(CH_2{=}CH_2)_2$, Et_2O, r.t., 6 h.

To mitigate the undesired selfreactivity of **2**, the corresponding 1,8-bis(trimethylsilyl) derivative **17** was scrutinized, albeit with some trepidation, as previous attempts at employing this diyne as a cocyclization partner had furnished the corresponding cyclobutadiene (**18**; Figure 1) and cyclopentadienone cobalt complexes, possibly the result of excessive steric hindrance.[4d,11] Gratifyingly, and after extensive optimization procedures toward **19**, the results summarized in Table 2 were collected. The desired cycloadducts formed as only one diastereomer in moderate to good yields (with the exception of **27**), and the mass balances were good to excellent, the bulk of the side products constituting **18**. Compared to the dominant stereochemistry at cobalt in Table 1, one notes that it is largely inverted in Table 2. This is illustrated by example **19**, for which the tertiary hydrogens give rise to an ^{1}H NMR signal at $\delta = 1.87$, in contrast to the corresponding hydrogens in **5** ($\delta = 0.68$), but almost identical to those in **54** (vide infra; $\delta = 1.91$), the constitution of which rests on an X-ray structural analysis. Inspection of the calculated structures of the relevant transition states to alkene insertion into the Co–C bond of the cobaltacyclopentadiene unit[4a,10] reveals near eclipsing of the substituent α to Co (in the present case TMS) with the *exo* substituent on the adjacent (inserting) alkene carbon, thus favoring an *endo* pathway. As expected, the stereochemistry of the oct-4-ene substrates is retained in the respective products **11** and **12**. Encouraging for further synthetic applications is the successful generation of **22**–**26** and the considerably reduced sensitivity of all of the silylated complexes to manipulation in air.



Scheme 2 *Reagents and conditions*: $CpCo(CO)_2$ (1.1 equiv), alkene (10 equiv), boiling Et_2O, *h*ν, 60 h.

Table 2 Cocyclizations of 1,8-Bis(trimethylsilyl)octa-1,7-diyne (**17**) with Various Alkenes[a]

Alkene	Products	Yield (%)	**18** (%)
	 **19**	55	19
	 **20**	21	36
	 **21**	17	55
	 **22**  **23**	82 (ratio 4:3)	10
	 **24**	42	39
	 **25**	31[b]	44
	 **26**	40	50
	 **27**	4[c]	81

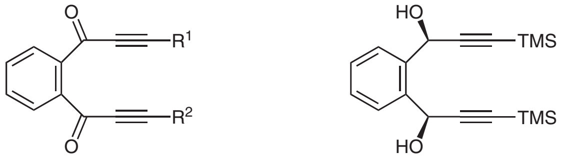
[a] $CpCo(CO)_2$ (1.1 equiv), alkene (10 equiv), boiling Et_2O, $h\nu$, 52 h.

[b] The stereochemistry at the hydroxy carbon is tentative and based on the assumption that in the intermediate cobaltacyclopentadiene cyclohexenol complex, the OH group is pointing away from the metal.

[c] In addition to **26** (2%).

In this vein, a brief excursion was made into testing the potential regioselectivity of an unsymmetrical diyne, namely the oxo derivative **28** (Figure 1), as a model for addressing the (more intricate) regiochemical problem embedded in Scheme 1 on route to **1**. This substrate could be synthesized readily by chromic acid oxidation of the known[12] alcohol precursor. Scheme 2 reveals that the presence of the symmetry breaking oxo group in **28** is inconsequential to the regio- (and stereo-) outcome of the cyclization, equimolar mixtures of both isomers being created, although in quite good yields. The regiochemical assignments of molecules **29** and **30** are tentative and are based on the observation of hindered rotation of the more deshielded TMS group in **29**. At room temperature, this phenomenon manifests itself in a severely broadened resonance at $\delta = 0.53$, sharpened on heating and decoalescing on cooling to three singlets ($\delta = 0.80$, 0.53, and 0.27). This signal was assigned to the silyl group β to the carbonyl function, the anisotropy of which should cause a relatively larger chemical shift, a supposition that is supported by the NMR spectra of a number of similar structures (vide infra). Molecular modeling (Chem 3D, MM2) indicates slightly greater crowding of this substituent in **29**, compared to **30**, leading to the respective structural choices. The presence of a similarly uniquely encumbered TMS moiety in **31** and related tentative arguments prompted the suggested connectivities of **31** and **32**. Hindered TMS-rotation in other CpCo-mediated cyclization products has been reported (and quantified) previously by us.[13]

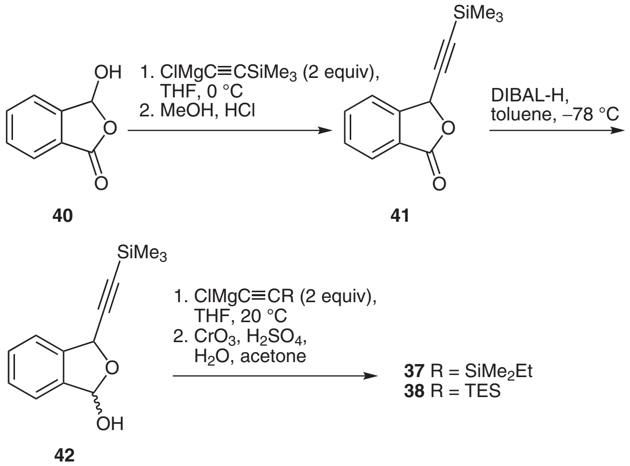
Undaunted by the unsolved issue of regioselectivity and encouraged by the reasonable yields, attention turned to cyclizations more directly addressing the topological features of Scheme 1 and involving the diynes shown in Figure 2. Of these diynes, **33**[14] and **34**[15] were known, and **35** and **36** were accessed in an analogous manner from benzenedicarboxaldehyde by alkynyl Grignard addition (sequential for **36**), followed by Cr(VI) oxidation. A selective sequence (Scheme 3)[16] was employed in the construction of **37** and **38**, starting from 3-hydroxyphthalide (**40**), via monoalkynylated **41**, its reduction to **42** (mixture of diastereomers and the hydroxy aldehyde isomer), and renewed one-pot alkynylation-oxidation. *Meso*-diol **39** is an intermediate on route to **34**, and was separated from its (minor; ratio 1.7:1) diastereomer by fractional crystallization.[17]



33 $R^1 = R^2 = H$
34 $R^1 = R^2 = TMS$
35 $R^1 = R^2 = SiMe_2(CMe_2CHMe_2)$
36 $R^1 = TMS, R^2 = SiMe_2(CMe_2CHMe_2)$
37 $R^1 = TMS, R^2 = SiMe_2Et$
38 $R^1 = TMS, R^2 = TES$

39

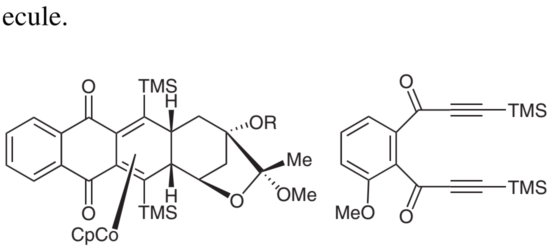
Figure 2 Diynes **33**–**39**



Scheme 3

The results of the cocycloadditions of these building blocks with various cyclohexenes are summarized in Table 3. In addition to the desired metallated dihydroanthraquinones, most runs also generated complexed cyclobutadienes and cyclopentadienones derived solely from the diyne substrate (see experimental section). Their proportion increased with the steric bulk of the diyne silyl groups or alkene component. Indeed, in attempted additions of **35** or **36** to cyclohexene or prop-2-en-1-ol, respectively, these were the only products isolated. In consonance with the results in Table 1, reaction of **33** was unselective and relatively low-yielding, compared to the corresponding transformations of **34** or **39**. Significantly, employment of the enantiomerically pure **47a**, which contains all the structural and stereochemical information embedded in the A ring,[18] furnished the corresponding (6a*R*,10a*R*)-dihydroanthracyclinone frames enantiospecifically. Disappointingly, however, attempts to exert regiocontrol, by means of two different silyl groups on the diyne, for example, using **37** or **38**, failed, the respective pairs of isomers **49**/**50** and **51**/**52** emerging in equimolar ratios. Nevertheless, **48**–**52** materialized with exquisite stereocontrol, established for **48** initially via extensive 2D NMR experiments and analysis of H–H coupling constants around the A ring (see experimental section). Eventually, two crystal structure analyses of analogues confirmed these assignments for the entire series (vide infra).[19] The structure of **54** was also ascertained by X-ray analysis, providing further confirmation of the configuration of the CpCo unit in all related complexes.[19]

As observed for **29** and **31** (Scheme 2), several of the products exhibited rotational encumbrance of (at least one) silyl group rotation on the NMR time scale, already visible at ambient temperature by either line broadening or decoalescence of the corresponding signal. The first example is **45** (broadened signal at r.t.; three singlets at –70 °C), for which VT NMR line shape analysis provided activation parameters $\Delta H^{\neq} = 8.42\ (\pm\ 0.04)\ \text{kcal mol}^{-1}$ and $\Delta S^{\neq} = -11.0\ (\pm\ 0.2)\ \text{cal mol}^{-1}\ \text{K}^{-1}$, comparable to those of previously scrutinized systems.[13] In the unsymmetrical **46**, only one TMS signal is broadened at 20 °C, assumed to be the one proximal to the benzoate function. The same TMS group in **48** (and all of its congeners, e.g., **50**, **52**, etc., vide infra) gives rise to three singlets at this temperature in both its ^1H and ^{13}C NMR spectra, evidently the result of increased encumbrance by the sterically rigid A ring. Relaxing this ring by quantitative conversion to the acetal **55** (Figure 3; CH_2Cl_2, MeOH) was inconsequential in this respect and served to illustrate the potential for functional group manipulations. The stereochemical assignment at the acetal carbon is tentative and predicated an attack by MeOH from the less hindered side of the molecule.



55 $R = SiMe_2(CMe_2CHMe_2)$

56

Figure 3 Acetal **55** and diyne **56**

Table 3 Cocyclizations of **33**–**39** with Various Cyclohexenes[a]

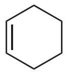
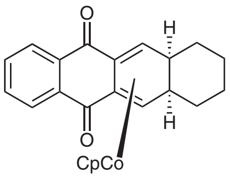
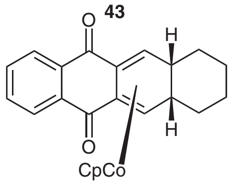
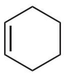
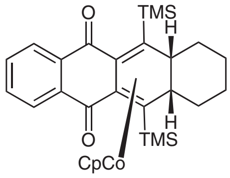
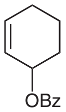
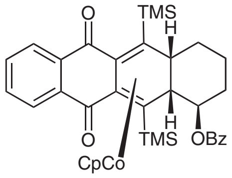
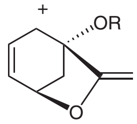
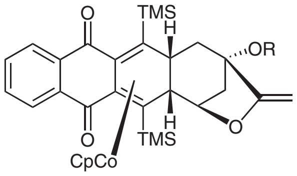
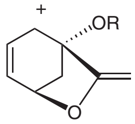
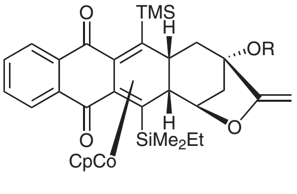
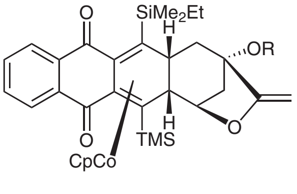
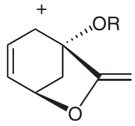
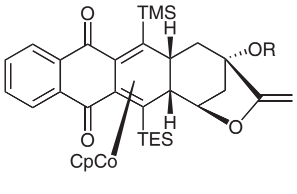
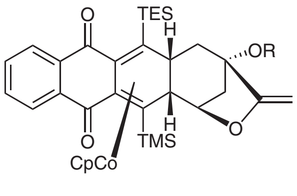
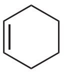
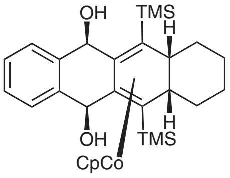
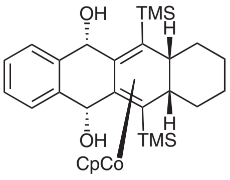
Substrates	Product	Yield (%)
33 + 	 **43**  **44** 1:1	19[b]

Table 3 Cocyclizations of **33**–**39** with Various Cyclohexenes[a] (continued)

Substrates	Product	Yield (%)
34 + 	 **45**	59[c]
34 + 	 **46**	31[c,d]
34 +  **47a**	 **48** R = $SiMe_2(CMe_2CHMe_2)$	44[e]
37 +  **47a**	 **49** R = $SiMe_2(CMe_2CHMe_2)$  **50** R = $SiMe_2(CMe_2CHMe_2)$ 1:1	16[f]
38 +  **47a**	 **51** R = $SiMe_2(CMe_2CHMe_2)$  **52** R = $SiMe_2(CMe_2CHMe_2)$ 1:1	18[f]
39 + 	 **53**  **54** 1:6	71[c]

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[a] $CpCo(CO)_2$ (1.3 equiv), alkene (10 equiv), solvent, r.t., *h*ν, 2–3 days. In the case of the valuable **47a**, most of the excess reagent could be recovered on chromatography.

[b] THF; inseparable mixture.

[c] Benzene.

[d] Stereochemistry at the benzoyloxycarbon tentative. See footnote b in Table 2.

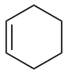
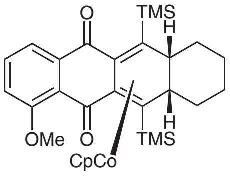
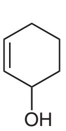
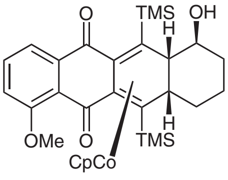
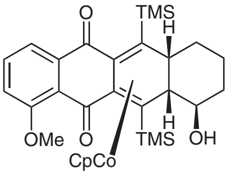
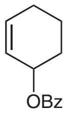
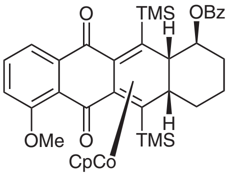
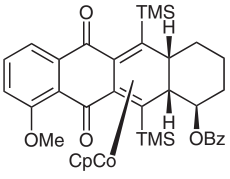
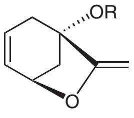
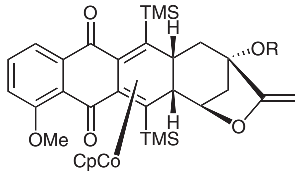
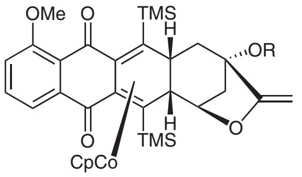
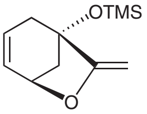
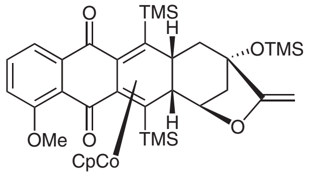
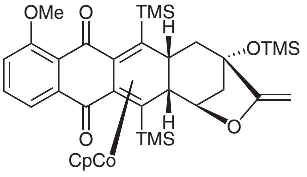
[e] Toluene.

[f] Boiling Et_2O.

The phenomenon of hindered ethyl(dimethyl)silyl rotation in **49** is particularly striking, as the different rotamers are, in fact, diastereomers. Indeed, at 20 °C, a complex set of resonances indicative of the presence of three isomers was visible by NMR spectroscopy. Specifically, the well separated signal due to the hydrogen next to the enol ether oxygen appeared as three doublets of doublets at $\delta = 4.82$, 4.79, and 4.76 (J = ~7, 4 Hz) in the ratio 1:2:2, reflecting the relative distribution of these rotamers. All these multiple signals (^1H and ^{13}C) coalesced to that of a single species at 100 °C. In contrast, the 'frozen', symmetrical TES substituent in **51** engendered simply three different sets of peaks for the ethyl groups.

In a last set of experiments, the remaining missing component of Scheme 1, the 4-methoxy appendage, was installed by way of diyne **56** (Figure 3), prepared in a manner identical to **34** from 3-methoxyphthalaldehyde.[20] The outcome of its cocyclizations is assembled in Table 4. Notably, but perhaps not surprisingly in light of the results obtained with **28**, **37**, and **38**, the desymmetrizing methoxy group in **56** did not influence the regioselectivity of the cycloaddition to unsymmetrical cyclohexenes, in all cases (nearly) equimolar mixtures being formed, although again with remarkable stereoselectivity. That the pairs **58**/**59** and **60**/**61** are indeed regio- and not stereoisomers was surmised by the near identity of the spectral data of the respective components in each pair, in addition to the likeness of the relevant spectral components with those of **25** and **46**. Similar arguments apply to the pair **62**/**63**. To cement them, a deliberate effort was made to obtain crystals of suitable derivatives amenable for X-ray crystal analysis. Such emerged by way of **47b** and its cyclization to isomers **64** and **65**, which, on treatment with TBAF furnished the crystalline alcohols **66** and **67** (Figure 4), respectively, the structures of which could be determined unambiguously.[19] This circuitous route was necessitated by the inertness of **47a**, **62**, and **63** to deprotection, using a variety of fluoride sources. Therefore, **47b** had to be made by modification of the route to **47a** from **68**,[18] as portrayed in Scheme 4.

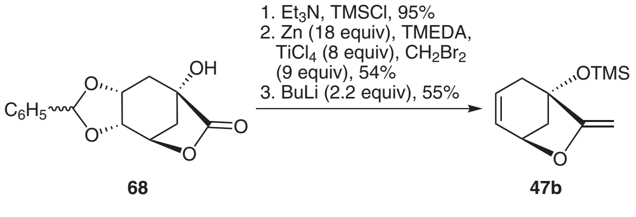
Table 4 Cocyclizations of **56** with Various Cyclohexenes[a]

Cyclohexene	Products	Yield (%)
	 **57**	43
	 **58**  **59** 5:6	56[b]
	 **60**  **61** 4:5	39[c]
 **47a**	 **62** R = $SiMe_2(CMe_2CHMe_2)$  **63** R = $SiMe_2(CMe_2CHMe_2)$ 1:1	20
 **47b**	 **64**  **65** 1:1	22

[a] $CpCo(CO)_2$ (1.1 equiv), alkene (10 equiv), boiling Et_2O, *hν*, 1–3 d.

[b] Stereochemistry at the hydroxycarbon tentative. See footnote b in Table 2.

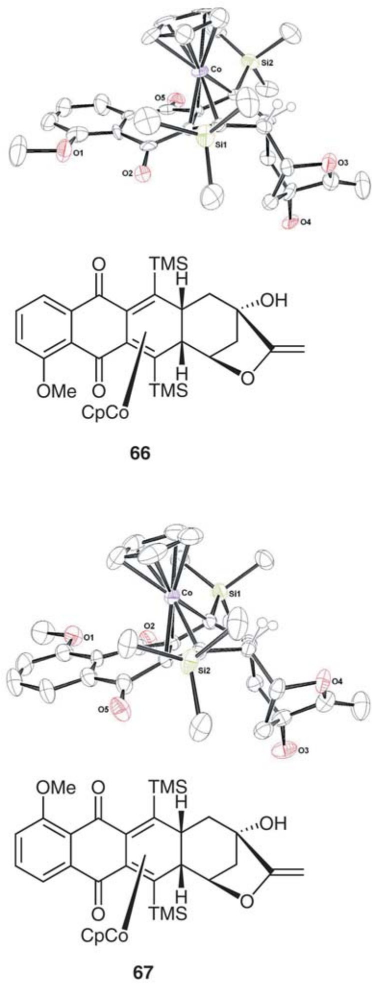
[c] Stereochemistry at the benzoyloxycarbon tentative. See footnote d in Table 3.



Scheme 4

Again, with the exception of **57**, all compounds in Table 4 and Figure 4 exhibited NMR data showing restricted rotation of one TMS group at room temperature (three singlets), assigned to be located proximal to the A ring oxygen substituent.

To demonstrate further synthetic utility of the complexes described so far and to further corroborate the structural



66

67

Figure 4 X-ray crystal structures of **66** and **67**

assignments, a representative sample of them was oxidatively demetallated, in most cases using copper(II) (Table 5). Monitoring these reactions by ^{1}H NMR showed high-yielding conversions, but isolated yields suffered either from the sensitivity of the products or the small scale of the experiments. It should be noted that all of these and other ligands reported in this paper were unknown. The stereoconvergent production of **69**–**71** from the pairs **5**/**6**, **7**/**8**, and **9**/**10**, respectively, confirmed the stereochemical assignments of the precursors as diverging only with respect to the disposition of the CpCo-unit. Conversely, **53**, **54**, **60**, and **61** each furnished a distinct respective isomer of ligand. All of the TMS containing products exhibited sharp singlets for this substituent, revealing free rotation on the NMR time scale. Interestingly, **53** underwent demetallation by simple dissolution in MeOH, conditions under which **54** (and **45**) are inert.

Several other exploratory reactions were performed, focusing primarily on **73** and its complex **45** as simplified representatives of the (6a,10a)-dihydroanthracyclinone core embedded in the examples in Table 4. Various tautomeric forms of this array have been implicated in the biological activity of the actual antitumor drugs.[21] As such, they constitute bisenone forms of the corresponding aromatic tetrahydrotetracenediols.[22] In this context, diene **73** was found to be remarkably resilient to aromatization. Mild acid left it intact, but dilute base caused a color change from yellow to red and eventual decomposition, indicative of the occurrence of redox processes[22b] and/or the generation of anions.[23] Treatment with excess NaH gave a red solution, which gradually turned green and gave rise to NMR spectra consistent with the presence of monoanion **78** (Figure 5). Attempted oxidation of **73** with MCPBA (3 equiv) in benzene furnished the monooxacyclopropane **79** (62%; stereochemistry surmised on mechanistic grounds), inert to further oxacyclopropanation. Other oxidizing agents (CAN, MnO$_2$, O$_2$) left **73** (and **76**/**77**) untouched. It is likely that the reluctance to aromatize the bissilylated cyclohexadiene moiety is due to the expected extreme buttressing expected on its planarization.[24] Consistent with this notion, exposure of complex **45** to BnNMe$_3^+$F$^-$ in THF (50 °C, 16 h) led to **44** (Table 3; 13%) and the known aromatic quinone **80** (65%).[25] Finally, the carbonyls in **45** may be subject to further stereoselective synthetic tinkering, as NaBH$_4$ (13 equiv, CH$_2$Cl$_2$, EtOH, r.t., 15 h) produced **81**, a larger excess of NaBH$_4$ (40 equiv) **53** (Table 3).

Table 5 Oxidative Demetallation of CpCo(cyclohexadiene) Complexes[a]

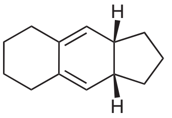
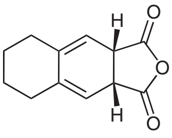
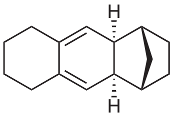
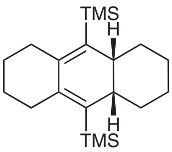
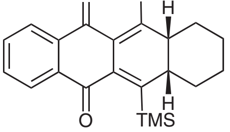
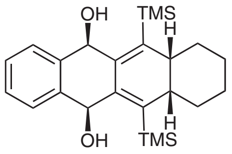
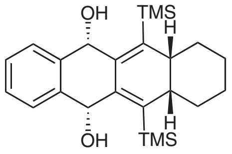
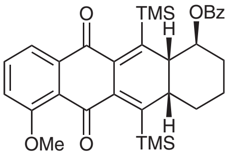
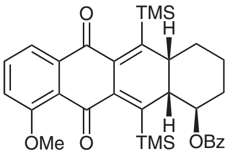
Complex	Free Diene	Yield (%)
3[b]	 **69**	17
7 + **8** (3:4)	 **70**	50[c]
9 + **10** (1:1)	 **71**	54
80	 **72**	91[d]
45	 **73**	74

Table 5 Oxidative Demetallation of CpCo(cyclohexadiene) Complexes[a] (continued)

Complex	Free Diene	Yield (%)
53	 **74**	52[e]
54	 **75**	46[f]
60 + **61** (4:5)	 **76**  **77** 4:5	71[g]

[a] CuCl$_2$·H$_2$O (5 equiv), Et$_3$N (5 equiv), THF, H$_2$O, 0 °C, 0.5–2.5 h, except as noted.

[b] A 2:1 mixture of **3** and **4** (Table 1) resulted in only **69**.

[c] CuCl$_2$·H$_2$O (5 equiv), EtOAc, MeCN, 0 °C, 5 min.

[d] 2 min.

[e] MeOH, r.t., 30 min.

[f] MCPBA, NaHCO$_3$, CH$_2$Cl$_2$, r.t., 2 min.

[g] Regiochemical assignments tentative.

In summary, we have filled a void in the literature of CpCo-mediated [2+2+2] cycloadditions by describing the reaction of α,ω-diynes (specifically octa-1,7-diynes) with (cyclo)alkenes to give linear di-, tri-, and tetracyclic cyclohexadiene complexes. Without silyl protection, the diynes give moderate yields of products, but bissilylation improves this outcome considerably. Using chiral, enantiomerically pure cyclohexene derivatives the method provides complexed analogues of the anthracyclinones. Some preliminary experiments demonstrate that these systems, in complexed or uncomplexed form, appear to be amenable to further synthetic manipulation.

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. THF, Et$_2$O, benzene, toluene, and *m*-xylene were distilled from sodium-benzophenone, while CH$_2$Cl$_2$ was purified over CaH$_2$. Maleic anhydride was recrystallized from Et$_2$O, norbornadiene was sublimed, while the remainder of the alkene starting materials and octa-1,7-diyne were purified by distillation. CpCo(CO)$_2$[26] (also commercially available) and CpCo(CH$_2$=CH$_2$)$_2$[27] were prepared by literature methods. BuLi and MeLi solutions were titrated with diphenylacetic acid. All reactions involving oxygen sensitive materials employed degassed solvents, the transfer of materials was carried out in a glove box, via syringe, or using standard Schlenk techniques, and the reaction mixtures were maintained under dry N$_2$, until workup. Irradiation was effected by a Sylvania ELH 300 W slide projector lamp, powered by a variable transformer at an applied potential of 40–60 V. Thin layer chromatography was done on EM Reagents Kieselgel 60 F254 or EM Reagents neutral Al$_2$O$_3$ 60 F254 sheets (0.2 mm coating). Flash chromatography employed EM Scientific SiO$_2$ (230–400 mesh), column chromatography Baker SiO$_2$ (60–200 mesh) or Alfa Al$_2$O$_3$ (60 mesh). High performance liquid chromatography (HPLC) was executed on an IBM LC/9533 instrument equipped with an LC/9522 fixed wavelength (254 nm) detector. For semi-preparative purposes, two columns, each 25 cm × 10 mm ID, packed with Microsorb 5 μm silica, were used two in sequence; preparative separations were carried out on 25 cm × 21.4 mm ID columns packed with Dynamax-60A 8 μm silica. Reverse phase HPLC relied on the same instrument but occurred on Microsorb 5 μm C18 (two columns in sequence) or Dynamax-60A 8 μm C18 packings under semipreparative and preparative conditions, respectively. Gas-liquid chromatography (GLC) was performed with a Hewlett-Packard 5880 instrument on a 6 ft × 2 mm ID glass column containing 3% OV-101 on Chromosorb W-HP (80/100 mesh), or a 30 m × 0.20 mm ID capillary column loaded with crosslinked 5% phenyl methyl silicone. Melting points were determined in open capillaries with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer model 241 polarimeter in a 10 cm quartz cell at ambient temperature. A Hewlett-Packard 8450A diode array spectrophotometer enabled the recording of UV-Vis spectra, while a Perkin-Elmer model 681 instrument facilitated related analyses in the IR range (polystyrene reference at 1601 cm^{-1}). ^{1}H and ^{13}C NMR (proton decoupled) spectra were collected on the UCB-200, UCB-250, BVX-300, AM-400, and AM-500 FT instruments. Although chemical shifts are reported in ppm downfield of TMS, they are referenced to the residual proton peak of the respective solvent for ^{1}H NMR, or the central peak of the solvent multiplet for ^{13}C NMR. In those cases in which DEPT ^{13}C NMR was employed, the chemical shift data are augmented by the labels in parentheses corresponding to the number of hydrogens directly bound to carbon. Selected assignments are based on additional 2D spectral correlations. The designation 'H$_{tert}$' refers to the complexed cyclohexadiene ring junction. Mass spectra were obtained on a Hewlett-Packard 5970A mass selective detector or provided by the Mass Spectral Service at UCB. Elemental analyses were performed by the UCB Analytical Service Facility. Products

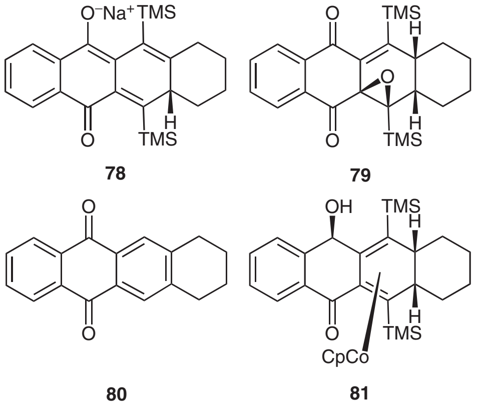


Figure 5 Compounds **78**–**81**

13,[28] and **14**[29] were known. Petroleum ether (PE) used refers to the fraction boiling in the range 30–40 °C.

Cocyclizations of Alkenes with Various Diynes; General Procedure

A 100 mL round-bottomed flask equipped with a magnetic stir bar and coil condenser was rinsed with hexamethyldisilazane and dried at 100 °C for 1 h. It was then charged with the alkene (5–10 equiv) in anhyd toluene (50 mL) or Et_2O (10 mL), degassed by three freeze-pump-thaw cycles, and the solution degassed by three freeze-pump-thaw cycles and brought to boil. Separately, a solution of diyne (1 equiv) in toluene or Et_2O (5 mL) was deoxygenated by a stream of dry N_2, $CpCo(CO)_2$ (1 equiv) added, and this mixture injected via syringe pump to the boiling, irradiated alkene solution over a period of 27–40 h. Heating and irradiation were continued for 3–12 h, the reaction mixture allowed to cool, and the volatile materials removed under vacuum. The crude, black residue was subjected to flash chromatography (50 g, hexanes) under N_2 to furnish the product(s), described in order of elution (for mixtures).

3

Red needles; mp 129–130 °C (MeOH).

IR (KBr): 2932, 2842, 1441, 1431, 1246, 802 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.61$ (s, 5 H), 2.78 (br s, 2 H, $H_{alkenyl}$), 2.37 (dt, *J* = 16.6, 6.0 Hz, 2 H), 2.15 (dt, *J* = 16.6, 6.0 Hz, 2 H,), 2.06 (m, 2 H), 1.73 (m, 5 H), 1.46 (m, 2 H), 1.08 (dtt, *J* = 18.0, 6.0, 6.0 Hz, 1 H), 0.95 (br t, *J* = 5.8 Hz, 2 H, H_{tert}).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 92.7$ (C), 80.2 (CH), 57.8 (CH), 41.4 (CH), 34.2 (CH_2), 29.2 (CH_2), 26.0 (CH_2), 23.6 (CH_2).

MS (EI, 70 eV): *m/z* (%) = 298 (100, $[M]^+$), 296 (77), 228 (46), 226 (30), 225 (23), 224 (65), 187 (17), 124 (20).

UV/Vis (MeOH): λ_{max} (log ε) = 263 (3.99), 338 (2.72), 402 nm (2.62).

Anal. Calcd for $C_{18}H_{23}Co$: C, 72.47; H, 7.77. Found: C, 72.39; H, 7.71.

4 (admixed with **3**)

^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.57$ (s, 5 H), 2.65 (br s, 2 H, $H_{alkenyl}$), the remainder of the resonances were obscured by those of **3**.

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 93.3$ (C), 81.0 (CH), 53.7 (CH), 45.6 (CH), 34.5 (CH_2), 30.0 (CH_2), 25.9 (CH_2), 23.8 (CH_2).

5

Red needles; mp 40–41 °C (MeOH).

IR (film): 2940, 2860, 2820, 1440, 1275, 1116, 809 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.64$ (s, 5 H), 2.54 (br s, 2 H), 2.36 (dt, *J* = 15.9, 6.2 Hz, 2 H), 2.22–2.01 (m, 4 H), 1.86–1.73 (m, 2 H), 1.62–1.48 (m, 4 H), 1.32–1.16 (m, 4 H), 0.68 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 92.8$, 80.1, 57.0, 37.2, 29.1, 26.5, 23.6, 20.0.

MS (EI, 70 eV): *m/z* (%) = 312 (77, $[M]^+$), 238 (100), 187 (11), 124 (6), 87 (10), 69 (10), 57 (12).

UV/Vis (MeOH): λ_{max} (log ε) = 263 (4.15), 341 (2.87), 398 nm (2.81).

Anal. Calcd for $C_{19}H_{25}Co$: C, 73.06; H, 8.07. Found: C, 72.77; H, 8.06.

6

Red-brown oil.

IR (film): 2907, 2841, 1443, 1346, 1240, 1111, 1007, 995, 801 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.61$ (s, 5 H), 2.43 (br s, 2 H), 2.42–2.30 (m, 2 H), 2.21–1.99 (m, 4 H), 1.86–1.71 (m, 4 H), 1.62–1.48 (m, 2 H), 1.44–1.12 (m, 8 H), 0.78 (br d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 92.6$, 79.9, 60.0, 42.6, 32.3, 31.1, 28.8, 26.2, 23.6.

MS (EI, 70 eV): *m/z* (%) = 340 (60, $[M]^+$), 266 (17), 216 (100), 214 (35), 145 (55), 131 (25), 117 (23), 91 (22).

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{21}H_{29}Co$: 340.1601; found: 340.1609.

UV/Vis (MeOH): λ_{max} (log ε) = 263 (4.13), 342 (2.95), 397 nm (2.85).

7

Red solid; mp 198–200 °C (25% EtOAc in hexanes).

IR (KBr): 2943, 1854, 1785, 1223, 1073, 1002, 910, 819, 729 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.67$ (s, 5 H), 3.09 (br s, 2 H), 2.44 (dt, *J* = 16.6, 6.1 Hz, 2 H), 2.24 (br t, *J* = 1.3 Hz, 2 H, H_{tert}), 2.21 (dt, *J* = 16.6, 6.1 Hz, 2 H), 2.04 (m, 2 H), 1.81 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 172.5$, 92.6, 81.1, 45.9, 44.4, 28.6, 23.2.

MS (EI, 70 eV): *m/z* (%) = 328 (22, $[M]^+$), 256 (29), 252 (11), 188 (11), 187 (17), 124 (100), 59 (16).

UV/Vis (MeOH): λ_{max} (log ε) = 266 (4.00), 338 (2.75), 392 nm (2.59).

Anal. Calcd for $C_{17}H_{17}CoO_3$: C, 62.20; H, 5.22. Found: C, 62.48; H, 5.26.

8

Reddish-brown solid; mp 178–179 °C (25% EtOAc in hexanes).

IR (KBr): 2928, 1850, 1770, 1265, 1213, 1055, 994, 910, 827 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.72$ (s, 5 H), 3.25 (dd, *J* = 3.0, 2.1 Hz, 2 H, H_{tert}), 3.00 (t, *J* = 2.5 Hz, 2 H), 2.46 (dt, *J* = 16.8, 6.2 Hz, 2 H), 2.19 (dt, *J* = 16.8, 6.2 Hz, 2 H), 2.02 (m, 2 H), 1.84 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.5$, 94.5, 81.2, 48.1, 44.0, 28.7, 23.1.

MS (EI, 70 eV): *m/z* (%) = 328 (67, $[M]^+$), 256 (74), 252 (60), 188 (61), 187 (72), 128 (60), 125 (40), 124 (100), 91 (32), 59 (78).

UV/Vis (MeOH): λ_{max} (log ε) = 266 (4.04), 338 (2.95), 394 nm (2.81).

Anal. Calcd for $C_{17}H_{17}CoO_3$: C, 62.20; H, 5.22. Found: C, 62.23; H, 5.11.

9

Red solid; mp 124–126 °C (MeOH).

IR (KBr): 2937, 2856, 1430, 1262, 1110, 803 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): $\delta = 4.48$ (s, 5 H), 3.84 (m, 1 H), 2.74 (s, 2 H, $H_{alkenyl}$), 2.30 (dt, *J* = 16.2, 6.1 Hz, 2 H), 2.02 (dt, *J* = 16.2, 6.3 Hz, 2 H), 1.98 (s, 2 H), 1.87 (m, 2 H), 1.61 (m, 2 H), 1.46 (m, 2 H), 1.00–0.91 (m, 3 H), 0.69 (s, 2 H, H_{tert}).

^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 91.0$ (C), 81.9 (CH), 53.5 ($CH_{alkenyl}$), 47.5 (CH, cyclohexadiene), 41.1 (CH, norbornane bridgehead), 33.1 (CH_2), 30.0 (CH_2), 28.9 (CH_2), 23.4 (CH_2).

MS (EI, 70 eV): *m/z* (%) = 324 (100, $[M]^+$), 322 (54), 252 (49), 124 (37), 59 (28).

UV/Vis (MeOH): λ_{max} (log ε) = 266 (4.21), 343 (2.92), 400 nm (2.83).

Anal. Calcd for $C_{20}H_{25}Co$: C, 74.06; H, 7.77. Found: C, 73.89; H, 7.64.

10 (admixed with **9**)

^{1}H NMR (500 MHz, C_6D_6): δ = 4.58 (s, 5 H), 2.81 (s, 2 H), 2.30 (m, 2 H), 2.11 (m, 2 H), 1.87 (m, 2 H), 1.78 (br s, 2 H), 1.75 (br s, 2 H), 1.61 (m, 2 H), 1.33 (m, 2 H), 1.09 (m, 1 H), 1.01 (m, 2 H), 0.60 (m, 1 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 93.2, 80.3, 53.3, 50.5, 44.1, 42.1, 30.5, 29.1, 24.1.

11

Red needles; mp 69–70 °C (MeOH).

IR (KBr): 2930, 2825, 1460, 1430, 1240, 1105, 795 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.62 (s, 5 H), 2.65 (br s, 2 H), 2.35 (dt, *J* = 15.5, 6.0 Hz, 2 H,), 2.12 (m, 4 H), 1.77 (m, 2 H), 1.48 (m, 2 H), 1.28 (m, 4 H), 1.12 (m, 2 H), 0.90 (t, *J* = 6.9 Hz, 6 H,), 0.69 (td, *J* = 5.1, 1.8 Hz, 2 H, H_{tert}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 93.2 (C), 80.0 (CH), 55.7 (CH), 39.4 (CH), 33.7 (CH_2), 29.1 (CH_2), 23.6 (CH_2), 21.4 (CH_2), 14.5 (CH_3).

MS (EI, 70 eV): *m/z* (%) = 342 (100, $[M]^+$), 340 (24), 299 (15), 273 (8), 272 (9), 270 (9), 244 (6), 201 (14), 187 (13), 124 (7), 67 (6).

UV/Vis (MeOH): λ_{max} (log ε) = 265 (4.04), 340 (2.84), 398 nm (2.76).

Anal. Calcd for $C_{21}H_{31}Co$: C, 73.66; H, 9.13. Found: C, 73.45; H, 9.12.

12

Red-brown oil.

IR (film): 2930, 2865, 1450, 1250, 1198, 797 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.57 (s, 5 H), 2.70 (d, *J* = 4.1 Hz, 1 H), 2.51 (d, *J* = 2.0 Hz, 1 H), 2.41–2.28 (m, 2 H), 2.25–2.02 (m, 4 H), 1.85–1.72 (m, 2 H), 1.44–1.22 (m, 4 H), 1.21–1.03 (m, 3 H), 1.00–0.81 (m, 2 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 0.75 (t, *J* = 7.2 Hz, 3 H), 0.27 (m, 1 H, H_{tert}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 92.8, 92.5, 80.1, 53.6, 53.4, 47.7, 42.6, 41.4, 40.2, 29.6, 29.2, 23.70, 23.68, 21.1, 20.3, 14.6, 14.5.

MS (EI, 70 eV): *m/z* (%) 342 (84, $[M]^+$), 340 (30), 299 (100), 233 (33), 218 (33), 201 (61), 175 (46), 133 (67), 91 (58).

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{21}H_{31}Co$: 342.1758; found: 342.1753.

UV/Vis (MeOH): λ_{max} (log ε) = 262 (4.04), 338 (2.90), 396 nm (2.85).

14[29]

Colorless solid; mp 95–96 °C (MeOH).

IR (KBr): 3400–3320, 2931, 2850, 1682, 1503, 1085, 1061, 1043 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (s, 1 H), 6.81 (s, 1 H), 4.72 (m, 1 H), 2.71 (m, 6H), 1.92 (m, 3 H), 1.78 (m, 5 H), 1.59 (d, *J* = 6.4 Hz, 1 H).

MS (EI, 70 eV): *m/z* (%) = 202 (100, $[M]^+$), 184 (97), 174 (95), 173 (82), 159 (6.3), 145 (69).

15

Red oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.64 (s, 5 H), 2.80 (d, *J* = 3.5 Hz, 1 H), 2.76 (d, *J* = 4.5 Hz, 1 H), 2.51 (dd, *J* = 10.8, 3.5 Hz, 1 H), 2.46–2.31 (m, 3 H), 2.22 (m, 2 H), 2.14–1.88 (m, 4 H), 1.78 (m, 2 H), 1.60–1.34 (m, 3 H), 0.98 (m, 1 H).

MS (EI, 70 eV): *m/z* (%) = 326 (39, $[M]^+$), 201 (100), 184 (91), 174 (57), 145 (63), 131 (48), 68 (56).

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{19}H_{23}CoO$: 326.1081; found: 326.1078.

16

Red oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.61 (s, 5 H), 3.65 (m, 4 H), 2.91 (s, 1 H), 2.80 (d, *J* = 3.0 Hz, 1 H), 2.65–1.20 (m, 15 H), 1.15 (d, *J* = 8.1 Hz, 1 H).

MS (EI, 70 eV): *m/z* (%) = 370 (48, $[M]^+$), 324 (28), 185 (28), 184 (100), 158 (38), 124 (60), 91 (42), 86 (66).

19

Brown plates; mp 115–116 °C (MeOH).

IR (KBr): 2925, 2855, 1448, 1263, 1249, 835, 799 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 4.57 (s, 5 H), 2.52 (dt, *J* = 15.5, 6.1 Hz, 2 H), 2.30 (dt, *J* = 15.5, 6.0 Hz, 2 H), 1.91 (m, 2 H), 1.87 (m, 2 H, H_{tert}), 1.76–1.62 (m, 2 H), 1.50–1.40 (m, 2 H), 1.19–0.98 (m, 6 H), 0.26 (s, 18 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 99.2, 81.0, 54.2, 41.6, 33.0, 31.3, 24.3, 23.8, 2.73.

MS (EI, 70 eV): *m/z* (%) = 456 (4, $[M]^+$), 383 (51), 317 (28), 310 (100), 73 (81).

UV/Vis (MeOH): λ_{max} (log ε) = 281 (3.90), 319 sh (3.27), 371 (2.73), 430 nm (2.64).

Anal. Calcd for $C_{25}H_{41}CoSi_2$: C, 65.75; H, 9.05. Found: C, 65.76; H, 8.97.

20

Brown solid; mp 70–71 °C (MeOH).

IR (film): 2964, 2939, 2878, 1252, 839, 803 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 4.56 (s, 5 H), 2.52 (dt, *J* = 16.2, 6.3 Hz, 2 H), 2.28 (dt, *J* = 15.9, 6.1 Hz, 2 H), 1.97 (d, *J* = 8.0 Hz, 2 H, H_{tert}), 1.93–1.82 (m, 2 H), 1.74–1.59 (m, 2 H), 1.39–1.17 (m, 4 H), 1.16–1.05 (m, 2 H), 0.95–0.80 (m, 2 H), 0.84 (t, *J* = 7.0 Hz, 6 H,), 0.30 (s, 18 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 99.0, 81.2, 55.3, 44.3, 37.7, 31.5, 24.2, 23.2, 15.0, 2.75.

MS (EI, 70 eV): *m/z* (%) = 486 (4, $[M]^+$), 413 (39), 340 (48), 215 (25), 187 (44), 145 (21), 73 (100).

Anal. Calcd for $C_{27}H_{47}CoSi_2$: C, 66.62; H, 9.73. Found: C, 66.34; H, 9.68.

21

Brown plates; mp 238–239 °C (MeOH).

IR (film): 2955, 2930, 2868, 2810, 1248, 999, 837, 803 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 4.60 (s, 5 H), 2.67 (dt, *J* = 16.2, 6.2 Hz, 1 H), 2.45–2.24 (m, 3 H), 1.99–1.57 (m, 6 H), 1.53–1.24 (m, 2 H), 1.20–1.02 (m, 2 H), 1.09 (t, *J* = 7.3 Hz, 3 H), 1.04 (d, *J* = 10.4 Hz, 1 H), 0.98 (d, *J* = 10.4 Hz, 1 H), 0.82 (t, *J* = 6.8 Hz, 3 H), 0.50–0.30 (m, 2 H), 0.21 (s, 9 H), 0.20 (s, 9 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 98.0 (C), 97.6 (C), 81.1 (CH), 57.6 (C), 55.1 (C), 48.8 (CH), 43.1 (CH_2), 42.4 (CH), 41.2 (CH_2), 32.2 (CH_2), 31.2 (CH_2), 24.7 (CH_2), 24.0 (CH_2), 23.8 (CH_2), 21.3 (CH_2), 15.3 (CH_3), 14.8 (CH_3), 2.61 (CH_3), 1.24 (CH_3).

MS (EI, 70 eV): *m/z* (%) = 486 (26, $[M]^+$), 413 (40), 73 (100), 59 (19).

Anal. Calcd for $C_{27}H_{47}CoSi_2$: C, 66.62; H, 9.73. Found: C, 66.79; H, 9.68.

22
Red-brown crystals; mp 115–119 °C (Et_2O–PE, 1:10).

IR (KBr): 3400–3300, 2940–2850, 1245, 1007, 836, 795 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 4.45 (s, 5 H), 3.30 (br d, J = 9.9 Hz, 1 H), 2.52 (dt, J = 15.8, 5.9 Hz, 1 H), 2.44 (br t, J = 8.5 Hz, 1 H), 2.37–2.25 (m, 2 H), 2.21 (dt, J = 15.7, 5.7 Hz, 1 H), 1.95–1.79 (m, 2 H), 1.74 (m, 2 H, H_{tert} and CHH_{endo}), 1.67 (m, 1 H), 1.58 (m, 1 H), 1.14 (dd, J = 13.1, 6.5 Hz, 1 H, CHH_{exo}), 0.70 (br s, 1 H), 0.21 (s, 9 H), 0.18 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 98.6, 98.5, 80.7, 66.8, 51.3, 48.5, 41.3, 35.9, 31.4, 30.5, 24.3, 23.9, 2.09, 0.50.

MS (EI, 70 eV): m/z (%) = 432 (8, $[M]^+$), 359 (42), 286 (27), 273 (26), 189 (20), 145 (45), 73 (100), 59 (54).

Anal. Calcd for $C_{22}H_{37}CoOSi_2$: C, 61.08; H, 8.62. Found: C, 60.86; H, 8.53.

23
Red-brown crystals; mp 113–114 °C (Et_2O–PE, 1:10).

IR (KBr): 3450, 2950–2830, 1245, 831, 804 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 4.55 (s, 5 H), 3.73 (m, 1 H), 3.59 (m, 1 H), 3.28 (br s, 1 H), 2.47–2.15 (m, 4 H), 1.76 (m, 2 H), 1.65 (m, 1 H), 1.46 (m, 2 H), 0.95 (m, 1 H, H_{tert}), 0.37 (m, 1 H, CHH_{exo}), 0.30 (s, 9 H), 0.23 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 99.5, 98.3, 81.0, 67.9, 53.0, 51.2, 42.9, 32.1, 31.2, 30.5, 24.4, 23.4, 3.62, 0.61.

MS (EI, 70 eV): m/z (%) = 432 (9, $[M]^+$), 416 (27), 189 (59), 129 (44), 124 (15), 73 (100), 59 (70).

Anal. Calcd for $C_{22}H_{37}CoOSi_2$: C, 61.08; H, 8.62. Found: C, 61.01; H, 8.57.

24
Red-brown oil.

IR (film): 3420, 2950, 2880, 1250, 1015, 840, 800 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 4.54 (s, 5 H), 3.20 (m, 1 H), 2.75 (m, 1 H), 2.55 (m, 1 H), 2.45–2.13 (m, 3 H), 1.91 (td, J = 7.4, 2.7 Hz, 1 H, H_{tert}), 1.90–1.78 (m, 1 H), 1.73–1.48 (m, 3 H), 1.54 (br d, J = 7.4 Hz, 1 H, H_{tert}), 1.28–1.04 (m, 3 H), 0.98–0.85 (m, 1 H), 0.91 (t, J = 7.0 Hz, 3 H), 0.42 (br s, 1 H), 0.31 (s, 9 H), 0.24 (s, 9 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 100.6 (C), 96.9 (C), 81.3 (CH), 64.8 (CH_2), 56.0 (C), 50.4 (C), 48.0 (CH), 42.8 (CH), 37.2 (CH_2), 31.7 (CH_2), 31.0 (CH_2), 24.3 (CH_2), 24.0 (CH_2), 22.7 (CH_2), 14.9 (CH_3), 3.28 (CH_3), 1.96 (CH_3).

MS (EI, 70 eV): m/z (%) = 474 (4, $[M]^+$), 401 (53), 328 (41), 259 (14), 245 (13), 187 (11), 73 (100), 59 (22).

Anal. Calcd for $C_{25}H_{43}CoOSi_2$: C, 63.25; H, 9.13. Found: C, 63.39; H, 9.05.

25
Brown solid; mp 157–158 °C (EtOAc–hexanes, 1:1).

IR (film): 3340, 2935, 2860, 1250, 838, 800 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 4.54 (s, 5 H), 3.88 (br s, 1 H), 2.63 (dt, J = 16.0, 5.8 Hz, 1 H), 2.40–2.28 (m, 2 H), 2.25 (br d, J = 7.5 Hz, 1 H, H_{tert}), 2.15 (dt, J = 15.8, 5.6 Hz, 1 H), 1.97–1.80 (m, 3 H, including H_{tert}), 1.77–1.55 (m, 3 H), 1.54–1.41 (m, 1 H), 1.37–1.19 (m, 2 H), 1.06–0.95 (m, 2 H), 0.58–0.42 (m, 1 H), 0.26 (s, 9 H), 0.22 (s, 9 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 101.2, 97.5, 81.2, 70.2, 53.7, 52.7, 51.1, 34.3, 33.3, 31.8, 30.7, 28.8, 24.4, 23.7, 19.5, 5.07, 2.15.

MS (EI, 70 eV): m/z (%) = 472 (5, $[M]^+$), 399 (15), 257 (22), 243 (13), 183 (48), 73 (100), 59 (15).

Anal. Calcd for $C_{25}H_{41}CoOSi_2$: C, 63.52; H, 8.74. Found: C, 63.60; H, 8.71.

26
Brown solid; mp 134–135 °C (EtOAc–hexanes, 1:1).

IR (film): 2956, 2874, 1701, 1254, 844, 811 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 4.54 (s, 5 H), 2.70 (dt, J = 16.1, 6.1 Hz, 1 H), 2.68 (d, J = 10.5 Hz, 1 H, H_{tert}), 2.58 (ddd, J = 16.0, 7.6, 5.8 Hz, 1 H), 2.39–2.17 (m, 3 H), 1.93–1.79 (m, 4 H), 1.78–1.68 (m, 2 H), 1.55–1.47 (m, 1 H), 1.31–1.23 (m, 1 H), 1.20–1.09 (m, 1 H), 0.68 (dddd, J = 13.6, 10.6, 9.2, 3.1 Hz, 1 H), 0.24 (s, 9 H), 0.16 (s, 9 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 211.4, 100.8, 99.1, 81.1, 55.7, 54.6, 46.5, 46.2, 39.3, 33.3, 31.2, 30.9, 24.2, 23.9, 23.2, 2.65, 1.85.

MS (EI, 70 eV): m/z (%) = 470 (4, $[M]^+$), 397 (11), 329 (10), 273 (20), 257 (21), 183 (13), 73 (100), 59 (22).

Anal. Calcd for $C_{25}H_{39}CoOSi_2$: C, 63.79; H, 8.35. Found: C, 63.60; H, 8.39.

27
Red-brown oil.

IR (film): 2940, 2860, 1248, 1098, 1043, 936, 844, 800 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 4.62 (s, 5 H), 3.53 (m, 1 H), 3.47–3.26 (m, 3 H), 2.69–2.54 (m, 2 H), 2.48 (d J = 8.4 Hz, 1 H), 2.38 (ddd, J = 13.6, 8.4, 4.6 Hz, 1 H), 2.28 (dt, J = 15.5, 5.6 Hz, 1 H), 2.09 (ddd, J = 13.6, 8.4, 4.6 Hz, 1 H), 1.99–1.83 (m, 2 H), 1.82–1.71 (m, 1 H), 1.70–1.57 (m, 2 H), 1.56–1.40 (m, 1 H), 1.33–1.13 (m, 3 H), 0.78–0.61 (m, 1 H), 0.48 (s, 9 H), 0.23 (s, 9 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 110.8, 103.4, 97.5, 81.4, 64.5, 63.0, 54.4, 52.8, 51.7, 38.3, 33.4, 31.9, 30.9, 30.7, 24.6, 23.8, 22.8, 5.25, 2.16.

MS (EI, 70 eV): m/z (%) = 514 (7, $[M]^+$), 441 (56), 124 (16), 99 (13), 86 (80), 73 (100), 59 (20).

28
Colorless oil; bp 86–91 °C/0.5 mm.

IR (film): 2964, 2900, 2175, 1680, 1254, 1113, 845, 762 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (t, J = 6.9 Hz, 2 H), 1.96 (t, J = 6.4 Hz, 2 H), 1.63 (quint, J = 6.8 Hz, 2 H), 0.17 (s, 9 H), 0.04 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.5, 106.6, 103.0, 96.1, 85.6, 44.1, 22.8, 19.2, 0.27, –0.90.

MS (EI, 70 eV): m/z (%) = 264 (1, $[M]^+$), 249 (29), 157 (27), 133 (29), 125 (44), 97 (33), 73 (100).

Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.14. Found: C, 63.74; H, 9.12.

29
Red-brown solid; mp 110–112 °C (EtOAC–hexanes, 1:1).

IR (film): 3440, 2960, 2865, 1671, 1395, 1250, 1033, 1020, 845, 807 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 4.57 (s, 5 H), 3.15 (ddd, J = 10.3, 4.0, 2.7 Hz, 1 H), 2.68 (ddd, J = 10.7, 8.0, 5.0 Hz, 1 H), 2.64–2.54 (m, 1 H), 2.31 (m, 1 H), 2.24 (t, J = 8.7 Hz, 1 H, H_{tert}), 2.17–2.02 (m, 4 H, including H_{tert}), 1.67 (m, 1 H), 1.53–1.42 (m, 2 H), 1.19 (m, 1 H), 0.90 (m, 1 H), 0.85 (t, J = 7.0 Hz, 3 H), 0.51 (br s, 9 H), 0.37 (br t, J = 5.1 Hz, 1 H), 0.19 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 205.2, 108.6, 88.1, 81.6, 64.0, 59.4, 58.5, 46.3, 44.7, 39.7, 37.3, 29.6, 23.0, 22.5, 14.9, 3.61, 2.23.

MS (EI, 70 eV): *m*/*z* (%) = 488 (9, [M]$^+$), 415 (15), 399 (10), 347 (31), 259 (27), 185 (16), 75 (29), 73 (100), 59 (16).

Anal. Calcd for $C_{25}H_{41}CoO_2Si_2$: C, 61.44; H, 8.46. Found: C, 61.21; H, 8.47.

30

Deep brown solid; mp 163–164 °C (EtOAC–hexanes, 1:1).

IR (film): 3490, 2930, 2850, 1660, 1250, 990, 835, 810 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 4.55 (s, 5 H), 3.12 (m, 1 H), 2.62–2.50 (m, 2 H), 2.36–2.15 (m, 3 H), 2.12–1.95 (m, 3 H), 1.67–1.44 (m, 3 H), 1.28–1.07 (m, 2 H), 0.90 (t, *J* = 6.8 Hz, 3 H), 0.63 (br t, *J* = 4.8 Hz, 1 H), 0.42 (s, 9 H), 0.22 (s, 9 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 205.6, 111.2, 85.8, 81.4, 65.5, 64.5, 52.5, 49.6, 41.2, 39.5, 36.9, 29.2, 22.7, 22.4, 14.7, 3.20, 2.32.

MS (EI, 70 eV): *m*/*z* (%) = 488 (10, [M]$^+$), 347 (13), 321 (33), 305 (22), 275 (21), 75 (73), 73 (100), 66 (74), 59 (22).

Anal. Calcd for $C_{25}H_{41}CoO_2Si_2$: C, 61.44; H, 8.46. Found: C, 61.50; H, 8.40.

31

Brown solid; mp 151–152 °C (EtOAC–hexanes, 1:1).

IR (film): 2945, 2800, 1700, 1675, 1250, 842, 812 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 4.55 (s, 5 H), 2.71 (ddd, *J* = 15.8, 11.5, 4.3 Hz, 1 H), 2.70 (d, *J* = 10.5 Hz, 1 H, H_{tert}), 2.63–2.53 (m, 2 H), 2.49 (dddd, *J* = 15.9, 5.6, 4.2, 1.2 Hz, 1 H), 2.20 (ddd, *J* = 16.8, 11.7, 5.0 Hz, 1 H), 2.06 (m, 1 H), 1.78 (d, *J* = 5.7 Hz, 1 H), 1.76 (d, *J* = 6.3 Hz, 1 H), 1.74–1.63 (m, 2 H), 1.24–1.06 (m, 2 H), 0.65 (dddd, *J* = 13.8, 10.4, 10.2, 4.1 Hz, 1 H), 0.40 (br s, 9 H), 0.14 (s, 9 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 210.9, 205.1, 111.0, 87.2, 81.5, 57.8, 55.0, 54.4, 47.8, 39.8, 39.5, 33.5, 29.6, 22.9, 22.6, 3.65, 1.66.

MS (EI, 70 eV): *m*/*z* (%) = 484 (7, [M]$^+$), 345 (21), 271 (49), 243 (17), 73 (76), 58 (63).

Anal. Calcd for $C_{25}H_{37}CoO_2Si_2$: C, 61.95; H, 7.69. Found: C, 62.01; H, 7.64.

32

Dark brown solid; mp 173–174 °C (EtOAC–hexanes, 1:1).

IR (film): 2932, 2900, 1695, 1672, 1397, 1250, 839, 810 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 4.54 (s, 5 H), 2.94 (d, *J* = 10.1 Hz, 1 H, H_{tert}), 2.67 (m, 1 H), 2.35–1.98 (m, 5 H), 1.94–1.77 (m, 2 H), 1.62 (m, 1 H), 1.45 (m, 1 H), 1.25–1.06 (m, 2 H), 0.60 (dddd, *J* = 13.5, 10.4, 9.4, 3.6 Hz, 1 H), 0.43 (s, 9 H), 0.06 (s, 9 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 209.6, 204.3, 108.6, 89.1, 81.4, 66.7, 64.0, 56.0, 46.4, 39.9, 39.0, 33.1, 29.6, 23.2, 22.4, 2.63, 2.38.

MS (EI, 70 eV): *m*/*z* (%) = 484 (9, [M]$^+$), 411 (5), 345 (15), 271 (60), 107 (13), 75 (39), 73 (100), 59 (13).

Anal. Calcd for $C_{25}H_{37}CoO_2Si_2$: C, 61.95; H, 7.69. Found: C, 61.69; H, 7.85.

35

Pale yellow oil.

IR (film): 2960, 2864, 2158, 1771, 1646, 1468, 1249, 1017, 825, 778 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (AA′m, 2 H), 7.58 (BB′m, 2 H), 1.65 (sept, *J* = 6.8 Hz, 2 H), 0.91 (s, 12 H), 0.88 (d, *J* = 6.8 Hz, 12 H), 0.22 (s, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.5, 139.0, 131.9, 129.7, 102.5, 101.7, 34.5, 23.6, 20.7, 18.6, –3.10.

MS (EI, 70 eV): *m*/*z* (%) = 466 (0.4, [M]$^+$), 396 (3), 382 (22), 297 (69), 269 (69), 84 (60), 73 (63), 69 (49), 57 (100).

Anal. Calcd for $C_{28}H_{42}O_2Si_2$: C, 72.04; H, 9.07. Found: C, 71.98; H, 9.19.

36

Colorless solid; mp 36–40 °C (EtOAC–hexanes, 1:1).

IR (film): 2965, 2870, 2155, 1649, 1253, 1019, 849, 827 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (m, 2 H), 7.59 (m, 2 H), 1.64 (sept, *J* = 6.9 Hz, 1 H), 0.91 (s, 6 H), 0.87 (d, *J* = 6.9 Hz, 6 H), 0.23 (s, 9 H), 0.22 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.52, 178.48, 139.1, 138.8, 131.9, 131.8, 129.7, 129.6, 102.5, 101.8, 101.4 (2 C), 34.4, 23.6, 20.6, 18.6, –0.84, –3.11.

MS (EI, 70 eV): *m*/*z* (%) = 396 (1, [M]$^+$), 311 (100), 297 (15), 237 (19), 155 (9), 73 (36).

Anal. Calcd for $C_{23}H_{32}O_2Si_2$: C, 69.64; H, 8.13. Found: C, 69.84; H, 8.20.

Compound 37 from 40 via 41 and 42

41**:** To ice-cooled **40** (15.4 g, 103 mmol) in THF (50 mL) was added a solution of ClMgC≡CSiMe$_3$ (210 mmol) in THF (160 mL) over 15 min and the mixture stirred for another 30 min. The solution was quenched with aq 3.0 N HCl (100 mL), the aqueous phase extracted with Et_2O (2 × 100 mL), then aq 1.0 N HCl (2 × 100 mL), and dried ($MgSO_4$). The crude product was dissolved in MeOH (50 mL), aq 1.0 N HCl (5.0 mL) added, and the pale yellow solution stirred at r.t. overnight. Aqueous workup gave **41** (19.9 g, 84%); colorless solid; mp 55–57 °C (Et_2O–PE).

IR (KBr): 2960, 1765, 1471, 1283, 1254, 1069, 968, 850, 748, 712 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.6 Hz, 1 H), 7.72 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.55 (m, 2 H), 6.04 (s, 1 H), 0.15 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.4, 146.8, 134.6, 129.7, 125.6, 125.0, 122.5, 97.5, 94.4, 70.3, –0.48.

MS (EI, 70 eV): *m*/*z* (%) = 230 (23, [M]$^+$), 215 (79), 200 (82), 187 (100), 128 (44), 105 (34).

Anal. Calcd for $C_{13}H_{14}O_2Si$: C, 67.79; H, 6.13. Found: C, 67.74; H, 6.08.

42: To a stirred solution of **41** (1.00 g, 4.34 mmol) in toluene (20 mL) at –78 °C was added DIBAL-H (1.5 M in toluene, 3.0 mL, 4.5 mmol) over 2 min. The stirring was continued for 45 min, MeOH added (1.0 mL), and the mixture subjected to acidic (aq 0.1 N HCl, Et_2O) workup, furnishing a waxy mixture of the diastereomeric lactols **42** contaminated by a small amount of its hydroxy aldehydic form (937 mg, 93%; 7:5:1); colorless wax; mp 62–70 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (major diastereomer) = 7.41–7.34 (m, 4 H), 6.54 (d, *J* = 5.4 Hz, 1 H), 6.02 (s, 1 H), 3.79 (d, *J* = 7.0 Hz, 1 H), 0.15 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (major diastereomer) = 139.7, 138.5, 129.7, 128.6, 122.8, 121.8, 102.2, 101.4, 91.3, 72.4, –0.29.

^{1}H NMR (400 MHz, $CDCl_3$): δ (minor diastereomer) = 7.41–7.34 (m, 4 H), 6.35 (d, *J* = 9.5 Hz, 1 H), 5.73 (s, 1 H), 3.54 (d, *J* = 9.6 Hz, 1 H), 0.14 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (minor diastereomer) = 139.5, 138.7, 129.8, 128.7, 123.0, 121.9, 103.3, 101.1, 91.4, 72.0, –0.32.

^{1}H NMR (400 MHz, $CDCl_3$): δ (hydroxy aldehyde isomer) = 10.13 (s, 1 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 7.80 (d, *J* = 7.1 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.53 (t, *J* = 7.1 Hz, 1 H), 5.85 (d, *J* = 6.2 Hz, 1 H), 4.34 (d, *J* = 6.6 Hz, 1 H), 0.17 (s, 9 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ (hydroxy aldehyde isomer) = 194.4, 141.4, 135.0, 134.5, 133.5, 128.8, 128.7, 103.6, 92.1, 62.9, –0.32.

37: To **42** (5.08 g, 21.9 mmol) in THF (20 mL) at r.t. was added a solution of ClMgC≡CSiMe$_2$Et (45.5 mmol)[30] in THF (50 mL) over 5 min, and the mixture stirred overnight and then subjected to standard aqueous workup. The crude product was dissolved in acetone (100 mL), cooled in an ice-water bath, and a solution of Jones reagent[31] (35.2 mL, 143.6 mmol) was added over 30 min. After stirring for 2 h at r.t., aqueous workup yielded **37** (6.89 g, 93%); pale orange oil.

IR (film): 2965, 2158, 1647, 1248, 1015, 846 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.79 (m, 2 H), 7.59 (m, 2 H), 1.00 (t, *J* = 7.8 Hz, 3 H), 0.66 (q, *J* = 7.8 Hz, 2 H), 0.24 (s, 9 H), 0.21 (s, 6 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 178.59, 178.56, 139.0, 138.9, 131.9 (2 C), 129.7 (2 C), 101.9, 101.6, 101.5, 101.0, 7.3, 7.2, –0.81, –2.93.

MS (EI, 70 eV): *m/z* (%) = 340 (14, [M]$^+$), 312 (100), 297 (25), 237 (35), 73 (43).

Anal. Calcd for $C_{19}H_{24}O_2Si_2$: C, 67.01; H, 7.10. Found: C, 67.09; H, 7.37.

38

The procedure described for **37** was repeated using ClMgC≡CSiEt$_3$ to render **38**; colorless oil.

IR (film): 2960, 2875, 2150, 1648, 1250, 1018, 847 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.79 (m, 2 H), 7.58 (m, 2 H), 0.99 (t, *J* = 8.1 Hz, 9 H), 0.66 (q, *J* = 8.1 Hz, 6 H), 0.23 (s, 9 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 178.6, 178.4, 139.0, 138.9, 131.9 (2 C), 129.7, 129.6, 102.7, 101.43, 101.40, 99.8, 7.3, 3.76, –0.88.

MS (EI, 70 eV): *m/z* (%) = 368 (6, [M]$^+$), 353 (14), 340 (79), 339 (100), 311(18), 283 (29), 165 (17), 73 (30).

39

This intermediate on route to **34**[15] was crystallized from a mixture (*meso*/*d,l* = 1.7:1) containing its *d,l* isomer [^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.59 (AA′m, 2 H), 7.34 (BB′m, 2 H), 5.99 (s, 2 H), 3.48 (br s, 2 H), 0.20 (s, 18 H)]; colorless solid; mp 88–93 °C (PE).

IR (KBr): 3530, 3365, 2960, 2898, 2170, 1422, 1248, 1031, 990, 973, 840, 760 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.79 (AA′m, 2 H), 7.38 (BB′m, 2 H), 5.83 (s, 2 H), 3.18 (br s, 2 H), 0.21 (s, 18 H).

^{13}C NMR (125 MHz, CDCl$_3$): δ = 137.6, 129.1, 128.1, 103.9, 92.8, 62.3, –0.24.

MS (EI, 70 eV): *m/z* (%) = 330 (1, [M]$^+$), 312 (12), 214 (15), 147 (25), 75 (29), 73 (100).

Anal. Calcd for $C_{18}H_{26}O_2Si_2$: C, 65.40; H, 7.93. Found: C, 65.63; H, 8.08.

43 and 44 (1:1)

Red solid; mp 149–155 °C (EtOAc–hexanes, 1:3).

IR (KBr): 2939, 2862, 1663, 1592, 1412, 1323, 1285, 1265, 961, 814, 733 cm^{-1}.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 8.36 (m, 4 H), 7.16 (m, 4 H), 4.34 (d, *J* = 3.4 Hz, 2 H, H$_{\text{alkenyl}}$), 4.225 (s, 5 H), 4.222 (s, 5 H), 4.13 (br s, 2 H, H$_{\text{alkenyl}}$), 1.89 (m, 2 H, **44**-H$_{\text{tert}}$), 1.54 (m, 2 H), 1.46 (m, 2 H), 1.36–1.21 (m, 8 H), 1.02 (m, 2 H), 0.93 (m, 2 H), 0.72 (m, 2 H, **43**-H$_{\text{tert}}$).

^{13}C NMR (125 MHz, C$_6$D$_6$): δ = 188.9, 188.8, 134.9 (2 C), 133.3 (2 C), 126.6 (2 C), 84.8 (2 C), 82.9, 82.7, 65.3, 62.5, 38.5, 37.7, 30.5, 26.5, 21.0, 20.0.

MS (EI, 70 eV): *m/z* (%) = 388 (17, [M]$^+$), 386 (100), 320 (20), 262 (37), 207 (69), 124 (35), 69 (56), 57 (60), 55 (56).

UV/Vis (MeOH): λ$_{\text{max}}$ (log ε) = 263 (4.22), 297 sh (3.93), 327 sh (3.81), 438 nm (3.18).

Anal. Calcd for $C_{23}H_{21}CoO_2$: C, 71.13; H, 5.45. Found: C, 70.88; H, 5.30.

45

Red needles; mp 189–191 °C (EtOAc).

IR (KBr): 2934, 2860, 1656, 1589, 1335, 1297, 1245, 845, 807, 729 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.13 (AA′m, 2 H), 7.71 (BB′m, 2 H), 4.61 (s, 5 H), 2.19 (br s, 2 H, H$_{\text{tert}}$), 1.51 (m, 2 H), 1.07 (m, 6 H), 0.26 (br s, 18 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 191.0 (C), 134.4 (C), 133.3 (CH), 126.0 (CH), 92.6 (C), 82.6 (CH), 71.0 (C), 41.6 (CH), 32.8 (CH$_2$), 23.2 (CH$_2$), 2.65 (CH$_3$).

MS (EI, 70 eV): *m/z* (%) = 532 (45, [M]$^+$), 408 (30), 392 (15), 319 (30), 73 (100).

UV/Vis (MeOH): λ$_{\text{max}}$ (log ε) = 279 (4.26), 312 sh (4.02), 345 sh (3.77), 472 nm (3.26).

Anal. Calcd for $C_{29}H_{37}CoO_2Si_2$: C, 65.39; H, 7.00. Found: C, 65.38; H, 6.81.

A second product (6%) was the CpCo(cyclopentadienone) complex (Figure 6) derived from **34**.

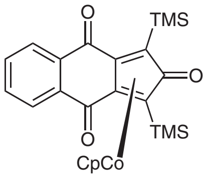


Figure 6 CpCo[1,3-bis(trimethylsilyl)-1*H*-cyclopenta[*b*]naphthalene-2,4,9-trione]

Red-orange solid; mp 203–204 °C (EtOAc).

IR (KBr): 2216, 1672, 1621, 1586, 1552, 1392, 1243, 1227, 1003, 849, 728, 642 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.21 (AA′m, 2 H) 7.77 (BB′m, 2 H), 4.94 (s, 5 H), 0.43 (s, 18 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 224.4, 134.6, 134.0, 126.9, 91.4, 83.1, 50.7, 0.26 [1 C (C=O) not detected].

MS (EI, 70 eV): *m/z* (%) = 478 (46, [M]$^+$), 463 (14), 434 (13), 339 (10), 237 (13), 198 (10), 124 (15), 73 (51).

HRMS-EI: *m/z* [M]$^+$ calcd for $C_{24}H_{27}CoO_3Si_2$: 478.0831; found: 478.0822.

UV/Vis (THF): λ$_{\text{max}}$ (log ε) = 258 (4.20), 303 (4.05), 404 nm (3.23).

Anal. Calcd for $C_{24}H_{27}CoO_3Si_2$: C, 60.24; H, 5.67. Found: C, 60.22; H, 5.60.

46

Reddish-brown powder; mp 206–210 °C (EtOAc).

IR (KBr): 2945, 2900, 1715, 1667, 1597, 1270, 1109, 970, 851, 813, 732, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (dd, J = 7.0, 1.7 Hz, 1 H), 8.11 (dd, J = 7.0, 1.1 Hz, 1 H), 8.03 (d, J = 7.0 Hz, 2 H), 7.74 (m, 2 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.47 (t, J = 7.2 Hz, 2 H), 5.68 (br s, 1 H), 4.63 (s, 5 H), 2.70 (br d, J = 7.2 Hz, 1 H, H_{tert}), 2.26 (ddd, J = 11.6, 7.4, 4.9 Hz, 1 H, H_{tert}), 1.79 (m, 1 H), 1.62 (m, 1 H), 1.38 (m, 1 H), 1.28–1.10 (m, 2 H), 0.53 (m, 1 H), 0.38 (br s, 9 H), 0.28 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0 (C), 190.8 (C), 165.2 (C), 134.6 (C), 134.2 (C), 133.6 (CH), 133.4 (CH), 132.8 (CH), 130.8 (C), 129.6 (CH), 128.4 (CH), 126.13 (CH), 126.09 (CH), 95.1 (C), 91.4 (C), 82.9 (CH), 72.8 (CH), 70.6 (C), 65.4 (C), 50.4 (CH), 34.5 (CH_2), 33.0 (CH), 25.3 (CH_2), 20.0 (CH_2), 3.10 (br, CH_3), 1.75 (CH_3).

MS (EI, 70 eV): m/z (%) = 652 (1, $[M]^+$), 586 (8), 530 (23), 406 (45), 392 (35), 194 (36), 189 (64), 179 (100), 147 (53), 135 (58), 124 (37), 105 (55).

Anal. Calcd for $C_{36}H_{41}CoO_4Si_2$: C, 66.23; H, 6.33. Found: C, 66.23; H, 6.34.

48

Dark red oil.

IR (KBr): 2955, 1667, 1596, 1251, 1165, 996, 846, 830, 808 cm^{-1}.

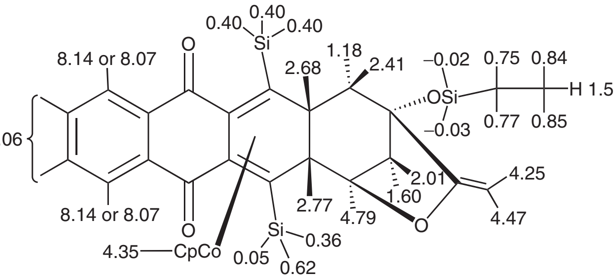


Figure 7 ^{1}H NMR assignments by 2D NMR

^{1}H NMR [400 MHz, C_6D_6, assignments by 2D NMR (Figure 7)]: δ = 8.14 (m, 1 H), 8.07 (m, 1 H), 7.06 (m, 2 H), 4.79 (dd, J = 6.7, 3.6 Hz, 1 H), 4.47 (br s, 1 H), 4.35 (s, 5 H), 4.25 (d, J = 1.2 Hz, 1 H), 2.77 (dd, J = 8.4, 3.6 Hz, 1 H), 2.68 (ddd, J = 10.6, 8.5, 7.0 Hz, 1 H), 2.41 (ddd, J = 12.2, 7.0, 3.0 Hz, 1 H), 2.01 (ddd, J = 10.2, 6.7, 3.0 Hz, 1 H), 1.60 (d, J = 10.2 Hz, 1 H), 1.55 (sept, J = 6.9 Hz, 1 H), 1.18 (dd, J = 12.1, 10.7 Hz, 1 H), 0.85 (d, J = 6.9 Hz, 3 H), 0.84 (d, J = 6.9 Hz, 3 H), 0.77 (s, 3 H), 0.75 (s, 3 H), 0.62 (s, 3 H), 0.40 (br s, 9 H), 0.36 (s, 3 H), 0.05 (s, 3 H), −0.02 (s, 3 H), −0.03 (s, 3 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 190.7, 190.6, 166.5, 134.6, 134.4, 133.6, 133.3, 126.5, 126.3, 94.8, 91.9, 82.8, 79.4, 78.7, 76.8, 67.9, 64.5, 51.0, 39.0, 34.8, 34.4, 32.3, 25.0, 20.5, 20.4, 18.84, 18.75, 3.92, 3.83, 2.45, 1.68, −0.09, −0.37.

MS (FAB, NBA): m/z (%) = 730 $[M]^+$.

Anal. Calcd for $C_{39}H_{55}CoO_4Si_3$: C, 64.08; H, 7.58. Found: C, 64.47; H, 7.84.

49

Red brown powder; mp 59–64 °C (EtOAc–hexanes); $[\alpha]_D^{20}$ +177 (c 1.65 × 10^{-3}, $CHCl_3$).

IR (KBr): 2960, 2875, 1668, 1597, 1259, 833, 810 cm^{-1}.

^{1}H NMR (300 MHz, toluene-d_8, +100 °C): δ = 8.07 (m, 1 H), 7.98 (m, 1 H), 7.20 (m, 2 H), 4.69 (dd, J = 6.6, 3.6 Hz, 1 H), 4.44 (s, 5 H), 4.26 (br t, J = 1.0 Hz, 1 H), 4.07 (br d, J = 1.3 Hz, 1 H), 2.70 (dd, J = 8.3, 3.5 Hz, 1 H), 2.60 (ddd, J = 10.5, 8.4, 6.9 Hz, 1 H), 2.28 (ddd, J = 12.2, 6.9, 3.0 Hz, 1 H), 1.92 (ddd, J = 9.6, 6.8, 3.1 Hz, 1 H), 1.55 (sept, J = 6.8 Hz, 1 H), 1.53 (d, J = 9.9 Hz, 1 H), 1.11 (br t, J = 7.4 Hz, 3 H), 1.06 (dd, J = 12.1, 10.6 Hz, 1 H), 0.9–0.8 (m, 2 H), 0.82 (d, J = 6.8 Hz, 6 H), 0.76 (s, 3 H), 0.75 (s, 3 H), 0.5–0.3 (br s, 6 H), 0.34 (s, 9 H), −0.02 (s, 6 H).

^{13}C NMR (75 MHz, toluene-d_8, +100 °C): δ = 190.6 (2 C), 166.7, 135.2, 135.1, 133.6, 133.3, 126.7, 126.5, 100.4, 95.6, 83.2, 79.8, 79.0, 76.7, 51.5, 51.3, 39.6, 35.4, 34.9, 25.6, 20.8, 20.7, 19.01, 18.97, 10.8 (br), 8.6 (br), 2.60 (2 C), 0.12, 0.0 (br), −0.97 (the signals for the terminal diene carbons were not observed).

MS (FAB, NBA): m/z (%) = 744 $[M]^+$.

UV/Vis (MeOH): λ_{max} (log ε) = 280 (4.38), 310 sh (4.14), 345 sh (3.85), 474 nm (3.34).

Anal. Calcd for $C_{40}H_{57}CoO_4Si_3$: C, 64.48; H, 7.71. Found: C, 64.58; H, 8.10.

50

Red-brown powder; mp 74–79 °C (EtOAc–hexanes); $[\alpha]_D^{20}$ +285 (c 4.00 × 10^{-4}, $CHCl_3$).

IR (KBr): 2960, 2870, 1667, 1599, 1257, 832, 812 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 8.13 (m, 1 H), 8.07 (m, 1 H), 7.07 (m, 2 H), 4.78 (dd, J = 6.6, 3.8 Hz, 1 H), 4.45 (s, 1 H), 4.36 (s, 5 H), 4.23 (s, 1 H), 2.77 (dd, J = 8.3, 3.7 Hz, 1 H), 2.66 (dt, J = 10.6, 7.5 Hz, 1 H), 2.37 (ddd, J = 11.8, 7.0, 2.7 Hz, 1 H), 2.00 (ddd, J = 9.6, 6.9, 2.7 Hz, 1 H), 1.60 (d, J = 10.3 Hz, 1 H), 1.54 (sept, J = 6.8 Hz, 1 H), 1.17 (t, J = 7.6 Hz, 3 H), 1.16 (m, 1 H), 0.90 (m, 2 H), 0.85 (d, J = 6.8 Hz, 3 H), 0.84 (d, J = 6.8 Hz, 3 H), 0.76 (s, 3 H), 0.75 (s, 3 H), 0.61 (s, 3 H), 0.39 (br s, 3 H), 0.37 (s, 3 H), 0.31 (s, 3 H) 0.05 (s, 3 H), −0.026 (s, 3 H), −0.029 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.7, 190.4, 166.4, 134.53, 134.48, 133.6, 133.3, 126.5, 126.3, 97.7, 92.1, 82.9, 79.4, 78.7, 76.8, 68.1, 64.4, 51.0, 50.8, 39.0, 34.7, 34.4, 25.0, 20.5, 20.4, 18.85, 18.75, 10.0, 8.81, 3.94, 3.79, 1.67, 0.01, −0.09, −0.14, −0.37.

MS (FAB, NBA): m/z (%) = 744 $[M]^+$.

UV/Vis (MeOH): λ_{max} (log ε) = 279 (4.20), 307 sh (3.97), 341 sh (3.70), 470 nm (3.16).

Anal. Calcd for $C_{40}H_{57}CoO_4Si_3$: C, 64.48; H, 7.71. Found: C, 64.43; H, 7.99.

The experiment generating **49** and **50** also gave, as the slowest eluting component on column chromatography, the CpCo(cyclopentadienone) complex (Figure 8) (11%) derived from **37**.

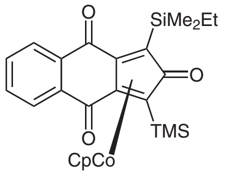


Figure 8 CpCo[1-(ethyldimethylsilyl)-3-(trimethylsilyl)-1*H*-cyclopenta[*b*]naphthalene-2,4,9-trione]

Red powder; mp 169–172.5 °C (EtOAc–hexanes).

IR (KBr): 2960, 2910, 1683, 1609, 1394, 1248, 1231, 1010, 829, 708 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 8.12 (m, 2 H), 7.09 (m, 2 H), 4.33 (s, 5 H), 1.22 (m, 5 H), 0.64 (s, 3 H), 0.62 (s, 9 H), 0.55 (s, 3 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 187.42, 187.41, 175.7, 135.17, 135.15, 133.5 (2 C), 126.7 (2 C), 91.8, 82.4, 80.7, 71.0, 70.7, 8.18, 8.13, 0.39, −1.69, −2.11.

MS (EI, 70 eV): m/z (%) = 492 (5, $[M]^+$), 235 (8), 221 (11), 161 (49), 147 (100), 133 (79), 73 (48).

UV/Vis (MeOH): λ_{max} (log ε) = 257 (4.40), 300 (4.30), 402 (3.48), 474 nm (3.12).

Anal. Calcd for $C_{25}H_{29}CoO_3Si_2$: C, 60.96; H, 5.93. Found: C, 61.00; H, 6.00.

51

Red-brown powder; mp 75–81 °C (EtOAc–hexanes); $[\alpha]_D^{20}$ +329 (*c* 7.0×10^{-4}, $CHCl_3$).

IR (KBr): 2965, 2878, 1668, 1598, 1255, 999, 832, 811 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 8.13 (m, 1 H), 8.05 (m, 1 H), 7.08 (m, 2 H), 4.82 (dd, *J* = 6.3, 3.4 Hz, 1 H), 4.47 (s, 1 H), 4.38 (s, 5 H), 4.25 (s, 1 H), 2.77 (dd, *J* = 8.5, 3.5 Hz, 1 H), 2.71 (ddd, *J* = 10.6, 8.5, 7.1 Hz, 1 H), 2.42 (ddd, *J* = 12.1, 7.0, 2.9 Hz, 1 H), 2.03 (ddd, *J* = 9.6, 6.6, 2.7 Hz, 1 H), 1.61 (d, *J* = 10.2 Hz, 1 H), 1.60–1.53 (m, 1 H), 1.54 (sept, *J* = 6.9 Hz, 1 H), 1.30 (t, *J* = 7.8 Hz, 3 H), 1.22 (t, *J* = 7.8 Hz, 6 H), 1.18 (dd, *J* = 12.2, 10.8 Hz, 1 H), 1.09 (dq, *J* = 15.0, 7.5 Hz, 1 H), 0.97–0.91 (m, 2 H), 0.85 (d, *J* = 6.9 Hz, 3 H), 0.84 (d, *J* = 6.9 Hz, 3 H), 0.77 (s, 3 H), 0.75 (s, 3 H), 0.69 (dq, *J* = 15.0, 7.8 Hz, 1 H), 0.40 (br s, 9 H), 0.29 (dq, *J* = 15.0, 7.8 Hz, 1 H), –0.02 (s, 3 H), –0.03 (s, 3 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 190.8, 190.7, 166.4, 134.7, 134.4, 133.6, 133.3, 126.5, 126.3, 95.2, 91.5, 82.9, 79.3, 79.0, 76.8, 67.4, 65.7, 51.2, 50.8, 39.2, 35.0, 34.4, 25.0, 20.5, 20.4, 18.9, 18.8, 10.1, 9.69, 9.43, 8.26, 7.62, 6.79, 2.58, –0.09, –0.38.

MS (FAB, NBA): *m/z* (%) = 772 $[M]^+$.

UV/Vis (MeOH): λ_{max} (log ε) = 280 (4.28), 306 sh (4.07), 340 sh (3.79), 470 nm (3.26).

Anal. Calcd for $C_{42}H_{61}CoO_4Si_3$: C, 65.25; H, 7.95. Found: C, 64.95; H, 8.11.

52

Red-brown powder; mp 68–72 °C (EtOAc–hexanes); $[\alpha]_D^{20}$ +370 (*c* 1.2×10^{-4}, $CHCl_3$).

IR (KBr): 2963, 2878, 1667, 1600, 1255, 1168, 1001, 817 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 8.14 (m, 1 H), 8.05 (m, 1 H), 7.08 (m, 2 H), 4.78 (dd, *J* = 6.6, 3.9 Hz, 1 H), 4.44 (s, 1 H), 4.38 (s, 5 H), 4.23 (s, 1 H), 2.79 (dd, *J* = 8.2, 3.7 Hz, 1 H), 2.66 (dt, *J* = 10.9, 7.6 Hz, 1 H), 2.34 (ddd, *J* = 12.1, 6.8, 2.9 Hz, 1 H,), 2.00 (ddd, *J* = 10.3, 6.8, 2.3 Hz, 1 H), 1.64 (d, *J* = 10.3 Hz, 1 H), 1.55 (sept, *J* = 6.9 Hz, 1 H), 1.27 (t, *J* = 7.9 Hz, 9 H), 1.18 (t, *J* = 11.6 Hz, 1 H), 1.00 (dq, *J* = 15.1, 7.6 Hz, 3 H), 0.89–0.83 (m, 3 H), 0.86 (d, *J* = 6.9 Hz, 3 H), 0.85 (d, *J* = 6.9 Hz, 3 H), 0.78 (s, 3 H), 0.75 (s, 3 H), 0.61 (s, 3 H), 0.38 (s, 3 H), 0.03 (s, 3 H), –0.01 (s, 3 H), –0.03 (s, 3 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 190.9, 189.8, 166.4, 134.5 (2 C), 133.6, 133.3, 126.6, 126.2, 94.6, 92.6, 83.0, 79.4, 78.7, 76.8, 69.1, 64.4, 51.3, 50.4, 39.2, 34.7, 34.5, 25.0, 20.6, 20.4, 18.9, 18.8, 9.47, 7.07, 4.02, 3.73, 1.68, –0.17, –0.40.

UV/Vis (MeOH): λ_{max} (log ε) = 281 (4.33), 307 sh (4.12), 340 sh (3.87), 474 nm (3.32).

MS (FAB, NBA): *m/z* (%) = 772 $[M]^+$.

Anal. Calcd for $C_{42}H_{61}CoO_4Si_3$: C, 65.25; H, 7.95. Found: C, 65.18; H, 7.82.

The experiment generating **51** and **52** also gave, as the slower eluting components on column chromatography, the CpCo(cyclobutadiene) (33%) and (cyclopentadienone) complexes (Figure 9) (7%) derived from **38**.

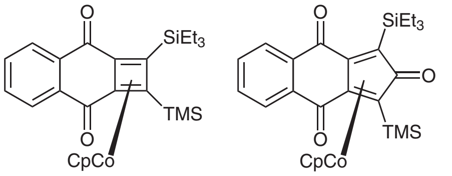


Figure 9 CpCo[1-(triethylsilyl)-2-(trimethylsilyl)cyclobuta[*b*]naphthalene-3,8-dione] and CpCo[1-(triethylsilyl)-3-(trimethylsilyl)-1*H*-cyclopenta[*b*]naphthalene-2,4,9-trione]

CpCo[1-(triethylsilyl)-2-(trimethylsilyl)cyclobuta[b]naphthalene-3,8-dione]

Red powder; mp 114–115 °C (EtOAc–hexanes).

IR (KBr): 2950, 2875, 1663, 1597, 1463, 1218, 842, 820, 715 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 8.21 (m, 2 H), 7.10 (m, 2 H), 4.43 (s, 5 H), 1.08 (t, *J* = 7.8 Hz, 9 H), 0.94 (dq, *J* = 15.2, 7.6 Hz, 3 H), 0.80 (dq, *J* = 15.3, 7.7 Hz, 3 H), 0.35 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 186.1, 186.0, 136.8 (2 C), 132.43, 132.41, 126.30, 126.28, 81.7, 80.6, 78.6, 78.51, 78.46, 8.16, 5.12, 0.59.

MS (EI, 70 eV): *m/z* (%) = 492 (46, $[M]^+$), 463 (30), 435 (21), 87 (49), 73 (71), 59 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 255 sh (4.38), 274 (4.43), 326 (4.27), 383 (3.59), 470 nm (2.99).

Anal. Calcd for $C_{26}H_{33}CoO_2Si_2$: C, 63.39; H, 6.75. Found: C, 63.75; H, 6.89.

CpCo[1-(triethylsilyl)-3-(trimethylsilyl)-1*H*-cyclopenta[*b*]naphthalene-2,4,9-trione]

Red-brown powder; mp 140.5–144 °C (EtOAc–hexanes).

IR (KBr): 2955, 2875, 1672, 1627, 1595, 1393, 1230, 1005, 826, 730 cm^{-1}.

^1H NMR (500 MHz, C_6D_6): δ = 8.13 (m, 2 H), 7.15 (m, 2 H), 4.38 (s, 5 H), 1.27 (dq, *J* = 13.5, 6.7 Hz, 3 H), 1.23 (t, *J* = 6.7 Hz, 9 H), 1.06 (dq, *J* = 13.5, 6.7 Hz, 3 H), 0.60 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 187.5, 187.4, 175.8, 135.2, 135.1, 133.5 (2 C), 126.8, 126.7, 91.83, 91.79, 82.5, 71.1, 70.4, 8.53, 4.69, 0.39.

MS (EI, 70 eV): *m/z* (%) = 520 (100, $[M]^+$), 505 (20), 491 (92), 237 (24), 198 (24), 124 (58), 73 (52), 59 (53).

HRMS-EI: *m/z* $[M]^+$ calcd for $C_{27}H_{33}CoO_3Si_2$: 520.1300; found: 520.1308.

UV/Vis (MeOH): λ_{max} (log ε) = 258 (4.35), 299 (4.22), 402 (3.42), 472 nm (3.09).

53

Red-black solid; mp 184–189 °C (EtOAc–hexanes).

IR (KBr): 3360, 2930, 2855, 1418, 1250, 982, 928, 836, 806, 757 cm^{-1}.

^1H NMR (300 MHz, C_6D_6): δ = 7.19 (AA′m, 2 H), 6.98 (BB′m, 2 H), 5.05 (d, *J* = 6.3 Hz, 2 H), 4.86 (s, 5 H), 3.96 (d, *J* = 6.3 Hz, 2 H), 1.91 (br t, *J* = 5.9 Hz, 2 H, H_{tert}), 1.28–1.17 (m, 2 H), 0.85–0.67 (m, 4 H), 0.65–0.45 (m, 2 H), 0.36 (s, 18 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 142.3, 128.8, 108.0, 81.0, 71.6, 58.5, 41.2, 32.9, 23.2, 2.03 (one aromatic carbon resonance was obscured by solvent).

MS (EI, 70 eV): *m/z* (%) = 536 (1, $[M]^+$), 518 (4), 445 (4), 376 (10), 305 (27), 289 (28), 231 (31), 75 (59), 73 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 269 (4.23), 329 sh (3.41), 381 (2.93), 428 nm (2.86).

Anal. Calcd for $C_{29}H_{41}CoO_2Si_2$: C, 64.89; H, 7.70. Found: C, 64.94; H, 7.60.

54

Red-brown powder; mp 183–186 °C (EtOAc–hexanes).

IR (KBr): 3460–3300, 2945, 2858, 1417, 1253, 963, 834, 806, 759, 681, 633 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (AA′m, 2 H), 7.35 (BB′m, 2 H), 5.26 (d, *J* = 6.5 Hz, 2 H), 4.16 (s, 5 H), 3.11 (d, *J* = 6.5 Hz, 2 H, exchangeable with D_2O), 1.91 (br s, 2 H, H_{tert}), 1.45 (m, 2 H), 1.20–1.08 (m, 4 H), 1.04 (m, 2 H), 0.28 (s, 18 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 140.0, 128.4, 127.7, 98.5, 80.6, 73.2, 60.5, 41.0, 32.8, 23.1, 2.72.

MS (EI, 70 eV): *m*/*z* (%) = 536 (11, [M]$^+$), 463 (43), 305 (53), 231 (49), 136 (48), 121 (56), 105 (47), 91 (48), 73 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 264 (4.19), 315 sh (3.67), 412 (2.99), 544 nm (2.50).

Anal. Calcd for $C_{29}H_{41}CoO_2Si_2$: C, 64.89; H, 7.70. Found: C, 64.61; H, 7.81.

The crude solution of the cyclization experiment generating **53** and **54** formed a precipitate of a CpCo(cyclopentadienone) complex (Figure 10) (10%) derived from **39**.

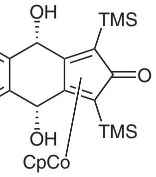


Figure 10 CpCo[4,9-dihydroxy-1,3-bis(trimethylsilyl)-4,9-dihydro-2*H*-cyclopenta[*b*]naphthalen-2-one]

Orange-yellow powder; mp 250–253 °C (C_6H_6).

IR (KBr): 3400–3200, 2950, 2895, 1511, 1438, 1247, 1012, 861, 835, 825, 738 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.48 (m, 2 H), 7.34 (m, 2 H), 5.23 (s, 2 H), 4.58 (s, 5 H), 0.32 (s, 18 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 172.3, 137.6, 129.7, 127.7, 98.9, 81.0, 66.2, 64.7, –0.31.

MS (EI, 70 eV): *m*/*z* (%) = 482 (45, [M]$^+$), 449 (16), 375 (15), 325 (14), 133 (26), 75 (41), 73 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 288 (4.28), 365 (3.40), 428 nm (3.08).

Anal. Calcd for $C_{24}H_{31}CoO_3Si_2$: C, 59.73; H, 6.47. Found: C, 59.61; H, 6.45.

Attempted cocyclization of **35** with cyclohexene gave only the CpCo(cyclobutadiene) complex (Figure 11) of **35** (54%).

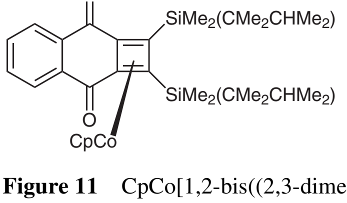


Figure 11 CpCo[1,2-bis((2,3-dimethylbutan-2-yl)dimethylsilyl)cyclobuta[*b*]naphthalene-3,8-dione]

Red needles; mp 191–193 °C (CH_2Cl_2–MeOH).

IR (KBr): 2958, 2864, 1659, 1597, 1452, 1400, 1253, 1213, 952, 815, 777, 713 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (AA′m, 2 H), 7.59 (BB′m, 2 H), 4.77 (s, 5 H), 1.77 (sept, *J* = 6.8 Hz, 2 H), 0.94 (s, 6 H), 0.92 (s, 6 H), 0.86 (d, *J* = 6.8 Hz, 6 H), 0.84 (d, *J* = 6.8 Hz, 6 H), 0.50 (s, 6 H), 0.28 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.3, 136.0, 132.5, 126.1, 85.0, 82.7, 78.9, 33.9, 24.6, 21.8, 21.6, 18.9, 18.3, –1.03, –1.10.

MS (EI, 70 eV): *m*/*z* (%) = 590 (0.5, [M]$^+$), 505 (85), 435 (76), 421 (95), 361 (58), 360 (50), 73 (95), 43 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 275 (4.19), 327 (3.96), 386 (3.28), 470 sh nm (2.67).

Anal. Calcd for $C_{33}H_{47}CoO_2Si_2$: C, 67.08; H, 8.02. Found: C, 66.99; H, 8.00.

Attempted cocyclization of **36** with cyclohexene gave only the CpCo(cyclobutadiene) complex (Figure 12) of **36** (33%).

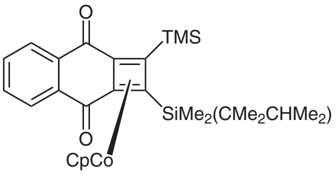


Figure 12 CpCo{1-[(2,3-dimethylbutan-2-yl)dimethylsilyl]-2-(trimethylsilyl)cyclobuta[*b*]naphthalene-3,8-dione}

Red-brown powder; mp 111–113 °C (EtOAc–hexanes).

IR (KBr): 2970, 1661, 1600, 1460, 1259, 1214, 958, 821, 718 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 8.19 (m, 2 H), 7.12 (m, 2 H), 4.41 (s, 5 H), 1.69 (sept, *J* = 6.9 Hz, 1 H), 1.01 (s, 3 H), 0.97 (s, 3 H), 0.91 (d, *J* = 6.9 Hz, 6 H), 0.63 (s, 3 H), 0.37 (s, 9 H), 0.17 (s, 3 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 186.2, 185.8, 136.8, 136.7, 132.5, 132.4, 126.4, 126.3, 82.7, 81.9, 81.5, 79.4, 78.8, 35.0, 24.9, 22.1, 21.7, 19.10, 19.09, 0.75, –1.32, –1.45.

MS (EI, 70 eV): *m*/*z* (%) = 520 (0.5, [M]$^+$), 505 (0.8), 435 (100), 361 (26), 73 (57).

UV/Vis (MeOH): λ_{max} (log ε) = 256 sh (4.40), 273 (4.46), 326 (4.27), 386 (3.61), 470 sh nm (3.04).

Anal. Calcd for $C_{28}H_{37}CoO_2Si_2$: C, 64.59; H, 7.16. Found: C, 64.78; H, 7.30.

55

Dark red solid; mp 198–203 °C (CH_2Cl_2–MeOH).

IR (KBr): 2950, 1665, 1598, 1333, 1250, 842, 813 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 8.18 (m, 1 H), 8.12 (m, 1 H), 7.07 (m, 2 H), 4.57 (dd, *J* = 7.0, 4.1 Hz, 1 H), 4.38 (s, 5 H), 3.18 (s, 3 H), 2.77 (dd, *J* = 8.7, 4.0 Hz, 1 H), 2.65 (ddd, *J* = 10.6, 8.6, 7.7 Hz, 1 H), 2.54 (ddd, *J* = 9.7, 7.1, 2.6 Hz, 1 H), 2.39 (ddd, *J* = 13.8, 7.6, 2.9 Hz, 1 H), 1.56 (sept, *J* = 6.9 Hz, 1 H), 1.42 (d, *J* = 9.9 Hz, 1 H), 1.34 (s, 3 H), 1.05 (dd, *J* = 13.8, 10.7 Hz, 1 H), 0.88 (d, *J* = 6.9 Hz, 3 H), 0.86 (d, *J* = 6.9 Hz, 3 H), 0.76 (s, 3 H), 0.74 (s, 3 H), 0.63 (s, 3 H), 0.44 (br s, 9 H), 0.35 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H), –0.01 (s, 3 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 191.5, 191.2, 135.1, 135.0, 134.2, 133.9, 127.0, 126.9, 104.9, 95.6, 92.2, 83.2, 82.9, 77.4, 68.7, 66.2, 53.3, 48.3, 47.6, 35.9, 35.7, 35.2, 25.7, 21.2, 21.0, 19.4, 19.2, 15.0, 4.32, 4.20, 3.16, 2.17, 0.22, 0.08.

MS (FAB, HEDS): *m*/*z* (%) = 762 [M]$^+$.

Anal. Calcd for $C_{40}H_{59}CoO_5Si_3$: C, 62.96; H, 7.79. Found: C, 62.86; H, 8.18.

56

Colorless solid; mp 96–99 °C (CH_2Cl_2–PE).

IR (KBr): 2975, 2165, 1778, 1669, 1648, 1477, 1290, 1261, 1237, 1030, 858, 763 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (dd, *J* = 7.7, 0.6 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 1 H), 7.18 (d, *J* = 8.4 Hz, 1 H), 3.85 (s, 3 H), 0.28 (s, 9 H), 0.19 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.4, 176.4, 156.8, 135.9, 130.7, 130.1, 123.9, 117.0, 102.3, 101.8, 100.6, 98.3, 56.4, –0.70, –0.76.

MS (EI, 70 eV): *m*/*z* (%) = 356 (32, [M]$^+$), 341 (50), 283 (29), 267 (26), 254 (31), 165 (24), 134 (27), 97 (25), 73 (100).

Anal. Calcd for $C_{19}H_{24}O_3Si_2$: C, 64.00; H, 6.78. Found: C, 64.17; H, 6.59.

57

Red brown solid; mp 172–175 °C (EtOAc–hexanes).

IR (KBr): 2935, 2858, 1663, 1586, 1283, 1252, 850, 813 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 7.7, 0.8 Hz, 1 H), 7.60 (t, *J* = 7.7 Hz, 1 H), 7.25 (d, *J* = 7.7 Hz, 1 H), 4.55 (s, 5 H), 3.97 (s, 3 H), 2.18–2.05 (m, 2 H, H_{tert}), 1.55–1.45 (m, 2 H), 1.20–1.00 (m, 6 H), 0.27 (s, 9 H), 0.24 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 190.0, 158.6, 136.8, 133.7, 123.4, 118.1, 116.8, 96.1, 92.1, 82.4, 70.0, 68.6, 56.6, 41.32, 41.31, 32.8, 32.7, 23.4, 23.2, 2.48, 2.38.

MS (EI, 70 eV): *m*/*z* (%) = 562 (3, [M]$^+$), 438 (3), 408 (5), 349 (9), 309 (26), 307 (16), 147 (20), 89 (100), 75 (26), 73 (27), 59 (74).

UV/Vis (MeOH): λ_{max} (log ε) = 276 (4.27), 313 sh (4.01), 354 (3.92), 470 nm (3.35).

Anal. Calcd for $C_{30}H_{39}CoO_3Si_2$: C, 64.03; H, 6.99. Found: C, 64.20; H, 6.78.

58

Reddish black solid; mp 164–166 °C (acetone–hexanes).

IR (KBr): 3540–3390, 2945, 1665, 1590, 1477, 1287, 855, 819 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.86 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.06 (t, *J* = 8.0 Hz, 1 H), 6.56 (d, *J* = 8.3 Hz, 1 H), 4.45 (s, 5 H), 4.03 (br s, 1 H), 3.32 (s, 3 H), 2.47 (d, *J* = 7.5 Hz, 1 H, H_{tert}), 2.27 (ddd, *J* = 11.7, 7.5, 4.8 Hz, 1 H, H_{tert}), 1.74 (m, 1 H), 1.42–1.30 (m, 2 H), 1.16–1.04 (m, 2 H), 0.90 (m, 1 H), 0.69 (d, *J* = 3.5 Hz, 1 H), 0.45 (br s, 9 H), 0.42 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 191.3, 189.1, 159.4, 137.4, 133.6, 124.7, 118.6, 117.4, 95.0, 94.6, 82.6, 70.1, 69.4, 64.7, 56.1, 52.6, 34.6, 33.6, 28.8, 19.4, 3.33, 2.19.

MS (FAB, TG-G): *m*/*z* (%) = 578 [M]$^+$.

UV/Vis (MeOH): λ_{max} (log ε) = 275 (4.32), 356 (3.96), 468 nm (3.40).

Anal. Calcd for $C_{30}H_{39}CoO_4Si_2$: C, 62.26; H, 6.79. Found: C, 61.89; H, 7.05.

59

Reddish brown foam.

IR (KBr): 3435, 2945, 1662, 1586, 1279, 1248, 840 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.93 (dd, *J* = 7.6, 0.9 Hz, 1 H), 7.10 (t, *J* = 8.0 Hz, 1 H), 6.56 (d, *J* = 8.2 Hz, 1 H), 4.44 (s, 5 H), 4.06 (br s, 1 H), 3.31 (s, 3 H), 2.52 (d, *J* = 7.3 Hz, 1 H, H_{tert}), 2.27 (ddd, *J* = 11.7, 7.3, 4.8 Hz, 1 H, H_{tert}), 1.72 (m, 1 H), 1.42–1.26 (m, 2 H), 1.16 (m, 1 H), 0.99–0.86 (m, 2 H), 0.49 (br s, 9 H), 0.40 (s, 9 H) (the OH signal was not observed).

^{13}C NMR (125 MHz, C_6D_6): δ = 191.1, 189.7, 159.2, 137.2, 133.8, 124.7, 118.5, 117.0, 98.9, 91.1, 82.7, 70.1, 68.3, 66.2, 56.0, 52.7, 34.8, 33.3, 28.8, 19.6, 3.58, 2.08.

MS (FAB, NBA): *m*/*z* (%) = 578 [M]$^+$.

HRMS-FAB (PEG): *m*/*z* [M]$^+$ calcd for $C_{30}H_{39}CoO_4Si_2$: 579.1797; found: 579.1800.

60

Red powder; 173–174.5 °C (EtOAc–hexanes).

IR (KBr): 2955, 1723, 1678, 1593, 1280, 857, 828, 724 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 8.23 (m, 2 H), 7.84 (dd, *J* = 7.4, 1.0 Hz, 1 H), 7.12–7.00 (m, 4 H), 6.57 (dd, *J* = 8.4, 0.6 Hz, 1 H), 6.02 (br s, 1 H), 4.39 (s, 5 H), 3.33 (s, 3 H), 2.81 (br d, *J* = 7.2 Hz, 1 H, H_{tert}), 2.34 (ddd, *J* = 12.0, 7.4, 4.8 Hz, 1 H, H_{tert}), 1.88 (m, 1 H), 1.63 (m, 1 H), 1.45 (m, 1 H), 1.22 (m, 1 H), 0.97 (m, 1 H), 0.59 (br s, 9 H), 0.50 (m, 1 H), 0.45 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.3, 188.8, 165.2, 159.4, 137.5, 133.7, 132.8, 131.5, 130.1, 125.2, 118.6, 117.4, 95.2, 94.7, 82.7, 73.1, 68.9, 63.1, 56.1, 50.8, 34.7, 33.5, 25.7, 20.5, 3.41, 2.09 (one aromatic carbon resonance was obscured by solvent).

MS (EI, 70 eV): *m*/*z* (%) = 436 (3, [M – (CpCo + $C_6H_5CO_2H$]$^+$), 179 (44), 147 (49), 89 (65), 73 (33), 59 (77).

MS (FAB, sulfolane): *m*/*z* (%) = 683 [MH]$^+$.

UV/Vis (MeOH): λ_{max} (log ε) = 273 (4.20), 355 (3.80), 462 nm (3.25).

Anal. Calcd for $C_{37}H_{43}CoO_5Si_2$: C, 65.08; H, 6.35. Found: C, 64.97; H, 6.32.

61

Red powder; mp 172–174 °C (EtOAc–hexanes).

IR (KBr): 2960, 1727, 1671, 1596, 1287, 995, 858, 827, 730 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 8.23 (m, 2 H), 7.94 (d, *J* = 7.7 Hz, 1 H), 7.13–7.00 (m, 4 H), 6.54 (d, *J* = 8.4 Hz, 1 H), 6.02 (br s, 1 H), 4.37 (s, 5 H), 3.29 (s, 3 H), 2.86 (br d, *J* = 7.5 Hz, 1 H, H_{tert}), 2.38 (ddd, *J* = 11.8, 7.2, 4.7 Hz, 1 H, H_{tert}), 1.85 (m, 1 H), 1.62 (m, 1 H), 1.51 (m, 1 H), 1.35 (m, 1 H), 0.96 (m, 1 H), 0.65 (br s, 9 H), 0.50 (m, 1 H), 0.43 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 190.9, 189.7, 165.2, 159.1, 137.1, 133.9, 132.8, 131.5, 129.8, 128.5, 124.0, 118.5, 117.1, 99.6, 90.9, 82.8, 73.1, 67.6, 64.6, 56.0, 50.8, 34.8, 33.2, 25.6, 20.5, 3.71 (br), 1.90.

MS (EI, 70 eV): *m*/*z* (%) = 436 (4, [M – (CpCo + $C_6H_5CO_2H$]$^+$), 179 (62), 135 (59), 105 (66), 89 (64), 77 (70), 73 (46), 59 (84).

UV/Vis (MeOH): λ_{max} (log ε) = 274 (4.28), 354 (3.88), 460 nm (3.34).

Anal. Calcd for $C_{37}H_{43}CoO_5Si_2$: C, 65.08; H, 6.35. Found: C, 64.87; H, 6.33.

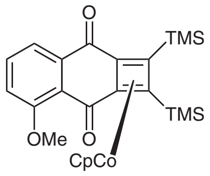


Figure 13 CpCo[4-methoxy-1,2-bis(trimethylsilyl)cyclobuta[*b*]naphthalene-3,8-dione]

Attempted cocyclization of **56** with 2-cyclohexenyl benzoate in THF gave only the CpCo(cyclobutadiene) complex (Figure 13) of **56** (12%).

Red-brown powder; mp 126–127 °C (EtOAc–hexanes).

IR (KBr): 2960, 1662, 1586, 1465, 1272, 1187, 975, 840, 818, 753 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 8.02 (dd, *J* = 7.7, 1.1 Hz, 1 H), 7.05 (t, *J* = 8.0 Hz, 1 H), 6.57 (d, *J* = 8.2 Hz, 1 H), 4.47 (s, 5 H), 3.36 (s, 3 H), 0.34 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.2, 185.6, 160.3, 139.6, 133.1, 125.0, 119.3, 117.8, 81.3, 80.1, 79.2, 78.3, 77.4, 56.1, 0.64, 0.57.

MS (EI, 70 eV): *m/z* (%) = 480 (69, [M]$^+$), 465 (12), 145 (17), 75 (57), 73 (100).

HRMS-EI: *m/z* [M]$^+$ calcd for $C_{24}H_{29}CoO_3Si_2$: 480.0987; found: 480.1006.

UV/Vis (MeOH): λ_{max} (log ε) = 274 (4.35), 328 (4.13), 364 sh (3.90), 394 sh (3.79), 466 sh nm (3.15).

Anal. Calcd for $C_{24}H_{29}CoO_3Si_2$: C, 59.98; H, 6.08. Found: C, 60.42; H, 6.05.

63

Red brown powder; mp 178–183 °C (EtOAc–hexanes); $[\alpha]_D^{20}$ +230 (*c* 3.2 × 10^{-4}, $CHCl_3$).

IR (KBr): 2962, 1674, 1593, 1278, 1257, 1004, 986, 843, 818 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.80 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.02 (t, *J* = 8.0 Hz, 1 H), 6.52 (d, *J* = 8.2 Hz, 1 H), 4.77 (dd, *J* = 6.7, 3.7 Hz, 1 H), 4.46 (s, 1 H), 4.41 (s, 5 H), 4.25 (d, *J* = 1.0 Hz, 1 H), 3.28 (s, 3 H), 2.71 (dd, *J* = 8.4, 3.6 Hz, 1 H), 2.64 (dt, *J* = 10.5, 7.1 Hz, 1 H), 2.41 (ddd, *J* = 12.2, 6.9, 2.8 Hz, 1 H), 2.00 (ddd, *J* = 9.7, 7.0, 2.6 Hz, 1 H), 1.65 (d, *J* = 10.2 Hz, 1 H), 1.56 (sept, *J* = 6.9 Hz, 1 H), 1.21 (dd, *J* = 12.1, 10.7 Hz, 1 H), 0.861 (d, *J* = 6.9 Hz, 3 H), 0.858 (d, *J* = 6.9 Hz, 3 H), 0.77 (s, 3 H), 0.76 (s, 3 H), 0.63 (s, 3 H), 0.41 (s, 9 H), 0.37 (s, 3 H), 0.05 (s, 3 H), 0.02 (s, 3 H), –0.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 189.0, 166.6, 159.4, 137.0, 133.8, 123.5, 118.5, 117.5, 95.0, 94.3, 82.6, 79.4, 78.8, 76.6, 66.5, 62.1, 56.0, 50.8, 50.6, 39.0, 34.6, 34.5, 25.0, 20.5, 20.4, 18.84, 18.79, 4.05, 3.35, 2.34, 1.36, –0.04, –0.37.

MS (FAB, sulfolane): *m/z* (%) = 761 [MH]$^+$.

UV/Vis (MeOH): λ_{max} (log ε) = 277 (4.32), 306 sh (4.09), 356 (3.91), 466 nm (3.37).

Anal. Calcd for $C_{40}H_{57}CoO_5Si_3$: C, 63.13; H, 7.55. Found: C, 62.97; H, 7.52.

62

Red brown solid; mp 68–72 °C (EtOAc–hexanes); $[\alpha]_D^{20}$ +340 (*c* 1.8 × 10^{-4}, $CHCl_3$).

IR (KBr): 2960, 1670, 1590, 1280, 1254, 979, 839, 812 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.87 (dd, *J* = 7.7, 1.0 Hz, 1 H), 7.04 (t, *J* = 7.8 Hz, 1 H), 6.49 (d, *J* = 7.7 Hz, 1 H), 4.77 (dd, *J* = 6.7, 3.8 Hz, 1 H), 4.46 (s, 1 H), 4.39 (s, 5 H), 4.25 (d, *J* = 1.1 Hz, 1 H), 3.26 (s, 3 H), 2.74 (dd, *J* = 8.3, 3.7 Hz, 1 H), 2.62 (dt, *J* = 15.4, 7.1 Hz, 1 H), 2.39 (ddd, *J* = 12.1, 7.0, 2.9 Hz, 1 H), 2.01 (ddd, *J* = 10.1, 7.0, 2.7 Hz, 1 H), 1.71 (d, *J* = 10.3 Hz, 1 H), 1.56 (sept, *J* = 6.9 Hz, 1 H), 1.23 (dd, *J* = 12.0, 9.3 Hz, 1 H), 0.861 (d, *J* = 6.9 Hz, 3 H), 0.857 (d, *J* = 6.9 Hz, 3 H), 0.78 (s, 3 H), 0.76 (s, 3 H), 0.66 (s, 3 H), 0.39 (s, 9 H), 0.35 (s, 3 H), 0.16 (s, 3 H), 0.01 (s, 3 H), 0.00 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 189.7, 166.6, 159.2, 137.0, 134.0, 123.5, 118.6, 117.1, 98.8, 91.0, 82.6, 79.4, 78.9, 76.6, 65.4, 63.6, 55.9, 50.74, 50.69, 39.0, 34.44, 34.41, 25.0, 20.5, 20.4, 18.84, 18.77, 4.62, 3.53, 2.22, 1.35, –0.08, –0.36.

MS (FAB, sulfolane): *m/z* (%) = 761 [MH]$^+$.

UV/Vis (MeOH): λ_{max} (log ε) = 276 (4.23), 305 sh (4.01), 357 (3.83), 464 nm (3.29).

Anal. Calcd for $C_{40}H_{57}CoO_5Si_3$: C, 63.13; H, 7.55. Found: C, 63.31; H, 7.80.

The experiment generating **63** and **62** (in order of elution on column chromatography) also gave the CpCo(cyclopentadienone) complex (Figure 14) (9%) derived from **56**.

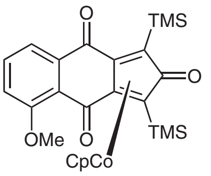


Figure 14 CpCo[5-methoxy-1,3-bis(trimethylsilyl)-1*H*-cyclopenta[*b*]naphthalene-2,4,9-trione]

Red powder; mp 201–203 °C (EtOAc–hexanes).

IR (KBr): 2960, 2904, 1679, 1611, 1592, 1287, 1248, 1199, 1013, 832, 736 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 7.90 (d, *J* = 7.5 Hz, 1 H), 7.12 (t, *J* = 8.1 Hz, 1 H), 6.62 (d, *J* = 8.1 Hz, 1 H), 4.39 (s, 5 H), 3.35 (s, 3 H), 0.61 (s, 18 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.7, 185.6, 175.3, 160.2, 137.6, 134.3, 123.4, 119.2, 117.9, 94.7, 90.7, 82.2, 70.9, 69.6, 56.1, 0.51, 0.48.

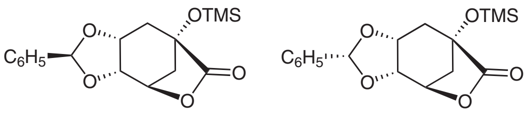
MS (EI, 70 eV): *m/z* (%) = 508 (29, [M]$^+$), 493 (10), 449 (13), 138 (11), 123 (21), 95 (21), 73 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 255 (4.30), 296 (4.22), 381 (3.80), 462 nm (3.14).

Anal. Calcd for $C_{25}H_{29}CoO_4Si_2$: C, 59.04; H, 5.75. Found: C, 59.37; H, 5.83.

47b

TMS-68a and TMS-68b: To a solution of the mixture of diastereomers **68** (13.5 g, 51 mmol)[18] in anhyd THF (80 mL) under N_2 at r.t. was slowly added Et_3N (14 mL, 2 equiv), followed by TMSCl (9 mL, 1.3 equiv), and the mixture was stirred for 12 h at r.t. Aqueous workup resulted in the two diastereomers of TMS-protected **68** (16.1 g, 95%), separated by column chromatography (silica gel) (Figure 15).



TMS-**68a** TMS-**68b**

Figure 15 TMS-**68a** and TMS-**68b**

TMS-68a: colorless oil.

IR (KBr): 3067, 3031, 3004, 2959, 2907, 1795, 1457, 1408, 1254, 1192, 1086, 1066, 971, 890, 839 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (m, 2 H), 7.42 (m, 3 H), 5.76 (s, 1 H), 4.76 (dd, *J* = 6.0, 2.4 Hz, 1 H), 4.52 (td, *J* = 7.6, 2.4 Hz, 1 H), 4.36 (dt, *J* = 6.8, 1.2 Hz, 1 H), 2.72 (d, *J* = 11.6 Hz, 1 H), 2.55 (ddd, *J* = 14.8, 7.6, 2.0 Hz, 1 H), 2.34 (ddt, *J* = 11.6, 6.4, 1.8 Hz, 1 H), 2.30 (dd, *J* = 14.8, 2.4 Hz, 1 H), 0.20 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.4, 135.8, 130.0, 128.8, 126.8, 103.9, 74.9, 73.5, 73.3, 73.0, 39.1, 35.7, 2.10.

HRMS-EI: *m/z* [M]$^+$ calcd for $C_{17}H_{22}O_5Si$: 334.1236; found: 334.1213.

*TMS-**68b***: Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (m, 5 H), 6.23 (s, 1 H), 4.84 (dd, *J* = 8.0, 4.4 Hz, 1 H), 4.56 (dt, *J* = 11.2, 7.6 Hz, 1 H), 4.35 (ddd, *J* = 8.0, 4.0, 1.2 Hz, 1 H), 2.56 (d, *J* = 15.6 Hz, 1 H), 2.52 (ddd, *J* = 18.8, 10.8, 3.6 Hz, 1 H), 2.44 (dddd, *J* = 15.6, 8.0, 3.2, 1.6 Hz, 1 H), 2.10 (dd, *J* = 18.8, 7.2 Hz, 1 H), 0.23 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.7, 137.9, 129.5, 128.7, 126.1, 103.9, 74.9, 73.4, 72.8, 72.4, 39.1, 37.1, 2.12.

*Methylene Derivative of TMS-**68a***: A 250 mL three-necked round-bottomed flask was loaded with Zn dust (5.60 g, 85.6 mmol), purged with dry N_2, charged with THF (50 mL) and TMEDA (22 mL), and cooled in an ice-water bath. $TiCl_4$ (7.6 g, 4 equiv) in CH_2Cl_2 (30 mL) was added cautiously and dissolved over 5 min. The cooling bath was removed and the light green solution stirred for 20 min. CH_2Br_2 (3.2 mL) was added via syringe and a solution of TMS-**68a** (3.26 g, 9.75 mmol) in THF (15 mL) injected slowly. The green mixture turned turquoise and gradually darkened after about 1 h. Workup with aq K_2CO_3 was followed by filtration through activated basic Al_2O_3 (50 g) and column chromatography (silica gel, hexane–Et_2O, 100:0 to 95:5) to furnish the methylene derivative of TMS-**68a** (1.75 g, 54%); colorless oil.

IR (KBr): 3117, 3082, 2962, 2925, 2892, 1686, 1655, 1459, 1404, 1250, 1175, 1083, 1065, 989, 833, 761 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (m, 2 H), 7.41 (m, 3 H), 5.80 (s, 1 H), 4.68 (dd, *J* = 6.0, 2.8 Hz, 1 H), 4.77 (ddd, *J* = 8.4, 7.2, 4.8 Hz, 1 H), 4.25 (dd, *J* = 6.4, 2.8 Hz, 1 H), 4.19 (br s, 1 H), 4.10 (br s, 1 H), 2.42 (m, 1 H), 2.39 (d, *J* = 10.8 Hz, 1 H), 2.18 (dd, *J* = 13.6, 4.8 Hz, 1 H), 2.16 (m, 1 H), 0.18 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 136.7, 129.8, 128.7, 126.8, 104.4, 78.7, 76.5, 76.4, 75.2, 73.6, 44.9, 36.9, 2.26.

HRMS-EI: *m/z* [M]$^+$ calcd for $C_{18}H_{24}O_4Si$: 332.1443; found: 332.1443.

47b: To a solution of the preceding methylene derivative (5.70 g, 17 mmol) in anhyd THF (150 mL) at –78 °C was added BuLi (2.50 M in hexanes, 14 mL, 2.06 equiv). The mixture was allowed to warm to –20 to –10 °C for 10 h and worked up with H_2O to give 1.4 g (55%, based on 1.7 g recovered starting material) of **47b**; colorless oil.

IR (neat): 3118, 3041, 2958, 2898, 1677, 1638, 1426, 1380, 1338, 1308, 1252, 1188, 1162, 1096, 998, 902, 878, 842, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.03 (m, 1 H), 5.86 (m, 1 H), 4.59 (td, *J* = 5.2, 1.2 Hz, 1 H), 4.21 (t, *J* = 1.6 Hz, 1 H), 4.12 (d, *J* = 1.6 Hz, 1 H), 2.61 (dt, *J* = 17.2, 2.8 Hz, 1 H), 2.46 (ddt, *J* = 17.2, 4.0, 1.6 Hz, 1 H), 2.40 (dd, *J* = 10.0, 5.6 Hz, 1 H), 2.02 (d, *J* = 9.6 Hz, 1 H), 0.17 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 131.5, 128.8, 79.5, 78.7, 73.4, 44.5, 42.4, 2.25.

MS (EI, 70 eV): *m/z* (%) = 210 (5, [M]$^+$), 195 (9), 167 (20), 151 (26), 115 (20), 105 (11), 73 (100).

64

Red solid.

IR (neat): 3084, 2956, 2923, 2855, 1666, 1586, 1470, 1446, 1316, 1297, 1277, 1251, 1208, 1163, 1050, 999, 842, 810, 756 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.84 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.00 (t, *J* = 8.0 Hz, 1 H), 6.45 (d, *J* = 8.5 Hz, 1 H), 4.73 (dd, *J* = 6.5, 3.5 Hz, 1 H), 4.44 (br s, 1 H), 4.35 (s, 5 H), 4.22 (d, *J* = 1.0 Hz, 1 H), 3.22 (s, 3 H), 2.71 (dd, *J* = 8.5, 3.5 Hz, 1 H), 2.58 (m, 1 H), 2.38 (ddd, *J* = 12.0, 7.0, 3.0 Hz, 1 H), 2.02 (ddd, *J* = 10.0, 7.0, 3.0 Hz, 1 H), 1.68 (d, *J* = 10.5 Hz, 1 H), 1.19 (m, 1 H), 0.62 (s, 3 H), 0.35 (br s, 9 H), 0.31 (s, 3 H), 0.13 (s, 3 H), 0.00 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 191.3, 190.0, 166.9, 159.6, 137.4, 134.4, 123.9, 119.0, 117.5, 99.1, 91.5, 83.1, 79.9, 79.2, 77.0, 65.9, 63.9, 56.3, 51.12, 51.09, 39.5, 34.7, 4.97, 3.97, 2.63, 2.52, 1.69.

HRMS-FAB (TG-G): *m/z* [M]$^+$ calcd for $C_{35}H_{47}CoO_5Si_3$: 690.2063; found: 690.2067.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 230 (4.59), 277 (4.63), 352 (4.21), 466 nm (3.58).

65

Red solid.

IR (neat): 3070, 2956, 2917, 2849, 1666, 1585, 1470, 1446, 1304 1278, 1251, 1164, 1076, 998, 982, 842, 810, 757 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.76 (dd, *J* = 7.5, 1.0 Hz, 1 H), 6.98 (t, *J* = 8.0 Hz, 1 H), 6.48 (d, *J* = 7.5 Hz, 1 H), 4.73 (dd, *J* = 6.5, 4.0 Hz, 1 H), 4.44 (br s, 1 H), 4.37 (s, 5 H), 4.22 (br d, *J* = 1.0 Hz, 1 H), 3.25 (s, 3 H), 2.68 (dd, *J* = 8.5, 3.5 Hz, 1 H), 2.59 (m, 1 H), 2.40 (ddd, *J* = 12.5, 7.0, 3.0 Hz, 1 H), 2.02 (ddd, *J* = 10.0, 6.5, 2.5 Hz, 1 H), 1.62 (d, *J* = 10.0 Hz, 1 H), 1.21 (m, 1 H), 0.58 (s, 3 H), 0.36 (br s, 9 H), 0.34 (s, 3 H), 0.02 (s, 3 H), 0.00 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 191.6, 189.3, 166.9, 159.8, 137.4, 134.1, 123.9, 118.9, 117.9, 95.5, 94.6, 83.0, 79.9, 79.0, 77.0, 67.0, 62.4, 56.4, 51.2, 50.9, 39.5, 34.9, 4.39, 3.78, 2.75, 2.54, 1.77.

HRMS-FAB (TG-G): *m/z* [M]$^+$ calcd for $C_{35}H_{47}CoO_5Si_3$: 690.2063; found: 690.2074.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 230 (4.76), 278 (4.59), 309 (4.34), 355 (4.16), 467 nm (3.57).

66

Red solid. Crystals suitable for X-ray crystallography were grown as purple plates over several days by slow cooling of a hexanes–CH_2Cl_2 solution to 5 °C.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.82 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.12 (1 H, partly masked by solvent), 6.53 (d, *J* = 8.5 Hz, 1 H), 4.65 (dd, *J* = 7.0, 4.0 Hz, 1 H), 4.40 (br s, 1 H), 4.30 (s, 5 H), 4.13 (d, *J* = 1.5 Hz, 1 H), 3.30 (s, 3 H), 2.64 (dd, *J* = 8.0, 3.5 Hz, 1 H), 2.50 (dt, *J* = 11.0, 7.0 Hz, 1 H), 2.10 (ddd, *J* = 12.0, 7.0, 3.0 Hz, 1 H), 1.81 (br s, 1 H), 1.68 (ddd, *J* = 10.0, 7.0, 3.0 Hz, 1 H), 1.42 (d, *J* = 10.5 Hz, 1 H), 0.84 (m, 1 H), 0.56 (s, 3 H), 0.30 (s, 9 H), 0.27 (s, 3 H), 0.08 (s, 3 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 190.9, 190.1, 166.8, 159.4, 137.1, 134.6, 123.7, 119.0, 117.3, 98.7, 91.3, 83.0, 79.2, 77.5, 76.4, 65.7, 64.1, 56.3, 51.1, 49.0, 39.8, 34.6, 4.93, 4.02, 2.66, 1.71.

HRMS-FAB (TG-G): *m/z* [M]$^+$ calcd for $C_{32}H_{39}CoO_5Si_2$: 618.1668; found: 618.1657.

67

Red solid. Crystals suitable for X-ray crystallography were grown as purple plates over several days by slow cooling of a hexanes–CH_2Cl_2 solution to 5 °C.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.79 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.03 (t, *J* = 8 Hz, 1 H), 6.53 (d, *J* = 8.0 Hz, 1 H), 4.64 (dd, *J* = 6.5, 4.0 Hz, 1 H), 4.35 (br s, 6 H), 4.03 (d, *J* = 1.5 Hz, 1 H), 3.28 (s, 3 H), 2.61 (dd, *J* = 8.5, 4.0 Hz, 1 H), 2.51 (dt, *J* = 11.0, 7.0 Hz, 1 H), 2.13 (ddd, *J* = 9.0, 7.0, 3.0 Hz, 1 H), 1.52 (m, 1 H), 1.27 (d, *J* = 10.5 Hz, 1 H), 0.86 (d, *J* = 11.0 Hz, 1 H), 0.52 (s, 3 H), 0.34 (s, 9 H), 0.30 (s, 3 H), 0.00 (s, 3 H) (OH signal could not be located).

^{13}C NMR (125 MHz, C_6D_6): δ = 191.3, 189.2, 166.8, 159.8, 137.5, 134.1, 123.8, 118.9, 117.9, 95.2, 94.4, 83.0, 78.9, 77.5, 76.4, 66.8, 62.4, 56.4, 53.6, 51.1, 39.6, 34.7, 4.32, 3.83, 2.76, 1.78.

HRMS-FAB (NBA): *m/z* [M]$^+$ calcd for $C_{32}H_{39}CoO_5Si_2$: 618.1668; found: 618.1651.

69

Unstable colorless oil.

IR (film): 2940, 2868, 1455, 1438, 831, 814 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.25 (br t, *J* = 2.0 Hz, 2 H), 2.53 (br s, 2 H), 2.25–2.11 (m, 4 H), 1.92–1.80 (m, 2 H), 1.58–1.49 (m, 4 H), 1.49–1.32 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7, 124.5, 37.8, 34.1, 30.6, 24.3, 23.2.

70

Unstable colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.46 (br s, 2 H), 3.88 (br s, 2 H), 2.32 (m, 4 H), 1.60 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5, 136.8, 111.9, 41.3, 29.8, 22.7.

MS (EI, 70 eV): *m/z* (%) = 204 (23, [M]$^+$), 132 (54), 104 (100), 91 (37).

71

Unstable colorless oil.

^{1}H NMR (500 MHz, C_6D_6): δ = 5.10 (s, 2 H), 2.41 (s, 2 H), 2.13 (s, 4 H), 1.96 (s, 2 H), 1.91 (dt, *J* = 9.4, 1.8 Hz, 1 H), 1.42 (m, 6 H), 1.22 (m, 2 H), 1.17 (dt, *J* = 9.4, 1.3 Hz, 1 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 132.1 (C), 123.1 (CH), 46.2 (CH), 43.9 (CH), 34.9 (CH_2), 30.5 (CH_2), 30.2 (CH_2), 23.8 (CH_2).

72

Colorless oil.

IR (film): 2925, 2855, 1445, 1250, 840 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 2.41 (m, 6 H), 1.74 (m, 2 H), 1.57 (m, 6 H), 1.42 (m, 4 H), 0.33 (s, 18 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 147.2, 134.9, 40.0, 31.1, 28.6, 24.8, 23.1, 1.96.

MS (EI, 70 eV): *m/z* (%) = 332 (3, [M]$^+$), 259 (3), 186 (12), 185 (80), 73 (100), 59 (26).

73

Yellow powder; mp 182–186 °C (CH_2Cl_2–PE).

IR (KBr): 2920, 2840, 1667, 1593, 1540, 1508, 1277, 1245, 962, 845, 719 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 8.13 (AA′m, 2 H), 7.09 (BB′m, 2 H), 2.52 (m, 2 H), 1.77 (m, 2 H), 1.43 (m, 2 H), 1.33 (m, 2 H), 1.26 (m, 2 H), 0.39 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.4, 164.7, 141.6, 135.7, 133.6, 127.1, 40.3, 27.3, 24.3, 0.98.

MS (EI, 70 eV): *m/z* (%) = 408 (35, [M]$^+$), 393 (25), 319 (15), 147 (17), 78 (13), 75 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 250 (4.24), 350 (3.68), 390 sh (3.42), 410 sh nm (3.22).

Anal. Calcd for $C_{24}H_{32}O_2Si_2$: C, 70.53; H, 7.89. Found: C, 70.53; H, 7.97.

74

Colorless solid; mp 160–165 °C (MeOH).

IR (KBr): 3490, 3010, 2935, 1485, 1291, 1009, 878, 800 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 7.03 (BB′m, 2 H), 5.43 (d, *J* = 6.1 Hz, 2 H), 3.32 (d, *J* = 6.0 Hz, 2 H), 2.48 (m, 2 H), 1.57 (m, 2 H), 1.35–1.08 (m, 6 H), 0.40 (s, 18 H) (the AA′ part of the aromatic proton signals was masked by solvent).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 143.0, 140.5, 72.7, 40.1, 28.0, 24.8, 2.89 (two sp^2 carbon signals were either masked by solvent or not observable).

MS (EI, 70 eV): *m/z* (%) = 412 (1, [M]$^+$), 376 (36), 304 (31), 232 (31), 147 (52), 107 (45), 78 (87), 77 (64), 75 (81), 73 (100).

Anal. Calcd for $C_{24}H_{36}O_2Si_2$: C, 69.85; H, 8.79. Found: C, 69.98; H, 8.63.

75

Colorless solid; mp 172–178 °C (EtOAc–hexanes).

IR (KBr): 3390, 2925, 1440, 1250, 967, 838, 754 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.04 (BB′m, 2 H), 5.48 (s, 2 H), 4.45 (br s, 2 H), 2.35 (m, 2 H), 1.95 (m, 2 H), 1.53 (m, 2 H), 1.45–1.28 (m, 4 H), 0.32 (s, 18 H) (the AA′ part of the aromatic proton signals was masked by solvent).

^{13}C NMR (100 MHz, C_6D_6): δ = 145.0 (br), 142.5 (br), 140.2, 128.4, 72.4, 40.2, 28.1, 24.7, 2.40 (one *sp*^{2} carbon signal was masked by solvent).

MS (EI, 70 eV): *m/z* (%) = 412 (5, [M]$^+$), 321 (9), 305 (7), 232 (79), 75 (76), 73 (100).

Anal. Calcd for $C_{24}H_{36}O_2Si_2$: C, 69.85; H, 8.79. Found: C, 69.24; H, 8.60.

76

Pale yellow solid; mp 213–218 °C (CH_2Cl_2–Et_2O).

IR (KBr): 2935, 1712, 1670, 1587, 1308, 1274, 1248, 986, 837, 718 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 8.21 (dd, *J* = 8.0, 1.5 Hz, 2 H), 7.90 (dd, *J* = 7.8, 1.0 Hz, 1 H), 7.08 (m, 3 H), 6.99 (t, *J* = 8.0 Hz, 1 H), 6.44 (d, *J* = 7.9 Hz, 1 H), 6.26 (br s,1 H), 3.29 (m, 1 H), 3.23 (s, 3 H), 2.95 (m, 1 H), 1.88–1.72 (m, 2 H), 1.60 (m, 1 H), 1.47–1.24 (m, 3 H), 0.53 (s, 9 H), 0.47 (s, 9 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 186.2, 183.1 (2 C), 165.2, 163.2, 159.5, 137.7, 134.0, 132.9, 131.3, 129.9, 128.6, 125.3, 119.8, 117.2, 71.8, 55.8, 43.9, 37.5, 28.5, 26.1, 19.5, 2.23, 0.41 (two sp^2 carbon signals were either masked by solvent or not observable).

MS (EI, 70 eV): *m/z* (%) = 558 (2, [M]$^+$), 543 (5), 436 (39), 421 (82), 406 (52), 362 (52), 347 (57), 324 (49), 179 (39), 160 (54), 105 (94), 77 (87), 73 (100).

77

Pale yellow solid; mp 223–227 °C (CH_2Cl_2–Et_2O).

IR (KBr): 2937, 1710, 1664, 1584, 1273, 1247, 980, 839, 705 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 8.18 (m, 2 H), 7.81 (d, *J* = 7.7 Hz, 1 H), 7.07 (m, 3 H), 6.97 (t, *J* = 8.0 Hz, 1 H), 6.43 (d, *J* = 7.7 Hz, 1 H), 6.09 (br s, 1 H), 3.23 (s, 3 H), 3.14 (m, 1 H), 2.96 (m, 1 H), 1.79 (m, 1 H), 1.71–1.59 (m, 3 H), 1.40–1.29 (m, 2 H), 0.48 (s, 9 H), 0.47 (s, 9 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 165.4, 160.4, 159.6, 138.4, 134.2, 132.9, 131.3, 129.9, 128.6, 124.5, 119.3, 117.2, 72.4, 55.9, 44.8, 38.0, 29.5, 26.6, 20.5, 1.71, 1.21 (signals for the three carbonyl and two sp^2 carbons were not observed).

MS (EI, 70 eV): *m/z* (%) = 558 (5, [M]$^+$), 543 (3), 436 (29), 428 (49), 406 (31), 105 (100), 77 (45), 73 (77).

78

^{1}H NMR (400 MHz, THF-d_8): δ = 7.91 (d, *J* = 6.2 Hz, 1 H), 7.85 (m, 1 H), 7.20 (m, 1 H), 7.04 (m, 1 H), 3.18 (d, *J* = 8.0 Hz, 1 H), 2.86 (br d, *J* = 9.7 Hz, 1 H), 2.04–1.96 (m, 2 H), 1.78–1.57 (m, 3 H), 1.37 (m, 1 H), 1.13 (app q, *J* = 8.0 Hz, 1 H), 0.25 (br s, 9 H), 0.19 (s, 9 H).

^{13}C NMR (100 MHz, THF-d_8): δ = 181.2, 154.5, 152.2, 140.7, 139.3, 138.8, 134.1, 127.9, 125.0, 124.2, 121.5, 120.4, 107.2, 45.6, 33.3, 32.5, 28.0, 23.7, 0.87 (br), –3.32.

79

Light yellow oil.

IR (KBr): 2950, 2875, 1704, 1663, 1600, 1302, 1259, 976, 860, 735 cm^{-1}.

^{1}H NMR (300 MHz, C_6D_6): δ = 8.16 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.94 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.02 (td, *J* = 7.5, 1.5 Hz, 1 H),6.95 (td, *J* = 7.5, 1.5 Hz, 1 H), 2.88 (br t, *J* = 4.5 Hz, 1 H), 2.34 (br d, *J* = 13.8 Hz, 1 H), 2.21 (ddd, *J* = 12.1, 6.6, 3.2 Hz, 1 H), 1.52–1.32 (m, 3 H), 1.07 (m, 2 H), 0.89 (m, 1 H), 0.72 (m, 1 H), 0.41 (s, 9 H), 0.40 (s, 9 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 192.6 (C), 183.1 (C), 179.1 (C), 145.2 (C), 136.5 (C), 134.7 (CH), 134.4 (C), 133.5 (CH), 126.9 (CH), 74.2 (C), 61.1 (C), 40.6 (CH), 39.7 (CH), 29.9 (CH_2), 25.9 (CH_2), 25.2 (CH_2), 24.3 (CH_2), 2.60 (CH_3), 0.21 (CH_3) (one signal was masked by solvent).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.6, 183.0, 180.7, 144.4, 136.1, 134.8, 133.7, 127.7, 126.9, 74.5, 61.2, 40.2, 39.5, 29.7, 25.6, 24.8, 23.9, 2.17, –0.31.

MS (EI, 70 eV): *m*/*z* (%) = 424 (7, [M]$^+$), 409 (60), 127 (28), 75 (41), 73 (100), 57 (38).

Anal. Calcd for $C_{24}H_{32}O_3Si_2$: C, 67.88; H, 7.59. Found: C, 68.01; H, 7.48.

81

Red-brown solid; mp 96–98 °C (EtOAc–hexanes).

IR (KBr): 3460–3320, 2928, 2852, 1635, 1601, 1247, 853, 832, 812 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 8.20 (d, *J* = 7.7 Hz, 1 H), 7.56 (d, *J* = 7.7 Hz, 1 H), 7.27 (t, *J* = 7.5 Hz, 1 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 5.13 (d, *J* = 9.9 Hz, 1 H), 4.43 (s, 5 H), 2.32 (dt, *J* = 8.0, 5.9 Hz, 1 H), 1.83 (ddd, *J* = 10.8, 8.2, 4.6 Hz, 1 H), 1.67 (m, 1 H), 1.53–1.41 (m, 3 H), 1.21 (dt, *J* = 12.5, 4.7 Hz, 1 H), 1.11 (m, 2 H), 0.99 (m, 1 H), 0.60 (m, 1 H), 0.52 (br s, 9 H), 0.32 (s, 9 H).

^{13}C NMR (125 MHz, C_6D_6): δ = 192.7, 144.0, 132.5, 132.3, 128.3, 126.1, 125.6, 105.9, 90.7, 81.1, 67.7, 62.2, 59.3, 44.4, 39.8, 32.9, 32.3, 24.8, 21.9, 3.82 (2 C).

MS (EI, 70 eV): *m*/*z* (%) = 534 (2, [M]$^+$), 518 (1), 443 (3), 408 (3), 320 (22), 305 (31), 75 (42), 73 (100).

UV/Vis (MeOH): λ_{max} (log ε) = 268 (4.21), 350 sh (3.50), 464 nm (3.05).

Anal. Calcd for $C_{29}H_{39}CoO_2Si_2$: C, 65.14; H, 7.35. Found: C, 65.33; H, 7.44.

Acknowledgment

This work was made possible by initial support from the NIH (GM-22479) and then by the NSF (CHE 0907800).

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