Tetrahedron 73 (2017) 6118–6137

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Steric buttressing in the Pauson-Khand reactions of benzyl enynes

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ARTICLE INFO

Article history:
Received 28 August 2017
Accepted 29 August 2017
Available online 4 September 2017

Keywords:
Cobalt-alkyne complex
Cycloaddition
Cyclopentenone
Diastereoselective
Oxidative

ABSTRACT

The application of the intramolecular Pauson-Khand reaction of 1,n-enynes provides a convenient method for the construction of polycyclic frameworks but this process has largely been limited to the formation of 5,5- and 5,6-fused ring systems. In this report, we describe the application of the Pauson-Khand cyclization to 1,8-enynes embedded in an aromatic ring system wherein it is determined that the presence of steric buttresses in the form of *t*-butyl groups facilitates the cycloaddition. These reactions proceed in good yields with either thermal or oxidative activation and in the former case, the diastereoselectivities are high. An investigation of the tolerance of this cycloaddition to substitution around the 1,8-enyne demonstrates that only 2,2-disubstitution does not result in productive cyclization. Cycloadditions with hydroxyl groups at the propargylic position while leading to fused rings are compromised by side reactions leading to reduction and in some cases tautomerization. However, these byproducts are easily minimized through conversion of the hydroxyl group to the corresponding silyl ether.

The Pauson-Khand (PK) reaction, the [2 + 2 + 1] co-cyclization of an alkene, an alkyne and carbon monoxide has evolved into a reliable method for the construction of cyclopentenones (**1**→**3**, Scheme 1).[1] In its original incarnation it involved the formation of the dicobalt hexacarbonyl complex **2** and thermolysis to afford the corresponding cyclopentenone (Scheme 1).[2] This reaction is known both intermolecularly and intramolecularly, and can be mediated or catalyzed by a variety of metal complexes in addition to the classical method with $Co_2(CO)_8$-derived complexes as initially reported by Pauson and Khand. Photochemical variants are known and it has even been extended to flow conditions.[3] During the development of this transformation other substrates have been found to engage in this reaction including, allenes,[4] dienes[5] and even some hetero cummulenes.[4,6] However, despite these notable advances, there still remain limitations with this cycloaddition that prevent the full realization of its synthetic potential.[7] For example, whereas there are many examples of intramolecular cyclizations which result in the formation of 5,5- and 5,6-fused bicyclic systems, the construction of larger fused rings had not been described until quite recently. Over the past fifteen years or so, several groups,[8] including ours have begun to identify strategies for overcoming these limitations, leading to reports of the construction of medium-sized rings annulated to the cyclopentenone.[9] Our initial approach to this problem was to use enynes which were constructed around an aromatic scaffold[10] as a means to pre-organize the reacting functional groups, in essence to increase the concentration of the reactive conformation (or conceivably decrease the concentration of non-productive conformations).[11] An advantage of this approach was that it permitted the evaluation of additional structural elements on the aromatic ring to further reduce the conformational degrees of freedom – using so-called steric buttressing.[11b–d] In our first generation studies of this approach, we employed aryl enynes e.g., **4** and found that in the presence of *ortho* substituents cyclization occurred to produce bridged ring systems e.g., **6** rather than the initially expected cycloadducts (Scheme 2).[11b,11c,12] In this manuscript, we describe the extension of this chemistry to the more conformationally flexible benzylic enynes where an additional methylene group is incorporated between the aryl ring and the alkyne to assess the limitations of this strategy.[11d]

Our studies commenced by the synthesis of the parent substrate starting from *o*-salicylaldehyde (**7**) which was allylated by treatment with allyl bromide and potassium carbonate (Scheme 3). The resulting aldehyde **8** was treated with acetylenic Grignard reagents (R = H, TMS, Ph) to provide the expected enynes **9**–**11** in generally good yields. Each enyne was converted to the corresponding $Co_2(CO)_6$-complex and then subjected to PK cyclization (Scheme 3) under either thermal conditions (PhMe, 70 °C, Condition A) or oxidative conditions (CH_2Cl_2, NMO, Condition B) (Table 1).[13] While the cobalt complexes were formed uneventfully, only one of these substrates **11** (R = Ph) delivered a cyclopentenone in 31% yield

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http://dx.doi.org/10.1016/j.tet.2017.08.053
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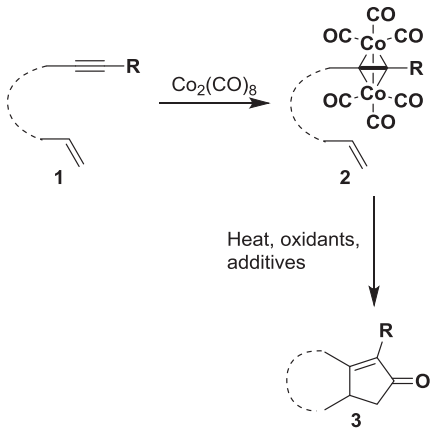


Scheme 1.

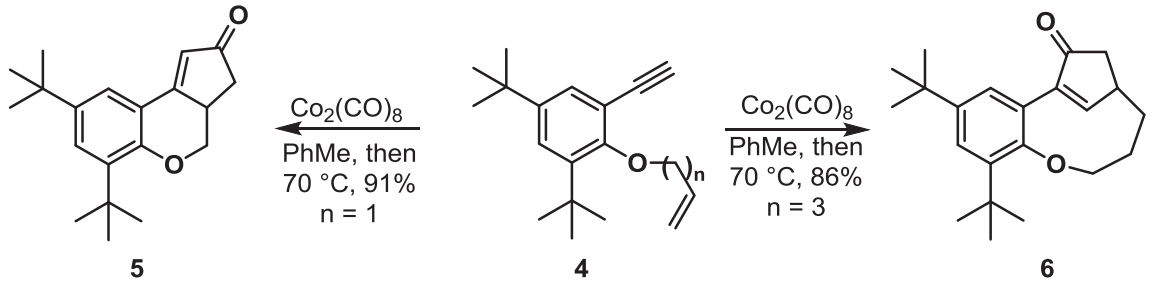
under thermal conditions (70 °C, PhMe) and 8% yield under oxidative conditions (NMO, CH_2Cl_2, 0 °C to rt). Interestingly, it was found that the corresponding TBS-ether **15** underwent thermal cycloaddition in a somewhat improved 50% yield. It is of note that Perez-Castells reported unsuccessful attempts to cyclize related substrates.[8b] Given that the cycloadditions of the parent substrate were on the whole poor, we turned our attention to substrates containing substituents *ortho* to the *O*-allyl moiety.

Table 1
Yields from the PK reactions of the *o*-salicylaldehyde derived enynes **9**–**11**.

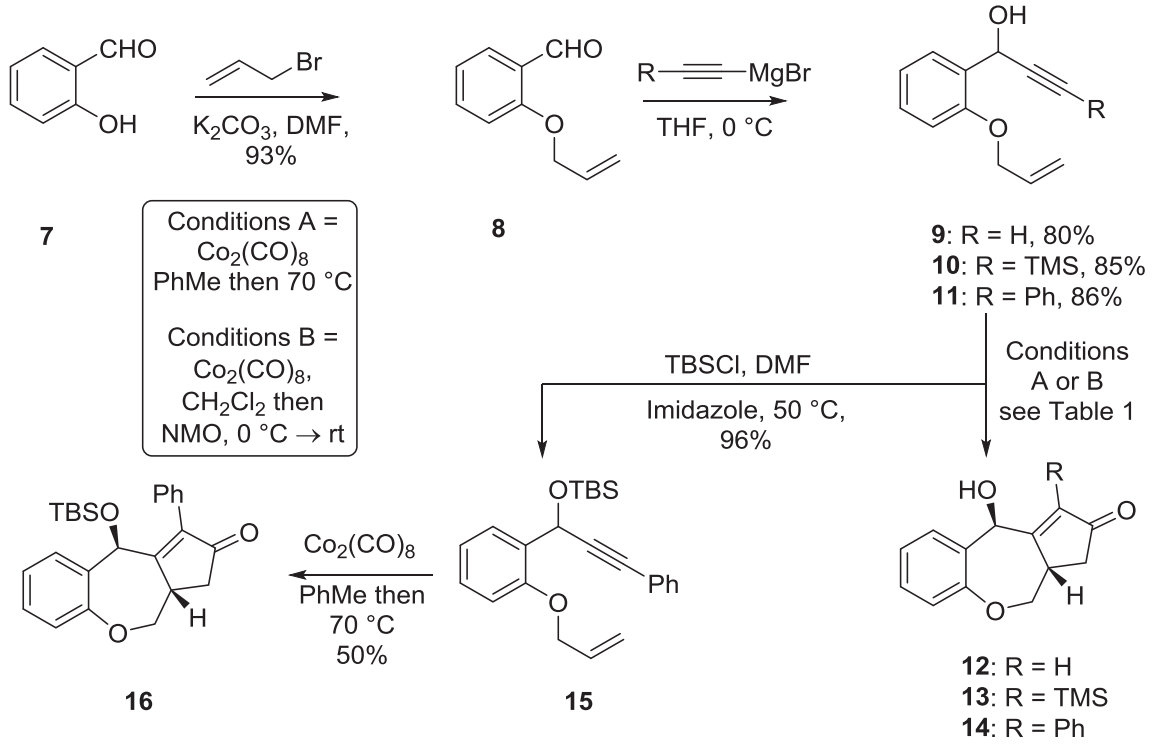
Entry	Substrate	Conditions[a]	Product	%-Yield
1	**9**	A	**12**	0
2	**9**	B	**12**	0
3	**10**	A	**13**	0
4	**10**	B	**13**	0
5	**11**	A	**14**	31
6	**11**	B	**14**	8

[a] Condition A = $Co_2(CO)_8$, PhMe, then 70 °C; Condition B = $Co_2(CO)_8$, CH_2Cl_2, then NMO.

Starting with 4,6-di-*tert*-butylsalicylaldehyde (**17**), it was converted to the allyl ether **18** in the same manner as the parent system **7** and then reaction with the same three Grignard reagents provided the corresponding propargylic alcohols **19**–**21** in good yields



Scheme 2.

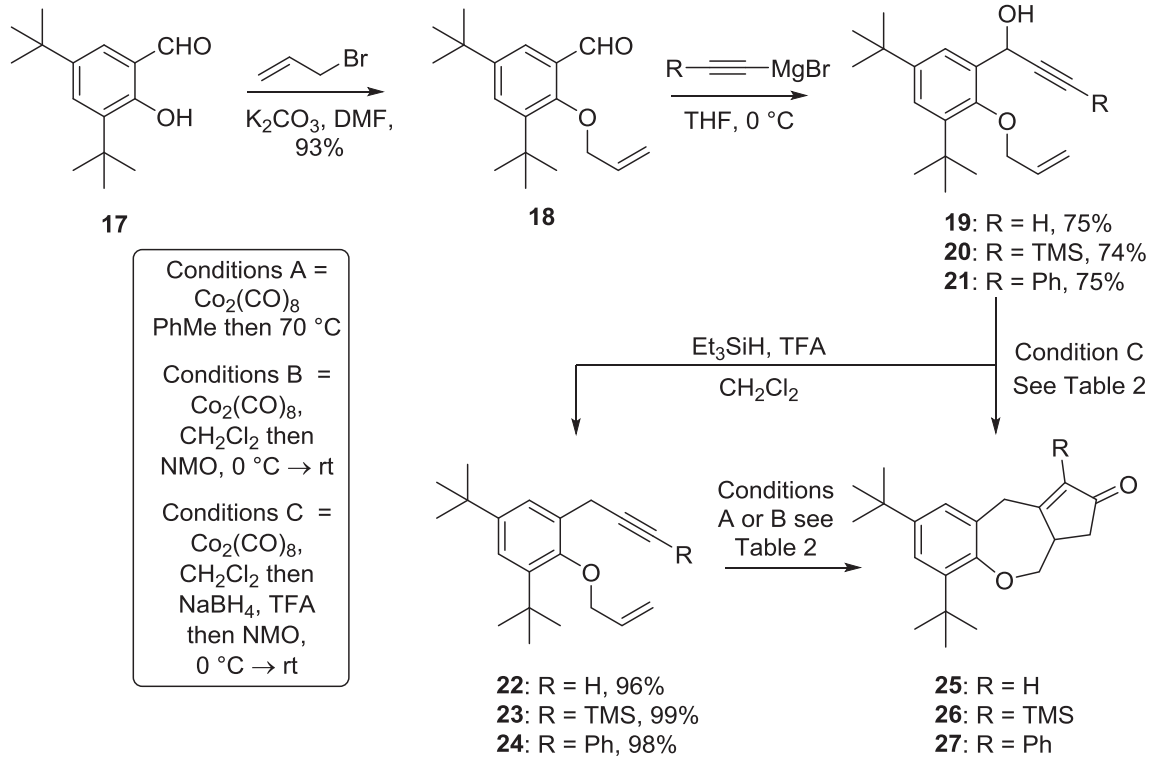


Scheme 3.

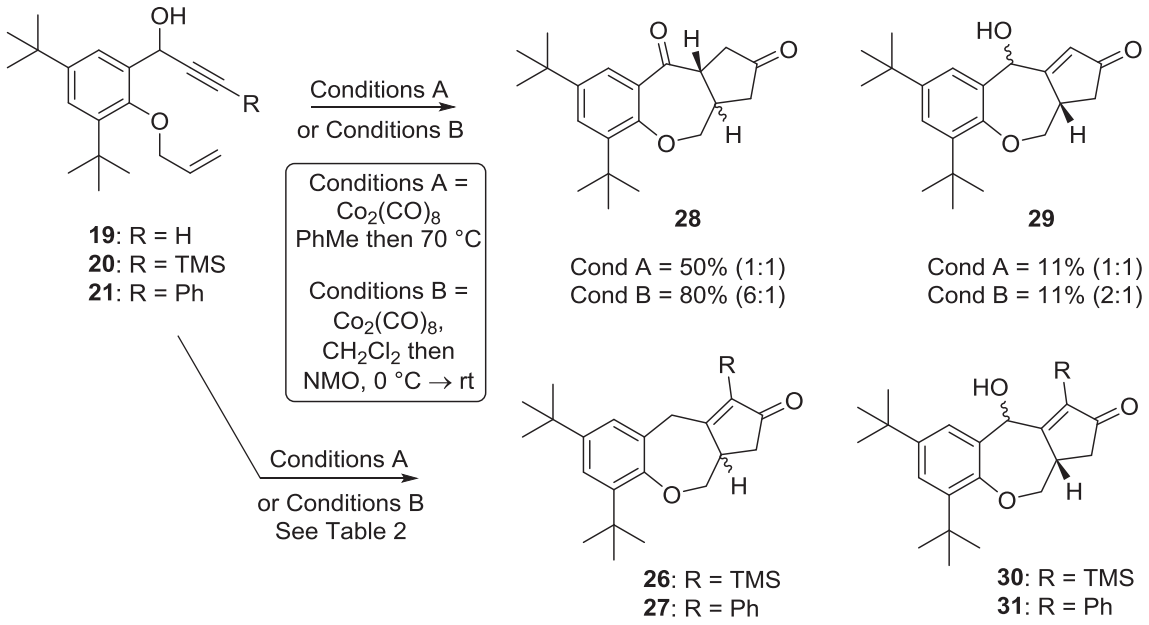
(Scheme 4). Initial attempts to effect PK reactions with these substrates were encouraging in that cycloaddition clearly occurred, but these reactions were complicated by the formation of several products, including 1,4-diketones derived from isomerization of the initial cycloadducts (see Scheme 5 and accompanying text below for details). To simplify product analysis, the hydroxyl group was removed reductively by treatment with TFA and Et_3SiH resulting in the formation of enynes **22**–**24** in essentially quantitative yield (Scheme 4). Conversion of these substrates to the cobalt complexes proceeded uneventfully and set the stage for cyclization reactions. The terminal alkyne **22** did not provide the expected cyclopentenone **25** under either thermal (Condition A) or oxidative conditions (Condition B), instead undergoing simple demetallation. On the other hand, the two internal alkynes participate in cycloaddition under both sets of conditions, delivering the anticipated enones **26** and **27** in similarly moderate yields (Table 2, entries 4–5 and 7–8). The phenyl-substituted product **27** was sufficiently crystalline allowing an X-ray structure to be obtained, which nicely illustrated the connectivity and the formation of the 5,7-bicyclic ring system (Fig. 1). As a further extension of this chemistry, we were cognizant of the fact that the cobalt cluster should promote ionization of the doubly activated hydroxyl group and that we might be able to harness this feature and telescope the reaction sequence.[14] Accordingly, we were able to convert the cobalt complexes of alcohols **20**–**21** directly into the reduced cycloadducts in comparable overall yields by treating the propargylic alcohols sequentially with $Co_2(CO)_8$, TFA/$NaBH_4$, and then NMO (Table 2, entries 6 and 9). Notably, the terminal alkyne **19** again failed to provide the cyclic adduct under these modified conditions.

With the products derived from successful cyclization fully characterized, we returned our attention to the parent alcohols. As noted previously, multiple products were obtained from all three substrates when subjected to either the thermal or oxidative conditions (Scheme 5, Table 2, entries 10–13). In the case of the parent substrate a small amount of the expected PK product **29** was obtained as a mixture of diastereomers (Scheme 5). The major product was the diketone **28**, again isolated as a mixture of diastereomers. Presumably, the diketone arises via a net 1,3-hydride shift followed by tautomerization to form the diketone (see Scheme 13 and accompanying text for further discussion). On the other hand, the internal alkynes **20**–**21** were better behaved, delivering the expected products **30** and **31**, accompanied by varying amounts of the reduction product (Table 2, entries 10–13). In the case of the silyl-substituted system **20** under oxidative conditions cyclopentenone **30** was obtained in 70% yield as a 2:1 mixture of stereoisomers along with 20% of the reduction product **26**. Interestingly, we found that the same substrate delivered cyclopentanone **30** as a single diastereomer under thermal conditions, although the yield was somewhat attenuated. On the other hand, the phenyl-substituted system **21** produced the reduction product as the major cycloadduct under oxidative conditions but in contrast under thermal conditions the expected cycloadduct was obtained in excellent yield as a single stereoisomer. An X-ray crystallographic structure determination on **31** revealed that this was the *exo*-diastereomer (Fig. 2).

A second approach to preventing these competitive side reactions was to convert the alcohols **19**–**21** into the corresponding silyl ethers **32**–**34** (Scheme 6), this was readily accomplished for all three substrates on exposure to TBSCl. Exposure of these enynes to $Co_2(CO)_8$ provided the corresponding cobalt complex which was then subjected to the PK reaction under either oxidative or thermal conditions (Table 3). Generally speaking, the cycloaddition reactions proceeded to produce the expected cycloadducts **35**–**37** in good to excellent yields. In the case of the phenylacetylene derivative **34**, accompanying the expected cyclopentenone under oxidative conditions was the formation of a small amount of the reduction product **27**. In addition, we noted that the reaction under thermal conditions led to higher diastereoselectivity than under



Scheme 4.



Scheme 5.

Table 2
PK Reactions of the allyl-derived substrates **19**–**24**.

Entry	Substrate	Conditions[a]	Product (% - exo:*endo*)	
1	**22**	A	**25** (0)	–
2	**22**	B	**25** (0)	–
3	**19**	C	**25** (0)	–
4	**23**	A	**26** (46)	–
5	**23**	B	**26** (43)	–
6	**20**	C	**26** (50)	–
7	**24**	A	**27** (45)	–
8	**24**	B	**27** (56)	–
9	**21**	C	**27** (48)	–
10	**20**	A	**26** (0)	**30** (58 – exo)
11	**20**	B	**26** (20)	**30** (70–2:1)
12	**21**	A	**27** (0)	**31** (99 – exo)
13	**21**	B	**27** (55)	**31** (26–1:1)

[a] Condition A = $Co_2(CO)_8$, PhMe, then 70 C; Condition B = $Co_2(CO)_8$, CH_2Cl_2, then NMO. Condition C = $Co_2(CO)_8$, CH_2Cl_2; TFA, $NaBH_4$ then NMO.

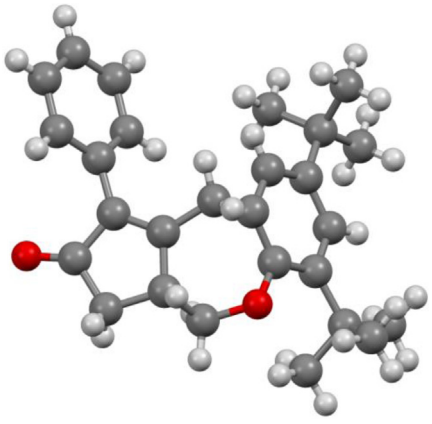


Fig. 1. X-ray crystal structure of **27**.

oxidative conditions (10:1 vs 5:1). To confirm the stereochemistry of the major diastereomer, the TBS ether **37** was treated with TBAF to deliver the same alcohol *exo*-**31** which was characterized by X-ray crystallography, thereby confirming the relative stereochemistry of cycloadduct **37**. The TMS-substituted enyne **33** provided a single cycloadduct **36** in moderate yield under oxidative conditions, but no cyclization appeared to occur under thermal conditions. The simple propargyl ether **32** provided the anticipated cycloadduct **35** in moderate to good yield as a mixture of diastereomers under both conditions.

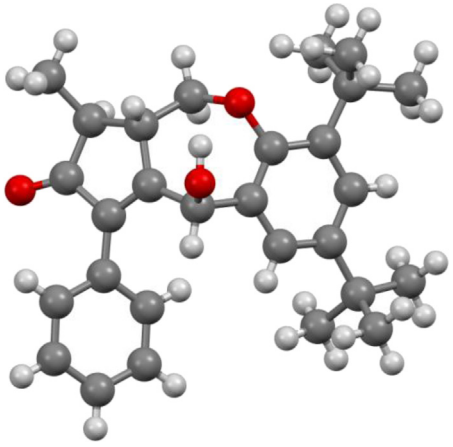
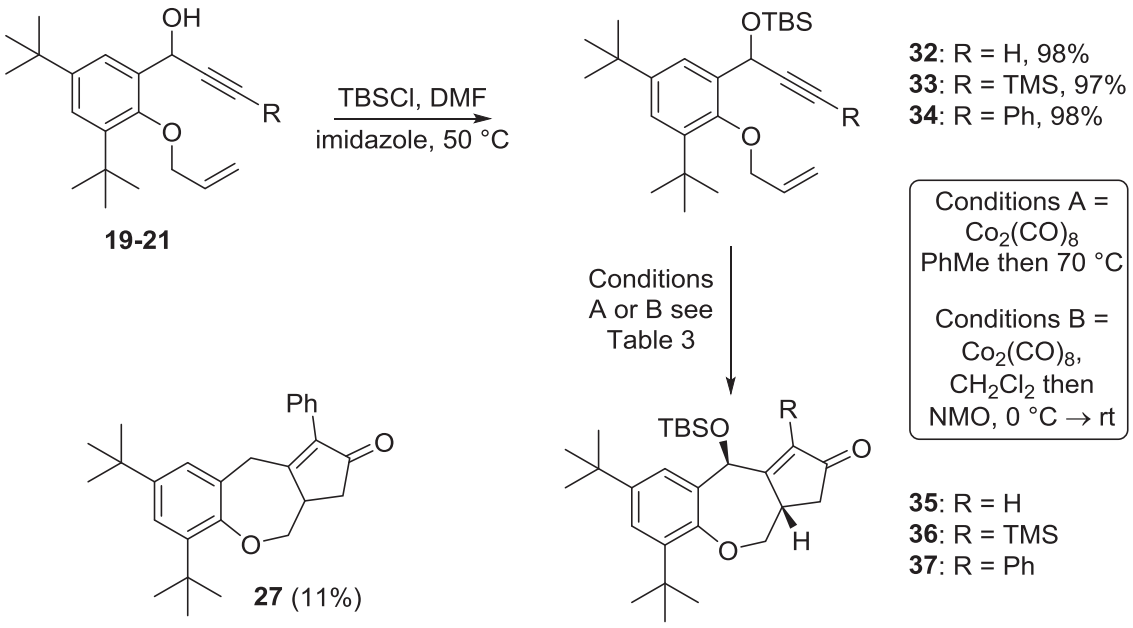


Fig. 2. X-ray crystal structure of **31**.

In our initial report on this chemistry, our efforts focused on using simple allylic systems and thus we now wanted to extend our investigation to substituted systems.[15] Accordingly, we prepared three substituted allylic systems. The two sets of methyl substituted derivatives were prepared in a similar fashion to the parent systems from the corresponding salicylaldehyde **17** and either methylallyl or crotyl bromide in the presence of K_2CO_3 in DMF delivering the corresponding ethers **38** and **42** in excellent yield (Scheme 7). Subsequent treatment of the ethers with the same series of ethynyl Grignard reagents provided the requisite enynes **39**–**41** and **43**–**45** in good yields (Scheme 7). Unfortunately, attempts to use this strategy to obtain the related cinnamyl systems **49**–**50** were unsuccessful, leading to the formation of dark and uncharacterizable



Scheme 6.

Table 3
PK reaction yields of TBS-Ethers **32**–**34**.

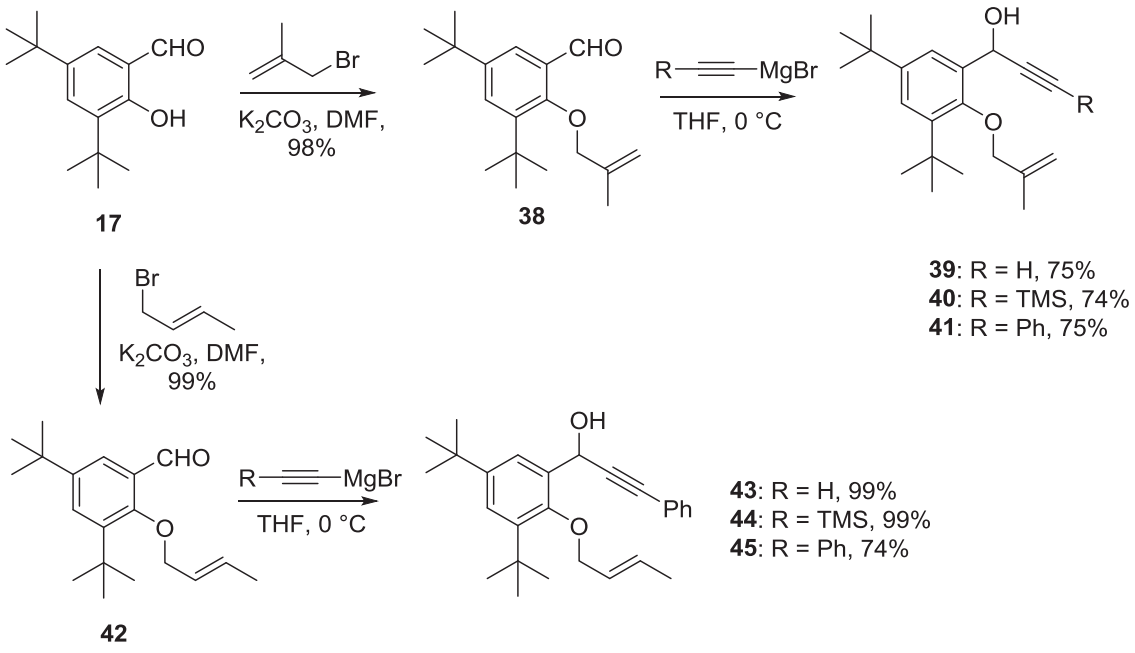
Entry	Substrate	Conditions[a]	Product (% - *exo*:*endo*)
1	**32**	A	**35** (80–1:1)
2	**32**	B	**35** (52–2:1)
3	**33**	A	**36** 0
4	**33**	B	**36** (60 – *exo*)
5	**34**	A	**37** (95–10:1)
6	**34**	B	**37** (60–5:1)

[a] Condition A = $Co_2(CO)_8$, PhMe, then 70 C; Condition B = $Co_2(CO)_8$, CH_2Cl_2, then NMO.

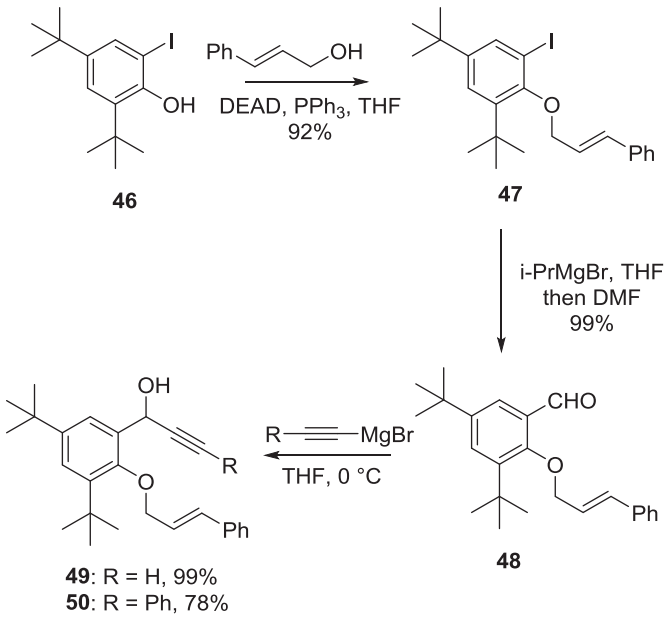
product mixtures from attempted allylation. However, it was found that the required enynes could be obtained via a slightly different sequence involving a Mitsunobu reaction of iodophenol derivative **46**[11a,11c] with cinnamyl alcohol followed by formylation of the resulting aryl iodide **47** by treatment with *i*-PrMgBr and then DMF to deliver the aldehyde **48** (Scheme 8). Reaction of the resulting aldehyde **48** with ethynyl Grignards provided the corresponding enynes **49**–**50** in good yield (Scheme 8).

As before, once the enynes were in hand, they were converted into the corresponding cobalt complex and subjected to PK reaction under either thermal (Condition A) or oxidative conditions (Condition B). We found that the internally substituted allyl substrates **39**–**41** did not participate in cyclization under either set of conditions. While examples of internally substituted alkenes are known to undergo cyclization in the PK reaction, they generally appear to be less reactive in this chemistry. Indeed, we have found this to be so in systems related to the ones under investigation here.[11a,11c,16] On the other hand, the terminally substituted systems did engage quite well in this cycloaddition chemistry (Scheme 9, Table 4). Globally, the results with the phenyl acetylene derivative **41** mirrored those obtained in the parent systems in that two or three products were obtained depending on the cyclization conditions. Under oxidative conditions, the reduction product **52** was obtained in 18% yield along with an almost 1:1 mixture of separable epimeric alcohols *endo*-**54** and *exo*-**56** (36% and 45% respectively, Table 4, entry 3). The alcohol produced in slightly larger amounts was nicely crystalline which permitted an X-ray crystal structure determination thus allowing the assignments of the relative stereochemistry of the three chiral centers (Fig. 3). Interestingly, under thermal conditions the cyclization was substantially more selective resulting in the formation of the two epimeric alcohols, favoring *exo*-**56** (*exo*:*endo* = 9:1, Table 4, entry 4). In comparison, the TMS-substituted derivative **44** was a relatively poor substrate, resulting in the formation of the *exo*-alcohol **55** in approximately 10% yield under both sets of conditions (Table 4, entries 5–6). The terminal alkyne underwent cyclization to again produce an epimeric mixture of 1,4-diketones **58** along with a reduction product **57** (only under oxidative conditions). In this case, the epimeric diketones could be partially separated to give pure samples of both epimers for characterization. Fortunately, we were able obtain NOESY data on the major diketone which revealed that the ring junction had a *cis* fusion. Similarly to the unsubstituted allylic systems, the propargylic alcohols were protected as the TBS-ethers **59**–**61** (Scheme 9), converted to the cobalt complexes and subjected to the PK reaction. The phenyl-substituted system **61** underwent cyclization under both sets of conditions to give the *exo*-silyl ether **65** as the major or sole product (Scheme 10 and entries 9 and 10, Table 4). The stereochemistry of the major product was confirmed by silylating the major cycloadduct obtained from the free alcohol **56**; this material was identical to **65** obtained from **61** (Scheme 10). The TMS-substituted derivative **60** behaved similarly in the cyclization chemistry to the unprotected system, a single cycloadduct **64** was formed but in low yield (Scheme 10, entries 7 and 8, Table 4). Finally, the silyl ether of unsubstituted enyne **59** underwent fairly efficient cyclization (≥80%) but the diastereoselectivity was poor, providing essentially 1:1 mixtures of the two epimeric silyl ethers (Scheme 10, entries 5 and 6, Table 4).

The final group of substrates that we examined were the cinnamyl systems **49** and **50** (Scheme 11). Since the TMS-substituted derivatives **44** and **60** performed poorly with the crotyl derivatives, we only investigated the non-substituted **49** and phenyl **50** systems. Gratifyingly, we found that the phenyl-substituted system **50** engaged effectively in a PK reaction under thermal and oxidative conditions (Scheme 11). Thermally (Condition A), a 10:1



Scheme 7.



Scheme 8.

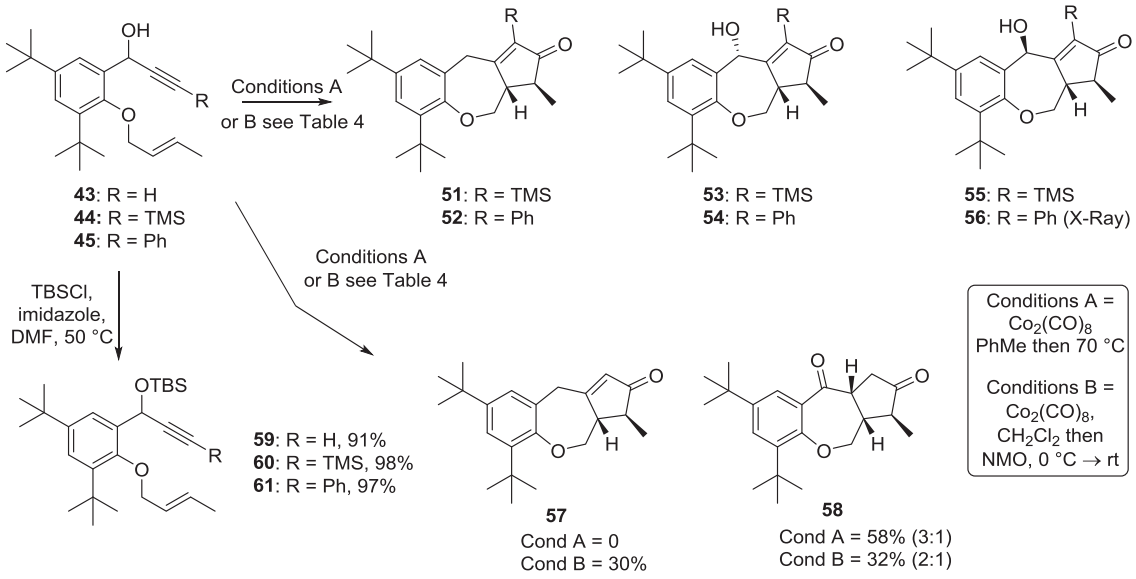
mixture of cycloadducts was obtained, the major diastereomer was assigned by analogy with **45** as the *exo*-alcohol **66**. Under oxidative conditions an essentially equal mixture of two products was obtained of the reduction product **66** and the *exo*-alcohol **66** (Scheme 11). The terminal alkyne **49** predominantly formed the diketone product **68** under both thermal and oxidative conditions. A small amount of the direct PK-product **67** was obtained under thermal conditions. Whereas the mixture of the 1,4-diketones was difficult to separate chromatographically, a small amount of the major adduct was obtained and characterized. A NOESY experiment indicated that the ring fusion was *cis*, similar to diketone **58** (Scheme 9). Finally, cyclization of both substrates was investigated after conversion to the corresponding TBS-ethers **69** and **70** (Scheme 11), the outcomes here mirrored those observed with the crotyl systems wherein the phenyl-substituted acetylene derivative provided a single cycloadduct **72** in moderate to excellent yield as the *exo*-diastereomer. The unsubstituted system formed the expected cycloadducts **73** as essentially 1:1 mixtures of diastereomers in much improved yields.

1. Discussion

Several issues emerged in the course of these investigations that require further comment, specifically the diastereoselectivity of the cycloaddition and the formation of initially unanticipated products.

1.1. Diastereocontrol

In general terms the diastereocontrol follows the patterns seen in other PK reactions wherein the newly formed stereocenter of the cyclopentenone and any substituents on the tether tend to end up *syn* to one another,[8b,17] in other words, they display *exo* selectivity[18]; this is also what we observed. However, we also note that the relative diastereoselectivity is dependent on the reaction conditions with the thermal conditions resulting in the higher selectivity compared to oxidative reactions. These results stand in contrast to the formation of smaller fused rings where oxidative conditions appear to be more selective. As we considered possible rationales for these observations we were struck by a couple of considerations. First, it must be borne in mind that the reaction conditions are substantially different in terms of what might be expected as the active metal containing species. While the full details of the mechanism of this reaction remain to be demonstrated experimentally,[19] it is generally accepted that the reaction involves the loss of carbon monoxide and coordination of the olefin to the vacated coordination site on the metals, **73**→**74** + **77** (Scheme 12).[20] Migratory insertion affords the metallacycles **75** and **78**; carbon monoxide insertion, reductive elimination and loss of the cobalt cluster complete the reaction. Under thermal conditions,



Scheme 9.

Table 4
PK reactions of substituted Allyl systems **44**–**45** and **59**–**61**.

Entry	Substrate	Conditions[a]	Product (%)		
1	**44**	A	**51** (0)	**53** (0)	**55** (12)
2	**44**	B	**51** (0)	**53** (0)	**55** (7)
3	**45**	A	**52** (0)	**54** (9)	**56** (90)
4	**45**	B	**52** (18)	**54** (36)	**56** (45)
5	**59**	A			**62** (86–4:5)
6	**59**	B			**62** (80–5:4)
7	**60**	A			**63** (10)
8	**60**	B			**63** (7)
9	**61**	A			**64** (68)
10	**61**	B			**64** (45–4:1)

[a] Condition A = $Co_2(CO)_8$, PhMe, then 70 C; Condition B = $Co_2(CO)_8$, CH_2Cl_2, then NMO.

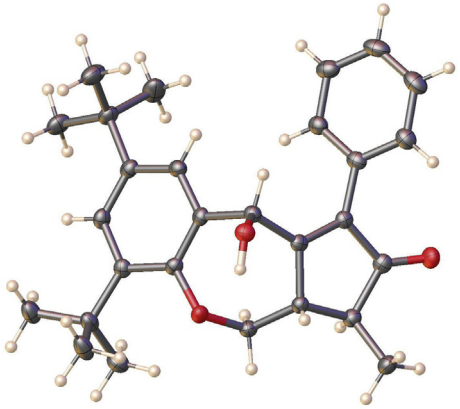
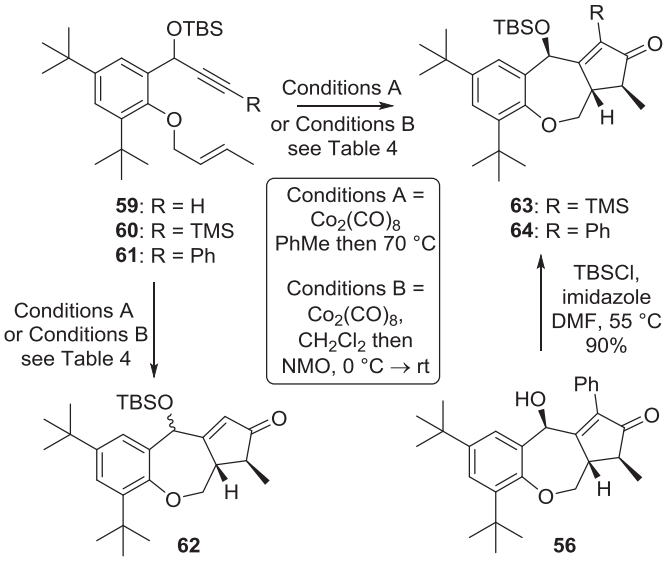


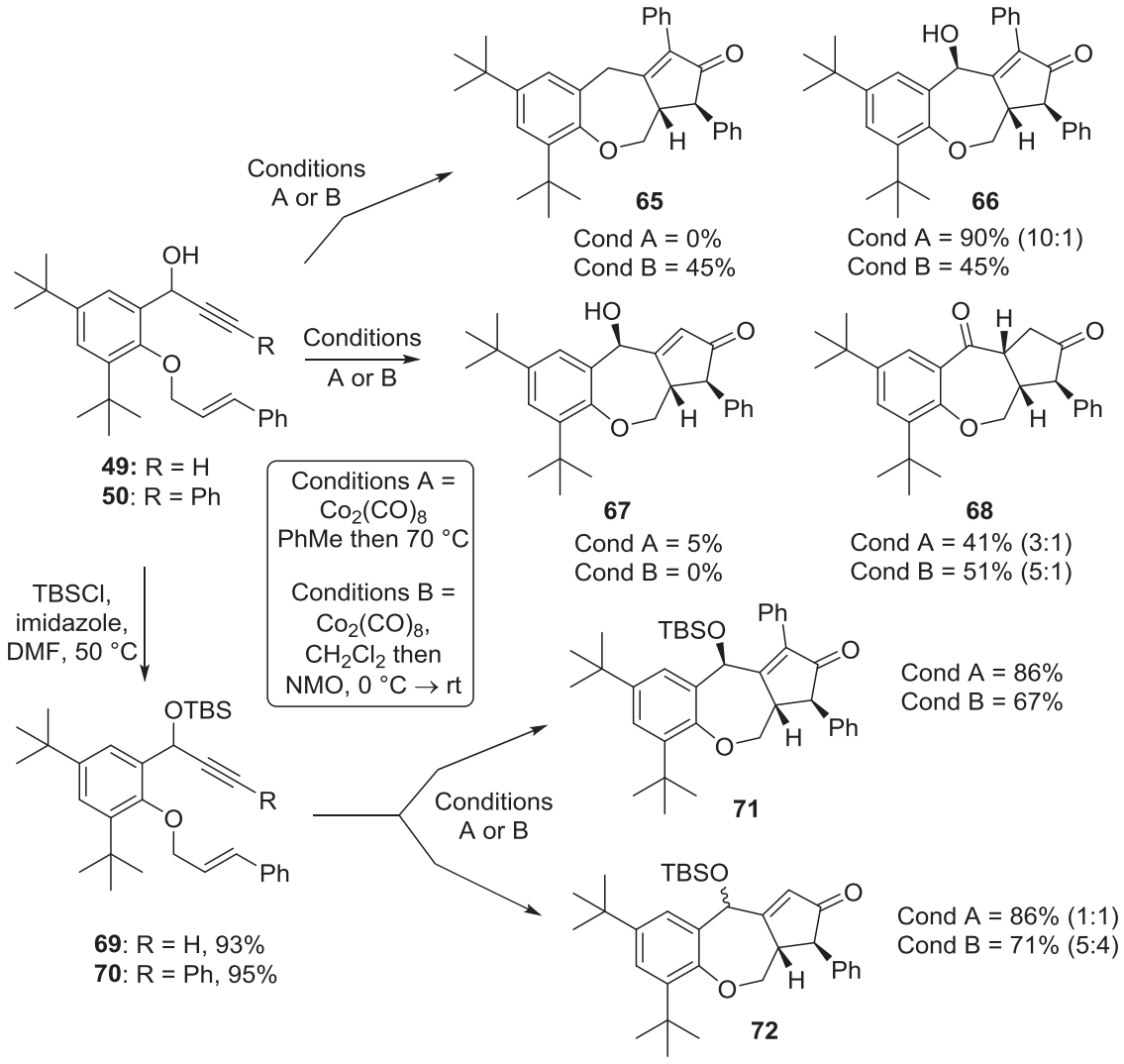
Fig. 3. X-ray crystal structure of **56.**

the loss of CO is expected to be relatively slow, controlled and more importantly potentially reversible whereas in the case of oxidative conditions, the CO is converted irreversibly to CO_2 and presumably lost to the atmosphere and the oxidant, the amine oxide leaves an amine behind which may potentially be involved in coordination to the metal cluster. Moreover, an excess of NMO is used meaning that



Scheme 10.

other CO ligands are lost irreversibly which in turn means the active cobalt species will likely be different under oxidative conditions. These thoughts lead to a conclusion that one set of conditions are more kinetic-like (oxidative) and the other more thermodynamic-like (thermal). Accordingly, we hypothesize that in the case of the oxidative conditions the alkene-coordinated cluster is less stable and immediately undergoes the Co-insertion and decomplexation whereas under thermal conditions this complex is more stable and undergoes reversible olefin coordination (i.e., 74 ⇔ 77) really need an equilibrium arrow here, with the rate (and product) determining step being Co insertion and formation of the cobaltacycles **75** and **78** (Scheme 12). Co-insertion is generally thought to be irreversible and thus the developing interactions in the cobaltacycle **75** and **78** drive the observed stereoselectivity, specifically the interaction between the propargylic substituent and substituent on the terminus of the alkyne. When R^1 = TMS or



Scheme 11.

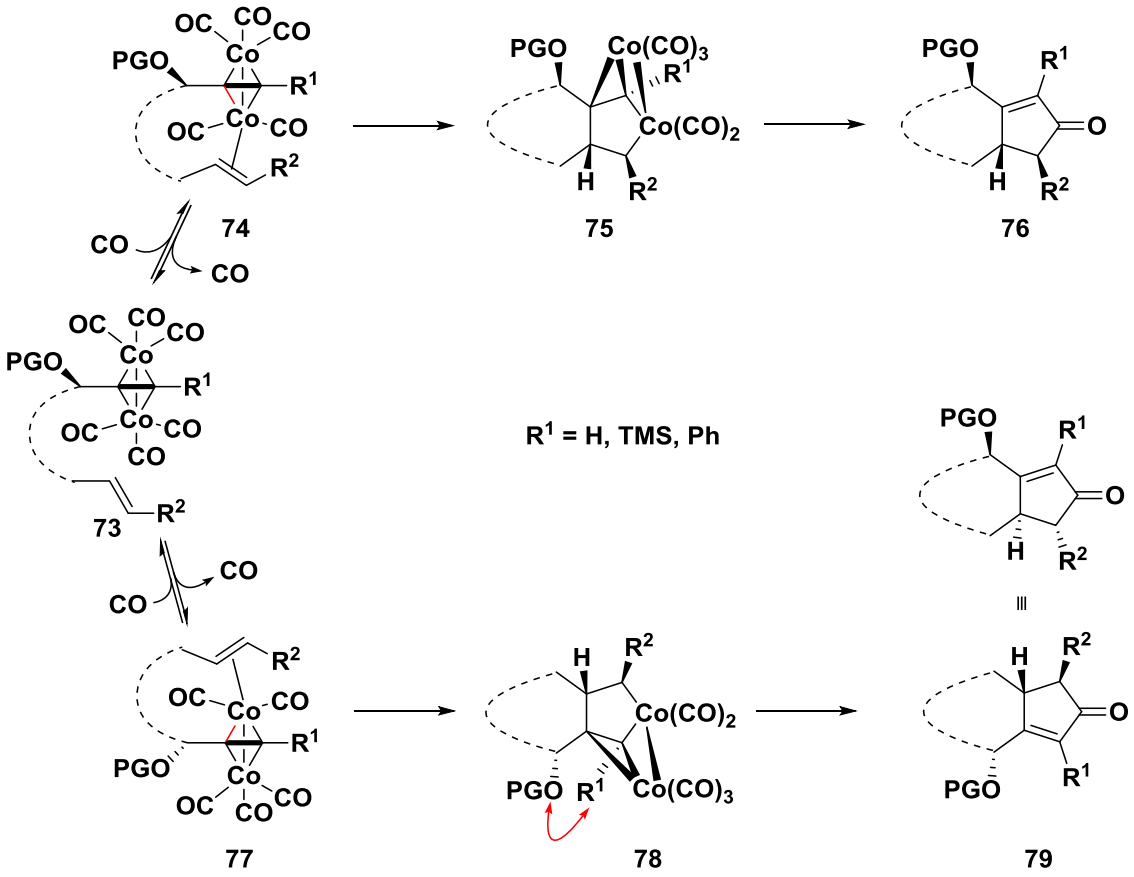
Ph, good diastereoselectivities are observed as a result of a substantial destabilizing interaction with the propargylic group, whereas when $R^1 = H$, there is essentially no diastereoselectivity which is consistent with minimal interaction with the propargylic substituent.

1.2. Product selectivity

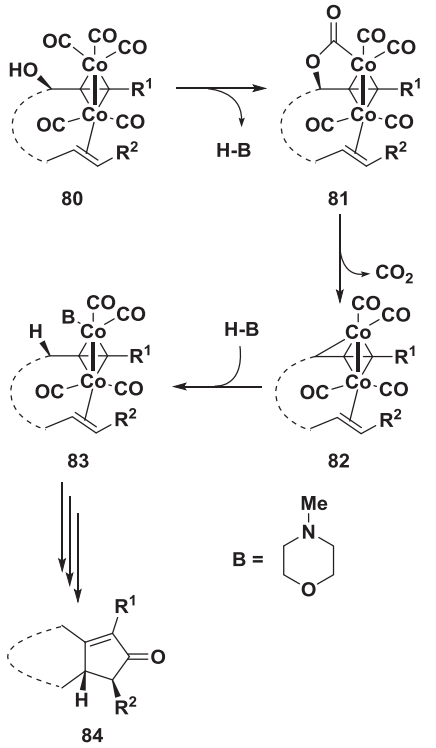
In addition to the formation of the expected cycloadduct adduct, we also observed the formation of two byproducts, resulting from the reduction of the propargylic hydroxyl group or from tautomerism of the hydroxy enone to provide the dione when the free alcohols are employed.[21] Counterintuitively, perhaps, the reduction product was observed predominantly under oxidative conditions. As noted above, when the PK reaction is performed under oxidative conditions, it is not entirely clear what the reactive species is, but presumably when the hydroxyl group is *syn* to the cobalt cluster it can react with a carbonyl ligand and then undergoes cobalt-assisted decarboxylation to produce **82** via **81** (Scheme 13). Reductive cleavage of the Co-carbon bond leading to **83** and decomplexation completes the sequence by providing **84**. Presumably, the *N*-methyl morpholine byproduct serves as both the base, acid and then ligand. It is assumed that this reduction occurs pre-cyclization as we have already shown that the cobalt complex can be reduced and that it is a competent cyclization precursor. It is also worth noting that the reduction product is more prominent in the case of the phenyl-substituted systems.

The second type of byproduct observed is the formation of the 1,4-dione **90** (Scheme 14), which is only formed from substrates containing a terminal alkyne. In a general sense, the formation of the dione can be understood through the participation of a cobalt hydride species through oxidative addition **86**→**87**, isomerization and subsequent reductive elimination **87**→**88**. Decomplexation followed by tautomerization gives rise to the diketone; the facial selectivity of the protonation dictating the stereochemistry of the ring fusion. The precise identity of the metallic species involved is unclear, it is also unclear whether the tautomerization occurs prior to decomplexation of the cobalt cluster immediately after the cycloaddition, i.e. “intramolecular” catalysis or whether it is the result of the participation of an “intermolecular” cobalt species derived from post cycloaddition decomplexation. These details notwithstanding, a pathway to the diketones can be articulated through a net 1,3-hydride shift-tautomerization sequence.

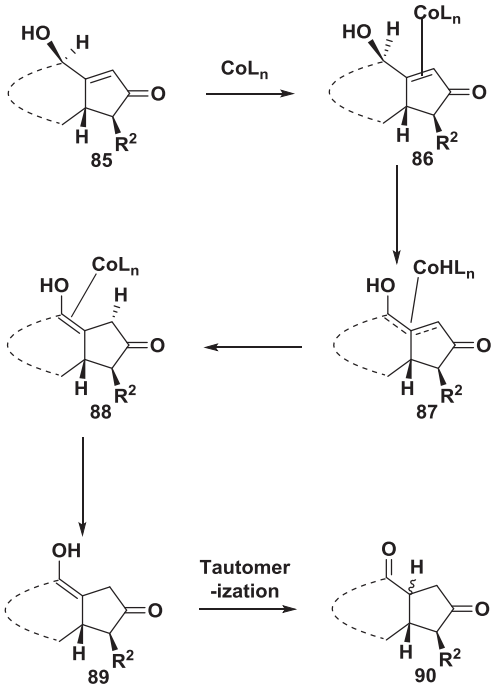
In summary, we have demonstrated that oxahydroazulenes can



Scheme 12. Rationale for the observed diastereoselectivity.



Scheme 13.



Scheme 14.

be constructed through intramolecular PK reactions in moderate to excellent yields. High diastereoselectivities can be obtained under thermal conditions and this outcome has been rationalized in terms of thermodynamic-like control. Substrates containing free propargylic alcohols participate in these cyclizations but lead to the formation of other types of products, resulting from reduction at the propargylic position and isomerization. These unwanted side reactions can be reduced by protection of the alcohol as a silyl ether. We have also examined the tolerance of this variant of the PK reaction to substitution on the olefin which indicates that internal alkenes are competent substrates but 2,2-disubstitution is not tolerated.

2. Experimental - general methods

All reagents were purchased from commercial suppliers and were used as received unless otherwise noted. Solvents were dried either by distillation over appropriate drying agents: tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone ketyl; benzene and dichloromethane were distilled over calcium hydride or purified using Innovative Technologies Inc Pure Solv SPS-400-05 solvent purification system. ^{1}H and ^{13}C NMR (δ in ppm) spectra were recorded in $CDCl_3$ (unless otherwise noted) at 500 and 125.8 MHz, respectively (unless otherwise noted); using a JEOL Eclipse+ 500 spectrometer. In some cases ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz respectively; using a JEOL Eclipse 300 spectrometer. Residual $CHCl_3$ (δ = 7.26) as reference for ^{1}H NMR and carbon absorption of $CDCl_3$ (δ = 77.0) as internal reference for ^{13}C NMR were used. Infrared spectra were recorded either as neat films or as KBr pellets using a Bruker Vector 22 FT-IR spectrometer. High resolution mass spectra (HR-MS) were measured at the University of Florida, Gainesville, Florida. Analytical thin layer chromatography (TLC) was performed on silica gel 60F_{254} aluminum precoated plates (0.25 mm layer). All chromatographic purifications were performed using ICN silica gel (200–400 mesh).

2.1. General procedure for O-alkylation reactions

The bromoalkene (11.0 mmol) was added to a suspension of K_2CO_3 (14.4 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (11.0 mmol) in DMF (50 mL) and stirred at room temperature for 12 h. The mixture was diluted with CH_2Cl_2 (25 mL) and washed twice with water, dried using Na_2SO_4 (anhydrous) and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2: hexane/EtOAc, 15:1 unless indicated otherwise).

2.2. General procedure for Grignard reactions

The Grignard reagent (1.5 equiv) was added to a solution of aldehyde in dry THF (10 mL) under an N_2 at 0 °C. The mixture was stirred and gradually allowed to warm up to room temperature and stirred for an additional 3 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and then extracted with CH_2Cl_2. The organic extracts were then washed with water, brine and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc, 4:1).

2.3. General procedures for the Pauson-Khand cyclization

2.3.1. Thermal Pauson-Khand reactions (procedure A)

1.1–1.2 equiv. of $Co_2(CO)_8$ was added to a stirred solution of enyne in toluene under N_2 and stirred for 5 h at room temperature. The reaction mixture was then heated at 70 °C overnight. The reaction mixture was poured into a sintered glass funnel packed with Celite and SiO_2 (*ca.* 1:1 v/v) and first washed with hexane to remove the alkyne•$Co_2(CO)_6$ remaining and then washed with ethyl acetate to remove the cyclized product. After rotary evaporation of the filtrate, the crude product was purified by flash chromatography (hexane/EtOAc, 20/1.5 unless indicated otherwise).

2.3.2. Oxidative Pauson-Khand method (procedure B)

1.1–1.2 equiv. of $Co_2(CO)_8$ was added to a stirred solution of enyne in CH_2Cl_2 under N_2 at room temperature. The reaction mixture was stirred for 5 h. The reaction mixture was cooled to 0 °C before NMO (12 equiv) was added in three portions at 30 min intervals and then left to stir for 2 h. The reaction mixture was then poured into a sintered glass funnel packed with Celite and SiO_2 (ca. 1:1) and washed with EtOAc. The crude product was purified by flash chromatography (hexane/EtOAc, 20/1.5 unless indicated otherwise).

2.3.3. Reductive PKR (procedure C)

1.1–1.2 equiv. of $Co_2(CO)_8$ was added to a stirred solution of enyne in CH_2Cl_2 under N_2 at room temperature. The reaction mixture was stirred for 5 h at rt. The reaction mixture was then cooled to 0 °C before adding $NaBH_4$. Subsequently, TFA was added over 10 min at 0 °C. The reaction mixture was decanted into 300 mL iced water and the organic solution was separated, washed with water and dried (Na_2SO_4). The organic layers were concentrated and cooled to 0 °C before NMO (12 equiv) was added and stirred for 2 h. The reaction mixture was then poured onto a sintered glass funnel with Celite and SiO_2 (ca. 1:1) and filtered. The solid packing was washed with EtOAc to extract the cycloadduct. The filtrates were combined and concentrated under reduced pressure. The crude product was purified by flash chromatography (hexane/EtOAc, 20/1.5 unless indicated otherwise).

2.3.4. 2-(2-Propenyloxy)benzaldehyde (**8**)

Allyl bromide (19.8 g, 160 mmol) was added to a suspension of K_2CO_3 (23.0 g) and 2-hydroxybenzaldehyde (20.0 g, 160 mmol) in DMF (100 mL) and stirred for 12 h according to the general alkylation procedure. The crude product was purified by flash chromatography to give **8** as a brown oil (18.5 g, 70%). ^{1}H NMR: δ = 10.41 (s, 1H), 7.70 (dd, J = 1.4, 7.8 Hz, 1H), 7.40 (dt, J = 1.8, 8.7 Hz, 1H), 6.90 (t, J = 7.8 Hz, 1H), 6.86 (d, J = 8.7 Hz, 1H), 6.95 (ddt, J = 5.5, 10.5, 17.0 Hz, 1H), 5.33 (dd, J = 1.4, 17.4 Hz, 1H), 5.21 (dd, J = 1.4, 10.5 Hz, 1H), 4.52 (d, J = 5.0 Hz, 2H); ^{13}C NMR: δ = 189.7, 161.0, 136.1, 132.6, 128.4, 125.1, 120.9, 118.1, 113.1, 69.2; IR (neat, cm^{-1}) = 3079, 2866, 1685, 1599, 1483, 1286, 995, 759; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{10}H_{11}O_2$ (m/z): 163.0759. Found 163.0749.

2.3.5. 2-(1-Hydroxy-2-propynyl)-(2-propenyloxy) benzene (**9**)

A 0.5 M solution of ethynylmagnesium bromide (55.6 mL, 28.0 mmol) in THF was added at 0 °C to a solution of **8** (3.00 g, 19.0 mmol) in THF (20 mL) under N_2 atmosphere. The reaction was worked up according to the general procedure to give **9** (3.31 g, 95%) as a brown oil after chromatographic purification. ^{1}H NMR: δ = 7.57 (dd, J = 1.8, 7.3 Hz, 1H), 7.28 (dt, J = 1.8, 7.3 Hz, 1H), 6.98 (dt, J = 1.0, 7.3 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.05 (ddt, J = 5.5, 10.5, 17.0 Hz, 1H), 5.73 (d, J = 2.3 Hz, 1H), 5.45 (dq, J = 1.8, 17.0 Hz, 1H), 5.30 (dq, J = 1.4, 10.5 Hz, 1H), 4.58 (ddt, J = 1.4, 3.2, 5.0 Hz, 2H), 3.44 (s, 1H), 2.61 (d, J = 2.3, 1H); ^{13}C NMR: δ = 153.2, 133.0, 129.8, 128.7, 128.0, 121.2, 118.0, 112.3, 83.4, 74.2, 69.2, 60.9; IR (neat, cm^{-1}) = 3392, 3287, 3077, 2870, 2116, 1648, 1601, 1490, 1453; HRMS (CI): Calcd. For $[M^+]$ $C_{12}H_{12}O_2$ (m/z): 188.0837. Found 188.0829.

2.3.6. 2-(1-Hydroxy-3-trimethylsilyl-2-propynyl)-(-2-propenyloxy) benzene (**10**)

Trimethylsilylethynylmagnesium chloride in dry THF was

prepared by adding ethynyltrimethylsilane (3.33 g, 34.0 mmol) to 2.0 M solution of isopropylmagnesium chloride (14.0 mL, 28.0 mmol) under N_2 at 0 °C and the mixture was stirred for 30 min before allowing to gradually warm up to room temperature and then stirred further for 10 min. To this thus prepared solution of trimethylsilylethynylmagnesium chloride was added a solution of **8** (3.00 g, 19.0 mmol) in dry THF (20 mL) under N_2 atmosphere at −78 °C and then stirred for 2.5 h at −78 °C. The reaction was then allowed to warm up to room temperature and stirred overnight. The reaction was worked up according to the general procedure to give **10** (4.97 g, 93%) as a brown oil. ^{1}H NMR (300 MHz), δ = 7.56 (dd, J = 1.7, 7.6 Hz, 1H), 7.27 (dt, J = 1.7, 8.3 Hz, 1H), 6.99 (dt, J = 1.0, 7.2 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 6.02 (ddt, J = 4.8, 10.7, 17.2 Hz, 1H), 5.71 (s, 1H), 5.46 (dq, J = 1.7, 17.2 Hz, 1H), 5.31 (dq, J = 1.4, 10.7 Hz, 1H), 4.58 (ddt, J = 1.7, 3.5, 5.2 Hz, 2H), 3.09 (s, 1H), 0.20 (s, 9H). ^{13}C NMR (75 MHz): δ = 160.0, 132.9, 129.7, 129.0, 128.2, 121.2, 117.8, 112.3, 104.7, 90.9, 69.1, 61.9, −0.1; IR (neat, cm^{-1}) = 3403, 2960, 2173, 1601, 1490, 1455, 1249; HRMS (ESI): Calcd. for [M+Na]$^+$ $C_{15}H_{20}O_2Na$ (*m/z*): 283.1125. Found 283.1124.

2.3.7. 2-(1-Hydroxy-3-phenyl-2-propynyl)-(2-propenyloxy) benzene (**11**)

1.0 M solution of phenylethynylmagnesium bromide (24.6 mL, 25.0 mmol) in THF was added at 0 °C to a solution of 2 (3.00 g, 19.0 mmol) in THF (20 mL) under N_2 atmosphere and worked up according to the general procedure to give **11** (2.04 g, 47%) as a brown oil. ^{1}H NMR: δ = 7.64 (dd, J = 1.8, 7.8 Hz, 1H), 7.47 (dd, J = 2.3, 7.3 Hz, 2H), 7.32 (m, 4H), 7.02 (dt, J = 1.0, 7.3 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.07 (ddt, J = 5.0, 10.5, 17.4 Hz, 1H), 5.96 (d, J = 6.0 Hz, 1H), 5.47 (dd, J = 1.4, 17.4 Hz, 1H), 5.32 (dq, J = 1.4, 10.5 Hz, 1H), 4.65 (ddt, J = 1.8, 3.7, 5.0 Hz, 2H), 3.25 (d, J = 6.0 Hz, 1H). ^{13}C NMR: δ = 156.0, 133.0, 131.9, 129.7, 129.3, 128.5, 128.4, 128.2, 122.9, 121.2, 117.9, 112.3, 88.7, 86.0, 69.2, 62.0; IR (neat, cm^{-1}) = 3413, 3079, 2870, 2198, 1560, 1490; HRMS (ESI): Calcd. For [M+Na]$^+$ $C_{18}H_{16}O_2Na$ (*m/z*): 287.1043. Found 287.1038.

2.3.8. 10-Hydroxy-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f] azulen-2-one (**14**)

The Pauson-Khand cyclization was carried out according to the General Procedures A and B. The enyne **11** (200 mg, 0.76 mmol) was dissolved in 10 mL of the appropriate solvent and $Co_2(CO)_8$ (285 mg, 0.83 mmol) and NMO (975 mg, 8.30 mmol) were added following the general procedures. The crude product was purified by flash chromatography (silica gel, *n*-hexane/EtOAc, 9:1) to afford **8** (17.6 mg, 8% using procedure A and 70.0 mg, 31% using procedure B) as a light yellow waxy solid. ^{1}H NMR: δ = 7.57 (m, 4H), 7.09 (m, 5H), 5.59 (d, J = 6.0 Hz, 1H), 4.68 (dd, J = 5.5, 11.5 Hz, 1H), 3.99 (m, 1H), 3.67 (app.t, J = 10.5 Hz, 1H), 2.97 (d, J = 6.0 Hz, 1H), 2.75 (dd, J = 7.0, 19.0 Hz, 1H), 2.09 (d, J = 20.0 Hz, 1H); ^{13}C NMR: δ = 205.5, 171.1, 159.8, 140.2, 132.1, 130.6, 130.5, 130.1, 129.4, 128.5, 128.5, 125.1, 123.0, 76.7, 72.3, 39.3, 37.1; IR (neat, cm^{-1}) = 3418, 3058, 2953, 1702, 1601, 1486, 1016; HRMS (ESI): Calcd. for [M+H]$^+$ $C_{19}H_{17}O_3$ (*m/z*): 293.1178. Found 293.1166.

2.3.9. 2-(-1-tert-Butyldimethylsilyloxy -3-phenyl-2-propynyl)-(2-propenyloxy)benzene (**15**)

Tert-Butyldimethylsilyl chloride (1.51 g, 1.00 mmol) was added at room temperature to a mixture of **11** (880 mg, 3.33 mmol) and imidazole (600 mg, 1.00 mmol) in DMF (10 mL). Then the mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of $NaHCO_3$ and extracted with Et_2O. The organic layer separated, washed with water, brine and dried with Na_2SO_4 (anhydrous). The organic layer was concentrated to give a dark colored liquid. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc, 19:1) to give **15** (1.21 g, 96%) as viscous brown liquid. ^{1}H NMR: δ = 7.76 (dd, J = 1.4, 7.3 Hz, 1H), 7.42 (dd, J = 2.3, 4.1 Hz, 2H), 7.29 (m, 4H), 7.02 (t, J = 7.3 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.07 (m, 2H), 5.48 (dq, J = 1.4, 17.4 Hz, 1H), 5.29 (dq, J = 1.4, 10.5 Hz, 1H), 4.63 (app. t, J = 4.6 Hz, 2H), 0.99 (s, 9H), 0.29 (s, 3H), 0.20 (s, 3H). ^{13}C NMR: δ = 154.9, 133.5, 131.7, 130.7, 128.8, 128.3, 128.1, 127.6, 123.5, 121.0, 117.3, 111.8, 90.7, 84.2, 69.0, 59.9, 26.0, 18.5, −4.4, −4.7; IR (neat, cm^{-1}) = 3080, 2929, 2857, 2175, 1601, 1490; HRMS (ESI): Calcd. for [M+Na]$^+$ $C_{24}H_{30}O_2SiNa$ (*m/z*): 401.1907. Found 401.1902.

2.3.10. 10-tert-Butyldimethylsilyloxy-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**16**)

The Pauson-Khand cyclization was carried out according to the General Procedures A and B. The enyne **15** (200 mg, 0.53 mmol) was dissolved in 10 mL of appropriate solvent, $Co_2(CO)_8$ (200 mg, 0.58 mmol) and NMO (680 mg, 5.85 mmol) were added following the general procedures. The crude product was purified by flash chromatography (hexane/EtOAc, 9:1) to afford **10** (110 mg, 50%) using procedure B as a light brown waxy solid. Procedure A gave no cyclized product with only starting material being recovered. ^{1}H NMR: δ = 7.36 (m, 3H), 7.26 (dt, J = 1.8, 9.2 Hz, 1H), 7.19 (dd, J = 1.8, 7.3 Hz, 1H), 7.10 (m, 2H), 7.08 (d, J = 7.3 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 5.63 (s, 1H), 4.71 (d, J = 7.5 Hz, 1H), 3.86 (m, 2H), 2.79 (dd, J = 6.4, 18.8 Hz, 1H), 2.27 (d, J = 18.8 Hz, 1H), 0.80 (s, 9H), −0.07 (s, 3H), −0.18 (s, 3H); ^{13}C NMR: δ = 206.1, 172.3, 160.4, 139.0, 131.0, 130.9, 130.7, 130.1, 129.1, 128.4, 123.8, 122.5, 110.9, 72.6, 60.2, 40.2, 38.1, 25.8, 18.1, −4.6, −4.8; IR (neat, cm^{-1}) = 2954, 1711, 1486, 1251, 1068, 836; HRMS (ESI): Calcd. For [M+H]$^+$ $C_{25}H_{31}O_3Si$ (*m/z*): 407.2037. Found 407.2030.

2.3.11. 3,5-Di-tert-butyl-2-(-2-propenyloxy)benzaldehyde (**18**)

Allyl bromide (1.29 g, 11.0 mmol) was added to a suspension of K_2CO_3 (2.00 g, 14.4 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (**17**) (2.50 g, 11.0 mmol) in DMF (50 mL) and stirred at room temperature for 12 h according to the general alkylation procedure. The crude product was purified by flash chromatography (hexane/EtOAc, 15:1) to give **18** as a light yellow oil (2.72 g, 93%). ^{1}H NMR: δ = 10.29 (s, 1H), 7.74 (d, J = 2.8 Hz, 1H), 7.65 (d, J = 2.8 Hz, 1H), 6.08 (ddt, J = 4.6, 11.0, 17.0 Hz, 1H), 5.51 (dq, J = 1.8, 17.0 Hz, 1H), 5.31 (dq, J = 1.4, 10.5 Hz, 1H), 4.47 (dt, J = 1.4, 5.0 Hz, 2H), 1.42 (s, 9H), 1.31 (s, 9H); ^{13}C NMR: δ = 190.9, 159.8, 146.5, 143.1, 140.3, 132.9, 130.9, 129.4, 123.9, 117.5, 79.4, 35.4, 31.4, 30.9; IR (neat, cm^{-1}); 2962, 2871, 1690, 1472, 1231, 928; HRMS (ESI): Calcd. for [M+H]$^+$ $C_{18}H_{26}O_2$ (*m/z*): Calcd. For $C_{18}H_{27}O_2$ (*m/z*): 275.2006. Found 275.1995.

2.3.12. 4,6-Di-tert-butyl-2-(1-hydroxy-2-propynyl)-(2-propenyloxy)benzene (**19**)

0.5 M solution of ethynylmagnesium bromide (30.0 mL, 15.0 mmol) THF was added to a solution of **18** (2.72 g, 9.92 mmol) in dry THF (20 mL) under N_2 atmosphere at 0 °C after work-up and purification according to the general procedure gave **19** (2.75 g, 92%) as a light yellow solid, mp: 95–96 °C. ^{1}H NMR: δ = 7.58 (d, J = 2.8 Hz, 1H,), 7.36 (d, J = 2.3 Hz, 1H,), 6.10 (ddt, J = 4.6, 11.0, 17.0 Hz, 1H), 5.76 (d, J = 2.3 Hz, 1H), 5.55 (dq, J = 1.8, 17.0, 1), 5.30 (dq, J = 1.4, 10.5, 1H), 4.59 (ddt, J = 1.8, 4.6, 13.3 Hz, 1H), 4.43 (ddt, J = 1.8, 5.0, 13.3 Hz, 1H), 2.62 (d, J = 1.8 Hz, 1H), 2.46 (s,1H), 1.41 (s, 9H), 1.30 (s, 9H); ^{13}C NMR: δ = 153.2, 146.7, 142.4, 133.8, 125.3, 123.6, 116.8, 84.6, 76.1, 74.3, 59.8, 35.6, 34.8, 31.6, 31.3 (only 15 signals out of 16 carbon types were observed); IR (neat, cm^{-1}) = 3304, 2960, 2219, 1470, 1281, 989; HRMS (CI): Calcd. for [M]$^+$ $C_{20}H_{28}O_2$ (*m/z*): 300.2089. Found 300.2091.

*2.3.13. 4,6-Di-tert-butyl-2-(1-hydroxy-3-trimethylsilyl-2-propynyl)-(-2-propenyloxy) benzene (**20**)*

A solution of trimethylsilylethynylmagnesium chloride in dry THF was prepared by adding ethynyltrimethylsilane (2.47 g, 25.0 mmol) to 3.0 M solution of ethylmagnesium chloride (8.40 mL, 25.0 mmol) in THF under N_2 at 0 °C and stirred for 30 min before allowing the reaction to warm up to room temperature and stirred for additional 10 min. To this thus prepared solution of trimethylsilylethynylmagnesium chloride, was added a solution of **18** (3.00 g, 11.0 mmol) in dry THF (20 mL) under N_2 atmosphere at −78 °C. The reaction mixture was stirred for 2.5 h at −78 °C before allowing to warm up to rt. The reaction was then stirred overnight and worked up according to the general procedure to give **20** (3.05 g, 75%) as a light yellow solid, mp: 94–95 °C. ^{1}H NMR: δ = 7.61 (d, J = 2.3 Hz, 1H), 7.35 (d, J = 2.3 Hz, 1H), 6.09 (ddt, J = 5.0, 10.5, 17.0 Hz, 1H), 5.73 (d, J = 5.5 Hz, 1H), 5.52 (dq, J = 1.4, 17.0 Hz, 1H), 5.28 (dq, J = 1.4, 10.5 Hz, 1H), 4.64 (ddt, J = 1.8, 5.0, 13.0 Hz, 1H), 4.43 (ddt, J = 1.8, 5.0, 13.0 Hz, 1H), 2.50 (d, J = 5.5 Hz, 1H), 1.41 (s, 9H), 1.30 (s, 9H), 0.19 (s, 9H); ^{13}C NMR: δ = 153.4, 146.5, 142.3, 134.0, 133.9, 125.19, 124.1, 116.7, 106.0, 91.1, 76.1, 60.6, 35.6, 34.8, 31.5, 31.3, −0.09; IR (neat, cm^{-1}) = 3454, 2960, 2172; HRMS (ESI): Calcd. for $[M+Na]^+$ $C_{23}H_{36}O_2SiNa$ (*m/z*): 395.2377. Found 395.2373.

*2.3.14. 4,6-Di-tert-butyl-2-(1-hydroxy-3-phenyl-2-propynyl)-2-propenyloxybenzene (**21**)*

1.0 M solution of phenylethynylmagnesium bromide (15.0 mL, 15.0 mmol) was added at 0 °C to the solution of **18** (3.00 g, 11.0 mmol) in dry THF (20 mL) under N_2 atmosphere according to the general procedure to give **21** (3.07 g, 75%) as a light yellow solid, mp 92–93 °C. ^{1}H NMR: δ = 7.69 (d, J = 2.8 Hz, 1H), 7.46 (m, 2H), 7.38 (d, J = 2.8 Hz, 1H), 7.30 (m, 3H), 6.13 (ddt, J = 4.6, 11.0, 17.0 Hz, 1H), 5.98 (s, 1H), 5.55 (dq, J = 1.8, 17.4 Hz, 1H), 5.32 (dq, J = 1.8, 10.5 Hz, 1H), 4.65 (ddt, J = 1.8, 4.6, 13.3 Hz, 1H), 4.50 (ddt, J = 1.8, 4.6, 13.3 Hz, 1H), 2.58 (d, J = 5.5 Hz, 1H), 1.44 (s, 9H), 1.34 (s, 9H); ^{13}C NMR: δ = 171.3, 153.3, 146.6, 142.4, 134.4, 133.9131.8, 128.4, 125.1, 123.9, 122.8, 116.8, 89.7, 86.1, 76.3, 60.6, 35.6, 34.8, 31.6, 31.3; IR (neat, cm^{-1}) = 3414, 2959, 2223, 1479, 1280; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{26}H_{33}O_2$ (*m/z*): 377.2475. Found 377.2471.

*2.3.15. 4,6-Di-tert-butyl-2-prop-2-ynyl-(2-propenyloxy)benzene (**22**)*

Triethylsilane (1.24 g, 10.7 mmol) was added at room temperature to the solution of **19** (1.60 g, 5.30 mmol) in CH_2Cl_2 (10 mL) under N_2 atmosphere. Then trifluoroacetic acid (2.43 g, 21.3 mmol) was added and stirred for 20 min. The reaction mixture was quenched with aqueous $NaHCO_3$ and then extracted with CH_2Cl_2 (2 × 10 mL) to give a yellow liquid. The crude product was purified by flash chromatography (hexane/EtOAc 95:5) to give **22** as a light yellow liquid (1.45 g, 96%). ^{1}H NMR: δ = 7.39 (d, J = 2.8 Hz, 1H), 7.25 (d, J = 2.8 Hz, 1H), 6.07 (ddt, J = 5.0, 10.5, 17.0 Hz, 1H), 5.51 (dq, J = 1.8, 17.0 Hz, 1H), 5.29 (dq, J = 1.8, 10.5 Hz, 1H), 4.38 (dt, J = 1.4, 5.0 Hz, 2H), 3.58 (d, J = 2.3 Hz, 2H), 2.12 (t, J = 2.8 Hz, 1H), 1.39 (s, 9H), 1.32 (s, 9H); ^{13}C NMR: δ = 148.9, 142.0, 133.5, 128.9, 125.0, 122.9, 116.6, 83.0, 73.9, 69.7, 35.5, 34.6, 31.6, 31.3, 6.7, 5.9; IR (neat, cm^{-1}) = 3312, 2959, 2872, 2176, 1715, 1507; HRMS (CI): Calcd. For $[M^+]$ $C_{20}H_{28}O^+$ (*m/z*): 284.2135. Found 284.2132.

*2.3.16. 4,6-Di-tert-butyl-2-(3-trimethylsilyl-2-propynyl)-(-2-propenyloxy) benzene (**23**)*

Triethylsilane (1.24 g, 10.7 mmol) was added at room temperature to a solution of **20** (1.98 g, 5.30 mmol) in CH_2Cl_2 (10 mL) under N_2 atmosphere. Then trifluoroacetic acid (2.43 g, 21.3 mmol) was added and the reaction was stirred for 20 min. The reaction mixture was quenched with aqueous $NaHCO_3$ and extracted with dichloromethane (2 × 10 mL) to give a yellow liquid after removal of the solvent. The crude product purified by flash chromatography (hexane/EtOAc, 95:5) to give **23** as a light yellow liquid (1.87 g, 99%). ^{1}H NMR: δ = 7.47 (d, J = 2.5 Hz, 1H), 7.25 (d, J = 2.5 Hz, 1H), 6.05 (ddt, J = 5.0, 10.5, 17.0 Hz, 1H), 5.49 (dq, J = 1.8, 17.0 Hz, 1H), 5.26 (dq, J = 1.8, 10.5 Hz, 1H), 4.35 (dt, J = 1.8, 5.0 Hz, 2H), 3.64 (s, 2H), 1.39 (s, 9H), 1.32 (s, 9H), 0.18 (s, 9H); ^{13}C NMR (75 MHz): δ = 153.6, 145.9, 141.9, 133.9, 129.5, 125.4, 123.1, 116.5, 105.5, 86.8. 73.9, 35.5, 34.8, 31.6, 31.3, 21.4, 0.2; IR (neat, cm^{-1}) = 2960, 2874, 2177; HRMS (ESI): Calcd. For $[M+H]^+$ $C_{23}H_{37}OSi$ (*m/z*): 357.2608. Found 357.2618.

*2.3.17. 4,6-Di-tert-butyl-2-(-3-phenyl-2-propynyl)-2-propenyloxybenzene (**24**)*

Triethylsilane (1.24 g, 10.7 mmol) was added at room temperature to a solution of **21** (2.0 g, 5.3 mmol) in CH_2Cl_2 (10 mL) under N_2 atmosphere. Then trifluoroacetic acid (2.43 g, 21.3 mmol) was added and stirred for 20 min. The reaction mixture was quenched with aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (2 × 10 mL) to give a yellow liquid. The crude product was purified by flash chromatography (hexane/EtOAc, 95:5) to give **24** as a light yellow liquid (1.87 g, 98%). ^{1}H NMR: δ = 7.52 (d, J = 2.5 Hz, 1H), 7.44 (m, 2H), 7.30 (d, J = 2.5 Hz, 1H), 7.29 (d, J = 3.0 Hz, 3H), 6.11 (ddt, J = 4.6, 11.0, 17.0 Hz, 1H), 5.55 (dq, J = 1.8, 17.4 Hz, 1H), 5.32 (dq, J = 1.8, 10.5 Hz, 1H), 4.46 (dt, J = 1.8, 4.6 Hz, 2H), 3.83 (d, J = 5.0 Hz, 2H), 1.46 (s, 9H), 1.38 (s, 9H); ^{13}C NMR: δ = 153.6, 146.1, 142.0, 134.0, 131.7, 129.9, 128.3, 127.8, 125.5, 124.0, 123.2, 116.5, 88.7, 82.1, 74.1, 35.5, 34.7, 31.6, 31.3, 20.9; IR (neat, cm^{-1}) = 2959, 2870, 1451, 1225, 991, 755; HRMS (ESI): Calcd. For $[M+H]^+$ $C_{26}H_{33}O$ (*m/z*): 361.2526. Found 361.2538.

*2.3.18. 6,8-Di-tert-butyl-1-trimethylsilyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**26**)*

The Pauson-Khand cyclization was carried out according to the general procedures A and B. The enyne **23** (124 mg, 0.35 mmol) was dissolved in 10 mL of the appropriate solvent. $Co_2(CO)_8$ (200 mg, 0.59 mmol) and NMO (408 mg, 3.48 mmol) were added according to the General Procedure B. The crude product was purified by flash chromatography (silica gel, hexane/EtOAc, 90:10) to afford **26** (75.0 mg, 56% using Procedure A and 60.0 mg, 45% using Procedure B) as a yellow solid.

General Procedure C: $Co_2(CO)_8$ (506 mg, 1.47 mmol) was added to a solution of **20** (500 mg, 1.34 mmol) in CH_2Cl_2 (10 mL) was under N_2 and stirred at room temperature for 5 h. The reaction mixture was then cooled in an ice bath before adding $NaBH_4$ (153 mg, 4.03 mmol). Subsequently, TFA (15 mL) was added over 10 min at 0 °C and then worked up. The organic extracts were concentrated, redissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C before NMO (2.08 g. 17.8 mmol) was added in three portions and then left to stir for 2 h. Usual work-up and purification of the crude product was purified by flash chromatography (hexane/EtOAc, 20:1.5) to afford 23 (240 mg, 48%) as a yellow solid. mp: 89–91 °C; ^{1}H NMR: δ = 7.24 (s, 1H), 7.10 (s, 1H), 4.54 (dd, J = 5.3, 5.6 Hz, 1H), 3.91 (s, 2H), 3.41 (m, 1H), 3.24 (t, J = 11.4 Hz, 1H), 2.52 (dd, J = 7.1, 18.8 Hz, 1H), 1.82 (dd, J = 1.6, 18.8 Hz, 1H), 1.38 (s, 9H), 1.30 (s, 9H), 0.31 (s, 9H); ^{13}C NMR: δ = 211.8, 184.9, 156.5, 146.3, 141.6, 139.2, 129.6, 125.2, 123.0, 76.0, 47.5, 38.4, 38.2, 35.2, 34.6, 31.6, 30.7, −0.03; IR (neat, cm^{-1}) = 2958.3, 1693.5, 1587.2, 1249.7; HRMS (ESI): Calcd. for $[M+Na]^+$ $C_{24}H_{36}O_2SiNa$ 407.2377, Found 407.2376.

*2.3.19. 6,8-Di-tert-butyl-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**27**)*

The Pauson-Khand cyclization was carried out according to the General Procedures A and B. The enyne **24** (130 mg, 0.36 mmol) was dissolved in 10 mL of the appropriate solvent. $Co_2(CO)_8$ (136 mg, 0.40 mmol) and NMO (460 mg, 3.93 mmol) were added according to the general procedure. The crude product was purified by flash

chromatography (silica gel, *n*-hexane/EtOAc, 9:1) to afford **27** (60 mg, 43% using procedure A and 64 mg, 46% using procedure B) as a yellow solid.

General Procedure C: $Co_2(CO)_8$ (136 mg, 0.40 mmol) was added to a solution of **21** (290 mg, 0.77 mmol) in CH_2Cl_2 (10 mL) under N_2 and stirred at room temperature for 5 h. The reaction mixture was then cooled in an ice bath before adding $NaBH_4$ (88.0 mg, 2.31 mmol). Subsequently, TFA (10 mL) was added over 10 min at 0 °C and then worked-up. The dried organic extracts were concentrated, redissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C before NMO (1.22 g. 10.4 mmol) was added in three portions and then left to stir for 2 h. Usual work-up and purification of the crude product (hexane/EtOAc, 20:1.5) provided **27** (150 mg, 50%) as a yellow solid. mp: 160–162 °C; ^{1}H NMR: δ = 7.46 (t, J = 7.8 Hz, 2H). 7.40 (d, J = 2.8 Hz, 1H), 7.34 (d, J = 2.8 Hz, 2H), 7.30 (s, 1H), 7.14 (s, 1H), 4.67 (dd, J = 5.5, 11.5 Hz, 1H), 3.91 (d, J = 12.8 Hz, 1H), 3.76 (d, J = 12.8 Hz, 1H), 3.54 (m, 1H), 3.35 (t, J = 11.5 Hz, 1H), 2.75 (dd, J = 7.1, 18.9 Hz, 1H), 2.03 (dd, J = 2.8, 18.8 Hz, 1H), 1.41 (s, 9H), 1.35 (s, 9H); ^{13}C NMR: δ = 205.5, 172.0, 156.8, 146.7, 141.9, 139.7, 131.3, 129.7, 129.6, 128.3, 128.2, 125.3, 123.0, 76.2, 44.1, 36.9, 36.7, 35.2, 34.7, 31.6, 30.7; IR (neat, cm^{-1}) = 2958, 1705, 1474, 758; HRMS (ESI): Calcd. for $[M+Na]^+$ $C_{27}H_{32}O_2Na$ (*m/z*): 411.2295. Found 411.2266.

2.3.20. Cyclization of 4,6-di-tert-butyl-2-(1-hydroxy-2-propynyl)-(2-propenyloxy)benzene (**19**)

The Pauson-Khand cyclization of the enyne **19** (80 mg, 0.27 mmol) in 10 mL of the appropriate solvent, was carried out following the General Procedures A and B. $Co_2(CO)_8$ (100 mg, 0.29 mmol) and NMO (312 mg, 2.67 mmol) were added according to the general procedures and then worked up as described. The crude product was purified by flash chromatography (silica gel, hexane/EtOAc, 9:1) to afford the PK product **29** (15 mg, 17% as a 1:1 mixture of epimers) and the 1,4-diketone **28** (80 mg, 80% as a 1:6 mixture of the *syn*- and *anti*-isomers) using the oxidative procedure B. On the other hand, when the enyne was heated to 70 °C for 1 day in toluene under the thermal procedure A, it gave the PK product of **29** (10 mg, 11% in a 2:1 ratio of *exo*:*endo* epimers) along with the diketone product **28** (44 mg, 50% as a 1:1 mixture of the *syn* and *anti* isomers).

2.3.21. 6,8-Di-tert-butyl-1,1a,4,4a-tetrahydro-3H-5-oxabenzo[f] azulen-2,10-dione (cis-28)

Yellow waxy solid, ^{1}H NMR: δ = 7.57 (d, J = 2.3 Hz, 1H), 7.49 (d, J = 2.3 Hz, 1H), 4.71 (dd, J = 6.0, 12.4 Hz, 1H), 3.85 (dt, J = 2.8, 8.7 Hz, 1H), 3.76 (dd, J = 10.1, 12.4 Hz, 1H), 3.33 (dddd, J = 6.0, 8.7, 10.1, 18.8 Hz, 1H), 2.91 (d, J = 18.8 Hz 1H), 2.41 (dd, J = 8.3, 18.3 Hz, 1H), 2.29 (dd, J = 8.7, 18.8 Hz, 1H), 2.04 (dd, J = 10.1, 17.4 Hz, 1H), 1.40 (s, 9H), 1.30 (s, 9H); ^{13}C NMR: δ = 215.3, 200.9, 160.1, 144.6, 139.9, 128.4, 127.5, 124.3, 51.0, 42.4, 39.5, 39.4, 35.4, 34.7, 31.5, 30.7, 30.2; IR (neat, cm^{-1}) = 2960, 2871, 1750, 1678, 1597, 1474, 1439, 1365; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{21}H_{29}O_3$ (*m/z*): 329.2111. Found 329.2098.

2.3.22. 6,8-Di-tert-butyl-1,1a,4,4a-tetrahydro-3H-5-oxabenzo[f] azulen-2,10-dione (trans-28)

Yellow waxy solid, ^{1}H NMR: δ = 7.83 (d, J = 2.3 Hz, 1H), 7.61 (d, J = 2.3 Hz, 1H), 4.25 (m, 2H), 3.67 (dd, J = 11.5, 19.3 Hz, 1H), 2.87 (dd, J = 11.5, 19.3 Hz, 1H), 2.66 (t, J = 8.3 Hz, 2H), 2.63 (s, 1H), 2.27 (dt, J = 3.2, 14.7 Hz, 1H), 1.43 (s, 9H), 1.32 (s, 9H); ^{13}C NMR: δ = 214.4. 198.7, 167.6, 146.4, 142.8, 130.0, 129.9, 124.8, 74.3, 52.0, 44.3, 39.8, 39.6, 35.6, 34.8, 31.4, 30.8; IR (neat, cm^{-1}) = 2960, 2871, 1750, 1678, 1597, 1474, 1439, 1365; HRMS (ESI): Calcd. For $C_{42}H_{56}NaO_6^+$ (*m/z*): 679.3969. Found 679.4005 $[2M + Na]^+$.

2.3.23. 6,8-Di-tert-butyl-10-hydroxyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**29**)

Yellow oil, ^{1}H NMR: δ = 7.56 (d, J = 2.3 Hz, 1H), 7.48 (d, J = 2.3 Hz, 1H), 6.29 (s, 1H), 4.71 (dd, J = 6.0, 11.5 Hz, 1H), 3.85 (td, J = 2.8, 11.5 Hz, 1H), 3.55 (m, 1H), 2.93 (d, J = 19.3 Hz, 1H), 2.38 (dd, J = 8.3, 17.9 Hz, 1H), 2.04 (dd, J = 11.0, 22.5 Hz, 1H), 1.38 (s, 9H), 1.31 (s, 9H); ^{13}C NMR: δ = 205.4, 181.9, 152.6, 147.5, 140.6, 134.3, 128.4, 122.5, 120.6, 77.4, 74.6, 42.3, 36.5, 35.1, 31.6, 30.7, 25.5; HRMS (ESI): Calcd. for $C_{21}H_{28}NaO_3^+$ (*m/z*): 351.1931. Found 351.1957 $[M+Na]^+$.

2.3.24. Cyclization 4,6-di-tert-butyl-2-(1-hydroxy-3-trimethylsilyl-2-propynyl)-(-2-propenyloxy)benzene (**20**)

The Pauson-Khand cyclization of the enyne **20** (102 mg, 0.27 mmol) in 10 mL of the appropriate solvent, was carried out following the General Procedures A and B. $Co_2(CO)_8$ (103 mg, 0.30 mmol) and NMO (230 mg, 2.74 mmol) were added according to the general procedures and worked up as described. The crude product was purified by flash chromatography (hexane/EtOAc, 90:10) to afford the reduced PK product **26** (21.0 mg, 20%) and the expected PK product **30** (78.0 mg, 70% as a 1:2 mixture of *exo* and *endo* epimers) using the oxidative Procedure B. However, when enyne **20** was subjected to Procedure A only the *exo*-product of **30** (64.0 mg, 58%) was isolated.

2.3.25. 6,8-Di-tert-butyl-10-hydroxy-1-trimethylsilyl-4,4a-dihydro-3H,10H-5-oxabenzo[f] azulen-2-one (**30**)

A light yellow solid, mp: 110–112 °C; ^{1}H NMR: δ = 7.32 (d, J = 2.3 Hz, 1H), 7.17 (d, J = 2.3 Hz, 1H), 5.68 (d, J = 9.2 Hz, 1H), 4.58 (dd, J = 6.0, 11.5 Hz, 1H), 3.96 (m, 1H), 3.37 (t, J = 11.5 Hz, 1H), 3.25 (d, J = 9.2 Hz, 1H), 2.55 (dd, J = 7.3, 18.8 Hz, 1H), 1.82 (dd, J = 2.8, 18.3 Hz, 1H), 1.37 (s, 9H) 1.30 (s, 9H), 0.29 (s, 9H); ^{13}C NMR (125 MHz): δ = 211.4, 185.1, 155.9, 147.1, 142.5, 140.0, 132.9, 125.0, 124.9, 77.6, 75.0, 41.8, 37.7, 35.3, 34.9, 31.5, 30.7, −0.12; IR (neat, cm^{-1}) = 3396, 2958, 1710, 1606, 1471, 1367, 1236, 1013; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{24}H_{37}O_3Si$ (*m/z*): 401.2506. Found 401.2500.

2.3.26. Cyclization of 4,6-di-tert-butyl-2-(1-hydroxy-3-phenyl-2-propynyl)-2-propenyloxy benzene (**21**)

The Pauson-Khand cyclization of the enyne **21** (250 mg, 0.67 mmol) in 10 mL of the appropriate solvent, was carried out following the General Procedures A and B. $Co_2(CO)_8$ (250 mg, 0.73 mmol) and NMO (1.22 g, 10.4 mmol) were added according to the general procedures. Usual work-up and purification (silica gel, hexane/EtOAc, 90:10) gave the reduced PK product **27** (142 mg, 55%) and the expected PK product **31** (70 mg, 26% as a 1:1 mixture of epimers) using the Procedure B. Under Procedure A the reaction only gave the *exo*-product **31** (255 mg, 99%).

2.3.27. 6,8-Di-tert-butyl-10-hydroxy-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**31**)

A light yellow solid, mp: 171–173 °C; ^{1}H NMR: δ = 7.46 (m, 3H), 7.35 (d, J = 2.8 Hz, 1H), 7.23 (m, 2H), 7.14 (d, J = 2.8 Hz, 1H), 5.49 (d, J = 9.2 Hz, 1H), 4.61 (dd, J = 5.7, 11.5 Hz, 1H), 4.09 (m. 1H), 3.51 (t, J = 11.9 Hz, 1H), 3.15 (d, J = 8.7 Hz, 1H), 2.76 (dd, J = 6.9, 19.3 Hz, 1H), 2.03 (dd, J = 2.8, 18.8 Hz, 1H), 1.40 (s, 9H), 1.32 (s, 9H); ^{13}C NMR: δ = 205.3, 172.3, 156.3, 147.3, 142.8, 139.6, 133.0, 130.7, 129.6, 128.5, 128.3, 125.1, 125.0, 77.9, 73.7, 38.8, 36.7, 35.3, 34.7, 31.5, 30.7; IR (neat, cm^{-1}) = 3435, 2959, 1702, 1598, 756; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{27}H_{33}O_3$ (*m/z*): 405.2424. Found 405.2425.

2.3.28. 4,6-Di-tert-butyl-2-(-1-tert-butyl-dimethylsilyloxy-2-propynyl)-(-2-propenyloxy) benzene (**32**)

tert-Butyldimethylsilyl chloride (0.750 g, 5.00 mmol) was added at room temperature to a mixture of **19** (0.500 g, 1.67 mmol) and imidazole (0.300 g, 5.00 mmol) in DMF (10 mL). The reaction

mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer was separated, washed with water and brine and dried (Na_2SO_4). The organic extracts were concentrated to give a dark liquid. The crude product was purified by flash chromatography (hexane/EtOAc; 19:1) to give **32** as a viscous brown oil, (0.680 g, 99%). ^{1}H NMR: δ = 7.56 (d, J = 2.8 Hz, 1H), 7.28 (d, J = 2.8 Hz, 1H), 6.06 (ddt, J = 4.6, 11.0, 17.0 Hz, 1H), 5.69 (d, J = 2.3 Hz, 1H), 5.55 (dq, J = 1.8, 17.4 Hz, 1H), 5.29 (dq, J = 1.4, 10.5 Hz, 1H), 4.48 (ddt, J = 1.8, 4.6, 13.8 Hz, 1H), 4.42 (ddt, J = 1.8, 4.6, 13.8 Hz, 1H), 2.49 (d, J = 1.8 Hz, 1H), 1.39 (s, 9H), 1.31 (s, 9H), 0.82 (s, 9H), 0.07 (s, 3H), −0.08 (s, 3H); ^{13}C NMR: δ = 152.4, 146.3, 141.5, 135.5, 133.9, 124.2, 124.0, 116.1, 85.9, 75.8, 72.6, 59.3, 35.5, 34.8, 31.6, 31.1, 25.8, 18.3, −4.8, −5.0; IR (neat, cm^{-1}) = 3299, 2956, 2867, 2175, 1466, 1252, 1069; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{26}H_{43}O_2Si$ (*m/z*): 415.3027. Found 415.3045.

2.3.29. 4,6-Di-tert-butyl-2-(-1-tert-butyldimethylsilyloxy-3-trimethylsilyl-2-propynyl)-(2-propenyloxy)benzene (**33**)

tert-Butyldimethylsilyl chloride (0.500 g, 3.31 mmol) was added at room temperature to a mixture of **20** (0.410 g, 1.10 mmol) and imidazole (0.440 g, 3.31 mmol) in DMF (10 mL). Then the mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer was separated, washed with water and brine and dried (Na_2SO_4). The organic extracts were concentrated to give a dark liquid. The crude material was purified by flash chromatography (hexane/EtOAc; 19:1) to give **33** as a viscous brown oil (0.510 g, 95%). ^{1}H NMR: δ = 7.57 (d, J = 2.3 Hz, 1H), 7.28 (d, J = 2.3 Hz, 1H), 6.05 (ddt, J = 4.6, 10.5, 17.4 Hz, 1H), 5.70 (s, 1H), 5.51 (dq, J = 1.8, 17.4 Hz,1H), 5.29 (dq, J = 1.8, 10.5 Hz, 1H), 4.48 (dt, J = 1.4, 5.0 Hz, 2H), 1.39 (s, 9H), 1.32 (s, 9H), 0.83 (s, 9H), 0.15 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz): δ = 152.7, 146.0, 141.4, 135.6, 134.1, 124.7, 123.9, 116.0, 107.7, 85.9, 75.7, 60.2, 35.5, 34.8, 31.6, 31.2, 25.9, 18.4, −0.1, −4.4, −4.7; IR (neat, cm^{-1}) = 2960, 2173, 1470, 1252, 1070; HRMS (CI): Calcd. for $[M^+]$ $C_{29}H_{50}O_2Si_2$ (*m/z*): 486.3344. Found 486.3355.

2.3.30. 4,6-Di-tert-butyl-2-(-1-tert-butyl-dimethylsilyloxy -3-phenyl-2-propynyl)-(-2-propenyloxy)benzene (**34**)

tert-Butyldimethylsilyl chloride (0.410 g, 2.71 mmol) was added at room temperature to a mixture of **31** (0.340 g, 0.900 mmol) and imidazole (0.300 g, 2.71 mmol) in DMF (10 mL). The mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer was separated, washed with water and brine, dried with Na_2SO_4 (anhydrous). The organic layer was concentrated to give a dark colored liquid. The crude product was purified by flash chromatography (hexane/EtOAc; 19:1) to give **34** as viscous brown liquid (0.420 g, 95%). ^{1}H NMR: δ = 7.65 (d, J = 2.5 Hz, 1H), 7.41 (d, J = 2.5 Hz, 1H), 7.40 (d, J = 4.0 Hz, 1H), 7.27−7.30 (m, 4H), 6.09 (ddt, J = 4.6, 10.5, 17.4 Hz, 1H), 5.93 (s, 1H), 5.56 (dq, J = 1.8, 17.0 Hz, 1H), 5.29 (dq, J = 1.8, 10.5 Hz, 1H), 4.56 (ddt, J = 1.8, 4.6, 13.8 Hz, 1H), 4.50 (ddt, J = 1.8, 4.1, 13.8 Hz, 1H), 1.42 (s, 9H), 1.33 (s, 9H), 0.86 (s, 9H), 0.14 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz): δ = 152.5, 146.2, 141.5, 135.8, 134.0, 131.7, 128.3, 124.5, 123.9, 123.3, 116.5, 91.4, 84.7, 75.8, 60.1, 35.5, 34.8, 31.6, 31.2, 25.9, 18.4, −4.4, −4.8 (only 23 signals were observed out of 24 carbon types); IR (neat, cm^{-1}) = 2959, 2864, 1600, 1362, 1063; HRMS (CI): Calcd. for $[M^+]$ $C_{32}H_{46}O_2Si$ (*m/z*): 490.3262. Found 490.3277.

2.3.31. Cyclization of 4,6-di-tert-butyl-2-(-1-tert-butyl-dimethylsilyloxy-2-propynyl)-(-2-propenyloxy) benzene (**35**)

The Pauson-Khand cyclization of the enyne **32** (80 mg, 0.19 mmol) in 10 mL of the appropriate solvent, was carried out following the General Procedures A and B. $Co_2(CO)_8$ (91 mg, 0.27 mmol) and NMO (310 mg, 2.65 mmol) were added according to the general procedures. Normal work-up and purification of the crude product (hexane/EtOAc, 9:1) to afford the PK product **35** (45 mg, 52% as a 2:1 mixture of epimers) using Procedure B. Procedure A delivered the PK product **35** (68.3 mg, 80%) as a 1:1 mixture stereoisomers. Small amounts of the stereoisomers of **35** were separated by preparative thin layer chromatography to give the *exo*- and *endo*-products.

2.3.32. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (exo-35)

Brown waxy solid, ^{1}H NMR (300 MHz): δ = 7.55 (d, J = 2.1 Hz, 1H), 7.26 (d, J = 2.4 Hz, 1H), 6.25 (s, 1H), 5.75 (s, 1H), 4.51 (dd, J = 6.2, 11.4 Hz, 1H), 3.52 (m, 1H), 3.09 (t, J = 11.7 Hz, 1H), 2.58 (dd, J = 6.9, 18.6 Hz, 1H), 1.87 (dd, J = 2.8, 18.6 Hz, 1H), 1.34 (s, 9H), 1.31 (s, 9H), 1.00 (s, 9H), 0.07 (s, 6H), ^{13}C NMR (75 MHz): δ = 206.6, 182.8, 153.8, 146.6, 140.9, 133.0, 127.4, 123.4, 120.5, 75.8, 71.1, 43.1, 37.4, 35.0, 31.7, 30.8, 25.9, 18.4, −4.9, −5.1, only 20 carbons were observed out of 21 carbon types; IR (neat, cm^{-1}) = 2954, 2862, 1718, 1623, 1475; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{27}H_{43}O_3Si$ (*m/z*): 443.2976. Found 443.3002.

2.3.33. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (endo-35)

Brown waxy solid, ^{1}H NMR (300 MHz): δ = 7.29 (d, J = 2.1 Hz, 1H), 7.11 (d, J = 2.4 Hz, 1H), 6.06 (s, 1H), 5.61 (s, 1H), 4.49 (dd, J = 5.2, 11.0 Hz, 1H), 3.73 (m, 1H), 3.73 (t, J = 11.0 Hz, 1H), 2.62 (dd, J = 6.9, 18.9 Hz, 1H), 1.95 (dd, J = 2.1, 18.6 Hz, 1H), 1.36 (s, 9H), 1.30 (s, 9H), 0.85 (s, 9H), 0.04 (s, 3H), −0.19 (s, 3H); ^{13}C NMR (75 MHz): δ = 207.8, 181.2, 155.4, 145.7, 142.2, 132.2, 128.1, 124.9, 124.3, 75.2, 40.7, 38.0, 35.3, 34.6, 31.6, 30.6, 25.8, 18.3, −4.76, −4.8; IR (neat, cm^{-1}) = 2952, 2860, 1716, 1620, 1472; HRMS (ESI): Calcd. for $[2M + Na]^+$ $C_{54}H_{84}NaO_6Si_2^+$ (*m/z*): 907.5699. Found 907.5636.

2.3.34. Cyclization of 4,6-di-tert-butyl-2-(-1-tert-butyl-dimethylsilyloxy-3- trimethylsilyl -2-propynyl)-(-2-propenyloxy) benzene (**33**)

The Pauson-Khand cyclization of the enyne **33** (100 mg, 0.21 mmol) in 10 mL of the appropriate solvent, was carried out following the General Procedures A and B. $Co_2(CO)_8$ (141 mg, 0.41 mmol) and NMO (530 mg, 4.52 mmol) were added according to the general procedures, work-up and purification (hexane/EtOAc, 90:10) provided only the *exo*-isomer of the PK product **36** (58 mg, 61% yield). On the other hand, subjection of enyne **33** to thermal conditions resulted in no formation of any cycloadduct.

2.3.35. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-1-trimethylsilyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**36**)

Yellow, waxy paste, ^{1}H NMR: δ = 7.26 (d, J = 2.5 Hz, 1H), 7.07 (d, J = 2.3 Hz, 1H), 5.78 (s, 1H), 4.51 (dd, J = 4.6, 11.9 Hz, 1H), 4.18 (dd, J = 4.6, 8.7 Hz, 1H), 3.89 (m, 1H), 3.52 (t, J = 11.5 Hz, 1H), 2.56 (dd, J = 6.9, 18.8 Hz, 1H), 1.94 (d, J = 17.9 Hz, 1H), 1.34 (s, 9H), 1.29 (s, 9H), 0.82 (s, 9H), 0.23 (s, 9H), 0.03 (s, 3H), −0.21 (s, 3H); ^{13}C NMR: δ = 212.6, 186.9, 157.1, 145.0, 141.9, 138.5, 131.4, 126.3, 124.0, 75.4, 38.8, 38.7, 35.3, 34.5, 31.5, 30.4, 25.8, 18.2, 14.2, 11.0, −0.2, −4.6; IR (neat, cm^{-1}) = 3433.6, 2956.3, 2859.6, 1732.2, 1698.8, 1594.5, 1477.2, 1250.8; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{30}H_{51}O_3Si_2$ (*m/z*): 515.3371. Found 515.3389.

2.3.36. Cyclization of 4,6-di-tert-butyl-2-(-1-tert-butyldimethylsilyloxy -3-phenyl-2-propynyl)-(-2-propenyloxy) benzene (**34**)

The Pauson-Khand cyclization of the enyne **34** (101 mg,

0.21 mmol) in 10 mL of the appropriate solvent, was carried out following the General Procedures A and B. $Co_2(CO)_8$ (141 mg, 0.41 mmol) and NMO (529 mg, 4.52 mmol) were added according to the general procedures and after work-up and purification as usual gave the reduced PK product **27** (11.2 mg, 11%) and the PK product **37** (62.9 mg, 60% as a 1:5 mixture of epimers) using the oxidative Procedure B. Procedure A delivered only **37** (101 mg, 95% as a 1:10 mixture of epimers) was isolated. The isomers were separated by preparative thin layer chromatography.

2.3.37. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (exo-37)

Yellow oil, ^{1}H NMR: δ = 7.39 (m, 3H), 7.31 (d, J = 2.3 Hz, 1H), 7.21(dd, J = 1.8, 7.8 Hz, 2H), 7.05 (d, J = 2.8 Hz, 1H), 5.55 (s, 1H), 4.62 (dd, J = 5.0, 11.9 Hz, 1H), 4.01 (m, 1H), 3.54 (t, J = 10.5 Hz, 1H), 2.78 (dd, J = 7.3, 18.8 Hz, 1H), 2.10 (d, J = 18.8 Hz, 1H), 1.38 (s, 9H), 1.32 (s, 9H), 0.77 (s, 9H), −0.12 (s, 3H), −0.33 (s, 3H); ^{13}C NMR: δ = 206.3, 173.9, 157.3, 145.6, 142.4, 138.2, 132.0, 131.0, 129.5, 128.3, 126.1, 126.1, 124.3, 124.2, 74.2, 39.2, 37.3, 35.4, 34.6, 31.5, 30.5, 25.8, 18.2, −4.8; IR (neat, cm^{-1}) = 2959, 1709, 849; HRMS (ESI): Calcd. for $C_{33}H_{47}O_3Si$ (*m/z*): 519.3289. Found 519.3295 [M+H].

2.3.38. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (endo-37)

Yellow oil, ^{1}H NMR: δ = 7.69 (d, J = 2.5 Hz, 1H), 7.29–7.23 (m, 6H), 5.90 (s, 1H), 4.62 (dd, J = 5.5, 11.5 Hz, 1H), 3.53 (m, 1H), 3.23 (t, J = 11.5 Hz, 1H), 2.75 (dd, J = 6.9, 18.8 Hz, 1H), 1.94 (dd, J = 2.3, 18.8 Hz, 1H), 1.41 (s, 9H), 1.37 (s, 9H), 0.60 (s, 9H), −0.14 (s, 3H), −0.28 (s, 3H); ^{13}C NMR (125 MHz): δ = 205.4, 173.7, 146.5, 141.1, 138.2, 134.0, 132.2, 130.4, 127.7, 127.2, 126.2, 123.0, 120.9, 72.2, 61.8, 42.2, 36.6, 35.1, 35.0, 31.6, 30.8, 25.6, 18.1, −5.5; IR (neat, cm^{-1}) = 2959, 1709, 1623, 849; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{33}H_{47}O_3Si$ (*m/z*): 519.3289. Found 519.3250.

*2.3.39. 3,5-Di-tert-butyl-2-(2-methyl-2-propenyloxy)benzaldehyde (**38**)*

3-Chloro-2-methylpropene (1.16 g, 18.0 mmol) was added to a suspension of K_2CO_3 (2.00 g, 14.4 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol) in DMF (10 mL) and stirred for 12 h according to the general alkylation procedure. The crude product was purified by flash chromatography (hexane/EtOAc, 15:1) to give **38** (1.21 g, 98%) as a light yellow solid: mp: 49–51 °C, ^{1}H NMR (500 MHz): δ = 10.29 (s, 1H), 7.74 (d, J = 2.7 Hz, 1H), 7.65 (d, J = 2.7 Hz, 1H), 5.55 (s, 1H), 5.35 (s, 1H), 4.36 (s, 2H), 1.85 (s, 3H), 1.42 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (125 MHz): δ = 191.2, 159.6, 146.5, 143.1, 140.4, 130.9, 129.4, 123.6, 110.2, 82.2, 35.4, 34.8, 31.4, 30.9, 19.6; IR (neat, cm^{-1}) = 2962, 2869, 1688, 1597, 1478, 993, 896; HRMS (CI): Calcd. For $[M]^+$ $C_{19}H_{28}O_2^+$ (*m/z*): 288.2084. Found 288.2082.

*2.3.40. 4,6-Di-tert-butyl-2-(-1-hydroxy-3-phenyl-2-propynyl)-(2-methyl-2-propenyloxy) benzene (**41**)*

A 1.0 M solution of phenylethynylmagnesium bromide (15.6 mL, 16.0 mmol) in THF was added to a solution of **38** (3.00 g, 10.0 mmol) in THF (20 mL) under N_2 atmosphere at 0 °C according to the general procedure 3.1.2 to give **41** (4.00 g, 98%) as a light yellow solid, mp: 49–51 °C. ^{1}H NMR: δ = 7.71 (d, J = 2.7 Hz, 1H), 7.45 (m, 2H), 7.37 (d, J = 2.7 Hz, 1H), 7.30 (m, 3H), 6.01 (s, 1H), 5.30 (s, 1H), 5.05 (s, 1H), 4.59 (d, J = 13.1 Hz, 1H), 4.41 (d, J = 13.1 Hz, 1H), 2.62 (s, 1H), 1.89 (s, 3H), 1.45 (s, 9H), 1.37 (s, 9H); ^{13}C NMR: δ = 153.4, 146.6, 142.4, 141.5, 134.3, 131.8, 128.6, 128.4, 125.1, 123.9, 122.8, 111.4, 90.0, 86.1, 78.6, 60.5, 35.6, 34.9, 31.6, 31.3, 19.7; IR (neat, cm^{-1}) = 3452, 2963, 2908, 2224, 1658, 1599; HRMS (ESI): Calcd. for $[M+Na]^+$ $C_{27}H_{34}O_2Na^+$ (*m/z*): 413.2451. Found 413.2442.

*2.3.41. 3,5-Di-tert-butyl-2-(3-methyl-2-propenyloxy) benzaldehyde (**42**)*

Crotyl chloride (95% *trans*, 1.16 g, 18.0 mmol) was added to a suspension of K_2CO_3 (2.00 g, 14.4 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol) in DMF (10 mL) and stirred for 12 h according to the general alkylation procedure. The crude product was purified by flash chromatography (hexane/EtOAc, 15:1) to give **42** (1.22 g, 99%) as a brown oil. The proton NMR spectrum indicated that it was a 5:1 mixture of the *E/Z*-isomers. ^{1}H NMR data of the major isomer: δ = 10.29 (s, 1H), 7.69 (d, J = 2.7 Hz, 1H), 7.58 (d, J = 2.3 Hz, 1H), 5.88 (m, 1H), 5.80 (m, 1H), 4.39 (dd, J = 1.4, 6.0 Hz, 2H), 1.78 (dd, J = 1.4, 6.4 Hz, 3H), 1.42 (s, 9H), 1.31 (s, 9H); ^{13}C NMR: δ = 191.2, 160.0, 146.4, 143.1, 130.9, 130.7, 129.5, 126.0, 123.8, 79.7, 35.4, 34.8, 31.4, 31.0, 18.0; IR (neat, cm^{-1}) = 2958, 1690, 1593, 1460, 1374, 1220, 970; HRMS (ESI): Calcd. For $[M+Na]^+$ $C_{19}H_{28}NaO_2^+$ (*m/z*): 311.1981. Found 311.1951.

*2.3.42. 4,6-Di-tert-butyl-2-(-1-hydroxy-2-propynyl)-1-(-2-butenyloxy)benzene (**43**)*

A 0.5 M solution in THF of ethynylmagnesium bromide (12.7 mL, 6.35 mmol) was added at 0 °C to the solution of **42** (1.22 g, 4.23 mmol) in dry THF (10 mL) under N_2 atmosphere according to the general Grignard Procedure to give **43** as a viscous brown liquid (1.32 g, 99%). ^{1}H NMR (300 MHz): δ = 7.56 (d, J = 2.3 Hz, 1H), 7.35 (d, J = 2.7 Hz, 1H), 5.91 (q, J = 6.2 Hz, 1H), 5.81 (dt, J = 1.0, 5.5 Hz, 1H), 5.77 (d, J = 2.1 Hz, 1H), 4.51 (ddt, J = 1.0, 5.5, 11.7 Hz, 1H), 4.34 (ddt, J = 1.0, 5.9, 11.7 Hz, 1H), 2.61 (d, J = 2.4 Hz, 1H), 1.78 (d, J = 5.2 Hz, 3H), 1.40 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (75 MHz): δ = 153.3, 146.6, 142.4, 133.7, 129.8, 126.7, 125.3, 123.5, 84.4, 76.3, 74.2, 60.1, 35.6, 34.8, 31.5, 31.3, 18.0; IR (neat, cm^{-1}) = 3298, 2958, 2103, 1602, 1277; HRMS (ESI): Calcd. for $[2M + Na]^+$ $C_{42}H_{60}O_4Na^+$ (*m/z*): 651.4384. Found 651.4334.

*2.3.43. 4,6-Di-tert-butyl-2-(-1-hydroxy-3- trimethylsilyl -2-propynyl)-1-(-2- butenyloxy) benzene (**44**)*

A solution of trimethylsilylethynylmagnesium chloride in dry THF was prepared by adding ethynyltrimethylsilane (2.47 g, 25.0 mmol) to 3.0 M solution of ethylmagnesium chloride (8.27 mL, 25.0 mmol) THF under N_2 at 0 °C and stirred for 30 min before allowing the reaction to warm up to room temperature. The reaction was further stirred for 10 min at room temperature. To this aliquot of trimethylsilylethynylmagnesium chloride was added a solution of **42** (2.27 g, 7.87 mmol) in THF (20 mL) under N_2 atmosphere at −78 °C and stirred for 2.5 h at −78 °C before allowing it to warm up to rt. This was then stirred overnight and then worked up according to the general procedure to give **44** (3.00 g, 99%) as a light yellow waxy solid; ^{1}H NMR: δ = 7.54 (d, J = 2.7 Hz, 1H), 7.27 (d, J = 2.3 Hz, 1H), 5.84 (m, 1H), 5.75 (m, 1H), 5.68 (s, 1H), 4.47 (dd, J = 6.0, 11.5 Hz, 1H), 4.35 (dd, J = 6.0, 11.5 Hz, 1H), 1.71 (d, J = 6.4 Hz, 3H), 1.34 (s, 9H), 1.25 (s, 9H), 0.12 (s, 9H); ^{13}C NMR: δ = 153.5, 146.3, 142.2, 134.1, 129.6, 126.8, 125.1, 124.0, 106.0, 90.9, 76.2, 60.8, 35.5, 34.7, 31.5, 31.3, 18.0, −0.1; IR (neat, cm^{-1}) = 3361, 2960, 2172, 1462; HRMS (ESI): Calcd. For $[2M + Na]^+$ $C_{48}H_{76}O_4Si_2Na^+$ (*m/z*): 795.5178. Found 795.5212.

*2.3.44. 4,6-Di-tert-butyl-2-(-1-hydroxy-3-phenyl-2-propynyl)-(2-butenyloxy)benzene (**45**)*

A 1.0 M solution in THF of phenylethynylmagnesium bromide (15.6 mL, 16.0 mmol) was added to the solution of **42** (3.0 g, 10.0 mmol) in dry THF (20 mL) under N_2 atmosphere at 0 °C according to the general Grignard Procedure to give **45** (3.00 g, 74%) as a light yellow oil; ^{1}H NMR: δ = 7.75 (d, J = 2.3 Hz, 1H), 7.49 (m, 2H), 7.44 (d, J = 2.7 Hz, 1H), 7.32 (m, 3H), 6.03 (d, J = 4.0 Hz, 1H), 5.98 (m, 1H), 5.88 (m, 1H), 4.59 (dd, J = 6.0, 7.3 Hz, 1H), 4.44 (dd, J = 6.0, 7.3 Hz, 1H), 2.85 (d, J = 5.0 Hz, 1H), 1.80 (d, J = 5.5 Hz, 3H),

1.44 (s, 9H), 1.37 (s, 9H); ^{13}C NMR: δ = 153.4, 146.5, 142.4, 134.4, 131.8, 129.8, 128.5, 128.4, 126.9, 125.2, 123.8, 122.8, 89.9, 86.1, 76.4, 60.8, 35.6, 34.8, 31.6, 31.4, 18.0; IR (neat, cm^{-1}) = 3357, 2955, 2179, 1463, 1374, 1223; HRMS (ESI): Calcd. for [M+Na]$^+$ $C_{27}H_{34}O_2Na$ (*m/z*): 413.2451. Found 413.2461.

2.3.45. 1,5-Di-tert-butyl-3-iodo-2-(3-phenyl-2-propenyloxy) benzene (**47**)

A solution of diethyl azodicarboxylate (15.7 g, 90.4 mmol) in dry THF (50 mL) was added dropwise to a solution of iodophenol **46**[11c] (10.0 g, 30.1 mmol), cinnamyl alcohol (8.08 g, 60.2 mmol) and PPh_3 (23.7 g, 90.4 mmol) in dry THF (100 mL) at 0 °C and stirred for 3 h. The solvent was removed *in vacuo* at the end of the reaction. The crude product was purified by flash chromatography (hexane) to give the product **47** (12.4 g, 92%) as a white solid, mp: 120–122 °C; ^{1}H NMR (300 MHz): δ = (*E*-isomer) 7.69 (d, *J* = 2.4 Hz, 1H), 7.26–7.50 (m, 6H), 6.82 (d, *J* = 15.8 Hz, 1H), 6.50 (dt, *J* = 5.5, 16.2 Hz, 1H), 4.69 (d, *J* = 5.5 Hz, 2H), 1.43 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (75 MHz): δ = 155.1, 148.2, 143.9, 136.9, 135.4, 132.6, 128.7, 127.9, 126.7, 125.3, 124.9, 93.4, 73.9, 34.5, 34.0, 31.5, 31.3; IR (neat, cm^{-1}) = 3100, 2960, 2872, 1772, 1434, 1394, 1234, 1087, 963; HRMS (CI): Calcd. for [M$^+$] $C_{23}H_{29}IO$ (*m/z*): 448.1257. Found 448.1218.

2.3.46. 3,5-Di-tert-butyl-2-(3-phenyl-2-propenyloxy) benzaldehyde (**48**)

A solution of 1,5-di-*tert*-butyl-3-iodo-2-(3-phenyl-2-propenyloxy)benzene **47** (5.00 g, 11.2 mmol) in dry THF (20 mL) was cooled to −30 °C and 2.0 M solution of *i*-propylmagnesium chloride (1.38 g, 13.5 mmol) in THF was added and the reaction mixture stirred for 20 min at −30 °C. The reaction was then allowed to warm up to room temperature and stirred for 20 min. Next the reaction mixture was cooled to 0 °C and DMF (1.30 mL, 16.7 mmol) was added dropwise. The reaction was warmed up to room temperature and stirred for 2 h. The reaction was quenched with water and extracted with CH_2Cl_2. The organic layer was separated, concentrated under reduced pressure and dried ($MgSO_4$). The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc, 5:1) to give **48** (4.51 g, 98%) as a white solid, mp: 123–125 °C; ^{1}H NMR (300 MHz): δ = (*E*-isomer) 10.37 (s, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.26–7.47 (m, 5H), 6.80 (d, *J* = 15.8 Hz, 1H), 6.50 (dt, *J* = 5.5, 16.2 Hz, 1H), 4.64 (d, *J* = 5.9 Hz, 2H), 1.46 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (75 MHz); δ = 191.0, 159.8, 146.6, 143.2, 136.4, 133.0, 131.0, 129.4, 128.8, 128.1, 126.8, 124.1, 124.0, 79.4, 35.5, 34.8, 31.4, 31.0; IR (neat, cm^{-1}) = 3049, 2920, 1667, 1592, 1485, 1362, 1231, 915, 755, 687; HRMS (ESI): Calcd. for [M+H]+$C_{24}H_{31}O_2$ (*m/z*): 351.2319. Found 351.2325.

2.3.47. 4,6-Di-tert-butyl-2-(1-hydroxy-2-propynyl)-1-(-3-phenyl -2-propenyloxy) benzene (**49**)

A 0.5 M solution of ethynylmagnesium bromide (17.2 mL, 8.61 mmol) in THF was added at 0 °C to the solution of **48** (2.00 g, 5.71 mmol) in dry THF (20 mL) under N_2 atmosphere. The reaction mixture was allowed to warm up to rt and stirred for 3 h. The reaction was quenched with NH_4Cl and extracted with CH_2Cl_2. The organic extract was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc, 10:1) to give **49** (3.11 g, 99%) as a yellow solid, mp: 136–138 °C; ^{1}H NMR (300 MHz): δ = 7.26–7.61 (m, 7H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.46 (dt, *J* = 5.4, 16.2 Hz, 1H), 5.84 (s, 1H), 4.74 (ddd, *J* = 1.5, 5.7, 13.2 Hz, 1H), 4.58 (ddd, *J* = 1.5, 5.7, 13.2 Hz, 1H), 2.64 (d, *J* = 1.2 Hz, 1H), 2.52 (s, 1H), 1.44 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (75 MHz): δ = 153.3, 146.8, 142.4, 136.7, 133.8, 132.2, 128.7, 127.9, 126.7, 125.4, 125.0, 123.6, 84.5, 76.1, 74.4, 59.9, 35.7, 34.9, 31.6, 31.4; IR (neat, cm^{-1}) = 3550, 3279, 2962, 2159, 1476, 1362, 1230, 1159, 1118, 1021, 965, 884, 748; HRMS (ESI) Calcd. for [M+Na]$^+$ $C_{26}H_{36}O_2Na^+$ (*m/z*): 399.2295. Found 399.2293.

2.3.48. 4,6-Di-tert-butyl-2-(1-hydroxy-3-phenyl-2-propynyl)-1-(-3-phenyl-2-propenyloxy) benzene (**50**)

1.0 M solution of phenylethynylmagnesium bromide (8.59 mL, 8.59 mmol) in THF was added at 0 °C to a solution of **48** (2.00 g, 5.71 mmol) in dry THF (20 mL) under N_2 atmosphere. The reaction mixture was allowed to warm up to room temperature and stirred for 3 h. The reaction was quenched with NH_4Cl and extracted with CH_2Cl_2. The organic extract was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc, 10:1) to give **22b** (2.0 g, 78%) as a white solid. Mp: 133–134 °C; ^{1}H NMR (500 MHz): δ = 7.25–7.70 (m, 12H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.49 (dt, *J* = 5.5, 15.6 Hz, 1H), 6.04 (s, 1H), 4.81 (ddd, *J* = 1.8, 5.5, 12.8 Hz, 1H), 4.65 (ddd, *J* = 1.8, 5.5, 12.8 Hz, 1H), 2.60 (s, 1H), 1.45 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (75 MHz): δ = 153.3, 146.7, 142.4, 136.8, 134.4, 132.2, 131.8, 128.7, 128.6, 128.5, 128.4, 127.9, 126.7, 125.3, 125.2, 123.9, 89.8, 86.2, 76.1, 60.7, 35.7, 34.8, 31.6, 31.4; IR (neat, cm^{-1}) = 3441, 2961, 1599, 1444, 1362, 1222, 1159, 1119, 965, 883, 756; HRMS (ESI): Calcd. for [M+Na]$^+$ $C_{24}H_{31}O_2$ (*m/z*): 475.2608. Found 475.2613.

2.3.49. Cyclization of 4,6-di-tert-butyl-2-(1-hydroxy-3-phenyl-2-propynyl)-1-(-3-methyl-2-propenyloxy) benzene (**45**)

The Pauson-Khand cyclization of the enyne **45** (63 mg, 0.16 mmol) was carried out following the General Procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (61 mg, 0.18 mmol) and NMO (189 mg, 1.62 mmol) were added according to the general procedures, work-up and purification (hexane/EtOAc, 87:13) as usual provided the reduced PK product **52** (12 mg, 18%), the *endo*-product **54** (26 mg, 36%) and the *exo*-product **56** (31 mg, 45%) for procedure B. Procedure A produced the *endo*-product **54** (6.1 mg, 9%) and the *exo*-PK product **56** (60 mg, 90%).

2.3.50. 6,8-Di-tert-butyl-1-phenyl-3-methyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**52**)

Light yellow solid, mp: 80–82 °C; ^{1}H NMR: δ = 7.45 (t, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 6.9 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 2.3 Hz, 1H,), 7.14 (d, *J* = 1.8 Hz, 1H), 4.72 (dd, *J* = 5.5, 11.5 Hz, 1H), 3.87 (d, *J* = 12.8 Hz, 1H), 3.77 (d, *J* = 12.8 Hz, 1H), 3.37 (t, *J* = 11.5 Hz, 1H), 3.10 (m, 1H), 1.96 (dd, *J* = 2.8, 8.7 Hz, 1H), 1.42 (s, 9H), 1.36 (d, *J* = 7.8 Hz, 3H), 1.34 (s, 9H); ^{13}C NMR (125 MHz): δ = 207.7, 169.9, 157.0, 146.7, 141.8, 138.4, 131.5, 129.7, 128.3, 128.1, 125.3, 123.0, 75.5, 52.9, 42.4, 36.5, 35.2, 34.7, 31.6, 30.7, 15.3 (21 carbons were observed out of 22 carbon types); IR (Neat, cm^{-1}) = 2957, 1705, 1466, 752; HRMS (ESI): Calcd. for [M+H]$^+$ $C_{28}H_{35}O_2$ (*m/z*): 403.2632. Found 403.2636.

2.3.51. 6,8-Di-tert-butyl-10-hydroxy-3-methyl-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (54, endo-product)

Yellow oil, ^{1}H NMR: δ = 7.37 (m, 3H), 7.34 (d, *J* = 2.8 Hz, 1H), 7.20 (dd, *J* = 1.8, 8.3 Hz, 2H), 7.14 (d, *J* = 2.8 Hz, 1H), 5.53 (s, 1H), 4.73 (dd, *J* = 5.5, 11.5 Hz, 1H), 4.13 (d, *J* = 7.3 Hz, 1H), 4.10 (d, *J* = 7.3 Hz, 1H), 3.64 (t, *J* = 11.0 Hz, 1H), 2.83 (ddd, *J* = 7.3, 7.8, 11.5 Hz, 1H), 1.40 (s, 9H), 1.32 (s, 9H), 1.16 (d, *J* = 7.8 Hz, 3H); ^{13}C NMR: δ = 208.8, 171.5, 156.4, 147.3, 142.7, 138.5, 132.8, 130.9, 129.7, 128.4, 128.3, 125.3, 124.9, 73.5, 42.0, 41.7, 35.3, 34.7, 31.5, 30.7, 14.3, 10.5; IR (Neat, cm^{-1}) = 3434, 3055, 2960, 2870, 1703, 1477, 1444; HRMS (ESI): Calcd. for [2M + Na]$^+$ $C_{56}H_{68}NaO_6$ (*m/z*) 859.4908, Found 859.4955.

2.3.52. 6,8-Di-tert-butyl-10-hydroxy-3-methyl-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo [f]azulen-2-one (56, exo product)

Yellow solid, mp: 158–160 °C, ^{1}H NMR: δ = 7.42–7.35 (m, 3H), 7.34 (d, *J* = 2.8 Hz, 1H), 7.23 (d, *J* = 6.5 Hz, 2H), 7.18 (d, *J* = 2.8 Hz, 1H),

5.53 (d, J = 8.3 Hz, 1H), 4.76 (dd, J = 5.0, 11.0 Hz, 1H), 4.12 (dd, J = 7.3, 14.2 Hz, 1H), 3.60 (m, 1H), 3.54 (t, J = 11.0 Hz, 1H,), 3.14 (d, J = 8.7 Hz, 1H), 1.41 (s, 9H), 1.38 (d, J = 7.3 Hz, 3H), 1.32 (s, 9H); ^{13}C NMR: δ = 207.5, 170.0, 156.5, 147.3, 142.7, 138.5, 132.9, 130.9, 129.6, 128.4, 128.3, 125.2, 124.9, 73.5, 60.5, 47.7, 42.5, 35.3, 34.7, 31.5, 30.7, 15.2; IR (Neat, cm^{-1}) = 3498, 2955, 1701, 1468; HRMS (ESI): Calcd. for [M+H]$^+$ $C_{28}H_{35}O_3$ 419.2581, Found 419.2577.

2.3.53. Cyclization of 4,6-di-tert-butyl-2-(1-hydroxy-3-trimethylsilyl-2-propynyl)-1-(3-methyl-2-propenyloxy) benzene (**43**)

The Pauson-Khand cyclization of the enyne **43** (200 mg, 0.52 mmol) was carried out following the General Procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (195 mg, 0.57 mmol) and NMO (606 mg, 5.18 mmol) were added according to the general procedures, work-up and purification by flash chromatography (hexane/EtOAc, 87:13) afforded the PK product **55** (15 mg, 7%) for Procedure B whereas Procedure A gave **55** (25 mg, 12%).

2.3.54. 6,8-Di-tert-butyl-10-hydroxy-3-methyl-1-trimethylsilyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**55**)

Yellow liquid, ^{1}H NMR: δ = 7.32 (d, J = 2.8 Hz, 1H), 7.18 (d, J = 2.8 Hz, 1H), 5.69 (s, 1H), 4.65 (dd, J = 5.0, 11.0 Hz, 1H), 3.50 (ddd, J = 3.2, 5.0, 11.0 Hz, 1H), 3.47 (t, J = 11.0 Hz, 1H), 1.85 (ddd, J = 3.2, 7.3, 14.7 Hz, 1H), 1.38 (s, 9H), 1.29 (s, 9H), 1.23 (d, J = 7.8 Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (125 MHz): δ = 213.5, 182.6, 156.2, 146.9, 142.4, 139.0, 132.7, 125.1, 124.9, 75.0, 60.5, 50.6, 43.6, 35.3, 34.7, 31.5, 30.7, 15.0, −0.09; IR (neat, cm^{-1}) = 3498, 2960, 1697, 1590, 1478; HRMS (CI): Calcd. for [M$^+$] $C_{25}H_{38}O_3Si$ (m/z): 414.2590. Found 414.2593.

2.3.55. Cyclization of 4,6-di-tert-butyl-2-(-1-hydroxy-2-propynyl)-1-(-2-butenyloxy) benzene (**42**)

The Pauson-Khand cyclization of the enyne **42** (420 mg, 1.34 mmol) was carried out following General Procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (500 mg, 1.46 mmol) and NMO (1.72 g, 14.7 mmol) were added according to the general procedures, usual work-up and purification by flash chromatography (hexane/EtOAc, 87:13) delivered the reduced PK product **57** (131 mg, 30%) and the 1,4-diketone **58** (253 mg, 58% as a 1:3 mixture of *syn* and *anti* isomers) using Procedure B. Procedure A only gave **57** (146 mg, 32%, 1:2 mixture of *syn* and *anti* isomers). Preparatory TLC was used to separate the *syn*- and *anti*-products.

2.3.56. 6,8-Di-tert-butyl-3-methyl-1,1a,4,4a-tetrahydro-1H,3H-5-oxabenzo[f]azulen-2,10-dione (syn-58)

Brown solid, mp: 134–136 °C, ^{1}H NMR: δ = 7.56 (d, J = 2.8 Hz, 1H). 7.49 (d, J = 2.8 Hz, 1H), 4.84 (dd, J = 6.45, 11.9 Hz, 1H), 3.81 (dt, J = 1.8, 8.7 Hz, 1H), 3.70 (t, J = 11.9 Hz, 1H), 3.16 (dt, J = 1.8, 19.3 Hz, 1H), 2.93 (m, 1H), 2.25 (dd, J = 8.3, 19.3 Hz, 1H), 1.94 (m, 1H), 1.42 (s, 9H), 1.30 (s, 9H), 1.09 (d, J = 6.9 Hz, 3H); ^{13}C NMR: δ = 217.0, 200.5, 160.3, 144.4, 139.9, 128.3, 128.0, 124.3, 76.8, 50.0, 48.6, 44.4, 37.4, 35.4, 34.6, 31.5, 30.2, 12.8; IR (neat, cm^{-1}) = 2960, 1748, 1680, 1463, 757; HRMS (ESI): Calcd. for [M+H]$^+$.$C_{22}H_{31}O_3$ (m/z) 343.2268, Found 343.2272.

2.3.57. 6,8-Di-tert-butyl-3-methyl-1,1a,4,4a-tetrahydro-1H,3H-5-oxabenzo[f]azulen-2,10-dione (anti-58)

Yellow waxy solid, ^{1}H NMR: δ = 7.53 (d, J = 2.5 Hz, 1H,), 7.39 (d, J = 2.5 Hz, 1H), 4.45 (dd, J = 2.3, 12.8 Hz, 1H), 3.99 (dd, J = 3.7, 12.3 Hz, 1H), 3.59 (dt, J = 8.7, 10.5 Hz, 1H), 2.95 (tt, J = 2.8, 8.7 Hz, 1H), 2.49 (t, J = 8.7 Hz, 1H), 2.41 (ddd, J = 1.8, 8.7, 10.5 Hz, 1H), 2.33 (dd, J = 8.3, 19.3 Hz, 1H), 1.25 (s, 9H), 1.22 (s, 9H), 1.21 (d, J = 2.3 Hz, 3H); ^{13}C NMR: δ = 215.9, 202.7, 158.8, 145.1, 140.1, 128.6, 125.2, 125.0, 74.0, 51.1, 45.3, 45.1, 39.8, 35.2, 34.7, 31.5, 30.2, 10.3; IR (neat, cm^{-1}) = 2960, 1742, 1678, 1463, 755; HRMS (ESI): Calcd. for [2M + Na]$^+$ $C_{44}H_{60}NaO_6^+$ (m/z) 707.4282, Found 707.4352.

2.3.58. 6,8-Di-tert-butyl-3-methyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**57**)

Light yellow oily waxy solid, ^{1}H NMR: δ = 7.25 (d, J = 2.5 Hz, 1H), 7.06 (d, J = 2.5 Hz, 1H), 6.0 (s, 1H), 4.59 (dd, J = 5.5, 11.5 Hz, 1H), 3.94 (d, J = 13.3 Hz, 1H), 3.73 (d, J = 13.3 Hz, 1H), 3.24 (t, J = 11.9 Hz, 1H), 3.03 (m 1H), 1.86 (ddd, J = 3.2, 7.3, 14.7 Hz, 1H), 1.38 (s, 9H), 1.29 (s, 9H), 1.23 (d, J = 7.3 Hz, 3H); ^{13}C NMR: δ = 210.0, 176.5, 156.6, 146.6, 141.6, 129.2, 128.4, 125.2, 123.3, 75.0, 54.1, 43.6, 38.6, 35.1, 34.6, 31.6, 30.7, 14.9; IR (neat, cm^{-1}) = 2959, 1707, 1620, 1468, 1232, 1000; HRMS (ESI): Calcd. for [M+H]$^+$ $C_{22}H_{31}O_2$ (m/z): 327.2319. Found 327.2312.

2.3.59. 4,6-Di-tert-butyl-2-(-1-tert-butyl-dimethylsilyloxy-2-propynyl)-(2-butenyloxy) benzene (**59**)

tert-Butyldimethylsilyl chloride (2.20 g, 14.3 mmol) was added at room temperature to a mixture of **42** (1.50 g, 4.78 mmol) and imidazole (0.980 g, 14.3 mmol) in DMF (10 mL). The reaction mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer was separated, washed with water and brine and dried (Na_2SO_4). The organic layer was concentrated to give a dark liquid. The crude product purified by flash chromatography (hexane/EtOAc; 19:1) to give **59** as viscous brown oil, (2.03 g, 99%). ^{1}H NMR: δ = 7.58 (d, J = 2.8 Hz, 1H), 7.28 (d, J = 2.8 Hz, 1H), 5.94 (dq, J = 6.4, 15.1 Hz, 1H), 5.81 (dt, J = 6.0, 15.1 Hz, 1H), 5.73 (d, J = 2.3 Hz,1H), 4,28 (ddt, J = 1.4, 5.5, 10.5 Hz, 1H), 4.21 (ddt, J = 1.4, 5.5, 12.4 Hz, 1H), 2.49 (d, J = 2.3 Hz, 1H), 1.81 (dd, J = 6.5, Hz, 3H), 1.41 (s, 9H), 1.33 (s, 9H), 0.85 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ^{13}C NMR: δ = 152.6, 146.2, 141.5, 135.6, 128.8, 126.9, 124.1, 124.0, 86.0, 76.0, 72.6, 59.5, 35.5, 34.8, 31.6, 31.2, 25.8, 18.3, 18.0, −4.8, −5.0; IR (neat, cm^{-1}) = 3311, 2960, 2934, 2118, 1649, 1474; HRMS (ESI): Calcd. for [M+Na]$^+$$C_{27}H_{44}O_2SiNa$ (m/z): 451.3003. Found 451.3010.

2.3.60. 4,6-Di-tert-butyl-2-(-1-tert-butyl-dimethylsilyloxy-3-trimethylsilyl -2-propynyl)-(2-butenyloxy)benzene (**60**)

tert-Butyldimethylsilyl chloride (0.940 g, 6.22 mmol) was added at room, 6.22 mmol) in DMF (10 temperature to a mixture of **44** (0.800 g, 2.07 mmol) and imidazole (0.400 g mL). The reaction mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer was separated, washed with water and brine and dried (Na_2SO_4). The organic layer was concentrated to give a dark colored liquid. The crude product was purified by flash chromatography (hexane/EtOAc, 19:1) to give **60** as viscous brown oil, (1.02 g, 98%). ^{1}H NMR: δ = 7.58 (d, J = 3.0 Hz, 1H), 7.28 (d, J = 3.0 Hz, 1H), 5.94 (dq, J = 6.4, 15.5 Hz, 1H), 5.81 (dt, J = 6.0, 15.6 Hz, 1H), 5.73 (s, 1H), 4.52 (d, J = 4.5 Hz, 2H), 1.81 (d, J = 6.5 Hz, 3H), 1.40 (s, 9H), 1.30 (s, 9H), 0.85 (s, 9H), 0.16 (s, 9H), 0.12 (s, 3H), 0.02 (s, 3H); ^{13}C NMR: δ = 152.9, 145.6, 141.4, 135.7, 128.7, 127.2, 124.6, 123.8, 107.8, 89.4, 76.0, 60.3, 35.5, 34.8, 31.6, 31.2, 25.8, 18.4, 18.1, −0.1, −4.4, −4.6; IR (neat, cm^{-1}) = 2959, 2216, 1469, 1251; HRMS (ESI): Calcd. For [M+Na]$^+$ $C_{30}H_{52}O_2Si_2Na$ (m/z): 523.3398. Found 523.3412.

2.3.61. 4,6-Di-tert-butyl-2-(-1-tert-butyl-dimethylsilyloxy -3-phenyl-2-propynyl)-(-2-butenyloxy)benzene (**61**)

tert-Butyldimethylsilyl chloride (1.16 g, 7.69 mmol) was added at room temperature to a mixture of **45** (1.00 g, 2.60 mmol) and imidazole (0.460 g, 7.69 mmol) in DMF (10 mL). The reaction mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer was separated, washed with water and brine and dried (Na_2SO_4). The organic layer was concentrated to give a dark

liquid. The crude product was purified by flash chromatography (hexane/EtOAc, 19:1) to give **61** as viscous brown liquid (1.28 g, 98%). ^{1}H NMR: δ = 7.67 (d, 1H, J = 3.0 Hz), 7.47 (m, 2H), 7.31 (d, 1H, J = 3.0 Hz), 7.29 (m, 3H), 6.01 (m, 1H), 5.98 (s, 1H), 5.86 (m, 1H), 4.46 (dd, 2H, J = 5.5, 11.0 Hz), 1.83 (d, 3H, J = 6.5 Hz), 1.42 (s, 9H), 1.34 (s, 9H), 0.89 (s, 9H), 0.17 (s, 3H), 0.04 (s, 3H); ^{13}C NMR: δ = 152.7, 146.1, 141.5, 135.9, 131.7, 128.9, 128.3, 127.1, 124.5, 123.8, 123.4, 91.5, 84.6, 76.0, 60.2, 35.6, 34.8, 31.6, 31.2, 25.9, 25,8, 18.4, 18.1, −4.4, −4.7, IR (neat, cm^{-1}) = 2960, 2300, 1560, 1475, 1252, 1064; HRMS (ESI): Calcd. for [M+Na]$^+$ $C_{33}H_{48}O_2SiNa$ (*m/z*): 527.3316. Found 527.3345.

2.3.62. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-3-methyl-4,4a-dihydro-3H,10H-5-oxa benzo[f]azulen-2-one (**62**)

The Pauson-Khand cyclization of the enyne **59** (200 mg, 0.470 mmol) was carried out following the general procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (180 mg, 0.530 mmol) and NMO (620 mg, 5.30 mmol) were added according to the general procedures, normal work-up and purification was purified by flash chromatography (hexane/EtOAc, 87:13) affording the PK product **62** (170 mg, 80%, as a 5:4 mixture epimers) for Procedure B, Procedure A gave PK product **52** (180 mg, 85%, as a 5:4 mixture of isomers) as a brown waxy solid; ^{1}H NMR (300 MHz): δ = 7.29 (d, J = 2.5 Hz, 1H), 7.13 (d, J = 2.5 Hz, 1H), 6.06 (s, 1H), 5.63 (s, 1H), 4.59 (dd, J = 5.1, 11.4 Hz, 1H), 3.72 (app. t, J = 10.2 Hz, 1H), 3.20 (d, J = 3.5 Hz, 1H), 2.07 (d, J = 3.9 Hz, 1H), 1.31 (s, 9H), 1.30 (s, 9H), 1.23 (d, J = 3.9 Hz, 3H), 0.86 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz): δ = 210.2, 178.9, 153.9, 145.5, 142.0, 131.9, 127.1, 124.3, 120.6, 75.4, 71.1, 49.6, 44.1, 35.3, 34.6, 31.6, 30.7, 25.8, 18.3, 14.6, −4.7, −4.8; IR (neat, cm^{-1}) = 2957, 1712, 1624, 1474; HRMS (ESI): Calcd. for [M+H]$^+$ $C_{28}H_{45}O_3Si$ (*m/z*): 457.3132. Found 457.3131.

2.3.63. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-3-methyl-1-trimethylsilyl-4,4a-dihydro-3H,10H-5- oxabenzo[f]azulen-2-one (**63**)

The Pauson-Khand cyclization of the enyne **60** (100 mg, 0.200 mmol) was carried out following the General Procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (75 mg, 0.22 mmol) and NMO (260 mg, 2.20 mmol) were added according to the general procedures, usual work-up and purification by flash chromatography (SiO_2, hexane/EtOAc, 87:13) to afford only the *exo*-PK product **63** (7.8 mg, 7%) for the oxidative method. Thermal method gave also the *exo*-product **63** (10.4 mg, 10%) as a brown waxy solid, ^{1}H NMR: δ = 7.26 (d, J = 2.5 Hz, 1H), 7.06 (d, J = 2.5 Hz, 1H), 5.78 (s, 1H), 4.58 (dd, J = 4.6, 11.5 Hz, 1H), 3.71 (t, J = 9.5 Hz, 1H), 3.34 (m, 1H), 2.06 (m, 1H), 1.34 (s, 9H), 1.30 (s, 9H), 1.23 (d, J = 5.0 Hz, 3H), 0.83 (s, 9H), 0.21 (s, 9H), 0.06 (s, 3H), −0.14 (s, 3H); ^{13}C NMR: δ = 214.6, 177.1, 168.7, 163.0, 155.4, 138.6, 121.7, 114.5, 82.2, 71.8, 44.5, 35.4, 34.5, 33.2, 31.5, 30.4, 30.3, 29.8, 25.8, 18.2, 6.1, −0.2, −4.5; IR (neat, cm^{-1}) = 2957, 1709, 1465, 1066, 841; HRMS (ESI): Calcd. for [M+H]$^+$ $C_{31}H_{53}O_3Si_2$ (*m/z*): 529.3528. Found 529.3500.

2.3.64. 6, 8-di-tert-butyl-10-t-butyldimethylsilyloxy-3-methyl-1-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**64**)

The Pauson-Khand cyclization of the enyne **61** (210 mg, 0.400 mmol) was carried out following the General Procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (150 mg, 0.440 mmol) and NMO (510 mg, 4.36 mmol) were added according to the general procedures, usual a purification by flash chromatography (SiO_2, hexane/EtOAc, 87:13) provided the PK product **64** (100 mg, 45%, 1:4 mixture of the diastereomers) for Procedure B, Procedure A gave **64** (151 mg, 68%) as a brown waxy solid, ^{1}H NMR: δ = 7.36 (m, 3H), 7.31 (d, J = 2.5 Hz, 1H), 7.21 (d, J = 7.0 Hz, 2H), 7.09 (d, J = 2.5 Hz, 1H), 5.60 (s, 1H), 4.68 (dd, J = 5.0, 12.0 Hz, 1H), 3.68 (t, J = 9.5 Hz, 1H), 3.51 (d, J = 3.5 Hz, 1H), 2.15 (d, J = 5.0 Hz, 1H), 1.40 (s, 9H), 1.38 (d, J = 5.0 Hz, 3H), 1.33 (s, 9H), 0.78 (s, 9H), −0.11 (s, 3H), −0.27 (s, 3H); ^{13}C NMR: δ = 208.4, 171.5, 157.4, 145.4, 142.1, 137.2, 131.7, 131.1, 129.4, 128.2, 126.3, 124.2, 75.1, 73.8, 48.4, 43.2, 35.4, 34.6, 31.7, 31.6, 30.5, 25.8, 18.2, 15.1, −4.75, −4.79; IR (neat, cm^{-1}) = 2957, 1709, 1465, 1066, 841; HRMS (ESI): Calcd. for $C_{34}H_{49}O_3Si$ (*m/z*): 533.3445. Found 533.3468.

2.3.65. Cyclization of 4,6-di-tert-butyl-2-(1-hydroxy-3-phenyl-2-propynyl)-1-(-3-phenyl-2-propenyloxy) benzene (**50**)

The Pauson-Khand cyclization of the enyne **50** (110 mg, 0.240 mmol) was carried out following the General Procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (92 mg, 0.27 mmol) and NMO (310 mg, 2.65 mmol) were added according to the general procedures, work-up and purification by flash chromatography (SiO_2, hexane/EtOAc, 87:13) produced the reduced PK-product **65** (50 mg, 45%) and the *exo*-PK product **66** (60 mg, 51%) for the Procedure B, Procedure gave only the PK-product **66** (110 mg, 90%, 1:10 mixture of the epimers).

2.3.66. 6,8-Di-tert-butyl-1,3-diphenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**65**)

Yellow waxy solid, ^{1}H NMR (300 MHz): δ = 7.27−7.51 (m, 10H), 7.25 (d, J = 2.1 Hz, 1H), 7.19 (d, J = 2.4 Hz,1H), 4.78 (dd, J = 4.5, 10.2 Hz, 1H), 3.96 (d, J = 13.2 Hz, 1H), 3.84 (d, J = 12.9 Hz, 1H), 3.55 (m, 1H), 3.48 (t, J = 11.4 Hz, 1H), 3.13 (d, J = 3.0 Hz, 1H), 1.42 (s, 9H), 1.37 (s, 9H), ^{13}C NMR (75 MHz): δ = 204.7, 170.7, 157.0, 146.8, 141.9, 138.8, 138.6, 131.3, 129.8, 129.5, 129.1, 128.4, 128.3, 128.2, 127.4, 125.3, 123.1, 75.4, 54.2, 53.8, 36.6, 35.2, 34.7, 31.6, 30.7; IR (neat, cm^{-1}) = 3059, 3029, 2961, 2869, 1707, 1638, 1599, 1476; HRMS (ESI): Calcd. For $C_{33}H_{36}O_2Na$ (*m/z*): 487.2608. Found 487.2625 [M+Na]$^+$.

2.3.67. 6,8-Di-tert-butyl-10-hydroxy-1,3-diphenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f] azulen-2-one (**66**)

Yellow solid, mp: 173−175 °C. ^{1}H NMR: δ = 7.36 (m, 6H), 7.25 (m, 5H), 7.22 (d, J = 2.3 Hz, 1H), 5.60 (s, 1H), 4.81 (dd, J = 5.5, 11.5 Hz, 1H), 4.10 (m, 1H), 3.68 (t, J = 11.5 Hz, 1H), 3.17 (d, J = 2.8 Hz, 1H), 1.41 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (75 MHz): δ = 204.5, 170.9, 156.4, 147.4, 142.8, 138.7, 138.2, 132.7, 130.7, 129.7, 129.1, 128.6, 128.3, 128.2, 127.5, 125.2, 125.1, 73.5, 60.5, 54.2, 48.6, 35.4, 34.8, 31.5, 30.7; IR (neat, cm^{-1}) = 3450, 3058, 2956, 1700, 1638, 1600, 1477, 1361, 1266; HRMS (ESI): Calcd. for [M+Na]$^+$ $C_{33}H_{36}O_3Na$ (*m/z*): 503.2557. Found 503.2548.

2.3.68. Cyclization of 4,6-di-tert-butyl-2-(1-hydroxy-2-propynyl)-1-(-3-phenyl-2-propenyloxy) benzene (**49**)

The Pauson-Khand cyclization of the enyne **49** (200 mg, 0.530 mmol) was carried out following the general procedures A and B in 5 mL of the appropriate solvent. $Co_2(CO)_8$ (200 mg, 0.590 mmol) and NMO (680 mg, 5.85 mmol) were added according to the general procedures. The reaction mixture was filtered using a sintered glass funnel packed with a short layer of Celite and SiO_2. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc, 87:13) to afford the diketone product **68** (130 mg, 51%, 5:1 ratio of the *syn*- and *trans*-isomers), for the oxidative method. The thermal method gave the **68** (90 mg, 41%, 3:1 ratio of the *syn* and *trans*-isomers) and the normal PK product **67** (10 mg, 5%).

2.3.69. 6,8-Di-tert-butyl-3-phenyl-1,1a,4,4a-tetrahydro-3H-5-oxabenzo[f]azulen-2,10-dione (**68**)

For the major Isomer (obtained pure) as a yellow waxy solid. ^{1}H NMR (300 MHz): δ = 7.62 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.29 (m, 3H), 7.08 (d, J = 6.9 Hz, 2H), 4.67 (dd, J = 6.2, 12.0 Hz, 1H),

3.94 (dt, J = 1.2, 8.6 Hz, 1H), 3.73 (t, J = 12.0 Hz, 1H), 3.53 (ddt, J = 6.2, 8.6, 19.2 Hz, 1H), 3.29 (d, J = 19.2 Hz, 1H), 3.12 (d, J = 12.9 Hz, 1H), 2.40 (dd, J = 8.4, 18.9 Hz, 1H), 1.39 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (75 MHz): δ = 214.0, 200.4, 160.5, 144.5, 140.0, 136.0, 129.1, 128.5, 128.4, 128.1, 127.8, 124.3, 76.7, 56.4, 49.7, 48.4, 38.2, 35.4, 34.7, 31.5, 30.2, 29.8; IR (neat, cm^{-1}) = 3099, 2959, 2869, 2360, 1750, 1676, 1597, 1438; HRMS (ESI): Calcd. for $C_{27}H_{33}O_3^+$ (*m/z*): 405.2424. Found 405.2432 $[M+H]^+$.

2.3.70. 6,8-Di-tert-butyl-10-hydroxy-3-phenyl-4,4a-dihydro-3H,10H-5-oxabenzo[ff] azulen-2-one (**67**)

Yellow waxy solid, ^{1}H NMR (300 MHz): δ = 7.19–7.36 (m, 7H), 6.20 (s, 1H), 5.56 (s, 1H), 4.69 (dd, J = 5.4, 11.4 Hz, 1H), 4.21 (dd, J = 3.6, 5.4 Hz, 1H), 3.96 (m, 1H), 3.57 (t, J = 10.8 Hz, 1H), 3.08 (d, J = 3.3 Hz, 1H), 1.38 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (75 MHz): δ = 206.4, 177.8, 147.4, 142.6, 129.1, 128.9, 128.4, 128.1, 127.5, 125.4, 125.0, 111.2, 89.8, 77.3, 75.6, 50.4, 35.3, 34.8, 31.5, 30.7, 29.8; IR (neat, cm^{-1}) = 3451, 2959, 2926, 2869, 2360, 1712, 1476, 1362, 1269; HRMS (ESI): Calcd. For $[M+Na]^+$ $C_{27}H_{32}NaO_3$ (*m/z*): 427.2244. Found 427.2216.

2.3.71. 4,6-Di-tert-butyl-2-(1-tert-butyldimethylsilyloxy -2-propynyl)-1-(-3-phenyl -2-propenyloxy) benzene (**69**)

tert-Butyldimethylsilyl chloride (1.20 g, 7.98 mmol) was added at room temperature to a mixture of the **49** (1.0 g, 2.66 mmol) and imidazole (0.54 g, 7.98 mmol) in DMF (10 mL). Then the mixture was heated at 50 °C for 4.5 h. The reaction was quenched by the addition of aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer separated, washed with water and brine, dried with anhydrous Na_2SO_4 and then concentrated to give a dark liquid. Purification was by flash chromatography (hexane/EtOAc; 19:1) to give **69** (1.29 g, 99%) as dark red oil. ^{1}H NMR: δ = 7.59 (d, J = 2.8 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 2.3 Hz, 1H), 7.29 (d, J = 7.3 Hz, 1H), 6.85 (d, J = 16.0 Hz, 1H), 6.44 (dt, J = 5.1, 16.0 Hz, 1H), 5.76 (s, 1H), 4.62 (dd, J = 5.1, 13.8 Hz, 2H), 2.52 (s, 1H), 1.42 (s, 9H), 1.33 (s, 9H), 0.82 (s, 9H), 0.07 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (75 MHz): δ = 152.4, 146.4, 141.6, 136.9, 135.5, 131.5, 128.7, 127.8, 126.7, 125.3, 124.2, 124.1, 85.9, 75.7, 72.8, 59.5, 35.6, 34.8, 31.6, 31.2, 25.8, 18.3, −4.7, −4.9; IR (neat, cm^{-1}) = 3308, 3027, 2963, 2223, 1601, 1472, 1362, 1289, 1159, 1119, 1068, 965; HRMS (ESI): Calcd. For $C_{32}H_{47}O_2Si$ (*m/z*): 491.3340. Found 491.3343 $[M+H]^+$.

2.3.72. 4,6-Di-tert-butyl-2-(1-tert-butyldimethylsilyloxy-3-phenyl -2-propynyl)-1-(3-phenyl-2-propenyloxy) benzene (**70**)

tert-Butyldimethylsilyl chloride (1.00 g, 6.64 mmol) was added at room temperature to a mixture of **50** (1.00 g, 2.21 mmol) and imidazole (450 mg, 6.64 mmol) in DMF (10 mL). The reaction mixture was then heated at 50 °C for 4.5 h. The reaction was quenched with aqueous $NaHCO_3$ and extracted with Et_2O. The organic layer separated, washed with water and brine, dried (Na_2SO_4) and concentrated to give a dark liquid. The crude product was purified by flash chromatography (hexane/EtOAc, 19:1) to give **70** (1.23 g, 98%) as dark brown oil. ^{1}H NMR: δ = 7.73 (d, J = 2.8 Hz, 1H), 7.29–7.51 (m, 11H), 6.92 (d, J = 16.0 Hz, 1H), 6.53 (dt, J = 5.0, 15.6 Hz, 1H), 6.06 (s, 1H), 4.77 (ddd, J = 1.8, 5.5, 15.0 Hz, 1H), 4.70 (ddd, J = 1.8, 5.5, 15.0 Hz, 1H), 1.49 (s, 9H), 1.40 (s, 9H), 0.92 (s, 9H), 0.20 (s, 3H), 0.09 (s, 3H); ^{13}C NMR: δ = 152.6, 146.3, 141.6, 137.0, 135.9, 131.8, 131.6, 128.7, 128.3, 128.3, 127.8, 126.7, 125.5, 124.6, 124.0, 123.3, 91.5, 84.9, 75.8, 60.4, 35.6, 34.9, 31.7, 31.3, 26.0, 18.4, −4.3, −4.6; IR (neat, cm^{-1}) = 3102, 2928, 2709, 2223, 1946, 1659, 1599, 1472; HRMS (ESI): Calcd. for $[M+Na]^+$ $C_{38}H_{50}O_2SiNa$ (*m/z*): 589.3472. Found 589.3505.

2.3.73. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-1,3-diphenyl-4,4a-dihydro-3H,10H-5-oxabenzo[f]azulen-2-one (**71**)

The Pauson-Khand cyclization of the enyne **70** (200 mg, 0.35 mmol) was carried out following the General Procedures A and B in 10 mL of the appropriate solvent. $Co_2(CO)_8$ (140 mg, 0.41 mmol) and NMO (490 mg, 4.19 mmol) were added according to General Procedures A and B, usual work-up and purification by flash chromatography (hexane/EtOAc, 87:13) yielded only the *exo*-PK products of **71** (140 mg, 67%) for Procedure B, similarly Procedure A gave the *exo*-PK product **71** (180 mg, 86%) as a yellow viscous liquid. ^{1}H NMR (500 MHz): δ = 7.16–7.42 (m, 12H), 4.71 (s, 1H), 4.75 (dd, J = 4.6, 11.5 Hz, 1H), 4.10 (m, 1H), 3.83 (t, J = 10.0 Hz,1H), 3.31 (s, 1H), 1.42 (s, 9H), 1.37 (s, 9H), 0.81 (s, 9H), −0.05 (s, 3H), −0.24 (s, 3H); ^{13}C NMR (75 MHz); δ = 205.3, 172.5, 157.4, 145.6, 142.3, 138.7, 137.2, 131.9, 130.9, 129.6, 129.1, 128.4, 128.3, 128.2, 127.3, 126.3, 124.3, 73.9, 60.5, 54.6, 49.2, 35.5, 34.6, 31.6, 30.5, 25.8, 18.2, 14.3, −4.8; IR (neat, cm^{-1}) = 3098, 2955, 1712, 1600, 1477, 1361, 1254; HRMS (ESI): Calcd. For $[M+H]^+$ $C_{39}H_{51}O_3Si$ (*m/z*): 595.3602. Found 595.3605.

2.3.74. 6,8-Di-tert-butyl-10-t-butyldimethylsilyloxy-3-phenyl-4,4a-dihydro-3H,10H-5-oxa benzo[f]azulen-2-one (**72**)

The Pauson-Khand cyclization of the enyne **69** (200 mg, 0.410 mmol) was carried out following the General Procedures A and B in 10 mL of the appropriate solvent. $Co_2(CO)_8$ (153 mg, 0.450 mmol) and NMO (525 mg, 4.49 mmol) were added according to the general procedures, normal work-up and purification by flash chromatography (SiO_2, hexane/EtOAc, 87:13) produced the PK product **72** (150 mg, 71%, 1:0.8 mixture of the epimers) for Procedure B, the thermal conditions also gave the PK product **72** (180 mg, 86%, 1:1 ratio of epimers) as a viscous yellow liquid. ^{1}H NMR: δ = (1:1 mixture of *exo*- and *endo*-compound) 7.62 (d, J = 2.3 Hz, 1H), 7.27–7.36 (m, 8H), 7.19–7.15 (m, 5H), 6.38 (s, 1H), 6.17 (s, 1H), 5.83 (s, 1H), 5.69 (s, 1H), 4.67 (dd, J = 6.4, 11.5 Hz, 1H), 4.59 (dd, J = 6.4, 11.9 Hz, 1H), 3.82 (broad s, 2H), 3.62 (m, 1H), 3.32 (t, J = 11.9 Hz, 1H), 3.24 (s, 1H), 3.02 (d, J = 3.2 Hz, 1H), 1.41 (s, 9H), 1.38 (s, 9H), 1.35 (s, 9H), 1.34 (s, 9H), 1.06 (s, 9H), 0.89 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H),0.12 (s, 3H), −0.10 (s, 3H); ^{13}C NMR: δ = 207.0, 205.8, 181.6, 179.5, 155.8, 155.7, 153.9, 146.7, 145.6, 142.1, 141.0, 138.4, 138.3, 132.7, 131.6, 129.1, 129.0, 128.2, 127.9, 127.4, 127.3, 127.2, 126.3, 125.5, 124.4, 123.5, 120.6, 75.1, 71.1, 55.9, 54.9, 52.8, 50.8, 35.4, 35.1, 34.6, 31.7, 31.6, 30.9, 30.6, 26.0, 25.8, 18.5, 18.3, 14.3, −4.7, −4.7, −4.8, −5.1; IR (neat, cm^{-1}) = 3105, 2955, 1710, 1625, 1476, 1390, 1361, 1254, 1230; HRMS (ESI): Calcd. for $[M+H]^+$ $C_{33}H_{47}O_3Si^+$ (*m/z*), 519.3289. Found 519.3296.

2.4. X-ray crystallographic data

A suitable crystal covered with a layer of hydrocarbon/Paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data for compounds **27**, **31** and **56** were measured at 100(2) K on a SMART APEX II CCD area detector system equipped with an Oxford Cryosystems 700 series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Bruker ApexII program suite. Absorption corrections were applied by using SADABS. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14). Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using SHELXL.[22] All the non-hydrogen atoms were refined anisotropically. X-ray structural figures were generated using Olex2.[23] The hydrogen atoms of hydroxy groups were located in a Fourier difference synthesis and refined satisfactorily. All the remaining hydrogen atoms of compounds **27**, **31** and **56** were placed at calculated positions and refined using a

riding model. The CCDC 1552430–1552432 contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK).

Acknowledgements

We are grateful to the Robert A. Welch Foundation (Y-1289 and Y-1362) for supporting our research in this area. The NSF (CHE-0234811 and CHE-0840509) is thanked for partial funding of the purchase of NMR spectrometers employed in this work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2017.08.053.

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