Formation of Angularly-Fused Triquinanes by Successive Use of the Pauson-Khand Reaction and Radical Closure

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Angularly-fused triquinanes (see Table 1) are accessible by sequential use of the Pauson-Khand reaction and radical cyclization. The Pauson-Khand step works in the presence of homolyzable bonds, such as C-Br and C-SePh. The method seems best suited to the preparation of triquinanes containing heteroatoms, as the starting materials are then easily made. In one case the radical closure step (**15** → **16** and **17**) generated two five-membered rings fused in a *trans* manner; this stereochemistry was confirmed by X-ray analysis of the crystalline product.

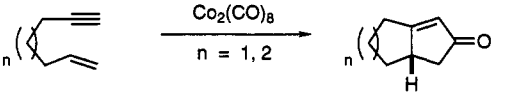
The intramolecular Pauson-Khand reaction[1] (**1** → **2**, Scheme 1) is often a convenient route to bicyclic enones. In order to apply the method to the construction of triquinanes, we have examined cases (Scheme 2) in which the starting enyne carries a chain terminating in a bromine atom (X = Br) or a phenylseleno group (X = PhSe). Both substituents turn out to be compatible[2] with the conditions of the Pauson-Khand reaction; therefore, treatment of enone **4** with a stannane generates a radical (**4** → **5**) which is correctly placed for cyclization (**5** → **6**)[3] to generate an angularly-fused triquinane.[4]

The stereochemical course of the Pauson-Khand reaction is known[1b,5] to follow the pattern shown in Scheme 2; in particular, the substituent at the starred carbon (see **4**) and the ring fusion hydrogen in **4** are *cis*, and this stereoselectivity is greatest for cases in which R is large, a result understandable by consideration of steric interactions in the organometallic intermediates of the process.

Preparation of Enynes for the Pauson-Khand/Radical-Closure Sequence. Most of the enynes we examined are listed in Table 1. In each case we used a phenylacetylene, the purpose of the phenyl group being to exert a steric influence that would enhance the stereoselectivity shown in Scheme 2.[6]

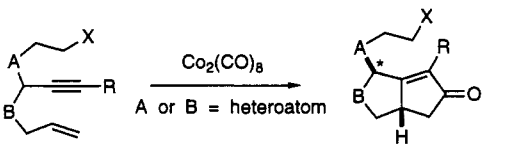
The route to **7** and **8** began with addition of lithium phenylacetylide to **7a** (Scheme 3). The resulting alcohol

Scheme 1

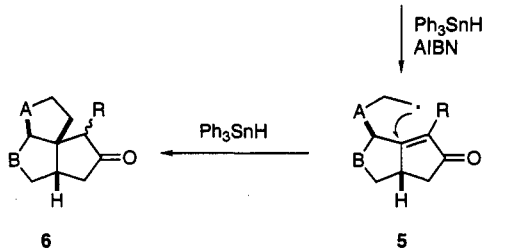


1 **2**

Scheme 2



3 **4**



6 **5**

7b was allylated (**7b** → **7c**), and then the tetrahydropyranyl ether was hydrolyzed (**7c** → **7d**). Alcohol **7d** was easily converted, under standard conditions, into bromide **7**[7] and selenide **8**.[8]

The corresponding enyne **14**, with an additional methyl substituent, was prepared (Scheme 4) in a similar way. Swern oxidation of alcohol **7b**, followed by reaction with methyllithium, proceeded without incident to give the tertiary alcohol **14b**. However, this compound did not afford the required allyl ether **14c** on treatment with allyl bromide and sodium hydride—conditions that had worked well with **7b**. Fortunately, use of powdered potassium hydroxide in warm DMSO as the base/solvent system[9] was successful, and the desired tertiary ether **14c** was isolated in acceptable yield (70%). Deprotection[10] (**14c**

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(2) Prior work had shown the compatibility of SR and SAr groups: Krafft, M. E.; Wright, C. *Tetrahedron Lett.* **1992**, *33*, 151. Krafft, M. E.; Juliano, C. A.; Scott, I. L.; Wright, C.; McEachin, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 1693. Krafft, M. E.; Scott, I. L.; Romero, R. H. *Tetrahedron Lett.* **1992**, *33*, 3829. Krafft, M. E.; Juliano, C. A. *J. Org. Chem.* **1992**, *57*, 5106. See also: Krafft, M.E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199.

(3) For one example of radical closure, using an enone related to those discused here, see: Rao, Y. K.; Nagarajan, M. *J. Org. Chem.* **1989**, *54*, 5678.

(4) For use of the Pauson-Khand reaction in other routes to angularly-fused triquinanes, see: Rowley, E. G.; Schore, N. E. *J. Org. Chem.* **1992**, *57*, 6853. Montaña, A.-M.; Moyano, A.; Pericas, M. A.; Serratosa, F. *Tetrahedron* **1985**, *41*, 5995. Review of polyquinane chemistry: Paquette, L. A.; Doherty, A. M. *Polyquinane Chemistry. Reactivity and Structure Concepts in Organic Chemistry*; Springer-Verlag: Berlin, 1987, Vol. 26.

(5) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851.

(6) For use of silyl groups, see: Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, *52*, 1483. Magnus, P.; Becker, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 7495. Mulzer, J.; Graske, K.-D.; Kirste, B. *Liebigs Ann. Chem.* **1988**, 891.

(7) *Cf.* Hayashi, H.; Nakanishi, K.; Brandon, C.; Marmur, J. *J. Am. Chem. Soc.* **1973**, *95*, 8749.

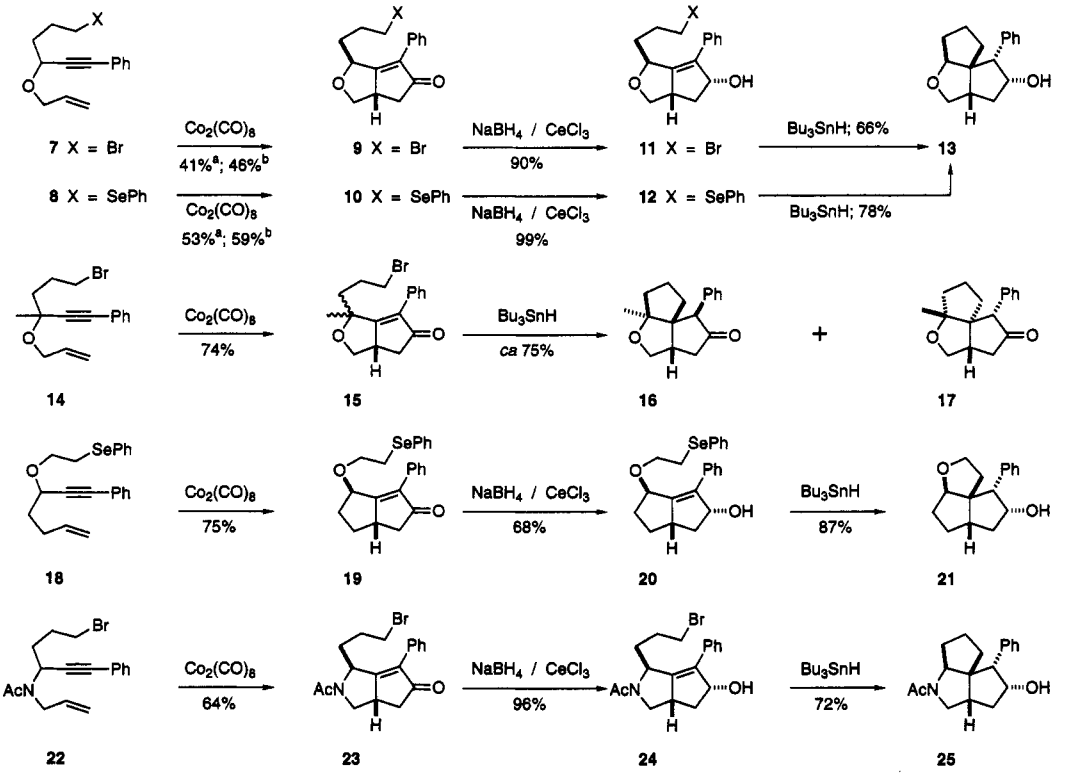
(8) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.

(9) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169.

(10) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

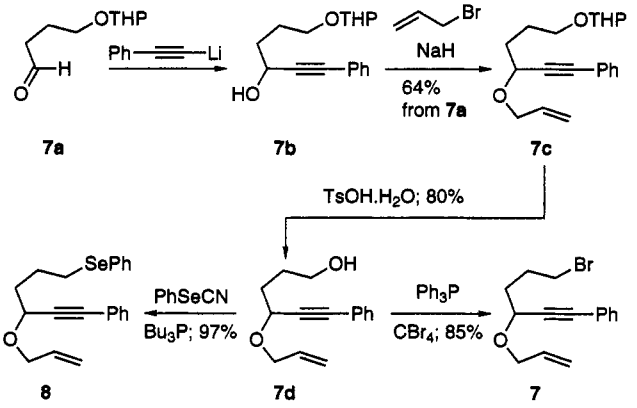
0022-3263/94/1959-1396$04.50/0

Table 1

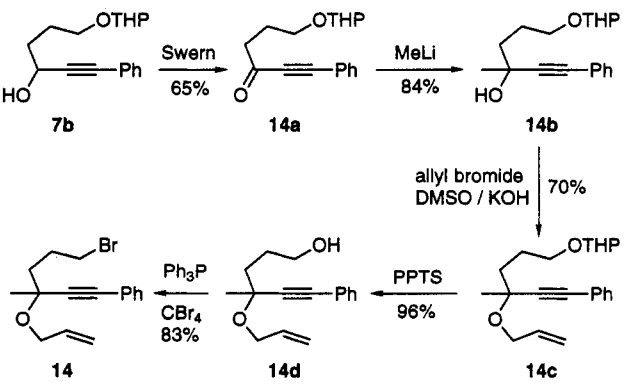


[a] Silica gel method. [b] NMO method.

Scheme 3



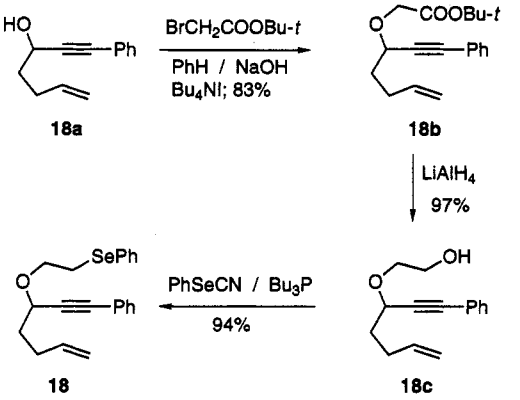
Scheme 4



→ **14d**) and replacement of the hydroxyl of **14d** by bromine were then done along the lines used with **7d** (*cf.* Scheme 3).

Formation of enyne **18** initially proved troublesome, but a simple route (Scheme 5) was soon found. Alcohol

Scheme 5



18a, assembled by reaction of bromomagnesium phenylacetylide with 4-pentenal, was alkylated under phase-transfer conditions[11] with *tert*-butyl bromoacetate. The resulting ester was reduced to the corresponding alcohol, which was then converted into the selenide in the usual way (**18a** → **18b** → **18c** → **18**).

The amide **22** was also made (Scheme 6) starting from aldehyde **7a**. Condensation with allylamine gave the imine **22a**. This reacted easily with lithium phenylacetylide in the presence of boron trifluoride etherate,[12] and the resulting secondary amine was acetylated. The tetrahydropyranyl ether **22c** was then converted directly, by a known procedure,[13] into bromide **22**.

The Pauson–Khand Reaction. When the enynes **7**

(11) Pietraszkiewicz, M.; Jurczak. T. *Tetrahedron* **1984**, *40*, 2967.
(12) Wada, M.; Sakurai, Y.; Akiba, K. *Tetrahedron Lett.* **1984**, *25*, 1083.
(13) Wagner, A.; Heitz, M.-P.; Mioskowski, C. *Tetrahedron Lett.* **1989**, *30*, 557.
(14) Montaña, A.-M.; Moyano, A.; Pericas, M. A.; Serratosa, F. *An. Quim., Ser. C* **1988**, *84*, 82. *Chem. Abstr.* **1989**, *111*, 23697g.

Scheme 6

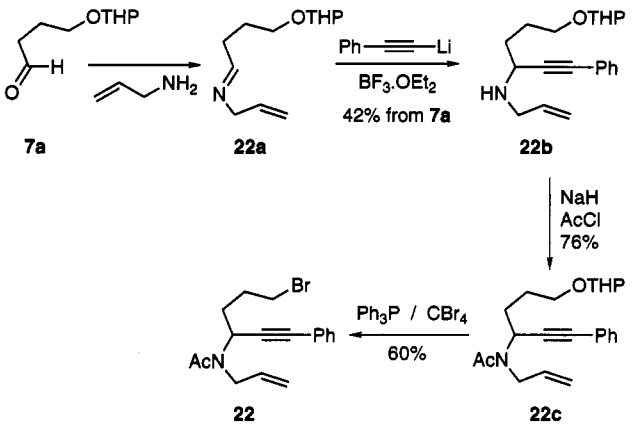


Table 2

compd	condns	yield (%) of 9 or 10
7	CO, *t*-BuPh, 170 °C, 3 h[14]	9, 26
7	SiO_2,[a] <5% H_2O, 45 °C, O_2[15]	9, 11
7	SiO_2,[a] 10% H_2O, 45 °C, O_2[15]	9, 33
7	SiO_2,[a] 20% H_2O, 45 °C, O_2[15]	9, 41
7	alumina,[b] 45 °C, argon[15]	9, 0
7	NMO, rt[16]	9, 47
8	SiO_2,[a] 20% H_2O, 45 °C, O_2[15]	10, 53
8	NMO, rt[16]	10, 59

[a] Merck silica gel for flash chromatography, type 60, 230–400 mesh. [b] Camag, aluminum oxide for chromatography, 507-C, neutral.

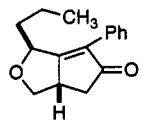
and 8 were individually stirred with octacarbonyldicobalt in benzene, chromatographable cobalt complexes were formed, and we then investigated (see Table 2) a number of the methods that have been reported for the Pauson–Khand reaction. From this survey, use of silica gel containing 20% w/w of water[15] or use of 4-methylmorpholine *N*-oxide[16] were judged to be the best conditions. However, yields with the silica gel method were sometimes difficult to reproduce, especially when the scale of the reaction was increased. Possibly, this effect is due to inefficient stirring of the dry reaction mixture.

In using 4-methylmorpholine *N*-oxide, it is important that the reagent be completely anhydrous, and so it was sublimed and stored under argon.

In each of these experiments (Table 2) the product (**9** or **10**) was a single isomer (see following text), as expected on the basis of prior work.[5]

The other Pauson–Khand reactions (see Table 1) proceeded as shown, under the conditions listed. For **14**, not unexpectedly, two isomers were formed (in a 1:1 ratio), but **18** and **22**[17] gave single products.

Radical Closure of the Pauson–Khand Products. When the enones **9** and **10** were treated with tributyltin hydride and AIBN in refluxing benzene, under standard conditions[18] used for radical cyclization, substantial amounts of the reduction product **26** were isolated. Possibly, one of the allylic hydrogens in the radical **27** is



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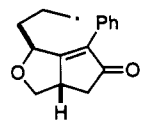

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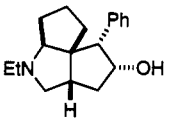
being abstracted intramolecularly.[19] We did not explore this point (by deuterium labeling experiments), however; instead, we deactivated the allylic hydrogens by reducing[20] enones **9** and **10** to the corresponding allylic alcohols **11** and **12**, respectively.[21] In each case the reduction ($NaBH_4$/$CeCl_3 \cdot 7H_2O$) produced a single isomer, with the indicated stereochemistry. Starting from alcohols **11** and **12**, radical cyclization proceeded smoothly (66% yield for the bromide and 78% for the selenide) to afford the angularly-fused triquinane **13**. The stereochemistry of **13**, and hence, of **11** and **12**, was established as described below.

When we treated the 1:1 mixture of bromides **15** with tributyltin hydride under our standard conditions, we obtained in good yield (*ca.* 84%) a separable mixture of two ketones **16** and **17** in a ratio of *ca.* 1:1. The stereochemistry of **16** and **17** was assigned on the basis of NOE and decoupling measurements (see below). However, as structure **17** has the unusual feature of two five-membered rings that were generated by a radical process *and* that are fused in a *trans* manner,[22] we confirmed our assignment by X-ray analysis (see Figure 1), the compound fortunately being nicely crystalline.[30]

With enone **19** we did not investigate direct radical cyclization[23] but reduced the compound to the corresponding allylic alcohol **20**, and this was then cyclized. Again, ^1H NMR decoupling and NOE measurements (see below) served to define the stereochemistry of the product **21**.

Treatment of enone **23** with tributyltin hydride[18] gave a complex mixture, but the derived alcohol **24** underwent radical cyclization (72% yield), the product **25** existing at room temperature as an inseparable 2:1 mixture of amide rotamers.[24] Treatment of the mixture with lithium aluminum hydride resulted in efficient conversion (99%) to a single amine, **28**.



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Stereochemical Assignments. We initially assumed that the Pauson–Khand reaction followed its usual stereochemical course so that the pendant that would even-

(15) Simonian, S. O.; Smit, W. A.; Gybin, A. S.; Shashkov, A. S.; Mikaelian, G. S.; Tarasov, V. A.; Ibragimov, I. I.; Caple, R.; Froen, D. E. *Tetrahedron Lett.* **1986**, *27*, 1245.

(16) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289. See also: Jeong, N.; Chung, Y. K.; Lee, B. Y.; Lee, S. H.; Yoo, S.-E. *Synlett.* **1991**, 204.

(17) For recent work on the Pauson–Khand reaction of amine derivatives, see: Brown, S. W.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1205. Becker, D. P.; Flynn, D. L. *Tetrahedron Lett.* **1993**, *34*, 2087. Jeong, N.; Yoo, S.-e.; Lee, S. J.; Lee, S. H.; Chung, Y. K. *Tetrahedron Lett.* **1991**, *32*, 2137.

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(20) Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.

(21) The stereochemistry of the reduction follows from the stereochemical assignment made to the radical cyclization product.

(22) Clive, D. L. J.; Cheshire, D. R.; Set, L. *J. Chem. Soc., Chem. Commun.* **1987**, 353. *Cf.* Chang, C.-P.; Gallucci, J. C.; Hart, D. J. *J. Org. Chem.* **1988**, *53*, 3210. Bachi, M. D.; Bosch, E. *J. Org. Chem.* **1992**, *57*, 4696.

(23) Three attempts at direct radical cyclization led to recovered starting material. We did not determine the reason for the failure of these experiments.

(24) For a discussion of barriers to N–C(O) bond rotation see Bennet, A. J.; Somayaji, V.; Brown, R. S.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1991**, *113*, 7563.

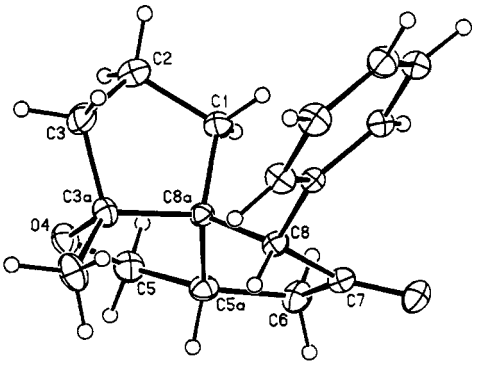
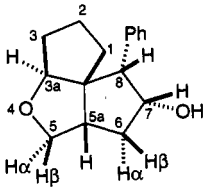


Figure 1.

tually undergo radical closure was taken to be *cis* to the newly-formed ring fusion hydrogen (except for one of the stereoisomers of **15**). The correctness of this assumption and the stereochemistry of all our bicyclic and tricyclic compounds was supported by a detailed ^{1}H NMR analysis (see Table 3) for **13**, **16**, **17**, **21**, and **25**.



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Compound 13. The hydroxyl hydrogen was identified by its change in chemical shift as a function of concentration and by exchange with D_2O. The following ^{1}H NMR decoupling measurements were made:

Irradiation of hydroxyl hydrogen: H(7) becomes a triplet, and was assigned on this basis. H(7) couples with H(8) and H(6β), but has negligible coupling with H(6α).

Irradiation of H(7): Hydroxyl hydrogen and H(8) become singlets, H(6β) becomes a doublet of doublets, and there is no change in H(6α). H(8) can be assigned on the basis of this information, as well as the value of its chemical shift, and the fact that it is a doublet [which collapses to a singlet on irradiation of H(7)].

Irradiation of H(3a): The only changes occur at high field (*ca.* δ 1.70); hence, on the basis of its chemical shift, H(3a) is assigned as shown.

Irradiation of H(5β): H(5α) becomes a singlet (with fine splitting) and H(5a) becomes a broad doublet.

Irradiation of H(5α): H(5a) becomes a doublet of doublets, and H(5β) becomes a doublet. On the basis of their chemical shifts and the fact that H(5β) and H(5α) have large and small couplings, respectively, with H(5a), they [i.e., H(5β) and H(5α)] are assigned as shown.

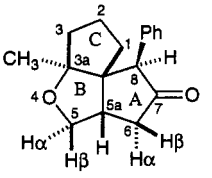
Irradiation of H(8): H(7) becomes a doublet of doublets.

Irradiation of H(5a): H(5β) becomes a doublet (with fine splitting), H(5α) becomes a doublet, H(6β) becomes simplified, and there is no change in H(6α).

Irradiation of H(6β): H(7) becomes a broad doublet, H(5a) becomes simplified, and H(6α) becomes a singlet (with fine splitting).

Evidently, H(5a) has large couplings with H(5β) and H(6β) and small couplings with H(5α) and H(6α).

Inspection of models shows that the five membered rings are quite rigid, with the angle between *cis* hydrogens being 0–30° and that between *trans* hydrogens being 70–100°. Therefore, a larger coupling is expected between vicinal *cis* hydrogens, and the relatively large sizes of J[H(5a)–H(6β)], J[H(6β)–H(7)], and J[H(7)–H(8)], compared with the almost negligible values of J[H(5a)–H(6α)] and J[H(7)–H(6α)], indicate that the molecule has the stereochemistry shown. This assignment is supported by NOE difference measurements: Saturation of H(8) produces signal enhancements of 4% for H(7), 2% for H(5a), and 4% for H(6β).



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Compound 16. The following ^{1}H NMR decoupling and NOE difference measurements were made:

Irradiation of H(5β): H(5α) and H(5a) change.

Irradiation of H(5α): H(5β) and H(5a) change.

Irradiation of H(8): H(6β) becomes a doublet of doublets, a small long-range coupling with H(8) being lost.

Irradiation of H(5a): H(5β) becomes a doublet and H(6β) simplifies [the H(6α) signal is too close to the irradiated signal for the changes in H(6α) to be diagnostic].

Irradiation of H(6β): H(5a) and H(6α) change and H(8) sharpens.

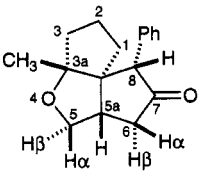
Irradiation of H(5β) produces a signal enhancement of 32% for H(5α) and 8% for H(5a).

Irradiation of H(8) produces a signal enhancement of 13% for the aromatic region and 5.6% for the CH_3 group, but no enhancement for H(5a).

Irradiation of H(5a) produces signal enhancements of 13% for H(6β), 5% for H(5β), 5% for the aromatic region (δ 7.01–7.06), and 7% for some of the hydrogens on ring C, but no enhancement for the CH_3 group or for H(8).

Irradiation of the CH_3 group produces signal enhancements of 3% for H(5α), 19% for H(8), 15% for the aromatic region (δ 7.01–7.06), and 19% for the hydrogens on ring C, but no enhancement for H(5a).

Irradiation of the aromatic signals (δ 7.01–7.06) produces signal enhancements of 14% for H(8), 7% (in total) for H(5a) and H(6β), 16% for the CH_3 group and for some of the hydrogens on ring C, and 37% for the aromatic region (δ 7.23–7.36).



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Compound 17. The stereochemistry of compound **17** was first determined by ^{1}H NMR decoupling and NOE difference measurements, and the spectral interpretation was then confirmed by X-ray analysis. [In the following text, the apparent change in the α and β faces with respect to structure **16** is a consequence of applying the priority rules of nomenclature.]

Irradiation of H(5α): H(5β) becomes a doublet and H(5a) changes. There is an NOE of 18% for H(5β), and 5% for H(5a).

Table 3. Chemical Shift (ppm) Data

compd 13		compd 16		compd 17		compd 21		compd 25	
H(3a)	4.58–4.63	H(5β)	4.09	H(5α)	4.08	H(3a)	4.69	H(3a′)	4.84
H(7)	4.35	H(5α)	3.59	H(5β)	3.63	H(7)	4.43	H(3a)	4.50–4.54
H(5β)	4.00	H(8)	3.71	H(8)	3.56	H(2)	3.69	H(7), H(7′)	4.38–4.47
H(5α)	3.80	H(5a)	2.70–2.79	H(5a)	2.71	H(2′)	3.46	H(5α)	4.01
Hydroxyl	3.45	H(6β)	2.39	H(6α)	2.55	H(8)	3.23	H(5′β)	3.56
H(8)	2.95	H(6α)	2.69	H(6β)	2.32	H(6β); H(5a)	2.37–2.49	H(5′α)	3.70
H(5a)	2.43					H(4α)	2.25–2.37	H(5β)	3.45
H(6β)	2.32					H(1)	2.15	H(8), H(8′)	2.97, 3.01
H(6α)	1.71					H(1′)	1.89–1.96	H(5a), H(5a′); H(6β), H(6′β)	2.38–2.53
						H(5β)	1.96–2.06		
						H(4β)	1.80	hydroxyls	2.22
						H(5α); hydroxyl	1.56–1.68	H(6α), H(6′α)	1.60, 1.67
						H(6α)	1.49		

Irradiation of H(5β): H(5α) becomes a doublet and H(5a) changes. On the basis of their chemical shifts, H(5α) and H(5β) are taken to be adjacent to the ether oxygen. They are coupled with each other and with H(5a), which was therefore assigned as the ring fusion hydrogen. The NOE between H(5α) and H(5a) indicates that they are *cis*.

Irradiation of H(8) produces signal enhancements of 11% in the aromatic region, 10% for H(5a), and 3% for the CH_3 group. On the basis of its chemical shift, and the fact that its signal is a singlet, H(8) is assigned as shown.

Irradiation of H(5a): H(5α) and H(6α) become doublets, and H(5β) and H(6β) change. There are signal enhancements of 8% for H(5α), 10% for H(8), 4.5% for H(6α), and 5.3% for the CH_3 group.

Irradiation of H(6α): H(6β) and H(5a) change. There are signal enhancements of 2% for H(5a) and 23% for H(6β).

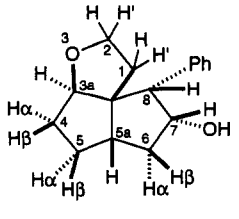
Irradiation of H(6β): H(6α) and H(5a) change. There is a signal enhancement of 23% for H(6α). On the basis of mutual NOEs, we conclude that H(5α), H(5a), H(6α), and H(8) are on the same face of the molecule.

Irradiation of the aromatic signal (δ 7.10–7.15) produces signal enhancements of 4.4% for H(8) and 3.6% for the CH_3 group.

Irradiation of the CH_3 group produces signal enhancements of 5% for the aromatic signal, 2.4% for H(8), and 3% for H(5a).

Only the structure shown fits the above data satisfactorily, and this interpretation was proved by X-ray analysis (see supplementary material).

We believe that the stereochemistries of **16** and **17** correspond to those generated in the radical cyclization; we noticed no evidence for epimerization [at C(8)] during chromatography.



21

Compound 21. The following ^1H NMR decoupling measurements were made:

Irradiation of H(3a): H(4α) becomes simplified. On the basis of its chemical shift and the fact that it does not couple to any low-field hydrogens, H(3a) is assigned as shown. It couples with H(4α) but not with H(4β), and so H(3a) and H(4α) are taken to be *cis*.

Irradiation of H(7): H(8) becomes a singlet, and the signal corresponding to H(6β) and H(5a) changes. H(7) is assigned on the basis of its chemical shift and the fact that when it is irradiated H(8) becomes a singlet. H(8) must be the benzylic hydrogen because of its chemical shift and multiplicity.

Irradiation of H(2): H(2′), H(1), and H(1′) are all simplified.

Irradiation of H(1): H(2), H(2′), and H(1′) change.

Irradiation of H(2′): H(2), H(1), and H(1′) are all simplified. On the basis of their chemical shifts and the fact that these four hydrogens are coupled to each other only, they are assigned as shown but their stereochemical relationship was not determined.

Irradiation of H(8): H(7) becomes a doublet. Hence, H(7) is coupled with only one other hydrogen, i.e., with H(6β). The coupling constants J[H(7)–H(6β)] and J[H(7)–H(8)] are equal, suggesting that the three hydrogens H(8), H(7), and H(6β) are all *cis*.

Irradiation of the signal corresponding to H(6β) and H(5a): H(7) becomes a doublet, H(5β) changes, and H(6α) becomes a singlet. Hence, one hydrogen producing the signal at δ 2.3–2.5 is assigned to H(6β) due to its coupling with H(7) and H(6α). The fact that H(6α) collapses to a singlet indicates that H(6α) is not significantly coupled with any other hydrogens. This is possible only if H(6α) is *trans* to H(7).

Irradiation of H(4α): H(3a) becomes a singlet, H(5β) changes slightly, and H(4β) and H(5α) change, a doublet [evidently due to H(5α)] forming at δ 1.62 (J = 10 Hz).

Irradiation at δ 2.0 [center of the signal corresponding to H(5β) and H(1′)]: [changes due to saturation of H(1′)] H(2), H(2′), and H(1) change; [changes due to saturation of H(5β)] H(6β) and H(5a) signals change [due to a change in the H(6β) component of the signal], H(4α) changes, H(4β) becomes a doublet [the large *gem* coupling with H(4α) remains], and the signal corresponding to H(5α) and the hydroxyl changes.

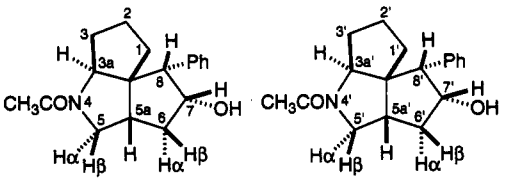
Irradiation of H(4β): H(4α) and H(5β) change.

Irradiation at δ 1.60 [center of the signal corresponding to H(5α) and the hydroxyl]: H(4α), H(5β), and the signal corresponding to H(6β) and H(5a) change.

Irradiation of H(6α): H(6β) and H(5a) change.

Since H(4α) is coupled with H(4β) and H(5α), and they, in turn, are both coupled with H(5β), these four hydrogens are assigned as shown.

Support for the above stereochemistry was gained from NOE difference measurements: irradiation of H(7) produces signal enhancements of 9% for H(8), 4% (in total) for H(6β) and H(5a), and 7% for the hydroxyl hydrogen.



Compounds 25. In solution, amide **25** is a mixture of two rotamers (2:1) as shown by its efficient conversion ($LiAlH_4$) to a single amine. The stereochemistry of compound **25** was determined by the following ^1H NMR decoupling and NOE difference experiments.

Irradiation of H(3a′) and H(3a) causes slight changes, and these are only in the high field region (*ca.* δ 1.5). Therefore, based on their chemical shifts, H(3a′) and H(3a) are assigned as shown.

Irradiation of H(7) and H(7′): Both H(8) and H(8′) doublets collapse to singlets, and the signal (δ 2.38–2.53) due to H(5a), H(5a′), H(6β) and H(6′β) changes. On the basis of their mutual coupling and chemical shifts, H(7), H(7′), H(8) and H(8′) are assigned as shown.

Irradiation of H(5α): H(5β) becomes a doublet, and the signal at δ 2.38–2.53 changes slightly.

Irradiation of H(5′β): H(5′α) becomes a singlet, and the signal at δ 2.38–2.53 changes slightly.

Irradiation of H(5′α): H(5′β) becomes a doublet,and the signal at δ 2.38–2.53 changes slightly.

Irradiation of H(5β): H(5α) becomes a singlet, and the signal at δ 2.38–2.53 changes slightly.

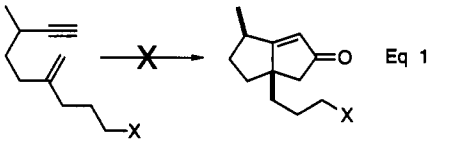
H(5α), H(5′β), H(5′α), and H(5β) are assigned as shown, on the basis of chemical shifts and the fact that H(5′β) and H(5β) are quartets which become doublets when the signal due to H(5a), H(5a′), H(6β), and H(6′β) is irradiated. H(5α) and H(5′α) are doublets (with fine splitting) which become sharp doublets when the signal at δ 2.38–2.53 [i.e., H(5a), H(5a′), H(6β) and H(6′β)] is irradiated, indicating negligible *trans* coupling.

Irradiation of H(8) and H(8′): H(7) and H(7′) change to a pair of doublets (one for each rotamer). Since the hydroxyl hydrogens are a broad singlet and do not couple with H(7) and H(7′), the remaining coupling of H(7) and H(7′) must be with H(6β) and H(6′β), respectively, with *J*[H(7)–H(6β)], *J*[H(7′)–H(6′β)], *J*[H(7)–H(8)], and *J*[H(7′)–H(8′)] approximately equal (4–5 Hz). This suggests that H(8), H(7), H(6β) and H(8′), H(7′), H(6′β) are *cis*.

Irradiation of the signal at δ 2.38–2.53 [i.e., corresponding to H(5a), H(5a′), H(6β), and H(6′β)]: H(5′β) and H(5β) become doublets, H(6α) and H(6′α) become a pair of singlets (one for each rotamer), and H(7) and H(7′) become a pair of doublets (one for each rotamer). Therefore, H(7) and H(7′) are not coupled to H(6α) or H(6′α), respectively. H(6α) and H(6′α) have only geminal couplings, i.e., no *trans* coupling. Irradiation of H(8) and H(8′) causes signal enhancements of 5.4% for H(7) and H(7′) and 14% for the aromatic signal.

Scope and Limitations. As indicated above, radical cyclization does not always work with enones; however, this problem can be circumvented by reducing the enone to an allylic alcohol.

Both bromides and phenyl selenides survive the conditions of the Pauson–Khand reaction, but there are some well-established limitations on the level of stereocontrol in this process and on the permissible substitution patterns of the starting materials. As the case of compound **14** illustrates, good stereoselectivity is observed only if one of the propargylic substituents is significantly larger than the other (e.g., alkyl versus hydrogen). The Pauson–Khand reaction does not always tolerate internal substitution of the olefin,[1cd,25] and we found, for example, that compounds **29** and **30**[26] (which would have served as precursors to propellanes) did not undergo the reaction (NMO or silica gel methods), although in each case a cobalt complex was formed.



29 X = SePh
30 X = $OSiPh_2Bu$-*t*

These limitations aside, our results show that heterocyclic triquinanes are fairly easily assembled by the Pauson–Khand/radical cyclization sequence.

Experimental Section

General. Argon was purified by passage through a column (3.5 × 42 cm) of R-311 catalyst[27] and then through a similar column of Drierite. Glassware was dried in an oven for at least 3 h before use (120 °C) and either cooled in a desiccator over Drierite or assembled quickly, sealed with rubber septa, and allowed to cool under a slight static pressure of argon. Reaction mixtures were stirred by Teflon-coated magnetic stirring bars.

Solvents for chromatography and extractions were distilled before use.

Products were isolated from solution by evaporation under water-aspirator vacuum at, or below, 30 °C using a rotary evaporator.

Melting points were determined on a Kofler block melting point apparatus.

Commercial thin-layer chromatography (TLC) plates (silica gel, Merck 60F254) were used. Spots were detected by spraying the plate with a solution of phosphomolybdic acid,[28] followed by charring on a hot plate, or by examination under UV light. Silica gel for flash chromatography was Merck type 60 (230–400 mesh).

Dry solvents were prepared under an inert atmosphere and transferred by syringe. Dry tetrahydrofuran (THF) and diethyl ether were distilled from sodium and benzophenone ketyl. Dry

(25) *Cf.* Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917.

(26) An annotated scheme showing the preparation of these compounds is given in the supplementary material. Compound **29** (crude) had: FT-IR (film) 2965, 2930, 2918, 1643, 1579, 1477, 1450, 1437 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.13 (d, *J* = 6.6 Hz, 3 H), 1.49 (q, *J* = 7.6 Hz, 2 H), 1.79 (d, *J* = 2.3 Hz, 3 H), 1.84 (quintet, *J* = 7.5 Hz, 2 H), 1.99–2.20 [m, including t (*J* = 7.4 Hz, 3 H) at δ 2.13, 4 H], 2.29–2.41 (m, 1 H), 2.90 (t, *J* = 7.4 Hz, 2 H), 4.73 (d, *J* = 13.4 Hz, 2 H), 7.17–7.31 (m, 3 H), 7.43–7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 3.54 (q′), 21.40 (d′), 25.71 (q′), 27.50 (t′), 28.17 (t′), 33.69 (t′), 35.38 (t′), 36.13 (t′), 75.88 (s′), 83.60 (s′), 109.71 (t′), 126.73 (d′), 129.03 (d′), 130.50 (s′), 132.57 (d′), 148.32 (s′); exact mass *m/z* calcd for $C_{18}H_{24}Se$ 320.1043, found 320.1037. Compound **30**: FT-IR (film) 3071, 2959, 2930, 2357, 1111 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.05 (s, 9 H), 1.13 (d, *J* = 7.0 Hz, 3 H), 1.50 (br q, *J* = 7.4 Hz, 2 H), 1.70 (br quintet, *J* = 7.0 Hz, 2 H), 1.78 (d, *J* = 2.4 Hz, 3 H), 2.00–2.22 (m, 4 H), 2.30–2.42 (m, 1 H), 3.68 (t, *J* = 6.3 Hz, 2 H), 4.71 (d, *J* = 5.0 Hz, 2 H), 7.28–7.46 (m, 6 H), 7.63–7.71 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 3.55 (q′), 19.29 (s′), 21.44 (d′), 25.75 (q′), 26.94 (q′), 30.87 (t′), 32.39 (t′), 33.92 (t′), 35.47 (t′), 63.68 (t′), 75.81 (s′), 83.71 (s′), 109,.01 (t′), 127.66 (d′), 129.58 (d′), 134.15 (s′), 135.63 (d′), 149.25 (s′); exact mass *m/z* calcd for $C_{28}H_{38}OSi$ 418.2692, found 418.2687. Anal. Calcd for $C_{28}H_{38}OSi$: C, 80.32; H, 9.15. Found: C, 80.43; H, 8.91.

(27) Supplied by Chemical Dynamics Corporation, South Plainfield, NJ.

(28) Phosphomolybdic acid (15 g) and ceric ammonium sulfate (2.5 g) dissolved in a mixture of water (985 mL) and concentrated sulfuric acid (15 mL).

benzene was distilled from sodium. Dry Et_3N, CH_2Cl_2, MeOH, and pyridine were distilled from CaH_2, the last solvent being distilled under water–aspirator vacuum. Commercial (Aldrich) solutions of *n*-BuLi and MeLi were assumed to have the stated molarity.

FT-IR measurements were made as casts from the specified solvent using potassium bromide plates.

The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate zero, one, two, or three attached hydrogens, respectively.

Mass spectra were recorded with an AEI Model MS-12 or MS-50 mass spectrometer at an ionizing voltage of 70 eV.

Microanalyses were performed by the microanalytical laboratory of this department.

General Procedure for Radical Cyclization. The substrate was placed in a round bottomed flask equipped with a Teflon-coated stirring bar and a reflux condenser that was sealed with a rubber septum. The system was flushed with argon for 5–10 min, and dry benzene was injected into the flask. The flask was placed in an oil bath preheated to 85 °C, and solutions of Bu_3SnH and AIBN in benzene were injected simultaneously by syringe pump over 8 h. Refluxing was continued for an arbitrary period of 2–4 h after the addition was complete. The reaction mixture was cooled, and the solvent was evaporated to give a residue which was processed as described for the individual experiments.

General Procedure for Pauson–Khand Reaction on Silica Gel.[15] Commercial flash chromatography silica gel (Merck type 60, 230–400 mesh) was used. The indicated amount of water was added, and the mixture was stirred for 30 min and then stored in a sealed container. The substrate was placed in a round bottomed flask that was then flushed with argon for 5–10 min. The indicated solvent was injected, and $Co_2(CO)_8$ was then tipped in. The resulting brown solution was stirred for 2–3 h at room temperature. This solution was then poured onto the specified amount of the hydrated silica gel which had been covered with ether. The solvent was removed below 25 °C. The flask was then flushed with oxygen for 5–10 min and heated under a slight static pressure of oxygen. After being cooled, the silica gel was extracted with ether (4 × 20 mL), and the extract was evaporated to give a residue which was purified as described in the individual experiments.

General Procedure for Pauson–Khand Reaction Using 4-Methylmorpholine *N*-Oxide (NMO).[16] The $Co_2(CO)_8$–alkyne complex was prepared as for the silica gel method. The brown solution was cooled to 0 °C, and NMO (which had been sublimed and stored under argon prior to use) was added. The cooling bath was removed, and the mixture was stirred at room temperature for the indicated time. The solvent was then evaporated and the residue was processed as described in each experiment.

1-Phenyl-3-[(2-propenyl)oxy]-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-hexyne (7c). *n*-BuLi (10.4 mL, 1.6 M, in hexanes, 16.7 mmol) was added to a stirred and cooled (−78 °C) solution of phenylacetylene (1.8 mL, 16.7 mmol) in THF (20 mL). After 10 min a solution of **7a**[29] (2.39 g, 13.9 mmol) in THF (10 mL) was added over 10 min. Stirring at −78 °C was continued for 1 h, and the mixture was then quenched with water (10 mL) and extracted with ether (2 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated to afford crude **7b**, which was used directly in the next step. [Compound **7b** was also made by a slightly different route (see below) and characterized spectroscopically.]

The crude material was dissolved in THF (20 mL), and NaH (1.1 g, 60% dispersion in oil, 27.5 mmol) followed by 3-bromopropene (2.4 mL, 27.7 mmol) were added with stirring. The mixture was refluxed for 1 h, cooled, quenched with water (10 mL), and extracted with ether (2 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 × 20 cm), using 10% EtOAc–hexane, gave **7c** (2.8 g, 64%) as an apparently homogeneous [^{13}C NMR (100.6 MHz)] colorless oil: FT-IR (CH_2Cl_2 cast) 2942 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.43–1.63 (m, 4 H), 1.63–1.76 (m, 1 H), 1.76–2.01 (m, 5 H), 3.38–3.54 (m, 2 H), 3.74–3.91 (m, 2 H), 4.00–4.09 (m, 1 H), 4.28–4.39 (m, 2 H), 4.59 (br s, 1 H), 5.20 (d quintet, J = 10.5, 1.4 Hz, 1 H), 5.33 (d quintet, J = 17.4, 1.7 Hz, 1 H), 5.89–6.01 (m, 1 H), 7.23–7.33 (m, 3 H), 7.39–7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.41 (t′), 25.38 (t′), 25.60 (t′), 30.59 (t′), 32.58 (t′), 62.01 (t′), 66.95 (t′), 69.01 (d′), 69.55 (t′), 85.72 (s′), 88.07 (s′), 98.57 (d′), 117.10 (t′), 122.68 (s′), 128.12 (two overlapping signals, d′), 131.60 (d′), 134.45 (d′); exact mass m/z calcd for $C_{20}H_{26}O_3$ 314.1882, found 314.1874.

6-Phenyl-4-[(2-propenyl)oxy]-5-hexyn-1-ol (7d). A solution of **7c** (1.6 g, 5.09 mmol) and *p*-toluenesulfonic acid monohydrate (5 mg, 0.03 mmol) in MeOH (20 mL) was refluxed for 10 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 20 cm), using 20% EtOAc–hexane, gave **7d** (0.94 g, 80%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3120–3600, 2950 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.74–1.98 (m, 4 H), 2.31 (br s, 1 H), 3.69 (t, J = 6.3 Hz, 2 H), 4.05 (ddt, J = 12.4, 6.3, 1.3 Hz, 1 H), 4.34 (ddt, J = 12.6, 5.1, 1.5 Hz, 1 H), 4.37 (t, J = 6.1 Hz, 1 H), 5.22 (dq, J = 10.4, 1.4 Hz, 1 H), 5.33 (dq, J = 17.4, 1.5 Hz, 1 H), 5.90–6.00 (m, 1 H), 7.27–7.34 (m, 3 H), 7.40–7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 28.64 (t′), 32.42 (t′), 62.45 (t′), 69.10 (d′), 69.76 (t′), 86.09 (s′), 87.74 (s′), 117.62 (t′), 122.61 (s′), 128.27 (d′), 128.36 (d′), 131.71 (d′), 134.23 (d′); exact mass m/z calcd for $C_{15}H_{17}O_2$ $(M-H)^+$ 229.1228, found 229.1227.

6-Bromo-1-phenyl-3-[(2-propenyl)oxy]-1-hexyne (7). Carbon tetrabromide (1.12 g, 3.37 mmol) and Ph_3P (0.88 g, 3.37 mmol) were added to a stirred and cooled (0 °C) solution of **7d** (0.648 g, 2.81 mmol) in CH_2Cl_2 (40 mL). The cooling bath was removed, and stirring was continued for 30 min. The solution was then filtered through a pad of silica gel (2 × 2 cm) with 10% EtOAc–hexane (50 mL). The filtrate was evaporated, and flash chromatography of the residue over silica gel (3 × 20 cm), using 20% EtOAc–hexane, gave **7** (0.70 g, 85%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 2800–3110, 1488 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.93–2.01 (m, 2 H), 2.08–2.17 (m, 2 H), 3.48 (t, J = 6.7 Hz, 2 H), 4.03 (ddt, J = 12.4, 6.2, 1.3 Hz, 1 H), 4.32 (ddt, J = 12.8, 5.0, 1.5 Hz, 1 H), 4.35 (t, J = 6.3 Hz, 1 H), 5.21 (dq, J = 10.3, 1.5 Hz, 1 H), 5.33 (dq, J = 17.3, 1.7 Hz, 1 H), 5.89–6.00 (m, 1 H), 7.27–7.34 (m, 3 H), 7.40–7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 28.69 (t′), 33.55 (t′), 34.29 (t′), 68.38 (d′), 69.71 (t′), 86.18 (s′), 87.57 (s′), 117.46 (t′), 122.54 (s′), 128.30 (d′), 128.45 (d′), 131.75 (d′), 134.37 (d′); exact mass m/z calcd for $C_{15}H_{17}{}^{81}BrO$ 294.0442, found 294.0419.

1-Phenyl-6-(phenylseleno)-3-[(2-propenyl)oxy]-1-hexyne (8). Bu_3P (1.83 mL, 7.36 mmol) and phenylselenocyanate (1.07 mL, 7.36 mmol) were added to a stirred and cooled (0 °C) solution of **7d** (565 mg, 2.45 mmol) in THF (20 mL). After 1 h at 0 °C, the mixture was diluted with ether (50 mL) and washed with water (1 × 10 mL). The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 10% EtOAc–hexane, gave **8** (884 mg, 97%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 2800–3040, 1480, 1477, 1437 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.88–2.02 (m, 4 H), 2.90-3.03 (m, 2 H), 4.01 (ddt, J = 12.2, 6.1, 1.2 Hz, 1 H), 4.27–4.36 (m, 2 H), 5.20 (dq, J = 10.2, 1.3 Hz, 1 H), 5.31 (dq, J = 17.2, 1.6 Hz, 1 H), 5.87–5.99 (m, 1 H), 7.17–7.25 (m, 3 H), 7.25–7.34 (m, 3 H), 7.34–7.42 (m, 2 H), 7.43–7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.97 (t′), 27.56 (t′), 35.70 (t′), 68.74 (d′), 69.69 (t′), 86.07 (s′), 87.88 (s′), 117.32 (t′), 122.76 (s′), 126.71 (d′), 128.25 (d′), 128.35 (d′), 129.00 (d′), 130.32 (s′), 131.75 (d′), 132.62 (d′), 134.46 (d′); exact mass m/z calcd for $C_{21}H_{22}OSe$ 370.0836, found 370.0823.

***cis*-1-(3-Bromopropyl)-3a,4-dihydro-6-phenyl-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (9). (a) Silica Gel Method.** The general method for the Pauson–Khand reaction with silica gel was followed, using **7** (129 mg, 0.44 mmol) in benzene (10 mL), $Co_2(CO)_8$ (225 mg, 0.66 mmol), and a reaction time of 2 h, and silica gel (5 g, containing 20% w/w water). The mixture was heated for 3 h at 45 °C. Flash chromatography of the crude product over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **9** (58.4 mg, 41%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–2800, 1709 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.86–1.99

(29) Uesato, S.; Kobayashi, K.; Inouye, H. *Chem. Pharm. Bull.* **1982**, *30*, 927.

(30) The author has deposited atomic coordinates for **17** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(m, 1 H), 2.01–2.15 (m, 3 H), 2.30 (dd, J = 17.9, 1.7 Hz, 1 H), 2.82 (dd, J = 17.9, 6.1 Hz, 1 H), 3.24–3.39 (m, 2 H), 3.42–3.53 (m, 2 H), 4.37 (t, J = 6.2 Hz, 1 H), 4.77–4.85 (m, 1 H), 7.30–7.53 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 28.55 (t'), 33.29 (t'), 33.53 (t'), 39.73 (t'), 42.57 (d'), 71.33 (t'), 75.28 (d'), 128.28 (d'), 128.57 (d'), 130.69 (s'), 135.47 (s'), 178.68 (s'), 207.09 (s'); exact mass m/z calcd for $C_{16}H_{17}O_2{}^{81}Br$ 322.0391, found 322.0390.

(b) 4-Methylmorpholine *N*-Oxide Method. The general procedure for the Pauson–Khand reaction with NMO was followed, using **7** (102 mg, 0.348 mmol) in CH_2Cl_2 (5 mL), $Co_2(CO)_8$ (1.7 mL, 0.3 M solution in CH_2Cl_2, 0.52 mmol), and a reaction time of 2 h, and NMO (244 mg, 2.09 mmol) and a reaction time of 24 h. Flash chromatography of the crude product over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **9** (52.3 mg, 46.8%) as a colorless oil, which was identical with material obtained by the silica gel method.

***cis*-3a,4-Dihydro-6-phenyl-1-[3-(phenylseleno)propyl]-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (10). (a) Silica Gel Method.** The general procedure for the Pauson–Khand reaction with silica gel was followed, using **8** (205 mg, 0.55 mmol) in benzene (10 mL), $Co_2(CO)_8$ (285 mg, 0.833 mmol), and a reaction time of 3 h, and silica gel (5 g, 20% w/w water). The mixture was heated for 3 h at 45 °C. Flash chromatography of the residue over silica gel (2 × 20 cm), using 50% EtOAc–hexane, gave **10** (116 mg, 53%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3120–2760, 1709 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.82–1.97 (m, 3 H), 1.97–2.11 (m, 1 H), 2.27 (dd, J = 17.7, 2.4 Hz, 1 H), 2.79 (dd, J = 17.8, 5.9 Hz, 1 H), 2.88–3.03 (m, 2 H), 3.28 (br d, J = 2.4 Hz, 2 H), 4.34 (t, J = 13.9 Hz, 1 H), 4.75–4.81 (m, 1 H), 7.20–7.30 (m, 3 H), 7.32–7.53 (m, 7 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.96 (t'), 27.64 (t'), 34.92 (t'), 39.76 (t'), 42.70 (d'), 71.32 (t'), 75.81 (d'), 126.95 (d'), 128.32 (d'), 128.52 (d'), 128.55 (d'), 129.07 (d'), 130.05 (s'), 130.87 (s'), 132.86 (d'), 135.35 (s'), 179.08 (s'), 207.07 (s'); exact mass m/z calcd for $C_{22}H_{22}O_2Se$ 398.0785, found 398.0790.

(b) 4-Methylmorpholine *N*-Oxide Method. The general procedure for the Pauson–Khand reaction with NMO was followed, using **8** (106 mg, 0.287 mmol) in CH_2Cl_2 (10 mL), $Co_2(CO)_8$ (1.4 mL, 0.3 M solution in CH_2Cl_2, 0.43 mmol), and a reaction time of 2 h, and NMO (201 mg, 1.72 mmol) and a reaction time of 12 h. Flash chromatography of the crude product over silica gel (2 × 20 cm), using 50% EtOAc–hexane, gave **10** (68 mg, 59%) as a colorless oil, which was identical with that obtained by the silica gel method.

(1α,3aα,5ββ)-1-(3-Bromopropyl)-3,3a,4,5-tetrahydro-6-phenyl-1*H*-cyclopenta[*c*]furan-5-ol (11). A mixture of **9** (38 mg, 0.118 mmol) and $CeCl_3{\cdot}7H_3O$ (48.5 mg, 0.130 mmol) in MeOH (5 mL) was stirred at room temperature for 30 min and then cooled to −78 °C. $NaBH_4$ (5 mg, 0.130 mmol) was added followed, after 1 h, by water (10 mL). The cooling bath was removed and, when the mixture had reached room temperature, it was extracted with ether (2 × 25 mL). The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 30% EtOAc–hexane, gave **11** (34.5 mg, 90%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600-3120, 2962, 2652 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.47 (dt, J = 12.0, 8.5 Hz, 1 H), 1.55–1.65 (m, 1 H), 1.71–1.81 (m, 1 H), 1.83–1.93 (m, 2 H), 2.01 (br s, 1 H), 2.91 (dt, J = 12.4, 6.3 Hz, 1 H), 3.07–3.19 (m, 1 H), 33.1 (dd, J = 10.5, 8.6 Hz, 1 H), 3.36 (t, J = 6.5 Hz, 2 H), 4.18 (t, J = 7.5 Hz, 1 H), 4.87–4.94 (m, 1 H), 5.50–5.60 (m, 1 H), 7.21–7.30 (m, 1 H), 7.32–7.45 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 28.63 (t'), 32.10 (t'), 33.52 (t'), 38.60 (t'), 47.62 (d'), 72.35 (t'), 74.36 (d'), 83.57 (d'), 127.31 (d'), 127.51 (d'), 128.66 (d'), 133.98 (s'), 134.17 (s'), 148.45 (s'); exact mass m/z calcd for $C_{16}H_{19}O_2{}^{81}Br$ 324.0548, found 324.0549.

(1α,3aα,5β)-3,3a,4,5-Tetrahydro-6-phenyl-1-[3-(phenylseleno)propyl]-1*H*-cyclopenta[*c*]furan-5-ol (12). The procedure for the preparation of **11** was followed, using **10** (63 mg, 0.158 mmol) in MeOH (10 mL), $CeCl_3{\cdot}7H_3O$ (65 mg, 0.175 mmol), and $NaBH_4$ (6.6 mg, 0.175 mmol). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 50% EtOAc–hexane, gave **12** (63.3 mg, 99%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–3080, 2963, 2933, 2856, 1477, 1437 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40–1.50 (m, 1 H), 1.56–1.78 (m, 4 H), 1.94 (br s, 1 H), 2.67 (dt, J = 12.0, 6.3 Hz, 1 H), 2.83 (td, J = 6.9, 2.0 Hz, 2 H), 3.08 (br quintet, J = 8.4 Hz, 1 H), 3.29 (dd, J = 10.4, 8.0 Hz, 1 H), 4.16 (t, J = 7.6 Hz, 1 H), 4.85–4.92 (m, 1 H), 5.51 (br q, J = 6.4 Hz, 1 H), 7.16–7.30 (m, 4 H), 7.32-7.43 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.84 (t'), 27.75 (t'), 33.50 (t'), 38.77 (t'), 47.64 (d'), 72.29 (t'), 74.75 (d'), 83.54 (d'), 126.76 (d'), 127.23 (d'), 127.48 (d'), 128.62 (d'), 128.62 (d'), 130.22 (s'), 132.76 (d'), 133.66 (s'), 134.23 (s'), 148.71 (s'); exact mass m/z calcd for $C_{22}H_{24}O_2Se$ 400.0942, found 400.0926.

Conversion of 11 into (3aα,5aβ,7α,8α,8aR*)-Octahydro-8-phenyl-5*H*-dicyclopenta[*b,c*]furan-7-ol (13). The general procedure for radical cyclization was followed using **11** (93.5 mg, 0.289 mmol) in benzene (20 mL), Bu_3SnH (0.12 mL, 0.434 mmol) in benzene (5 mL), and AIBN (5 mg, 0.030 mmol) in benzene (5 mL). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **13** (47 mg, 66%) as a colorless oil, which was identical with material obtained by radical cyclization of the selenide **12** (see the following experiment).

Conversion of 12 into (3aα,5aβ,7α,8α,8aR*)-Octahydro-8-phenyl-5*H*-dicyclopenta[*b,c*]furan-7-ol (13). The general procedure for radical cyclization was followed using **12** (182 mg, 0.469 mmol) in benzene (20 mL), Bu_3SnH (0.15 mL, 0.563 mmol) in benzene (5 mL), and AIBN (5 mg, 0.030 mmol) in benzene (5 mL). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **13** (87 mg, 78%) as a white solid: mp 74–76 °C; FT-IR (CH_2Cl_2 cast) 3600–3200, 2942, 2872 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37-1.60 (m, 3 H), 1.63–1.68 (m, 1 H), 1.71 (d, J = 14.8 Hz, 1 H), 1.73–1.80 (m, 1 H), 1.83–1.89 (m, 1 H), 2.32 (ddd, J = 14.8, 10.2, 4.4 Hz, 1 H), 2.43 (broad dd, J = 10.1, *ca* 7 Hz, 1 H), 2.95 (d, J = 3.6 Hz, 1 H), 3.45 (d, J = 10.5 Hz, 1 H), 3.80 (dd, J = 9.2, 2.0 Hz, 1 H), 4.00 (dd, J = 9.4, 6.7 Hz, 1 H), 4.35 (ddd, J = 10.5, 4.4, *ca* 3.6 Hz, 1 H), 4.58–4.63 (m, 1 H), 7.20–7.34 (m, 3 H), 7.57–7.64 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 24.95 (t'), 33.29 (t'), 37.91 (t'), 42.36 (t'), 50.95 (d'), 57.12 (d'), 64.73 (s'), 75.38 (t'), 76.74 (d'), 84.57 (d'), 126.57 (d'), 127.99 (d'), 130.44 (d'), 139.31 (s'); exact mass m/z calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1463.

1-Phenyl-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-hexyn-3-ol (7b). Ethylmagnesium bromide (2.0 M in THF, 3.8 mL, 7.6 mmol) was added to a stirred and cooled (0 °C) solution of phenylacetylene (0.84 mL, 7.67 mmol) in THF (20 mL). After 10 min a solution of aldehyde **7a**[29] (1.1 g, 6.39 mmol) in THF (10 mL) was added over 5 min. The solution was stirred at 0 °C for 1 h and then quenched by addition of water (10 mL). The layers were separated and the aqueous phase was washed with ether (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 20% EtOAc–hexane, gave **7b** (1.12 g, 64%) as a mixture of two diastereoisomers [^{13}C NMR (100.6 MHz)]. The material was a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–2960, 2945, 2889 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46-2.00 (m, 10 H), 3.27 (br s, 1 H), 3.42–3.57 (m, 2 H), 3.77–3.91 (m, 2 H), 4.57–4.70 (m, 2 H), 7.25–7.32 (m, 3 H), 7.37–7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.36 (t'), 25.34 (t'), 25.50 (t'), 25.56 (t'), 30.50 (t'), 30.52 (t'), 35.11 (t'), 62.14 (t'), 62.46 (t'), 67.11 (t'), 67.20 (t'), 84.57 (s'), 90.25 (s'), 98.60 (d'), 98.69 (d'), 112.76 (s'), 128.19 (d'), 131.60 (d'); exact mass m/z calcd for $C_{17}H_{22}O_3$ 274.1569, found 274.1572.

1-Phenyl-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-hexyn-3-one (14a). DMSO (4.3 mL, 60.6 mmol) was added over 10 min to a stirred and cooled (−78 °C) solution of $(COCl)_2$ (3.1 mL, 35.5 mmol) in CH_2Cl_2 (20 mL). A solution of **7b** (6.50 g, 23.7 mmol) in CH_2Cl_2 (10 mL) was then injected over 30 min. After 1 h, Et_3N (9.9 mL, 71.1 mmol) was added, and the cooling bath was removed. After a further 1 h the solvent was evaporated, and flash chromatography of the crude product over silica gel (4 × 20 cm), using 10% EtOAc–hexane, gave **14a** (4.2 g, 65%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 2942, 2870, 2202, 1671 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.43–1.63 (m, 4 H), 1.65–1.76 (m, 1 H), 1.76–1.90 (m 1 H), 2.03 (br quintet, J = 6.7 Hz, 2 H), 2.78 (td, J = 4.7, 1.7 Hz, 2 H), 3.40–3.54 (m, 2 H), 3.75–3.90 (m, 2 H), 4.58 (br t, J = 3.5 Hz, 1 H), 7.31–7.40 (m, 2 H), 7.40–7.48 (m, 1 H), 7.53–7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.43 (t'), 24.31 (t'), 25.37 (t'), 30.55 (t'), 42.40 (t'), 62.16 (t'), 66.12 (t'), 87.78 (s'), 90.50 (s'), 96.74 (d'), 119.98 (s'), 128.53 (d'), 130.54 (d'), 132.89 (d'), 187.36 (s'); exact mass, m/z calcd for $C_{17}H_{20}O_3$ 272.1412, found 272.1404.

3-Methyl-1-phenyl-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-hexyn-3-ol (14b). Methyllithium (3.6 mL, 1.4 M in ether, 5.0 mmol) was added to a stirred and cooled (−78 °C) solution of **14a** (1.15 g, 4.22 mmol) in THF (20 mL). After 1 h at −78 °C, water (10 mL) was added, and the cooling bath was removed. The layers were separated, and the aqueous phase was extracted with ether (1 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 20% EtOAc–hexane, gave **14b** (0.678 g, 84%) as a mixture of two diastereoisomers [^{13}C NMR (100.6 MHz)]. The material was a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–3040, 2940 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.46–2.11 [m, including s (3 H) at δ 1.60, 14 H], 3.41–3.60 (m, 2 H), 3.78–3.93 (m, 2 H), 4.66 (quintet, J = 3.6 Hz, 1 H), 7.26-7.35 (m, 3 H), 7.39–7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.30, 19.39, 25.25, 25.38, 25.48, 30.18, 30.35, 30.48, 41.25, 62.09, 62.16, 67.48, 67.55, 68.03, 68.11, 83.32, 83.39, 92.99, 93.03, 98.50, 98.63, 122.93, 128.13, 128.20, 131.62; exact mass m/z calcd for $C_{18}H_{24}O_3$ 288.1725, found 288.1716.

3-Methyl-1-phenyl-3-[(2-propenyl)oxy]-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-hexyne (14c). 3-Bromopropene (0.52 mL, 6.01 mmol) and potassium hydroxide (0.47 g, 8.37 mmol, freshly crushed) were added to a solution of alcohol **14b** (0.601 g, 2.08 mmol) in DMSO (20 mL).[9] The mixture was stirred at 55 °C for 30 min and then cooled and diluted with ether (30 mL). The solution was washed with saturated aqueous $NaHCO_3$ (10 mL) and water (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 10% EtOAc–hexane, gave **14c** (479 mg, 70%) as mixture of two diastereoisomers [^{13}C NMR (100.6 MHz)]. The material was a colorless oil: FT-IR (CH_2Cl_2 cast) 2959, 1120, 1068, 1033 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.45–1.64 [m, including s (3 H) at δ 1.55, 7 H], 1.66–1.78 (m, 1 H), 1.78–1.98 (m, 5 H), 3.40–3.56 (m, 2 H), 3.76–3.93 (m, 2 H), 4.00–4.15 (m, 2 H), 4.59 (t, J = 3.6 Hz, 1 H), 5.14 (dq, J = 10.8, 1.6 Hz, 1 H), 5.31 (dq, J = 17.1, 1.7 Hz, 1 H), 5.98 (ddt, J = 17.1, 10.6, 5.4 Hz, 1 H), 7.27–7.34 (m, 3 H), 7.38–7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.54 (t′), 24.86 (t′), 25.44 (t′), 26.37 (q′), 30.69 (t′), 38.46 (t′), 62.15 (t′), 65.23 (t′), 67.48 (t′), 73.60 (s′), 85.37 (s′), 90.51 (s′), 98.64 (d′), 98.71 (d′), 115.87 (t′), 122.83 (s′), 128.11 (d′), 128.14 (d′), 131.60 (d′), 135.58 (d′); mass (CI) m/z calcd for $C_{21}H_{28}O_3$ 328, found 346 $(M + 18)^+$.

4-Methyl-6-phenyl-4-[(2-propenyl)oxy]-5-hexyn-1-ol (14d). A solution of **14c** (442 mg, 1.35 mmol) and pyridinium *p*-toluenesulfonate[10] (10 mg, 0.04 mmol) in MeOH (10 mL) was refluxed for 1.5 h, cooled, and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 30% EtOAc–hexane, gave **14d** (317 mg, 96%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600-2920, 2933, 1059 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.54 (s, 3 H), 1.73–1.94 (m, 4 H), 2.34 (br s, 1 H), 3.69 (br t, J = 5.0 Hz, 2 H), 4.15 (ddt J = 12.1, 5.5, 1.5 Hz, 1 H), 4.23 (ddt, J = 12.1, 5.5, 1.5 Hz, 1 H), 5.31 (dq, J = 17.0, 1.7 Hz, 1 H), 5.16 (dq, J = 10.3, 1.5 Hz, 1 H), 5.97 (ddt, J = 17.2, 10.2, 5.6 Hz, 1 H), 7.26–7.35 (m, 3 H), 7.40–7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 26.48 (q′), 27.98 (t′), 38.66 (t′), 62.87 (t′), 65.49 (t′), 73.80 (s′), 85.75 (s′), 90.07 (s′), 116.60 (t′), 122.69 (s′), 128.30 (d′), 128.34 (d′), 131.70 (d′), 135.21 (d′); exact mass m/z calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1436.

6-Bromo-3-methyl-1-phenyl-3-[(2-propenyl)oxy]-1-hexyne (14). CBr_4 (1.74 mmol, 576 mg) and Ph_3P (1.74 mmol, 456 mg) were added to a stirred and cooled (0 °C) solution of **14d** (354 mg, 1.45 mmol) in CH_2Cl_2 (20 mL). The cooling bath was removed, and stirring was continued for 2 h. The mixture was then filtered through silica gel (2 × 3 cm) with 10% EtOAc–hexane (50 mL), and the filtrate was evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 10% EtOAc–hexane, gave **14** (372 mg, 83%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3120–2800, 1489, 1273 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.54 (s, 3 H), 1.87–1.97 (m, 2 H), 2.05–2.25 (m, 2 H), 3.42–3.54 (m, 2 H), 4.13 (ddt, J = 12.5, 5.6, 1.6 Hz, 1 H), 4.21 (ddt, J = 12.8, 5.2, 1.6 Hz, 1 H), 5.15 (dq, J = 10.5, 1.7 Hz, 1 H), 5.31 (dq, J = 17.1, 1.7 Hz, 1 H), 5.96 (ddt, J = 17.1, 10.2, 5.4 Hz, 1 H), 7.28–7.33 (m, 3 H), 7.40–7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 26.57 (q′), 28.16 (t′), 34.12 (t′), 40.66 (t′), 65.41 (t′), 73.33 (s′), 85. 81 (s′), 90.00 (s′), 116.21 (t′), 122.67 (s′), 128.32 (d′), 128.39 (d′), 131.74 (d′), 135.45 (d′); exact mass m/z calcd for $C_{15}H_{16}{}^{81}BrO$ $(M - CH_3)^+$ 293.0364, found 293.0361.

***cis*-1-(3-Bromopropyl)-3a,4-dihydro-1-methyl-6-phenyl-1*H*-cyclopenta[*c*]furan-5(3*H*)-one and *trans*-1-(3-Bromopropyl)-3a,4-dihydro-1-methyl-6-phenyl-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (15).** The general procedure for the Pauson–Khand reaction with NMO was followed, using **14** (214 mg, 0.696 mmol) and $Co_2(CO)_8$ (3.5 mL, 0.3 M, in CH_2Cl_2, 1.05 mmol) in CH_2Cl_2 (10 mL), and a reaction time of 2 h, and NMO (489 mg, 4.18 mmol) and a reaction time of 12 h. Flash chromatography of the crude product over silica gel (3 × 20 cm), using 70% EtOAc–hexane, gave **15** as a chromatographically inseparable 1:1 mixture of two diastereoisomers [^{13}C NMR (100.6)] (183 mg, 74%). The material was a colorless oil: FT-IR (CH_2Cl_2 cast) 3100–2800, 1711 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.09 (s, 3 × 0.5 H), 1.43–1.70 [m, including s (3 × 0.5 H) at δ 1.60, 3 H], 1.71–1.87 (m, 0.5 H), 1.90–2.03 (m, 1 H), 2.03–2.36 (m, 2 H), 2.70–2.86 (m, 1 H), 2.97–3.07 (m, 1 H), 3.27–3.60 (m, 3 H), 4.26–4.40 (m, 1 H), 7.20–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 23.36 (q′), 27.39 (t′), 28.01 (t′), 28.55 (q′), 33.27 (t′), 33.85 (t′), 35.81 (t′), 39.35 (t′), 39.75 (t′), 40.75 (t′), 43.36 (d′), 45.52 (d′), 69.86 (t′), 71.38 (t′), 80.61 (s′), 81.47 (s′), 128.49 (d′), 128.55 (d′), 128.59 (d′), 128.74 (d′), 129.03 (d′), 129.07 (d′), 130.50 (s′), 130.72 (s′), 136.45 (s′), 137.44 (s′), 181.56 (s′), 183.31 (s′), 207.15 (s′), 207.23 (s′); exact mass m/z calcd for $C_{17}H_{19}{}^{81}BrO_2$ 336.0548, found 336.0550. Anal. Calcd for $C_{17}H_{19}BrO_2$: C, 60.91; H, 5.71. Found: C, 60.82; H, 5.60.

(3aα,5aβ,8β,8aR*)-Hexahydro-3a-methyl-8-phenyl-5*H*-dicyclopenta[*b*,*c*]furan-7(8*H*)-one (16) and (3aα,5aα,8β,8aR*)-Hexahydro-3a-methyl-8-phenyl-5*H*-dicyclopenta[*b*,*c*]furan-7(8*H*)-one (17). The general procedure for radical cyclization was followed, using **15** (251.9 mg, 0.75 mmol) in benzene (25 mL), Bu_3SnH (290 μL, 1.05 mmol) in benzene (10 mL), and AIBN (49 mg, 0.30 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **16** (50.0 mg), a 4:5 mixture of **16** and **17** (59.6 mg), and **17** (53.0 mg) (*ca.* 84% yield in all). Each fraction contained a small amount [<9 mol% by ^1H NMR (400 MHz)] of tributyltin residues.

Further purification of **16** by flash chromatography over silica gel (1.0 × 20 cm), using 5% EtOAc–CH_2Cl_2, gave **16** as a pure [^1H NMR (400 MHz)], colorless oil: FT-IR (CH_2Cl_2 cast) 2956, 1742 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.29-1.44 [m, including s (3 H) at δ 1.37, 5 H], 1.45–1.61 (m, 2 H), 1.61–1.74 (m, 1 H), 1.94 (dd t, J = 15.2, 8.6, 1.9 Hz, 1 H), 2.39 (ddd, J = 18.7, 4.3, 1.3 Hz, 1 H), 2.69 (dd, J = 18.7, 9.6 Hz, 1 H), 2.70–2.74 (m, 1 H), 3.59 (dd, J = 9.0, 6.5 Hz, 1 H), 3.71 (s, 1 H), 4.09 (dd, J = 9.0, 6.2 Hz, 1 H), 7.01–7.06 (m, 2 H), 7.23–7.36 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.73 (t′), 24.12 (q′), 36.04 (t′), 40.68 (t′), 41.25 (t′), 47.62 (d′), 60.64 (d′), 62.96 (s′), 71.10 (t′), 93.31 (s′), 127.11 (d′), 128.50 (d′), 130.48 (d′), 137.19 (s′), 218.03 (s′); exact mass m/z calcd for $C_{17}H_{20}O_2$, 256.1463, found, 256.1461.

Recrystallization of **17** from 1:3 EtOAc–hexane afforded white cubic crystals: mp 131–133 °C; FT-IR (CH_2Cl_2 cast) 2982, 1745 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.11–1.31 (m, 2 H), 1.42–1.72 [m, including s (3 H) at δ 1.49, 6 H], 1.89 (dd, J = 11.2, 4.8 Hz, 1 H), 2.32 (dd, J = 17.4, 14.2 Hz, 1 H), 2.55 (dd, J = 17.2, 6.9 Hz, 1 H), 2.71 (dddd, J = 13.2, 11.0, 6.8, 6.8 Hz, 1 H), 3.56 (s, 1 H), 3.63 (dd, J = 11.4, 7.8 Hz, 1 H), 4.08 (dd, J = 7.3, 7.3 Hz, 1 H), 7.08–7.15 (m, 2 H), 7.23–7.30 (m, 1 H), 7.30–7.38 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.54 (q′), 22.25 (t′), 26.21 (t′), 38.57 (t′), 40.50 (t′), 47.10 (d′), 63.02 (d′), 64.36 (s′), 67.25 (t′), 89.12 (s′), 127.31 (d′), 128.44 (d′), 130.31 (d′), 135.48 (s′), 216.17 (s′); exact mass m/z calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1461.

We believe that the stereochemistries of **16** and **17** correspond to those generated in the radical cyclization; we noticed no evidence for epimerization during chromatography.

1-Phenyl-6-hepten-1-yn-3-ol (18a). Ethylmagnesium bromide (2.0 M solution in THF, 10 mL, 20 mmol) was added over 5 min to a stirred and cooled (0 °C) solution of phenylacetylene (2.0 mL, 18.2 mmol) in THF (20 mL). After 30 min, 4-pentenal (3.2 g, 38.0 mmol) in THF (5 mL) was added over 5 min, and the cooling bath was then removed. After a further 1 h, water (10 mL) was added, and the mixture was extracted with ether (2 × 25 mL). The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 × 20 cm),

using 10% EtOAc–hexane, gave **18a** (2.70 g, 80%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–3120, 1489 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.81–1.97 (m, 2 H), 2.27 (br q, J = 7.0 Hz, 2 H), 2.86 (br s, 1 H), 4.61 (q, J = 5.6 Hz, 1 H), 4.96–5.01 (m, 1 H), 5.07 (dq, J = 17.0, 1.6 Hz, 1 H), 5.83 (ddt, J = 17.0, 10.2, 6.7 Hz, 1 H), 7.20–7.30 (m, 3 H), 7.35–7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.41 (t'), 36.76 (t'), 62.20 (d'), 84.95 (s'), 89.92 (s'), 115.20 (t'), 122.56 (s'), 128.18 (d'), 128.27 (d'), 131.59 (d'), 137.60 (d'); exact mass m/z calcd for $C_{13}H_{13}O$ (M – H)$^+$ 185.0966, found 185.0967. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; 7.58. Found: C, 83.09; H, 7.37.

***tert*-Butyl [(1-Phenyl-6-hepten-1-yn-3-yl)oxy]acetate (18b).** Tetrabutylammonium iodide (150 mg, 0.406 mmol) and *tert*-butyl bromoacetate (0.20 mL, 1.24 mmol) were added to a stirred and cooled (10 °C) mixture of **18a** (150 mg, 0.805 mmol) in benzene (3 mL) and 50% w/v aqueous NaOH (2.5 mL). After 3 h, the mixture was diluted with ether (10 mL), and the organic layer was washed successively with 1 M hydrochloric acid (1 × 5 mL), saturated aqueous $NaHCO_3$ (1 × 5 mL), and water (1 × 5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 2% EtOAc–hexane, gave **18b** (201 mg, 83%) as a colorless oil: bp 150 °C (0.5 mmHg; Kugelrohr); FT-IR (CH_2Cl_2 cast) 1745, 1159, 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.50 (s, 9 H), 1.88–2.06 (m, 2 H), 2.33 (br q, J = 7.3 Hz, 2 H), 4.17 (d, J = 11.0 Hz, 1 H), 4.21 (d, J = 11.0 Hz, 1 H), 4.50 (t, J = 7.5 Hz, 1 H), 5.00 (ddt, J = 10.2, 2.0, 2.0 Hz, 1 H), 5.09 (dq, J = 17.0, 1.7 Hz, 1 H), 5.88 (ddt, 17.0, 10.2, 7.5 Hz, 1 H), 7.28–7.36 (m, 3 H), 7.41–7.49 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 28.15 (q'), 29.47 (t'), 34.86 (t'), 66.07 (t'), 69.76 (d'), 81.63 (s'), 86.64 (s'), 87.09 (s'), 115.12 (t'), 122.54 (s'), 128.32 (d'), 128.50 (d'), 131.80 (d'), 137.76 (d'), 169.55 (s'); exact mass m/z calcd for $C_{15}H_{15}O_3$ (M – C_4H_9)$^+$ 243.1021, found 243.1023.

2-[(1-Phenyl-6-hepten-1-yn-3-yl)oxy]ethanol (18c). $LiAlH_4$ (27 mg, 0.711 mmol) was added to a stirred and cooled (0 °C) solution of **18c** (175 mg, 0.583 mmol) in dry ether (10 mL). The mixture was stirred at 0 °C for 1 h, and then water (5 mL) and 5% NaOH (5 mL) were added. The layers were separated and the aqueous phase was washed with ether (1 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **18c** (131 mg, 97%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–3120, 2931, 1106 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.84–2.01 (m, 2 H), 2.92 (br q, J = 7.3 Hz, 2 H), 2.52 (br s, 1 H), 3.53-3.60 (m, 1 H), 3.77 (br s, 1 H), 3.88–3.94 (m, 2 H), 4.32 (t, J = 6.6 Hz, 1 H), 5.01 (dq, J = 10.2, 1.4 Hz, 1 H), 5.08 (dq, J = 17.0, 1.6 Hz, 1 H), 5.85 (ddt, J = 17.0, 10.2, 6.7 Hz, 1 H), 7.25–7.33 (m, 3 H), 7.40–7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.48 (t'), 34.72 (t'), 61.73 (t'), 69.82 (d'), 70.06 (t'), 86.09 (s'), 87.77 (s'), 115.17 (t'), 122.49 (s'), 128.21 (d'), 128.33 (d'), 131.64 (d'), 137.60 (d'); exact mass m/z calcd for $C_{15}H_{17}O_2$ (M – H)$^+$ 229.1228, found 229.1228.

1-Phenyl-3-[2-(phenylseleno)ethoxy]-6-hepten-1-yne (18). Phenylselenocyanate (0.16 mL, 1.13 mmol) and Bu_3P (0.28 mL, 1.13 mmol) were added to a stirred and cooled (0 °C) solution of **18c** (173 mg, 0.755 mmol) in THF (10 mL). The mixture was stirred at 0 °C for 1 h, and then water (10 mL) was added. The layers were separated, and the aqueous layer was washed with ether (1 × 30 mL). The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 5% EtOAc–hexane, gave **18** (261 mg, 94%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3090–2800, 1489, 1477, 1437, 1089 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.79–1.96 (m, 2 H), 2.27 (br q, J = 7.3 Hz, 2 H), 3.12 (t, J = 7.3 Hz, 2 H), 3.71 (dt, J = 10.0, 7.4 Hz, 1 H), 4.04 (dt, J = 10.2, 7.1 Hz, 1 H), 4.28 (t, J = 6.5 Hz, 1 H), 4.99 (br d, J = 10.2 Hz, 1 H), 5.07 (dq, J = 17.0, 5.1 Hz, 1 H), 5.83 (ddt, J = 17.2, 10.2, 6.6 Hz, 1 H), 7.14-7.24 (m, 3 H), 7.24–7.33 (m, 3 H), 7.33–7.42 (m, 2 H), 7.47–7.56 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 26.79 (t'), 29.48 (t'), 34.85 (t'), 68.29 (t'), 69.39 (d'), 86.03 (s'), 87.98 (s'), 115.21 (t'), 122.63 (s'), 126.86 (d'), 128.23 (d'), 128.32 (d'), 129.02 (d'), 129.92 (s'), 131.70 (d'), 132.56 (d'), 137.67 (d'); exact mass m/z calcd for $C_{21}H_{22}OSe$ 370.0836, found 370.0823.

***cis*-4,5,6,6a-Tetrahydro-3-phenyl-4-[2-(phenylseleno)-ethoxy]-2(1*H*)-pentalenone (19).** The general procedure for the Pauson–Khand reaction with NMO was followed, using **18** (141 mg, 0.382 mmol) and $Co_2(CO)_8$ (1.2 mL, 0.5 M solution in CH_2Cl_2, 0.6 mmol) in CH_2Cl_2 (10 mL) and a reaction time of 3 h, and NMO (270 mg, 2.30 mmol) and a reaction time of 12 h. Flash chromatography of the crude product over silica gel (2 × 18 cm), using 20% EtOAc–hexane, gave **19** (113.5 mg, 75%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3100–2800, 1704 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.03–1.15 (m, 1 H), 1.98–2.08 (m, 1 H), 2.24 (dd, J = 18.1, 2.8 Hz, 1 H), 2.25–2.38 (m, 2 H), 2.86 (dd, J = 18.1, 6.4 Hz, 1 H), 3.70 (dt, J = 9.8, 6.9 Hz, 1 H), 3.06–3.20 (m, 3 H), 3.83 (dt, J = 9.8, 6.8 Hz, 1 H), 4.49–4.54 (m, 1 H), 7.20–7.30 (m, 3 H), 7.30–7.42 (m, 3 H), 7.47–7.55 (m, 2 H), 7.62–7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 27.16 (t'), 29.04 (t'), 33.66 (t'), 41.36 (d'), 43.07 (t'), 66.26 (t'), 75.40 (d'), 127.11 (d'), 128.41 (d'), 128.95 (d'), 129.14 (d'), 129.64 (s'), 131.07 (s'), 132.66 (d'), 137.72 (s'), 176.46 (s'), 208.98 (s'); exact mass m/z calcd for $C_{22}H_{22}O_2Se$ 398.0785, found 398.0787.

(2α,4β,6aβ)-1,2,4,5,6,6a-Hexahydro-3-phenyl-4-[2-(phenylseleno)ethoxy]-2-pentalenol (20). The procedure for the preparation of **11** was followed, using **19** (47 mg, 0.118 mmol) in MeOH (8 mL), $CeCl_3{\cdot}7H_3O$ (48 mg, 0.130 mmol), and $NaBH_4$ (5 mg, 0.13 mmol). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **20** (32 mg, 68%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–3120, 2933, 2857, 1477, 1436 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.19 (dtd, J = 12.0, 9.3, 9.2 Hz, 1 H), 1.36 (dt, J = 12.8, 8.0 Hz, 1 H), 1.76 (br s, 1 H), 1.88–2.00 (m, 1 H), 2.06–2.16 (m, 1 H), 2.26–2.36 (m, 1 H), 2.78 (dt, J = 12.7, 6.9 Hz, 1 H), 2.86–3.02 (m, 3 H), 3.41–3.52 (m, 2 H), 4.62 (br t, J = 4.8 Hz, 1 H), 5.39 (br t, J = 7.2 Hz, 1 H), 7.17–7.30 (m, 4 H), 7.30–7.44 (m, 4 H), 7.44–7.52 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 27.05 (t'), 30.33 (t'), 34.99 (t'), 42.44 (t'), 45.55 (d'), 67.68 (t'), 74.47 (d'), 82.96 (d'), 126.87 (d'), 127.36 (d'), 128.02 (d'), 128.47 (d'), 129.02 (d'), 129.97 (s'), 132.58 (d'), 135.04 (s'), 138.20 (s'), 148.87 (s'); exact mass m/z calcd for $C_{22}H_{24}O_2Se$ 400.0942, found 400.0922.

(3aα,5aβ,7α,8α,8aS*)-Octahydro-8-phenyl-5(*H*)-pentaleno-[1,6a-*b*]furan-7-ol (21). The general procedure for radical cyclization was followed using **20** (56 mg, 0.145 mmol) in benzene (10 mL), Bu_3SnH (0.06 mL, 0.22 mmol) in benzene (5 mL), and AIBN (11 mg, 0.067 mmol) in benzene (5 mL). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 20% EtOAc–hexane, gave **21** (29.8 mg, 87%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3600–3200, 2394, 1033 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.49 (d, J = 10.8 Hz, 1 H), 1.56–1.68 (m, 2 H), 1.80 (dd, J = 13.9, 7.0 Hz, 1 H), 1.89–2.06 (m, 2 H), 2.15 (dt, J = 12.3, 7.7 Hz, 1 H), 2.25–2.37 (m, 1 H), 2.37–2.49 (m, 2 H), 3.23 (d, J = 4.5 Hz, 1 H), 3.46 (dt, J = 8.0, 5.2 Hz, 1 H), 3.69 (dt, J = 8.0, 6.9 Hz, 1 H), 4.43 (t, J = 4.6 Hz, 1 H), 4.69 (d, J = 5.4 Hz, 1 H), 7.23–7.30 (m, 1 H), 7.30–7.38 (m, 2 H), 7.43–7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 32.21 (t'), 32.62 (t'), 40.44 (t'), 41.52 (t'), 51.10 (d'), 59.31 (d'), 64.80 (s'), 67.64 (t'), 76.56 (d'), 85.80 (d'), 126.87 (d'), 128.58 (d'), 130.39 (d'), 138.60 (s'); exact mass m/z calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1460.

***N*-2-Propenyl-*N*-[1-phenyl-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-hexyn-3-yl]amine (22b).** Allylamine (2.3 mL, 30.2 mmol) was added to a stirred and cooled (0 °C) solution of **7a**[29] (2.6 g, 15.1 mmol) in benzene (50 mL). After 1 h, the cooling bath was removed, a side-arm addition funnel packed with 3-Å sieves (20 g) and carrying a condenser was fitted, and the solution was refluxed through the sieves for 2 h. The solution was cooled and evaporated to give crude imine **22a** (3.2 g): FT-IR (CH_2Cl_2 cast) 3010–2760, 1658 cm^{-1}.

n-BuLi (14.8 mL, 1.6 M, in hexanes, 23.6 mmol) was added to a stirred solution of phenylacetylene (2.5 mL, 23.6 mmol) in THF (50 mL) at −78 °C. After 30 min, boron trifluoride etherate (2.9 mL, 23.6 mmol) was added followed, after a further 10 min, by a solution of crude imine **22a** (2.5 g, 11.8 mmol) in THF (10 mL). The resulting solution was stirred at −78 °C for 1 h, the cooling bath was removed, and stirring was continued for 2 h. Water (10 mL) was added, and the layers were separated. The aqueous layer was washed with ether (20 mL), and the combined organic layers were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 × 20 cm), using 2% MeOH–CH_2Cl_2, gave **22b** (1.57 g, 42%) as a mixture of two diastereoisomers [^{13}C NMR (100.6 MHz)]. The material was a colorless oil: FT-IR (CH_2Cl_2 cast) 2941, 2869, 1489 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.32–1.96 (m, 11 H), 3.36 (ddt, J = 13.8, 6.2, 1.4 Hz, 1 H), 3.43–3.54 (m, 2 H), 3.57 (ddt, J = 14.0, 5.8, 1.4 Hz, 1 H),

3.64 (dd, J = 7.8, 5.3 Hz, 1 H), 3.78–3.92 (m, 2 H), 4.61 (t, J = 3.1 Hz, 1 H), 5.13 (dq, J = 10.0, 1.5 Hz, 1 H), 5.26 (dq, J = 17.0, 1.7 Hz, 1 H), 5.96 (ddt, J = 17.0, 10.2, 6.0 Hz, 1 H), 7.23–7.36 (m, 3 H), 7.39–7.51 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.49 (t'), 25.42 (t'), 26.41 (t'), 30.65 (t'), 32.89 (t'), 32.92 (t'), 49.90 (d'), 50.08 (t'), 62.13 (t'), 62.16 (t'), 67.09 (t'), 83.97 (s'), 90.56 (s'), 98.65 (d'), 116.22 (t'), 123.25 (s'), 127.86 (d'), 128.15 (d'), 131.59 (d'), 136.41 (d'); exact mass m/z calcd for $C_{20}H_{26}NO_2$ $(M - H)^+$ 312.1964, found 312.1962.

***N*-2-Propenyl-*N*-[1-phenyl-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-hexyn-3-yl]acetamide (22c).** NaH (0.26 g, 60% dispersion in oil, 6.49 mmol) was added to a stirred and cooled (0 °C) solution of **22b** (1.35 g, 4.33 mmol) and acetyl chloride (0.46 mL, 6.5 mmol) in THF (50 mL). The cooling bath was removed, and the mixture was stirred at room temperature for 2 h and then poured into ice–water (20 mL). The layers were separated, and the organic layer was washed with water (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 2% MeOH–CH_2Cl_2, gave **22c** (1.17 g, 76%) as a mixture of two isomers [^{13}C NMR (100.6 MHz)]. The material was a colorless oil: FT-IR (CH_2Cl_2 cast) 2940, 2868, 1653, 1405 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45–1.93 (m, 10 H), 2.12 (s) and 2.24 (s, 3 H in total), 3.37–3.54 (m, 2 H), 3.70-3.90 (m, 2 H), 3.99–4.23 (m, 2 H), 4.59 (t, J = 3.5 Hz, 1 H), 5.19–5.28 (m, 2 H), 5.72 (br t, J = 6.5 Hz, 1 H), 5.93 (ddt, J = 17.5, 10.4, 6.1 Hz, 1 H), 7.27–7.37 (m, 3 H), 7.37–7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) (major isomer only) δ 19.52 (t'), 21.94 (q'), 25.34 (t'), 26.43 (t'), 30.62 (t'), 31.27 (t'), 46.53 (d'), 46.56 (d'), 47.66 (t'), 62.20 (t'), 66.75 (t'), 84.59 (s'), 87.40 (s'), 98.74 (d'), 116.63 (t'), 122.67 (s'), 128.18 (d'), 128.26 (d'), 131.53 (d'), 134.84 (d'), 170.64 (s'); exact mass m/z calcd for $C_{22}H_{29}NO_3$ 355.2147, found 355.2141.

***N*-2-Propenyl-*N*-(6-bromo-1-phenyl-1-hexyn-3-yl)acetamide (22).** CBr_4 (1.5 g, 4.52 mmol) was added to a stirred solution of **22c** (1.01 g, 3.01 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After 10 min, Ph_3P (2.4 g, 9.0 mmol) was added, and the cooling bath was removed.[13] After 24 h the solution was filtered through silica gel (2 × 3 cm) with ether (50 mL). The filtrate was evaporated, and flash chromatography of the residue over silica gel (2 × 20 cm), using 30% EtOAc–hexane, gave **22** (0.61 g, 60%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3130–2800, 1651, 1407 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.80–2.15 [m, including s (3 H) at δ 2.11, 7 H], 3.46 (td, J = 6.1, 2.1 Hz, 2 H), 3.97–4.23 (m, 2 H), 5.21–5.28 (m, 2 H), 5.70 (t, J = 7.5 Hz, 1 H), 5.92 (ddt, J = 15.4, 10.5, 5.1 Hz, 1 H), 7.27–7.36 (m, 3 H), 7.36–7.44 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.98 (q'), 29.39 (t'), 33.04 (t'), 33.12 (t'), 46.61 (d'), 47.73 (t'), 85.08 (s'), 86.86 (s'), 116.92 (t'), 122.47 (s'), 128.30 (d'), 128.44 (d'), 131.62 (d'), 134.69 (d'), 170.77 (s'); exact mass m/z calcd for $C_{17}H_{20}{}^{81}BrNO$ 335.0708, found 335.0704.

***cis*-2-Acetyl-1-(3-bromopropyl)-2,3,3a,4-tetrahydro-6-phenylcyclopenta[*c*]pyrrol-5(1*H*)-one (23).** The general procedure for the Pauson–Khand reaction with NMO was followed, using **22** (104 mg, 0.311 mmol) and $Co_2(CO)_8$ (1.1 mL, 0.3 M, in CH_2Cl_2, 0.33 mmol) in CH_2Cl_2 (10 mL) and a reaction time of 2 h, and NMO (218 mg, 1.87 mmol) and a reaction time of 6 h. Flash chromatography of the crude product over silica gel (2 × 20 cm), using 80% EtOAc–hexane, gave **23** (72 mg, 64%), containing a small amount of another product (ca. 10% if it is an isomer) that was not characterized. The mixture had: FT-IR ($CHCl_3$) 1711, 1648, 1412 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (quintet, J = 7.2 Hz, 2 H), 2.00–2.19 [m, including s (3 H) at δ 2.08, 5 H], 2.39 (dd, J = 18.0, 3.7 Hz, 1 H), 2.91 (dd, J = 18.0, 6.7 Hz, 1 H), 3.14 (t, 9.7 Hz, 1 H), 3.33-3.46 (m, 2 H), 3.50–3.60 (m, 1 H), 4.07 (t, J = 9.2 Hz, 1 H), 5.15 (t, J = 6.1 Hz, 1 H), 7.33–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.48 (q'), 29.16 (t'), 32.94 (t'), 33.28 (t'), 40.06 (d'), 40.91 (t'), 52.43 (t'), 56.19 (d'), 128.28 (d'), 128.65 (d'), 128.76 (d'), 130.24 (s'), 136.03 (s'), 170.41 (s'), 174.08 (s'), 205.99 (s'); exact mass m/z calcd for $C_{18}H_{20}{}^{81}BrNO_2$ 363.0657, found 363.0668.

(1α,3aα,5β)-2-Acetyl-1-(3-bromopropyl)-1,2,3,3a,4,5-hexahydro-6-phenylcyclopenta[*c*]pyrrol-5-ol (24). The procedure for the preparation of **11** was followed, using crude **23** (83 mg, 0.23 mmol) in MeOH (10 mL), $CeCl_3{\cdot}7H_3O$ (128 mg, 0.34 mmol), and $NaBH_4$ (13 mg, 0.34 mmol). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 4% MeOH–EtOAc, gave **24** (80.5 mg, 96%) as a colorless oil that was probably a mixture of two rotamers [^{13}C NMR (100.6 MHz)]: FT-IR (CH_2Cl_2 cast) 3540–3120, 1621, 1444, 1425 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48–1.80 (m, 5 H), 1.93–2.12 [m, including s (3 H) at δ 2.08, 4 H], 2.84 (dt, J = 12.4, 6.9 Hz, 1 H), 3.09–3.24 (m, 3 H), 3.38–3.46 (m, 1 H), 3.89 (t, J = 8.4 Hz, 1 H), 5.03–5.11 (m, 1 H), 5.46–5.54 (m, 1 H), 7.21–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.59 (q'), 29.05 (t'), 32.05 (t'), 33.46 (t'), 40.34 (t'), 44.45 (d'), 53.49 (t'), 55.21 (d'), 81.95 (d'), 127.57 (d'), 127.67 (d'), 128:71 (d'), 134.09 (s'), 136.26 (s'), 143.57 (s'), 170.07 (s'); exact mass m/z calcd for $C_{18}H_{22}{}^{81}BrNO_2$ 365.0813, found 365.0827.

(3aα,5aβ,7α,8α,8aR*)-4-Acetyldecahydro-8-phenyldicyclopenta[*b,c*]pyrrol-7-ol (25). The general procedure for radical cyclization was followed using **24** (76.0 mg, 0.208 mmol) in benzene (10 mL), Bu_3SnH (0.083 mL, 0.312 mmol) in benzene (5 mL), and AIBN (17 mg, 0.10 mmol) in benzene (5 mL). Flash chromatography of the crude product over silica gel (2 × 20 cm), using 2.5% MeOH–EtOAc, gave **25**, containing a small amount of tributyltin species. The material was purified by flash chromatography over neutral alumina (1 × 15 cm), using 2.5% MeOH–EtOAc, to give **25** (43 mg, 72%) as a mixture (67:33) of two rotational isomers, at least in solution [^{1}H NMR (400 MHz)]: mp 149–153 °C; FT-IR (CH_2Cl_2 cast) 3560–3120, 2934, 2868, 1620, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31–1.54 (m, 4 H), 1.60 (br d, J = 11.4 Hz, 0.67 H), 1.67 (br d, J = 10.8 Hz, 0.33 H), 1.69–1.87 (m, 2 H), 2.06 (s, 3 × 0.33 H), 2.08 (s, 3 × 0.67 H), 2.22 (br s, 1 H), 2.38–2.53 (m, 2 H), 2.97 (d, J = 4.1 Hz, 0.67 H), 3.01 (d, J = 4.3 Hz, 0.33 H), 3.45 (dd, J = 12.3, 7.0 Hz, 0.67 H), 3.56 (br d, J = 10.8 Hz, 0.33 H), 3.70 (dd, J = 10.8, 7.1 Hz, 0.33 H), 4.01 (d, J = 12.0 Hz, 0.67 H), 4.38–4.43 (m, 0.33 H), 4.43-4.47 (m, 0.67 H), 4.50–4.54 (m, 0.67 H), 4.84 (br d, J = 6.4 Hz, 0.33 H), 7.25–7.37 (m, 3 H), 7.42–7.46 (m, 2 × 0.33 H), 7.49–7.54 (m, 2 × 0.67 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.06 (q'), 23.00 (q'), 24.66 (t'), 24.99 (t'), 34.56 (t'), 35.86 (t'), 39.06 (t'), 39.23 (t'), 42.17 (t'), 43.20 (t'), 48.51 (d'), 49.83 (d'), 53.04 (t'), 55.56 (t'), 58.98 (d'), 59.45 (d'), 63.21 (d'), 63.52 (s'), 64.50 (d'), 65.42 (s'), 75.80 (d'), 75.98 (d'), 126.97 (d'), 127.03 (d'), 128.32 (d'), 128.48 (d'), 130.45 (d'), 130.53 (d'), 138.14 (s'), 138.92 (s'), 168.75 (s'), 169.41 (s'); exact mass m/z calcd for $C_{18}H_{23}NO_2$ 285.1729, found 285.1728.

(3aα,5aβ,7α,8α,8aR*)-4-Ethyldecahydro-8-phenyldicyclopenta[*b,c*]pyrrol-7-ol (28). $LiAlH_4$ (1.6 mg, 0.041 mmol) was added to a solution of **25** (5.9 mg, 0.021 mmol) in ether 10 mL. The mixture was refluxed for 15 h and then cooled to room temperature. Water (5 mL) was added, and the layers were separated. The aqueous layer was extracted with ether (1 × 5 mL), and the combined ether layers were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (0.5 × 10 cm), using 5% MeOH–CH_2Cl_2, gave **28** (5.6 mg, 99%) as a colorless oil: FT-IR (CH_2Cl_2 cast) 3300–2600 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08–1.18 [m, including t (J = 7.6 Hz, 3 H) at δ 1.11, 4 H], 1.32–1.44 (m, 2 H), 1.54-1.76 (m, 4 H), 1.80 (dt, J = 11.2, 8.0 Hz, 1 H), 2.19–2.33 (m, 2 H), 2.50–2.70 (m, 3 H), 2.80 (br d, J = 8.8 Hz, 1 H), 2.89 (d, J = 3.2 Hz, 1 H), 3.47 (dd, J = 8.7, 4.8 Hz, 1 H), 4.19–4.29 (m, 1 H), 7.20–7.47 (m, 3 H), 7.63–7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.35, 23.16, 25.68, 38.16, 43.89, 44.41, 48.56, 57.59, 59.18, 64.05, 64.96, 76.19, 126.19, 127.81, 130.60; exact mass m/z calcd for $C_{18}H_{25}NO$ 271.1936, found 271.1934.

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Supplementary Material Available: Annotated scheme showing the preparation of **29** and **30** as well as NMR spectra for compounds that were not analyzed (64 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.