Acyl Radicals: Intermolecular and Intramolecular Alkene Addition Reactions

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A full study of the use of phenyl selenoesters as precursors to acyl radicals and their subsequent participation in intermolecular and intramolecular alkene addition reactions is detailed. Primary alkyl-, vinyl-, and aryl-substituted acyl radicals generated by Bu_3SnH treatment of the corresponding phenyl selenoesters participate cleanly in intermolecular addition reactions with alkenes bearing electron-withdrawing or radical-stabilizing substituents at rates that exceed those of the potentially competitive decarbonylation or reduction. Similarly, their intramolecular addition to activated or unactivated alkenes proceeds without significant competitive reduction or decarbonylation and at rates generally $\geq 1 \times 10^6$ s^{-1} with some occurring at rates $\geq 3 \times 10^7$ s^{-1}. Consistent with their behavior in intermolecular addition reactions, the 5-*exo*-*trig* cyclizations of secondary and tertiary alkyl-substituted acyl radicals to an unactivated olefin acceptor may be accompanied by varying degrees of decarbonylation, even under low-temperature free-radical reaction conditions. Studies are presented which suggest that the intramolecular additions of acyl radicals to alkenes under the conditions detailed herein may be regarded as irreversible, kinetically controlled processes which exhibit regioselectivity that is predictable based on well-established empirical rules set forth for the analogous free-radical cyclization reactions of alkyl radicals.

The generation of acyl radicals and their reaction with alkenes has long been recognized as a useful and practical method of carbon–carbon bond formation.[1-8] Since the initial report of the peroxide-initiated free radical addition of aldehydes to simple olefins,[9] the method was extended to the more productive use of electron-deficient alkenes.[10] Additional free-radical chain initiation methods have been introduced,[11] the use of acyl equivalents has been detailed,[19] and selected examples of intramolecular acyl radical–alkene addition reactions have been described.[13-19] The reemergence of acyl radicals as fundamental, functionalized free radicals has renewed interest in the development of methods for their productive generation. Herein, we report full details of a study of the generation of acyl radicals from phenyl selenoesters[20-22] and the scope of their participation in intermolecular and intramolecular alkene addition reactions.[23-26]

Intermolecular Alkene Addition Reactions. Primary alkyl-, vinyl-, and aryl-substituted acyl radicals generated by tri-*n*-butyltin hydride (Bu_3SnH) treatment of the corresponding phenyl selenoester were found to participate in productive intermolecular alkene addition reactions. The aryl acyl radicals generated by treatment of the phenyl selenoesters **1a–c** with Bu_3SnH exhibit nucleophilic character[9,10] and were found to react most productively with alkenes bearing electron-withdrawing or radical-stabilizing groups, eq 1 and Table I. The addition products **3** were formed in high yields (53–74%) with little or no competitive acyl radical reduction (0–5%)[27] or decarbonylation (0%) in reactions that proved surprisingly independent of additional alkene substitution (Table I, entries 4–6). More important was the observation that the slow rate of aryl acyl radical reduction[27] allowed the use of standard solution reaction conditions (method B: 1.3 equiv of Bu_3SnH, 0.1 equiv of AIBN, C_6H_6, 80 °C) for the intermolecular alkene addition reactions and provided results comparable to those obtained under reaction conditions that minimize the effective Bu_3SnH concentration (method A: syringe pump 1 h addition of 1.3 equiv of

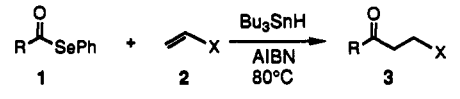

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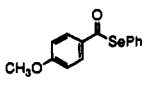
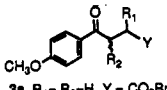
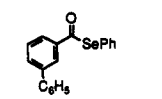
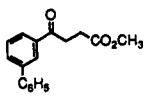
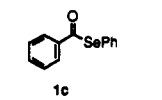
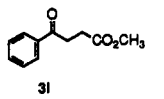
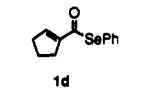
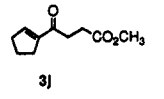
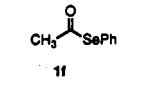
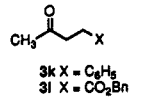
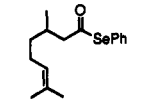
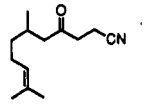
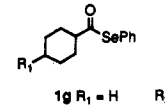
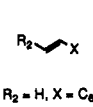
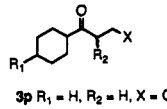
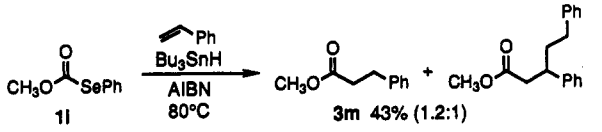
Table I. Intermolecular Acyl Radical–Alkene Addition Reactions

entry	phenyl selenoester	alkene	product	method[a]	yield[b] %
1	 1a		 3a R_1= R_2=H, Y = CO_2Bn	A	60
2			3b R_1= R_2=H, Y = CN	A	64
3			3c R_1= R_2=H, Y = C_6H_5	A	71
				B	64
4			3d R_1= H, R_2= CH_3, Y = CO_2CH_3	A	76
5			3e R_1= CH_3, R_2=H, Y = CO_2CH_3	A	55
6			3f R_1= $OSiMe_3$, R_2=H, Y = CO_2CH_3	A	54
7			3g R_1= R_2=H, Y = CO_2CH_3	A	54
8	 1b		 3h	A	62
9	 1c		 3i	A	58
10	 1d		 3j	A	68
11	 1f		 3k X = C_6H_5	B[e]	51
12			3l X = CO_2Bn	B	46
13	 1e		 3o	A[c]	71
14				A[d]	57
15	 1g R_1 = H	 R_2 = H, X = C_6H_5	 3p R_1 = H, R_2 = H, X = C_6H_5	B[e]	55
16				C[e]	54
17		R_2 = CH_3, X = CO_2CH_3	3q R_1 = H, R_2 = CH_3, X = CO_2CH_3	A	20
18					29
19	1h R_1 = tBu	R_2 = H, X = CO_2CH_3	3r R_1 = tBu, R_2 = H, X = CO_2CH_3	B	30

[a] 5.0 equiv of alkene. Method A: 0.1 equiv of AIBN, 0.2 M in benzene, 80 °C, slow addition (1 h) of 1.3 equiv of *n*-Bu_3SnH. Method B: 0.1 equiv of AIBN, normal addition of 1.3 equiv of *n*-Bu_3SnH, benzene, 80 °C. Method C: 0.1 equiv of AIBN, 1.3 equiv of *n*-Bu_3SnH, benzene, 25 °C, 275-W sunlamp irradiation. [b] All yields are based on pure material isolated by flash chromatography (SiO_2). [c] Reaction conducted with concentration of **1e** = 0.1 M. [d] Reaction conducted with concentration of **1e** = 0.01 M. [e] 2.5 equiv of alkene.

Bu_3SnH, 0.1 equiv of AIBN, C_6H_6, 80 °C), Table I. As anticipated, the reactions of the acyl radical derived from Bu_3SnH treatment of **1a** with electron-rich or neutral olefins including ethyl vinyl ether (18%), 1-octene (27%), allyl acetate (32%), cyclohexene (0%), and cyclohexenone (24%) provided low yields of the intermolecular alkene addition products accompanied by substantial amounts of 4-methoxybenzaldehyde (61–80%).

Similarly, treatment of the phenyl selenoesters **1d–f** with Bu_3SnH in the presence of alkenes substituted with activating groups (Table I, entries 10–14) provided the intermolecular alkene addition products (46–71%) with no evidence of primary or vinyl acyl radical reduction or decarbonylation. Moreover, the intermolecular addition reactions with activated alkenes proceeded at rates that exceed intramolecular 6-*exo-trig* addition to an unactivated alkene even under conditions (0.01 M) which would be expected to favor intramolecular addition over the bimolecular addition reaction (Table I, entry 14). In contrast, Bu_3SnH treatment of phenyl selenoesters **1g–h** in the presence of alkenes provided the addition products **3** in modest yields (20–55%) with no evidence of reduction but with evidence of competitive decarbonylation. Thus, Bu_3SnH treatment (method A) of **1h** in the presence of methyl acrylate provided the addition product **3r** (30% isolated) and *tert*-butylcyclohexane in a 1.4:1 ratio (GLC). Consistent with the well-defined relative rates of decarbonylation of acyl radicals (benzyl/allyl > tertiary > secondary ≫ primary ≫ aryl),[21] competitive decarbonylation and subsequent reduction of secondary acyl radicals were found to compete with intermolecular addition reactions to activated acceptor alkenes even under low temperature reaction conditions (method C: 25 °C, photochemical initiation).



(2)

In contrast to the results detailed above and the success of the intramolecular alkene addition reactions of alkoxycarbonyl radicals,[19] phenyl selenocarbonate **1i** proved to be a less dependable substrate for intermolecular alkene addition reactions, eq 3. Thus, although **1i** affords nearly equal amounts of mono- and bis-adducts **3m** with styrene as the alkene acceptor, the comparable reaction with benzyl acrylate provided the tri-*n*-butyltin addition product **4** with no evidence for formation of **3n**. Presumably, the alkoxycarbonyl radical generation from **1h** is slower or different[28] than that of aliphatic and aryl acyl radical generation.

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(19) Several acyl radical equivalents have been described: (a) Imidoyl radicals: Bachi, M. D.; Denenmark, D. *J. Am. Chem. Soc.* **1989**, *111*, 1886. (b) Dithioacetal radicals: Nishida, A.; Nishida, M.; Yonemitsu, O. *Tetrahedron Lett.* **1990**, *31*, 7035. Barton, D. H. R.; Clive, D. L. J.; Magnus, P. D.; Smith, G. *J. Chem. Soc. C* **1971**, 2193.

(20) The phenyl selenoesters described herein were prepared from the corresponding carboxylic acids using one of four different methods. (a) *N*-phenylselenophthalimide and tri-*n*-butylphosphine (THF, 25 °C), cf.: Grieco, P. A.; Jaw, J. Y.; Claremon, D. A.; Nicolaou, K. C. *J. Org. Chem.* **1981**, *46*, 1215. (b) Diphenyl selenide and tri-*n*-butylphosphine (THF, 25 °C), cf.: Masamune, S.; Hayase, Y.; Schilling, W.; Chan, W. K.; Bates, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 6756–6758. (c) (1) Oxalyl chloride; (2) selenophenol and pyridine (ether, 0 °C). (d) (1) Diethylchlorophosphate, Et_3N (THF, 25 °C); (2) NaSePh (THF, 25 °C).

(21) (a) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200. (b) Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 2555. (c) Schuh, H.; Hamilton, E. J., Jr.; Paul, H.; Fischer, H. *Helv. Chim. Acta* **1974**, *57*, 2011. (d) Lunazzi, L.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1983**, *87*, 529. (e) Gould, I. R.; Baretz, B. H.; Turro, N. J. *Ibid.* **1987**, *91*, 925. (f) Kerr, J. A.; Lloyd, A. C. *Trans. Faraday Soc.* **1967**, *63*, 2480. (g) Watkins, K. W.; Thompson, W. W. *Int. J. Chem. Kinet.* **1973**, *5*, 791.

(22) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328. Ryu, I.; Kusano, K.; Masumi, N.; Yamazaki, H.; Ogawa, A.; Sonoda, N. *Tetrahedron Lett.* **1990**, *31*, 6887.

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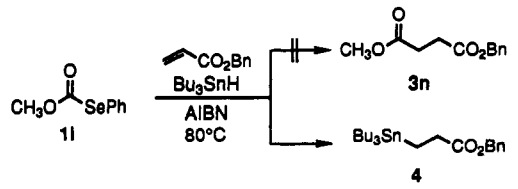
(24) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1989**, *54*, 1777.

(25) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4008.

(26) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003.

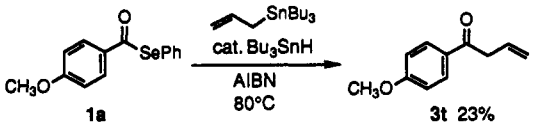
(27) The reaction of **1b** with *n*-Bu_3SnH (1.3 equiv, benzene, 80 °C, 0.05 equiv of AIBN) in the absence of alkene provided a 74% isolated yield of biphenyl-3-carboxaldehyde accompanied by 12% of biphenyl. The rate of intermolecular hydrogen abstraction from Bu_3SnH by the acetyl radical has been estimated to be at least ten times slower than hydrogen abstraction by alkyl radicals (ca. 2×10^6 s^{-1}). See: Lusztyk, J.; Lusztyk, E.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 2923.

(28) Enholm, E. J.; Prasad, G. *Tetrahedron Lett.* **1989**, *30*, 4939. Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron Lett.* **1990**, *31*, 3991.



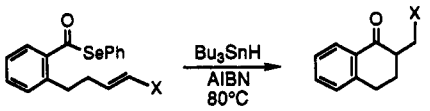
(3)

Attempts to extend the intermolecular addition of the acyl radical derived from **1a** to a self-propagating Bu_3SnH-catalyzed addition–elimination reaction proved only moderately successful, eq 4. Even under optimal conditions, the self-terminating intermolecular addition reactions were sluggish and inevitably resulted in incomplete consumption of phenyl selenoester **1a** presumably due to the premature termination of the free-radical chain reaction.



(4)

Intramolecular Alkene Addition Reactions. A wide variety of functionalized precursors suitable for initiation of intramolecular free-radical cyclization reactions have been introduced and include α-acylamino sulfides and selenides,[29] β-bromo acetals,[30] vinyl bromides and iodides,[31] and α-bromo or α-seleno ketones and esters.[32] Surprisingly, at the onset of our efforts only selected and isolated reports of the intramolecular alkene addition reactions of acyl radicals had been described despite their potential as a fundamental functionalized free radical.[13-19] Complementary to the concurrent efforts of Crich,[13] Bachi,[15] and Zard,[14] we have examined the scope of the intramolecular cyclization reactions of acyl radicals generated from phenyl selenoesters with substrates possessing a full range of proximal, unsaturated functionality (C=C, C≡C, C=N, C≡N). The results of our studies employing substrates bearing unactivated or activated alkenes are summarized in Table II. The intramolecular alkene addition reactions of the acyl radicals generated from phenyl selenoesters proceed efficiently, with little or no competitive reduction or decarbonylation, and more effectively than the corresponding reactions employing acid chlorides[17] or phenyl thioesters as precursors (entries 2 and 3). The intramolecular alkene addition reactions of the acyl radicals proved insensitive to the nature of the acceptor alkene and electron-deficient (C=$CHCO_2R$), unactivated (C=CH_2), and electron-rich (C=CHOR) π-systems serve as suitable acceptor groups. In the absence of directing functionality, the intramolecular acyl radical–alkene addition reactions follow a well-defined and useful level of regioselectivity: 5-*exo-trig* > 6-*endo-trig*, 6-*exo-trig* > 7-*endo-trig*, 7-*exo-trig* > 8-*endo-trig*. The exceptions to these generalizations represent predictable instances where the extent of the olefin substitution decelerates the preferred mode of cyclization, cf. Table II, entries 13 and 15. As anticipated based on earlier studies,[9,10] the intermediate acyl radicals derived from phenyl selenoesters undergo intramolecular cyclization reactions most effectively when the olefin acceptor is substituted with an electron-withdrawing substituent, eq 5. However, the six-membered-ring formation from **25g**[34] by intramolecular addition to an electron-rich alkene is notable and highlights the versatility of acyl radicals generated in this manner.



(5)

25e X = CO_2CH_3 **26e** X = CO_2CH_3 84%
25b X = H **26b** X = H 76%
25g X = OCH_3 **26g** X = OCH_3 64%

Reduction versus Cyclization. Although the majority of the cyclization reactions presented herein were conducted under conditions which minimize the effective hydride concentration (method A: syringe pump addition of 1.2 equiv of Bu_3SnH, 0.1 equiv of AIBN, C_6H_6, 80 °C), the slow rate[27] of intermolecular acyl radical hydrogen atom abstraction from Bu_3SnH permits the use of standard reaction conditions (method B: 1.2 equiv of Bu_3SnH, 0.1 equiv of AIBN, C_6H_6, 80 °C, 1–2 h) without recourse to syringe–pump techniques. Thus, in the cases examined, a comparable (Table II, entries 4–5 and 18–19) or considerably improved (entries 25–26) yield of product was obtained using standard reaction conditions without observation of competitive acyl radical reduction.

In contrast, treatment of phenyl selenoesters **33**[35] and **35**[36] under the normal conditions did not produce the anticipated cyclic products but rather provided aldehydes **34** and **36** resulting from direct reduction of the aryl acyl selenide, eq 6. The lack of observation of 6-*exo-dig* cyclization of sp^2-hybridized free radicals has been previously documented and has been attributed to an unfavorable approach trajectory for effective intramolecular addition of the free radicals.[13] Similarly, the nitrile acceptor moiety proved unreactive in 5-*exo-* and 7-*exo-dig* acyl radical cyclizations and Bu_3SnH treatment of **37** and **39**[37] gave rise to reduced products **38** and **40** upon attempted acyl radical cyclization, eqs 7–8.[38-40]

(29) (a) Hart, D. J.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1982**, *104*, 1430. (b) Choi, J.-K.; Burnett, D. A.; Hart, D. J.; Tsai, Y.-M. *Ibid.* **1984**, *106*, 8201. (c) Keck, G. E.; Enholm, E. J. *Tetrahedron Lett.* **1985**, *26*, 3311.

(30) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741.

(31) (a) Stork, G. *Selectivity: A Goal for Synthetic Efficiency*; Bartmann, W., Trost, B. M., Eds.; Verlag-Chemie: Weinheim, 1984; p 281. (b) Stork, G. *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon Press: Oxford, 1983; p 359.

(32) (a) Clive, D. L. J.; Cheshire, D. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1520. (b) Ihara, M.; Taniguchi, N.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1438. (c) Stork, G.; Mah, R. *Heterocycles* **1989**, *28*, 723.

(33) Full experimental details for the preparation of the carboxylic acid precursors to **25b–f** and **29** are provided in the supplementary material.

(34) Phenyl selenoester **25g** was prepared from α-tetralone, and experimental details are provided in the supplementary material.

(35) The carboxylic acid precursor to **33** was prepared by lithiation of 2-(2-methylphenyl)-4,4-dimethyl-Δ^2-oxazoline and subsequent treatment with 3-bromo-1-phenylpropyne followed by N-alkylation (MeI, CH_3NO_2) and hydrolysis (aqueous NaOH). Full details are provided in the supplementary material.

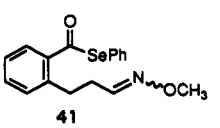
(36) Phenyl selenoester **35** was prepared from α-tetralone, and experimental details are provided in the supplementary material.

(37) Phenyl selenoester **39** was prepared from β-tetralone, and full experimental details are provided in the supplementary material.

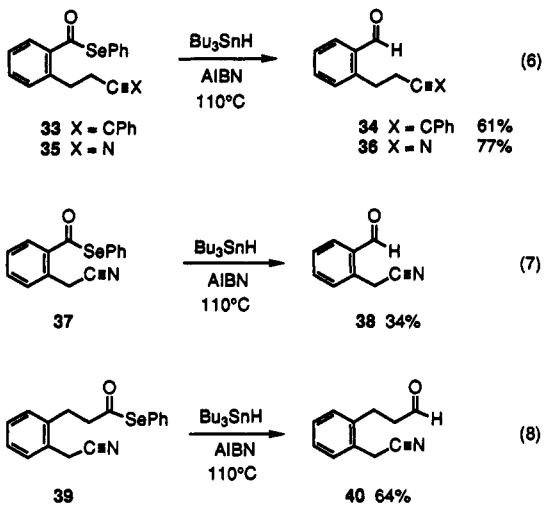
(38) The reactions of phenyl selenoesters **33**, **35**, **37**, and **39** with Bu_3SnH required temperatures (110 °C, toluene) in excess of that which was sufficient to effect the majority of the cyclization reactions described herein (80 °C, benzene). These reactions were sluggish and invariably required additional aliquots of AIBN and/or extended reaction times (3–6 h) to effect significant conversion to the observed reduction products.

(39) Chenera, B.; Chuang, C.-P.; Hart, D. J.; Hsu, L.-Y. *J. Org. Chem.* **1985**, *50*, 5409 and references cited therein.

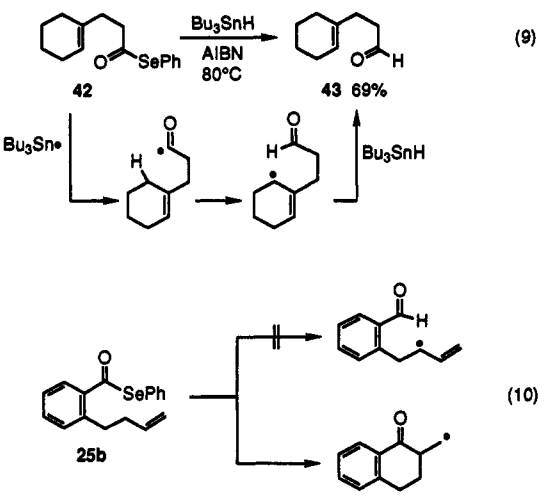
(40) A single attempt at intramolecular acyl radical addition to an oxime ether was unsuccessful. Treatment of **41** with Bu_3SnH and AIBN at 80 °C or 110 °C afforded only recovered starting material (51–60%) without production of identifiable cyclic products. For examples of intramolecular additions of alkyl radicals to oxime ethers, see: Bartlett, P. A.; McLaren, K. L.; Ting, P. C. *J. Am. Chem. Soc.* **1988**, *110*, 1633.



41

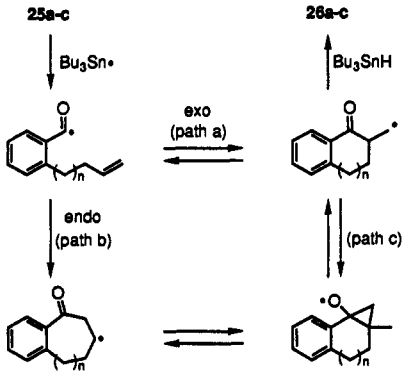


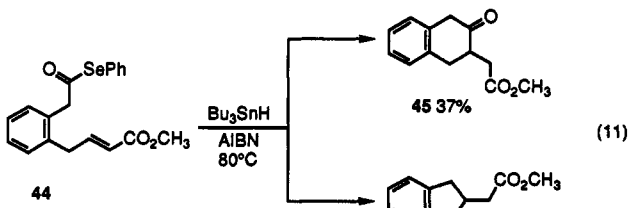
In only one example of an attempted acyl radical–alkene cyclization was competitive reduction of the intermediate acyl radical observed. This case represented an effort to promote a geometrically unfavorable acyl radical cyclization reaction with an unactivated alkene (5-*endo-trig* or 4-*exo-trig* cyclization) contained within a substrate **42**[41] possessing an allylic hydrogen atom five atoms removed from the acyl radical center, eq 9. This combination of a particularly slow intramolecular addition reaction and a strategically located allylic hydrogen atom permitted intramolecular hydrogen atom transfer to effectively compete with cyclization.[42,43] With the common cyclization reactions, this potentially competitive allylic hydrogen atom transfer reaction as well as the intermolecular hydrogen atom abstraction reaction with tri-*n*-butyltin hydride were not observed even with substrates bearing unactivated acceptor alkenes, e.g., eq 10.[44]

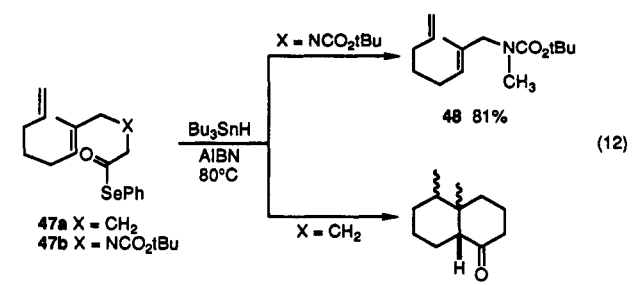


Decarbonylation versus Cyclization. Decarbonylation of acyl radicals can be a more serious competitive side reaction. Prior studies have established that the rates of decarbonylation of acyl radicals (at 80 °C) differ by several orders of magnitude (benzylic, allylic,[21d,e] (6–2.5) × 10^7 s^{-1}; tertiary,[21c] 1.4 × 10^6 s^{-1}; secondary,[21b] 8.4 × 10^5 s^{-1}; primary,[21f,g] (7.5–15) × 10^4 s^{-1}). Given the expectation that the rate of intramolecular acyl radical–unactivated alkene addition reactions would lie in the range of ca. 10^5–10^6 s^{-1} for the common cyclization modes (5-, 6-, 7-*exo-trig*), it can be anticipated that only systems capable of providing stabilized radicals will suffer from a potentially competitive decarbonylation reaction. Consistent with this expectation, **44**[45] provided a 1:1 mixture of **45** and **46** illustrating that the intramolecular 6-*exo-trig* cyclization of an acyl radical with an activated acrylate acceptor proceeds at a near identical rate as decarbonylation of a benzylic acyl radical (rate: 2.5 × 10^7 s^{-1}),[21d,e] eq 11. Similarly, although 6-*endo-trig* cyclization of the primary acyl radical generated from **47a** (X = CH_2) proceeds without competitive decarbonylation,[25] the decarbonylation reaction of the acyl radical derived from **47b** (X = NCO_2tBu)[46] to provide the heteroatom-stabilized primary radical precluded the observation of 6-*endo-trig* cyclization, eq 12. Thus, the rate of 6-*endo-trig* cyclization of primary acyl radicals with unactivated alkenes proved to be slower than decarbonylation of α-heteroatom-substituted acyl radicals.[47]

Scheme I







(41) Phenyl selenoester **42** was prepared from 1-(2-hydroxyethyl)-cyclohexene by one-carbon homologation (MsCl, Et_3N; NaCN, DMSO; aqueous KOH) followed by phenyl selenoester generation (supplementary material).

(42) Although the intramolecular allylic hydrogen atom transfer may not be expected to compete with 5-*exo* or 6-*endo-trig* cyclizations of acyl or alkyl radicals, this pathway can effectively compete with 6-*exo-trig* cyclizations of 6-heptenylicals, cf.: Leonard, W. R.; Livinghouse, T. *Tetrahedron Lett.* **1985**, *26*, 6431.

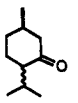
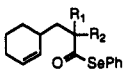
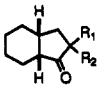
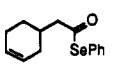
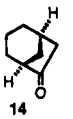
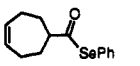
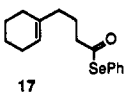
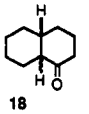
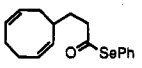
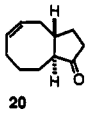
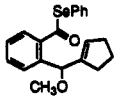
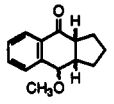
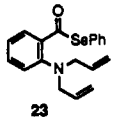
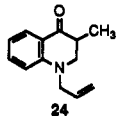
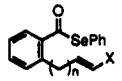
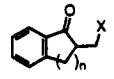
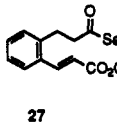
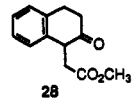
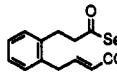
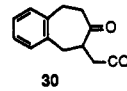
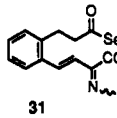
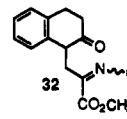
(43) The indirect generation and subsequent cyclization of alkyl radicals by 1,5-hydrogen atom abstraction has been described. See: Curran, D. P.; Kim, D.; Liu, H. T.; Shen, W. *J. Am. Chem. Soc.* **1988**, *110*, 5900. Snieckus, V.; Cuevas, J.-C.; Sloan, C. P.; Liu, H.; Curran, D. P. *Ibid.* **1990**, *112*, 896. Lathbury, D. C.; Parsons, P. J.; Pinto, I. *J. Chem. Soc., Chem. Commun.* **1988**, 81.

(44) Bachi, M. D.; Denenmark, D. *Heterocycles* **1989**, *28*, 583.

(45) Phenyl selenoesters **27** and **44** were prepared from β-tetralone, and experimental details are provided in supplementary material.

(46) Full experimental details for the preparation of the carboxylic acid precursor to **47b** are provided in the supplementary material.

Table II. Intramolecular Acyl Radical–Alkene Addition Reactions

entry	phenyl selenoester[a]	product	method[b]	% yield[c]
1	1e X=SePh		A	84[d]
2	1k X=SPh	6	A	NR[e]
3	1l X=Cl		A	59
4	 7 R_1= R_2= H	 8 R_1= R_2= H	A	86
5			B	76
6	9 R_1= CH_3, R_2= H	10 R_1= CH_3, R_2= H	A	68
7			C	59
8	11 R_1= R_2= CH_3	12 R_1= R_2= CH_3	A	49
9			C	51
10	 13	 14	A	69
11	 15	 16	A	58
12			C	48
13	 17	 18	A	82[f]
14	 19	 20	A	79
15	 21	 22	A	86
16	 23	 24	A	69
17	 25a n = 1, X = H	 26a n = 1, X = H	A	81
18	25b n = 2, X = H	26b n = 2, X = H	A	76
19			B	81
20	25c n = 3, X = H	26c n = 3, X = H	A	74
21	25d n = 1, X = CO_2CH_3	26d n = 1, X = CO_2CH_3	A	88
22	25e n = 2, X = CO_2CH_3	26e n = 2, X = CO_2CH_3	A	84
23	25f n = 3, X = CO_2CH_3	26f n = 3, X = CO_2CH_3	A	92
24	25g n = 2, X = OCH_3	26g n = 2, X = OCH_3	A	64
25	 27	 28	A	83
26			B	93
27	 29	 30	A	71
28	 31	 32	A	64

[a] For the preparation of phenyl selenoesters **25b–f**, **27**, and **29**, see refs 33 and 45. [b] Method A: 0.1 equiv of AIBN, 0.01 M in benzene, 80 °C, slow addition (1 h) of 1.2 equiv of *n*-Bu_3SnH. Method B: 0.1 equiv of AIBN, normal addition of 1.2 equiv of *n*-Bu_3SnH, benzene, 80 °C. Method C: 0.1 equiv of AIBN, 1.2 equiv of *n*-Bu_3SnH, benzene, 25 °C, photochemical initiation. [b] All yields are based on pure material isolated by flash chromatography (SiO_2). [d] 56:44 trans:cis ratio determined by gas chromatography. [e] No reaction. [f] 62:38 trans:cis ratio by gas chromatography.

The results of additional studies conducted in order to assess the relative rates of decarbonylation of acyl radicals possessing alkyl substituents in the α-position are summarized in Table II (entries 4–9) and provide further insight into the synthetic scope of acyl radical cyclization reactions. The isolated yields of products resulting from 5-*exo-trig* cyclization of the acyl radicals derived from **7**, **9**, and **11**[48] decreased slightly on increased α-substitution in accord with the expectation[21] of increased decarbonylation rates to generate successively more stable secondary and tertiary radicals (Scheme I). Nevertheless, useful yields of cyclic ketones were obtained under standard free-radical cyclization conditions. Similarly, the 5-*exo-trig* cyclization of the acyl radical derived from **15** proceeds at a rate which exceeds that of decarbonylation of a secondary alkyl-substituted acyl radical (8.4×10^5 s^{-1})[21b] and thus constitutes a convenient route to a range of bicyclic frameworks exemplified by **16** (Table II, entries 11–12). The employment of low-temperature, photochemical initiation conditions (method C) for the generation and subsequent cyclization of acyl radicals derived from the same substrates failed to improve the isolated yields of cyclic products as might be expected based on the well-documented temperature dependence observed for the rates of decarbonylation of acyl radicals.[21,22,49]

6-*Endo*- versus 5-*Exo*-*Trig* Cyclization. The preference for 5-hexenyl radicals to undergo predominant 5-*exo-trig* free-radical cyclizations is well documented[50] and has been attributed to a variety of factors including stereoelectronic,[50a–c] steric,[50g] and/or entropic[50h] effects, each of which favors the formation of 5-membered-ring products

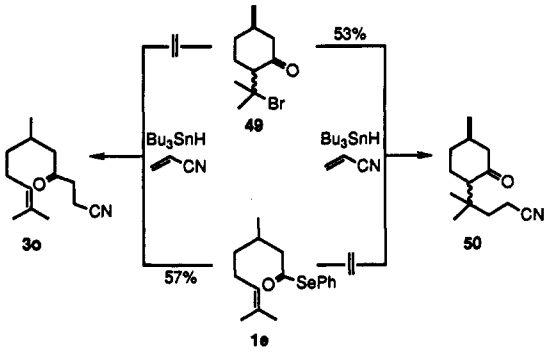
(47) Arrhenius parameters for the decarbonylation of the 2-hydroxy-2-methylpropanoyl radical have been determined (Lehni, M.; Fischer, H. *Int. J. Chem. Kinet.* **1983**, *15*, 733) and predict a decarbonylation rate of 6.4×10^6 s^{-1} at 80 °C. Thus, the decarbonylation of a α-hydroxy-substituted acyl radical is roughly six times faster than decarbonylation of its unsubstituted counterpart ($k = 1 \times 10^6$ s^{-1}; ref 21b).

(48) The carboxylic acid precursors to **9** and **11** were prepared by successive alkylations (LDA, THF–HMPA, –78 °C; MeI) of ethyl 3-(3-cyclohexenyl)propionate. Full details are provided in the supplementary material.

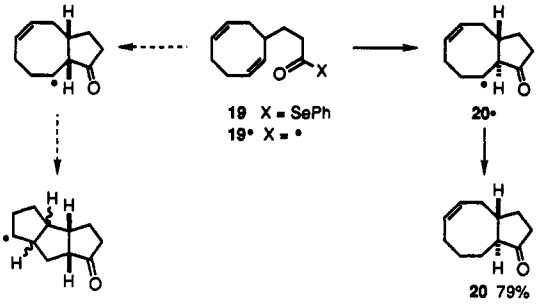
(49) Decarbonylation of the propanoyl radical is predicted to occur at a rate of (1–2) $\times 10^4$ s^{-1} at 80 °C and 250–500 s^{-1} at 25 °C; see refs. 21f,g.

(50) (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925. (c) Beckwith, A. L. J.; Lawrence, T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1535. (d) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* **1981**, *22*, 2811. (e) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. (f) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, 2251. (g) Julia, M.; Descoins, C.; Baillarge, M.; Jacquet, B.; Uguen, D.; Groeger, F. A. *Tetrahedron* **1975**, *31*, 1737. (h) Bischof, P. *Tetrahedron Lett.* **1979**, 1291.

Scheme II

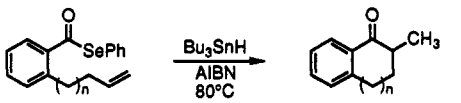


Scheme III



in the irreversible free-radical cyclizations. In these efforts, the mechanistic and synthetic studies have provided valuable, qualitative guidelines which allow the prediction of the regioselectivity of 5-hexenyl radical cyclizations.

Consistent with empirical rules for alkyl free-radical cyclizations, the intramolecular additions of acyl radicals to unsubstituted alkenes were found to exhibit exceptional regioselectivity favoring cyclization in the *exo* mode. For example, 5-*exo*, 6-*exo*, and 7-*exo* cyclizations are observed to the exclusion of significant amounts of 6-, 7-, and 8-*endo* cyclization, eq 13, despite the absence of directing func-



25a n = 0
25b n = 1
25c n = 2

26a n = 0 81%
26b n = 1 76%
26c n = 2 74%

tionality and the potential for thermodynamic partitioning of the intermediate primary alkyl radicals to the more stable secondary alkyl radicals through a reversible acyl radical cyclization (path a) or an intramolecular cyclopropyloxy rearrangement (path c, Scheme I).[51]

In contrast, the 5-hexenoyl radical generated from 5-hexenoyl chloride has been reported[17,52] to afford mixtures of 2-methylcyclopentanone and cyclohexanone, and the relative yields of cyclohexanone were variable but consistently higher than the proportion of product resulting from 6-*endo-trig* cyclization of the analogous 5-hexenyl radical.[53] The observation that the benzoyl peroxide initiated cyclization of 5-hexenal in cyclohexane at 80 °C afforded cyclohexanone as the only cyclic product led to the proposal that the enhanced amount of 6-*endo-trig* cyclization product can be attributed in part to reversion of the intermediate cyclopentanone-2-methylcarbinyl radical to the starting 5-hexenoyl radical.[52] Since acyl radicals are expectedly more stabilized than their alkyl radical counterparts,[54] the potential reversibility of their cyclization reactions with alkenes lacking directing substituents is reasonable.[27] However, the additional studies detailed below address the potential of a reversible acyl radical–alkene addition reaction and suggest that intramolecular alkene addition reactions of acyl radicals generated by reaction of phenyl selenoesters with Bu_3SnH proceed under conditions that can be considered irreversible and with a regioselectivity that is predictable based on empirical rules defined for alkyl radicals. Thus, subjecting **49**[55] to standard free radical cyclization conditions (Bu_3SnH, catalytic AIBN, benzene, 80 °C, 0.01 M) in the presence of 4 equiv of acrylonitrile led to the intermolecular addition product **50**, while phenyl selenoester **1e** afforded **3o** under identical reaction conditions (Scheme II). The absence of cyclic product **50** in the latter case highlights the unusual reactivity of acyl radicals in intermolecular additions to electron deficient olefins even under high dilution conditions, while the former observation suggests that an equilibrating, reversible acyl radical–alkene addition reaction is unlikely to be operative in intramolecular acyl radical additions to unactivated alkenes under the Bu_3SnH-mediated conditions.

In addition, Bu_3SnH treatment of phenyl selenoester **19**[56] leads to generation of acyl radical **19•** which undergoes clean 5-*exo-trig* cyclization to deliver predominantly the *trans*-bicyclo[6.3.0]undecenone **20** with little evidence for transannular cyclization of the intermediate bicyclo[6.3.0]undecenyl radical **20•** (Scheme III).[57,58] Since the observation of effective transannular cyclizations with this particular unsubstituted carbon framework has been demonstrated to be limited to substrates which are capable

(51) (a) Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666. Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565. (b) Dowd, P.; Choi, S.-C. *Ibid.* **1987**, *109*, 3493, 6548. Dowd, P.; Choi, S.-C. *Tetrahedron* **1989**, *45*, 77. Dowd, P.; Choi, S.-C. *Tetrahedron Lett.* **1989**, *30*, 6129. (c) Baldwin, J. E.; Adlington, R. M.; Kang, T. W.; Lee, E.; Schofield, C. J. *J. Chem. Soc., Chem. Commun.* **1987**, 104. Baldwin, J. E.; Adlington, R. M.; Robertson, J. *Ibid.* **1988**, 1404.

(52) (a) Julia, M.; Maumy, M.; Mion, L. *Bull. Soc. Chim. Fr.* **1967**, 2641–2642. (b) Julia, M.; Maumy, M. *Ibid.* **1969**, 2415, 2427.

(53) Čekovič reported[17a] that the reaction of 5-hexenoyl chloride (0.40 M in benzene, 80 °C) with Bu_3SnH (1 equiv) and AIBN (initiator) afforded cyclohexanone as the only cyclic product (36% yield). Under identical conditions, Walsh and co-workers[17b] obtained 2-methylcyclopentanone and cyclohexanone in a ratio of 84:16. The 5-hexenyl radical provides a 95:5 ratio of 5-*exo*:6-*endo* cyclization products.[50]

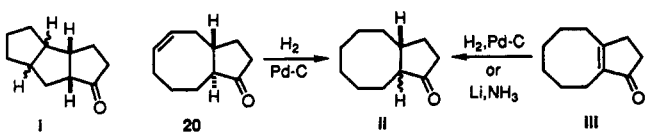
(54) The formation of the acetyl and benzoyl radicals has been characterized as having bond reorganizational energies (E_R) of −7.1 kcal mol^{-1}. Thus, acyl radicals are less stabilized than the benzylic radical (E_R = −13.9 kcal mol^{-1}) but more stabilized than the methoxy radical (E_R = −4.0 kcal mol^{-1}) and the *tert*-butyl radical (E_R = −1.7 kcal mol^{-1}). See: Sanderson, R. T. *J. Org. Chem.* **1982**, *47*, 3835.

(55) Overberger, C. G.; Kaye, H. *J. Am. Chem. Soc.* **1967**, *84*, 5640.

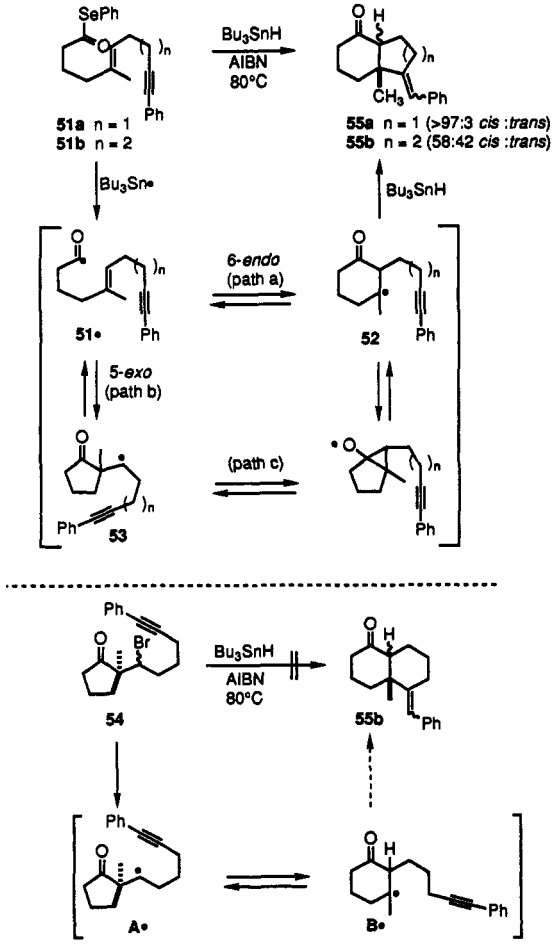
(56) Phenyl selenoester **19** was prepared from 3-(2-hydroxyethyl)-1,5-cyclooctadiene by one-carbon homologation (MsCl, Et_3N; NaCN, DMSO; aqueous KOH) followed by phenyl selenoester formation (N-PSP, Bu_3P). See the supplementary material for full details.

(57) Winkler, J. D.; Sridar, V. *J. Am. Chem. Soc.* **1986**, *108*, 1708; *Tetrahedron Lett.* **1988**, *29*, 6219.

(58) Capillary GC analysis of the crude reaction mixture indicated the presence of 80% of *trans*-**20**, 3% of the cis-fused bicyclic product *cis*-**20**, and two additional products (11% and 6% of total peak area) tentatively assigned the tricyclic structure i. The diastereomeric composition of **20** was unambiguously established by catalytic hydrogenation (H_2, Pd–C, EtOAc, 25 °C) of the free radical cyclization mixture and comparison of GC retention times with authentic sample of *trans*- and *cis*-ii independently prepared from the known enone iii. Full details are provided in the supplementary material.



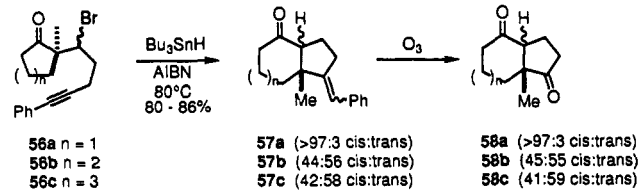
Scheme IV



of participating in an initial reversible 5-*exo-trig* cyclization subject to thermodynamic partitioning to an intermediate cis-fused bicyclic radical, the predominant formation of **20** is consistent with an irreversible 5-*exo* cyclization of acyl radical **19**•.

The intramolecular alkene addition reactions of 5-hexenoyl radicals bearing alkyl substitution at the 5-position results in preferential 6-*endo* cyclization (Table II, entries 13 and 15). The regioselectivity of such cyclization reactions may be attributed to kinetic deceleration of 5-*exo-trig* cyclization (steric effects) and/or acceleration of 6-*endo-trig* cyclization (radical stability).[50] The regiospecific 6-*endo-trig* cyclization of the additional acyl radical generated from **21**[59] further demonstrates the directing effect of an alkyl substituent at the 5-position of such acyl radicals and the stereoisomeric tricyclic products **22** were isolated to the complete exclusion of 5-*exo-trig* cyclization products (Table II, entry 15). The utility of six-membered-ring formation in such systems was recently demonstrated with the clean participation of acyl radicals in tandem cyclization reactions initiated with an initial 6-*endo* cyclization of a 5-substituted 5-hexenoyl radical (Scheme IV).[26] That the initial tertiary alkyl radical **52** results from a direct, 6-*endo-trig* acyl radical cyclization of **51**• (Scheme IV, path a) as opposed to an initial 5-*exo-trig* ring closure (path b) followed by free radical rearrangement of **53** (path c) was experimentally demonstrated by the lack of formation of **55b** upon subjecting **54** to identical free-radical cyclization conditions.

Scheme V



Thus, the intramolecular additions of acyl radicals derived from tributyltin hydride treatment of phenyl selenoesters are consistent with irreversible, kinetically controlled processes which, in the absence of directing functionality, proceed preferentially in the *exo* mode without subsequent rearrangement of the initial intermediate adduct radicals. In cases where *exo* ring closure is sterically decelerated by the presence of olefin substituents, preferential direct *endo* cyclization can be reliably expected.

Tandem Free-Radical Rearrangement and 5-Hexynyl Radical Cyclization: A Free-Radical Cyclopentanone Annulation. In conjunction with the investigation of the potential involvement of a tandem *exo* cyclization–rearrangement and/or reversible acyl radical–alkene addition pathway in the potential thermodynamic equilibration of cyclization products derived from **51** (5-*exo-trig* ⇄ 6-*endo-trig*), an examination of related systems resulted in the observation of the clean generation and rearrangement of the secondary alkyl radicals derived from β-bromo ketones **56a–c** (Scheme V).[60] Such rearrangements have been employed in the development of useful methodology to effect ring expansion of cyclic ketones and the majority of such studies have focused on systems bearing a radical-stabilizing substituent adjacent to the carbonyl.[52] The free-radical rearrangement of **56a–c** was found to cleanly generate the intermediate tertiary alkyl radicals which undergo subsequent 5-*exo-dig* cyclization onto a suitably positioned alkyne to provide high yields of the bicyclic products **57a–c**. Ozonolysis (O_3, CH_2Cl_2, −78 °C, Me_2S) of **57a–c** provided the bicyclic diones **58a–c**, thus establishing the tandem free-radical ring expansion, 5-*exo-dig* 5-hexenyl radical cyclization sequence as an effective method for the construction of useful 6,5-, 7,5-, and 8,5-bicyclic ring systems. The 5-*exo-dig* cyclization of the intermediate tertiary alkyl radical derived from **56a** provided **57a** with the exclusive cis ring fusion. The same process employing **56b** and **56c** provided **57b–c** with a slight predominance for the trans ring fusion product which could be subsequently enhanced by simple base-catalyzed equilibration of the cis:trans mixture.[61]

Ab Initio Treatment of the Structure of Acetyl Radical. Concurrent with studies on the synthetic applications of acyl radicals and in efforts to establish an accurate structural representation of the reactive intermediate, we have conducted ab initio calculations on acetyl radical. Initial low-level calculations established the most stable conformation as that possessing the syn, in plane hydrogen and sequential evaluations at increasingly higher level treatments provided accurate bond lengths and bond angles for the acetyl radical and a PSI/88 plot of the reactive molecular orbital (SOMO) (Table III and Figure 1).

(59) Phenyl selenoester **21** was prepared by condensation of 2-(2-lithiophenyl)-4,4-dimethyl-Δ^2-oxazoline with 1-cyclopentenecarboxaldehyde (THF, 0 °C) followed by O-methylation (NaH, MeI, THF), oxazoline hydrolysis (MeI, CH_3NO_2; aqueous NaOH, reflux) and phenyl selenoester formation (N-PSP, Bu_3P). Full details are provided in the supplementary material.

(60) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1990**, *55*, 5442.

(61) Base-catalyzed equilibration (catalytic NaOMe, MeOH, reflux) of **58b** and **58c** provided equilibrium ratios of 72:28 (**58b**) and 90:10 (**58c**) for the trans:cis ring fusion.

Table III. Summary of Computational Studies on Acetyl Radical

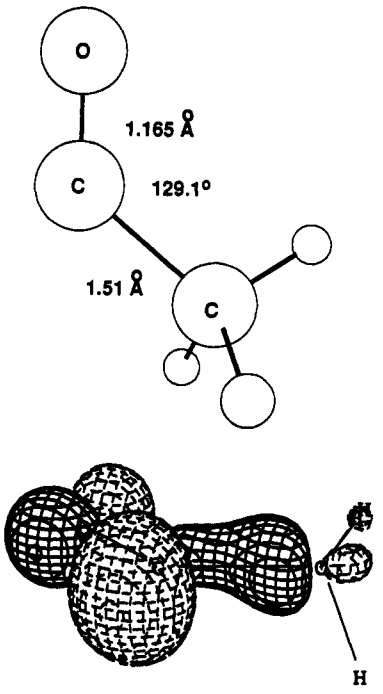
method[a]	r, Å C=O	r, Å C-C	r, Å C-H	∠(OCC), deg	E, h (SOMO, eV)	total energy, h	dipole, d
MNDO	1.19	1.47	1.11	147.9	-0.135 (-3.68)	-22.762140	2.23
AM1	1.20	1.45	1.12	143.5	-0.141 (-3.84)	-22.659855	2.54
UHF/STO-3G//STO-3G	1.25	1.53	1.09	128.4	-0.23620 (-6.43)	-150.331110	1.52
UHF/3-21G//3-21G	1.18	1.51	1.08	131.7	-0.32202 (-8.76)	-151.438417	2.98
UHF/3-21G(d)//3-21G(d)	1.18	1.51	1.08	131.7	-0.34520 (-9.39)	-151.438417	2.98
UHF/6-31G//6-31G	1.19	1.50	1.08	130.8	-0.35992 (-9.79)	-152.222822	3.37
UHF/6-31G(d)//6-31G(d)	1.165	1.51	1.08	129.1	-0.35197 (-9.58)	-152.297932	2.81
UHF/6-31G(d)(d)//6-31G(d)					-0.35162 (-9.57)	-152.302903	2.83
UMP2/6-31G(d)//6-31G(d)					-0.35198 (-9.58)	-152.708427	2.81
UMP3/6-31G(d)//6-31G(d)					-0.35198 (-9.58)	-152.720488	2.81
UMP4(SDTQ)//6-31G(d)//6-31G(d)					-0.35198 (-9.58)	-152.746736	2.81
UHF/6-31+G//6-31+G	1.19	1.50	1.08	131.1	-0.36439 (-9.92)	-152.228036	3.51
UHF/6-31+G(d)//6-31+G(d)	1.16	1.51	1.08	129.7	-0.35715 (-9.72)	-152.303721	2.99
UHF/6-31++G(d)//6-31++G(d)	1.16	1.51	1.08	129.5	-0.35703 (-9.72)	-152.303863	2.99

[a] MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. Gaussian 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Khan, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.

Experimental Section[62]

General Procedures for the Preparation of Phenyl Selenoesters. Method A:[20a] ***Se*-Phenyl 3,7-Dimethyloct-6-eneselenoate (1e).** A solution of citronellic acid[55] (255 mg, 1.50 mmol) in 8 mL of dry THF was treated sequentially with Bu_3P (0.75 mL, 606 mg, 3.0 mmol, 2.0 equiv) and *N*-phenylselenophthalimide[20a] (906 mg, 3.0 mmol, 2.0 equiv), and the orange solution was stirred at 25 °C for 4 h at which point TLC analysis (28:12:1 hexane–ether–formic acid eluant) indicated complete disappearance of the carboxylic acid. The solution was concentrated under reduced pressure, and the orange residue was stirred with 20 mL of hexane. The mixture was filtered, and the precipitated Bu_3PO was washed with 10 mL of hexane. The combined filtrates were concentrated under reduced pressure. Flash chromatography (SiO_2, 0–5% EtOAc–hexane eluant) afforded 376 mg (464 mg theoretical, 81%) of **1e** as a light yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.99 (3 H, d, J = 6.6 Hz, C3-CH_3), 1.25–1.45 (2 H, m, C4-H_2), 1.61 (3 H, s, C7-CH_3), 1.69 (3 H, s, C7-CH_3), 1.80–2.18 (3 H, m, C3-H and C5-H_2), 2.52 (1 H, dd, J = 14.9, 8.0 Hz, C*H*HCO), 2.71 (1 H, dd, J = 14.9, 5.8 Hz, CH*H*CO), 5.09 (1 H, m, C6-H), 7.30–7.60 (5 H, m, 5 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 19.5, 25.4, 25.7, 30.6, 36.5, 54.5, 124.0, 126.7, 128.7, 129.3, 131.7, 135.7, 199.7; IR (neat) ν_{max} 2965, 2925, 1726 (C=O), 1580, 1478, 1439, 1379, 986, 737 cm^{-1}; EIMS m/e (relative intensity) 157 (7), 153 (49, M^+ – SePh), 109 (35), 69 (base, $C_5H_9^+$), 55 (25); CIMS (2-methylpropane) m/e 311 ($M^+ + H$); EIHRMS m/e 310.0835 ($C_{16}H_{22}OSe$ requires 310.0836).

Method B: *Se*-Phenyl 3-(3-Cyclohexenyl)propaneselenoate (7). A solution of 3-(3-cyclohexenyl)propanoic acid[64] (0.770 g, 5.0 mmol) in 20 mL of dry THF was treated sequentially with Et_3N (0.84 mL, 607 mg, 6.0 mmol, 1.2 equiv) and $(EtO)_2P(O)Cl$ (0.88 mL, 1.04 g, 6.0 mmol, 1.2 equiv). After 4 h at 25 °C, the mixture was filtered under a N_2 atmosphere into a suspension of PhSeNa (9.0 mmol, 1.5 equiv) in 20 mL of dry THF. The orange solution was stirred at 25 °C for 12 h, concentrated under reduced pressure, and partitioned between Et_2O (50 mL) and H_2O (20 mL). The organic layer was separated, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography (SiO_2, 9–10% EtOAc–hexane eluant) provided 1.26 g (1.47 g theoretical, 86%) of **7** as a light yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19–2.20 (9 H, m), 2.74 (2 H, t, J = 7.8 Hz, CH_2CO), 5.52 (1 H, dd, J = 10.2, 2.1 Hz, *H*C=CH), 5.71 (1 H, dd, J = 10.2, 2.5 Hz, HC=C*H*), 7.23–7.60 (5 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 25.2, 28.6, 31.4, 34.4, 45.1, 128.0, 128.8, 129.2, 129.3, 130.5, 135.8, 200.4; IR (neat) ν_{max}



SOMO

Figure 1.

(62) For APT ^{13}C NMR, e = even and o = odd number of attached protons. Capillary GC analyses were performed on a Varian 3700 chromatograph equipped with a 30 m × 0.25 μm (film thickness) RSL-150 (column A) or DB-1 (column B) capillary column. Helium was used as the carrier gas (flow rate 1 mL/min) and peak area integrations are uncorrected for flame ionization detector response. Flash chromatography was performed on 230–400-mesh silica gel. Benzene and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from phosphorus pentoxide. Methanol (MeOH) was distilled from magnesium methoxide. All phenyl selenoesters were prepared from the corresponding carboxylic acids by the methods described in the experimental section. The following carboxylic acids were prepared by methods previously described: 3-biphenylcarboxylic acid,[63] citronellic acid,[55] 3-(3-cyclohexenyl)propanoic acid,[64] 2-(2-propenyl)benzoic acid,[65] 2-(*N*,*N*-diallylamino)benzoic acid,[66] *o*-carboxyphenylacetonitrile,[67] 4-cycloheptenecarboxylic acid,[68] 1-cyclopentenecarboxylic acid,[69] and 4-(1-cyclohexenyl)butanoic acid.[70] All other carboxylic acids are commercially available or were prepared by the methods outlined in the footnotes and detailed in the supplementary material.

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(64) Julia, M.; LeGoffic, F. *Bull. Soc. Chim. Fr.* **1965**, 1555.
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(66) Hodgkin, J. H.; Demerac, S. *Adv. Chem. Ser.* **1980**, *187*, 211.
(67) Price, C. C.; Rogers, R. G. *Organic Syntheses*; Wiley: New York, 1955; Collect Vol. III, p 174.
(68) Marquardt, D. J.; Newcomb, M. *Synth. Commun.* **1988**, *18*, 1193.
(69) Cook, A. H.; Linstead, R. P. *J. Chem. Soc.* **1934**, 956.
(70) Cook, J. W.; Lawrence, C. A. *J. Chem. Soc.* **1935**, 1637.

2927, 1723, 1477, 1439, 738 cm^{-1}; EIMS m/e (relative intensity) 294 (2, M^+), 157 (37), 137 (98, M^+ – SePh), 119 (71, M^+ – COSePh), 95 (98), 81 (96), 77 (73), 67 (base), 55 (67); CIMS (2-methylpropane) m/e 295 (base, $M^+ + H$); EIHRMS m/e 294.0521 ($C_{15}H_{18}OSe$ requires 294.0523).

Anal. Calcd for $C_{15}H_{18}OSe$: C, 61.43; H, 6.19. Found: C, 61.53; H, 6.35.

Method C: *Se*-Phenyl 4-Methoxybenzenecarboselenoate (1a). A solution of PhSeH (1.57 g, 1.10 mL, 10.0 mmol) and pyridine (0.97 mL, 0.95 g, 12.0 mmol) in 30 mL of dry Et_2O was cooled to 0 °C and treated dropwise with a solution of *p*-anisoyl chloride (1.71 g, 10.0 mmol) in 10 mL of dry Et_2O. The yellow mixture was stirred at 0 °C for 1 h and was allowed to warm to 25 °C over a period of 1 h. The mixture was diluted with 50 mL of Et_2O, filtered, and concentrated under reduced pressure. The resulting bright yellow solid was recrystallized from hot hexane to afford 2.19 g (2.94 g theoretical, 75%) of **1a** as a white crystalline solid: mp 61–63 °C (lit.[71] mp 62–63 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.89 (3 H, s, $ArOCH_3$), 6.96 (2 H, d, J = 8.9 Hz, C3-H and C5-H), 7.43 (3 H, m, 3 × phenyl H), 7.61 (2 H, m, 2 × phenyl H), 7.92 (2 H, d, J = 8.9 Hz, C2-H and C6-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.4, 114.0, 125.9, 128.8, 129.2, 129.5, 131.1, 136.3, 164.1, 191.1; IR (KBr) ν_{max} 1684 (C=O), 1602, 1576, 1506, 1258, 1210, 1168, 882 cm^{-1}; EIMS m/e (relative intensity) 157 (6, $PhSe^+$), 135 (base, $ArCO^+$), 107 (1), 92 (14), 77 (20); CIMS (2-methylpropane) m/e 293 (base, $M^+ + H$).

Anal. Calcd for $C_{14}H_{12}O_2Se$: C, 57.72; H, 4.16. Found: C, 58.00; H, 4.12.

***Se*-Phenyl benzenecarboselenoate (1c)**: white solid; mp 35–37 °C (lit.[71] mp 37–38 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.56 (5 H, m), 7.58–7.68 (3 H, m), 7.95 (2 H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 125.7, 127.3, 128.9, 129.0, 129.3, 133.8, 136.3, 138.4, 193.3; IR (neat) ν_{max} 1686 (C=O), 1580, 1476, 1446, 1440, 1174, 878 cm^{-1}; EIMS m/e (relative intensity) 262 (1, M^+), 157 (2), 105 (base, $C_6H_5CO^+$), 77 (24), 51 (11); CIMS (2-methylpropane) m/e 263 (72, $M^+ + H$), 105 (base, $C_6H_5CO^+$); CIHRMS m/e 258.9985 ($C_{13}H_{10}OSe$ requires 259.0001 based on Se^{76}).

Method D: *Se*-Phenyl Cyclohexanecarboselenoate (1g). A solution of cyclohexanecarboxylic acid (385 mg, 3.0 mmol) and $(PhSe)_2$ (1.87 g, 6.0 mmol, 2.0 equiv) in 15 mL of dry THF was treated dropwise with Bu_3P (1.50 mL, 1.21 g, 6.0 mmol, 2.0 equiv). After 14 h at 25 °C, the solution was concentrated under reduced pressure and the residue was triturated with hexane (2 × 30 mL). The combined hexane extracts were concentrated under reduced pressure. Flash chromatography (SiO_2, 0–10% EtOAc–hexane eluant) afforded 515 mg (804 mg theoretical, 64%) of **1g** as a light yellow, mobile oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18–2.04 (10 H, m, cyclohexyl CH_2), 2.64 (1 H, m, CHCO), 7.38 (3 H, m, 3 × ArH), 7.49 (2 H, m, 2 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) 25.3, 25.6, 29.3, 55.9, 126.3, 128.6, 129.2, 135.9, 203.9; IR (neat) ν_{max} 2932, 1722 (C=O), 1580, 1478, 1450, 1440, 954 cm^{-1}; EIMS m/e (relative intensity) 157 (12), 111 (53, M^+ – SePh), 83 (base, $C_6H_{11}^+$), 77 (15), 55 (59); CIMS (2-methylpropane) m/e 269 ($M^+ + H$), 111 (base, M^+ – HSePh); CIHRMS m/e 269.0444 $C_{13}H_{16}OSe$ requires 269.0454).

Method E: *Se*-Phenyl Ethaneselenoate (1f). A solution of $(PhSe)_2$ (6.24 g, 20.0 mmol) in THF (25 mL) under N_2 was treated with sodium metal (0.96 g, 40.0 mmol, 2.0 equiv), and the red mixture was warmed at reflux for 4 h. The orange slurry was cooled to 0 °C, treated with CH_3COCl (2.9 mL, 3.20 g, 40.0 mmol), and rewarmed at reflux for 1 h. After cooling to 0 °C and careful addition of 5 mL of CH_3OH, the mixture was poured into 20 mL of ice H_2O and extracted twice with Et_2O (70 mL × 2). The combined extracts were washed with 50 mL of saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced pressure. The red liquid was distilled under vacuum through a short Vigreux column to give 3.84 g (8.00 g theoretical, 48%) of pure **1f** as a light yellow liquid: bp 70–75 °C (0.40 mmHg) (lit.[72] bp 80 °C (0.5 mmHg)); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.45 (3 H, s, CH_3), 7.38 (3 H, m, 3 × ArH), 7.51 (2 H, m, 2 × ArH); IR (neat) ν_{max} 1726 (C=O), 1688, 1478, 1440, 1350, 1100, 938, 740 cm^{-1}; EIMS m/e (relative intensity) 200 (48, M^+), 158 (92, $M^+ - COCH_2$), 77 (base, $C_6H_5^+$), 51 (91); CIMS (2-methylpropane) m/e 201 base, $M^+ + H$).

Anal. Calcd for C_8H_8OSe: C, 48.24; H, 4.05. Found: C, 48.49; H, 4.31.

***O*-Methyl *Se*-phenyl carbonoselenoate (1i)**: light yellow liquid; bp 90–92 °C (1.5 mmHg) (lit.[72] bp 90–92 °C (3 mmHg)); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.86 (3 H, s, OCH_3), 7.40 (3 H, m, 3 × ArH), 7.61 (2 H, m, 2 × ArH); IR (neat) ν_{max} 2952, 1726 (C=O), 1440, 1428, 1120, 1074 cm^{-1}; EIMS m/e (relative intensity) 216 (49, M^+), 172 (30), 157 (base, $M^+ - CO_2CH_3$), 91 (49), 77 (74), 59 (87); CIMS (2-methylpropane) m/e 217 (base, $M^+ + H$); EIHRMS m/e 211.9725 (C_8H_8OSe requires 211.9716 based on Se^{76}).

Anal. Calcd for $C_8H_8O_2Se$: C, 44.64; H, 3.75. Found: C, 44.43; H, 3.75.

General Procedure for Intermolecular Addition Reactions of Phenyl Selenoesters 1 with Alkenes 2: Phenylmethyl 4-(4-Methoxyphenyl)-4-oxobutanoate (3a). A solution of **1a** (219 mg, 0.75 mmol), benzyl acrylate (608 mg, 3.75 mmol, 5 equiv), and AIBN (15 mg) in dry C_6H_6 (5 mL) was warmed at reflux and treated dropwise (syringe pump) with a solution of Bu_3SnH (0.27 mL, 1.00 mmol, 1.3 equiv) in C_6H_6 (3 mL) over a period of 1 h. After an additional 0.5 h, the solution was cooled to 25 °C and concentrated under reduced pressure. Flash chromatography (SiO_2, 20% EtOAc–hexane eluant) afforded 134 mg (224 mg theoretical, 60%) of **3a** as a colorless, viscous oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 2.79 (2 H, t, J = 6.6 Hz, C2-H_2), 3.25 (2 H, t, J = 6.6 Hz, C3-H_2), 3.82 (3 H, s, $ArOCH_3$), 5.13 (2 H, s, OCH_2Ph), 6.91 (2 H, d, J = 8.7 Hz, meta ArH), 7.33 (5 H, s, benzyl ArH), 7.94 (2 H, d, J = 8.7 Hz, ortho ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.3, 32.9, 55.4, 66.4, 113.7, 127.1, 128.2, 128.5, 128.6, 129.6, 130.3, 135.9, 163.5, 172.9, 196.5; IR (neat) ν_{max} 2938, 1736 (ester C=O), 1678 (ketone C=O), 1602, 1512 cm^{-1}; EIMS m/e (relative intensity) 298 (4, M^+), 191 (16), 135 (base, $ArCO^+$), 107 (13), 91 (27), 77 (30); CIMS (2-methylpropane) m/e 299 (base, $M^+ + H$); CIHRMS m/e 299.1280 ($C_{18}H_{18}O_4$ requires 299.1283).

General Procedure for Acyl Radical Generation and Intramolecular Free-Radical Cyclization (Method A): *cis*-Octahydro-1*H*-inden-1-one (8). A solution of phenyl selenoester **7** (253 mg, 0.863 mmol) and AIBN (8 mg) in dry C_6H_6 (100 mL) was warmed to reflux (bath temperature 90–92 °C) and treated dropwise (syringe pump, 1 h) with a solution of Bu_3SnH (302 mg, 1.03 mmol, 1.2 equiv) in C_6H_6 (10 mL). After an additional 0.5 h at reflux, the solution was cooled to 25 °C and concentrated under reduced pressure. Flash chromatography (SiO_2, 5–40% Et_2O–hexane eluant) afforded pure **8**[73] (102 mg, 86%) as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97–1.34 (4 H, m), 1.36–1.54 (2 H, m), 1.54–1.82 (3 H, m), 1.82–2.08 (2 H, m), 2.17–2.38 (3 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 22.8, 24.0, 25.6, 28.1, 34.8, 36.2, 49.6, 220.2; IR (neat) ν_{max} 2929, 1738 (C=O), 1447 cm^{-1}; EIMS m/e (relative intensity) 138 (41, M^+), 109 (26), 96 (56), 81 (66), 67 (base); CIMS (2-methylpropane) m/e 139 (base, $M^+ + H$).

An alternative procedure (method B) consisted of warming a solution of **7** (212 mg, 0.721 mmol), Bu_3SnH (0.23 mL, 0.865 mmol, 1.2 equiv), and AIBN (10 mg) in 60 mL of dry C_6H_6 at reflux for 30 min. In this manner, 78 mg (100 mg theoretical, 78%) of pure **8** was obtained.

***Se*-Phenyl 3-(3-cyclohexenyl)-2-methylpropaneselenoate (9)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.23 and 1.24 (3 H, two d, J = 6.8 and J = 6.9 Hz, diastereomeric C2-CH_3), 1.28–2.25 (9 H, m), 2.93 (1 H, m, C2-H), 5.57 (1 H, m, CH=C*H*), 5.69 (1 H, m, C*H*=CH), 7.38 (3 H, m, 3 × ArH), 7.51 (2 H, m, 2 × ArH); IR (neat) ν_{max} 2926, 1718 (C=O), 1438, 938, 738, 690 cm^{-1}; EIMS m/e (relative intensity) 308 (3, M^+), 151 (41, M^+ – SePh), 123 (27, M^+ – COSePh), 81 (base, $C_6H_9^+$), 67 (32), 55 (19); CIMS (2-methylpropane) m/e 309 ($M^+ + H$); CIHRMS m/e 305.0440 ($C_{10}H_{16}OSe$ requires 305.0444, based on Se^{76}).

General Procedure for Photochemically-Initiated Acyl Radical Cyclizations (Method C): *cis*-2-Methyl-1*H*-octahydroinden-1-one (10). A solution of **9** (308 mg, 1.0 mmol), Bu_3SnH (346, 0.32 mL, 1.2 equiv), and AIBN (16 mg, 0.10 mmol)

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in 45 mL of dry C_6H_6 was degassed, transferred to two separate Pyrex test tubes, and irradiated for 20 min in a Rayonet photoreactor equipped with 10 4.5-W lamps emitting at 350 nm. The two solutions were combined and concentrated under reduced pressure, and the residual oil was purified by flash chromatography (SiO_2, 0–6% Et_2O–hexane eluant) to afford 90 mg (152 mg theoretical, 59%) of **10** as a colorless, mobile oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.11 and 1.16 (3 H, two d, J = 7.2 and 7.0 Hz, respectively, diastereomeric C2-CH_3), 1.20–1.68 (11 H, m), 1.95–2.45 (2 H, m); IR (neat) ν_{max} 2932, 2854, 1737 (C=O), 1452, 1138 cm^{-1}; CIMS (2-methylpropane) m/e 153 (M^+ + H); CIHRMS m/e 153.1276 ($C_{10}H_{16}O$ requires 153.1279). Cyclization of **9** (230 mg, 0.747 mmol) according to method A afforded 79 mg (115 mg theoretical, 68%) of **10**.

***Se*-Phenyl 3-(3-cyclohexenyl)-2,2-dimethylpropaneselenoate (11)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (6 H, s, 2 × CH_3), 1.40–1.85 (6 H, m), 1.96 (2 H, m), 2.20 (1 H, m, C1′-H), 5.56 and 5.65 (2 H, two m, *HC*=C*H*), 7.38 (3 H, m, 3 × ArH), 7.51 (2 H, m, 2 × ArH); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 21.7 (e), 25.4 (e), 25.7 (o), 26.7 (o), 30.9 (e), 32.5 (o), 47.6 (e), 53.7 (e), 126.8 (e), 127.5 (o), 129.1 (o), 129.6 (o), 132.7 (o), 136.8 (o), 208.2 (e); IR (neat) ν_{max} 2928, 1702 (C=O), 1580, 1476, 1438, 906, 738, 690 cm^{-1}; EIMS m/e (relative intensity) 322 (1, M^+), 165 (11, M^+ – SePh), 157 (13, $SePh^+$), 137 (17), 81 (base, $C_6H_9^+$); CIMS (2-methylpropane) m/e 323 (M^+ + H), 165 (base, M^+ + H – HSePh); EIHRMS m/e 318.0863 ($C_{17}H_{22}OSe$ requires 318.0863, based on Se^{76}).

Anal. Calcd for $C_{17}H_{22}OSe$: C, 63.55; H, 6.90. Found: C, 63.79; H, 7.05.

***cis*-2,2-Dimethyl-1*H*-octahydroinden-1-one (12)**. Following the general procedure method B, **11** (81 mg, 0.252 mmol) afforded, after purification by flash chromatography (SiO_2, 0–10% ether–hexane eluant), 21 mg (41 mg theoretical, 51%) of **12** as an oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.04 and 1.15 (6 H, two s, two C2-CH_3), 1.24–1.80 (10 H, m), 1.91 (1 H, m), 2.26–2.34 (1 H, m); IR (neat) ν_{max} 2936, 2855, 1738 (C=O), 1436, 1140, 1082 cm^{-1}; EIMS m/e (relative intensity) 166 (31, M^+), 151 (10, $M^+ - CH_3$), 137 (6, $M^+ - C_2H_5$), 124 (13), 116 (28), 109 (25), 95 (29), 81 (52), 67 (base, $C_5H_7^+$); CIMS (2-methylpropane) m/e 167 (base, M^+ + H); EIHRMS m/e 166.1351 ($C_{11}H_{18}O$ requires 166.1357).

Using method A, **11** (161 mg, 0.50 mmol) afforded 41 mg (83 mg theoretical, 49%) of **12**.

***Se*-Phenyl 2-(3-cyclohexenyl)ethaneselenoate (13)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24–1.40 (3 H, m), 1.58 (2 H, m), 2.01–2.28 (2 H, m), 2.66 (2 H, d, J = 7.6 Hz, CH_2CO), 5.65 (2 H, m, HC=CH), 7.37 (3 H, m, 3 × ArH), 7.49 (2 H, m, 2 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.3, 27.9, 30.8, 31.0, 53.5, 125.3, 126.4, 126.6, 128.5, 129.0, 135.4, 199.2; IR (neat) ν_{max} 2914, 1723 (C=O), 1652, 1580, 738 cm^{-1}; EIMS m/e (relative intensity) 280 (1, M^+), 157 (10), 123 (69, M^+ – SePh), 95 (53), 79 (base, $C_6H_7^+$), 67 (31), 55 (16); CIMS (2-methylpropane) m/e 281 (base, M^+ + H); EIHRMS m/e 276.0390 ($C_{14}H_{16}OSe$ requires 276.0393, based on Se^{76}).

Bicyclo[3.2.1]octan-6-one (14). Following the general procedure (method A), **10** (200 mg, 0.727 mmol) afforded, after purification by sublimation (50–60 °C, 0.15 mmHg), 61 mg (89 mg theoretical, 69%) of **14** as a white solid: mp 153–155 °C (lit.[74] mp 155–157 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.44–2.05 (10 H, m), 2.44 (2 H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.5, 29.8, 30.4, 32.4, 36.9, 43.8, 46.4, 221.7; IR (CCl_4) ν_{max} 2933, 1726 (C=O), 1410 cm^{-1}; EIMS m/e (relative intensity) 124 (28, M^+), 81 (37), 80 (base), 67 (45), 54 (46); CIMS (2-methylpropane) m/e 125 (base, M^+ + H).

***Se*-Phenyl 4-cycloheptenecarboselenoate (15)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.71 (2 H, m), 2.11 (4 H, m), 2.32 (2 H, m), 2.87 (1 H, m, CHCO), 5.78 (2 H, m, *HC*=C*H*), 7.38 (3 H, m, 3 × ArH), 7.51 (2 H, m, 2 × ArH); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 26.5 (e), 29.3 (e), 59.9 (o), 126.4 (e), 128.7 (o), 129.2 (o), 131.5 (o), 135.8 (o), 203.5 (e); IR (neat) ν_{max} 2930, 2840, 1720 (C=O), 1580, 1478, 1438, 1064, 1022, 998, 928, 912, 782, 736, 690 cm^{-1}; EIMS m/e (relative intensity) 157 (13, $PhSe^+$), 123 (50, M^+ – SePh), 95 (base, $C_7H_{11}^+$), 77 (15), 67 (28); CIMS (2-methylpropane) m/e 281 (M^+ + H), 123 (base, M^+ + H – HSePh); EIHRMS m/e 276.0397 ($C_{14}H_{16}OSe$ requires 276.0393, based on Se^{76}).

Bicyclo[3.2.1]octan-8-one (16). Following the general procedure (method A), **15** (504 mg, 1.50 mmol) afforded, after purification by flash chromatography (SiO_2, 0–20% Et_2O–hexane eluant), 108 mg (186 mg theoretical, 58%) of **16** as a white solid: mp 138–140 °C (lit.[75] mp 141.5–143.2 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50–1.61 (2 H, m), 1.75–2.05 (8 H, m), 2.24 (2 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.3 (e), 22.8 (e), 37.1 (e), 44.8 (o), 222.1 (e); IR (KBr) ν_{max} 2930, 1720 (C=O), 1438, 1106 cm^{-1}; EIMS m/e (relative intensity) 124 (60, M^+), 81 (66), 67 (91), 54 (base, $C_4H_6^+$); CIMS (2-methylpropane) m/e 125 (base, M^+ + H).

***Se*-Phenyl 4-(1-cyclohexenyl)butaneselenoate (17)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.47 (4 H, m), 1.69 (2 H, m), 1.79 (2 H, m), 1.88 (4 H, m), 2.55 (2 H, t, J = 7.4 Hz, CH_2CO), 5.31 (1 H, s, C2-H), 7.25 (3 H, m, 3 × ArH), 7.40 (2 H, m, 2 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 22.8, 23.1, 25.1, 27.9, 36.8, 46.8, 122.1, 126.5, 128.6, 129.1, 135.6, 136.1, 199.9; IR (neat) ν_{max} 2927, 1724 (C=O), 1579, 1477, 1438, 863, 802 cm^{-1}; EIMS m/e (relative intensity) 314 (2, M^+), 151 (94, M^+ – SePh), 133 (42), 107 (20), 91 (45), 81 (49), 67 (base), 55 (67); CIMS (2-methylpropane) m/e 309 (M^+ + H), 151 (base, M^+ + H – SePh); CIHRMS m/e 305.0784 ($C_{16}H_{20}OSe$ requires 305.0784, based on Se^{76}).

Octahydro-1(2*H*)-naphthalenone (18). Following the general procedure (method A), **17** (200 mg, 0.650 mmol) afforded, after purification by flash chromatography (SiO_2, 0–10% Et_2O–hexane eluant), 81 mg (99 mg theoretical, 82%) of **18** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18–2.36 (16 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.0, 23.4, 24.6 (cis), 25.0, 25.2 (trans), 25.3 (cis), 25.7, 26.4 (trans), 29.1, 29.2 (cis), 32.9, 34.3 (trans), 39.1, 40.6 (cis), 41.7, 44.9 (trans), 50.7 (cis), 55.0, 212.6 (trans), 213.4 (cis); IR (neat) ν_{max} 2936, 2860, 1706 (C=O), 1450 cm^{-1}; EIMS m/e (relative intensity) 152 (58, M^+), 123 (20), 109 (77), 97 (92), 81 (87), 67 (base, $C_3H_3CO^+$), 55 (59); CIMS (2-methylpropane) m/e 153 (base, M^+ + H). All properties were consistent with those previously reported.[76]

***Se*-Phenyl 3-(2,6-cyclooctadienyl)propaneselenoate (19)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60–1.84 (2 H, m, C3-H_2), 2.14–2.24 (2 H, m, C4′-H_2 or C5′-H_2), 2.26–2.40 (3 H, m), 2.44–2.58 (1 H, m), 2.76 (3 H, overlapping 2 H, t, J = 7.3 Hz, C2-H_2 and 1 H, m, C1′-H), 5.29 (1 H, dd, J = 10.1 and 7.2 Hz, C2′-H), 5.55 (3 H, m, C3′-H, C6′-H, and C7′-H), 7.39 (3 H, m, 3 × ArH), 7.49 (2 H, m, 2 × ArH); IR (neat) ν_{max} 3058, 1724 (C=O), 1480, 1438, 1204, 962, 740 cm^{-1}; EIMS m/e (relative intensity) 163 (56, M^+ – SePh), 119 (28), 91 (49), 79 (97), 67 (base, $C_5H_7^+$), 55 (48); CIMS (2-methylpropane) m/e 321 (M^+ + H); CIHRMS m/e 317.0789 ($C_{17}H_{20}OSe$ requires 317.0784 based on Se^{76}).

2,3,3aα,4,7,8,9,9a,β-Octahydro-1*H*-cyclopentacycloocten-1-one (20). Following the general procedure (method A), **19** (210 mg, 0.656 mmol) afforded, after purification by flash chromatography (SiO_2, 0–10% Et_2O–hexane eluant), 85 mg (108 mg theoretical, 79%) of **20** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21 (2 H, m, C5-H_2), 1.38–1.66 (5 H, m), 1.92–2.24 (7 H, m), 5.58 (1 H, m, C5-H or C6-H), 5.77 (1 H, m, C6-H or C5-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.6 (e), 24.7 (e), 26.0 (e), 27.6 (e), 31.5 (e), 37.2 (e), 46.3 (o), 55.9 (o), 128.4 (o), 130.3 (o), 219.3 (e); IR (neat) ν_{max} 2930, 2858, 1740 (C=O), 1462 (C=C), 1164, 730 cm^{-1}; EIMS m/e (relative intensity) 164 (40, M^+), 135 (21), 123 (13), 122 (32), 120 (14), 79 (99), 67 (base), 53 (61); CIMS (2-methylpropane) m/e 165 (base, M^+ + H); EIHRMS m/e 164.1200 ($C_{11}H_{16}O$ requires 164.1201).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.15; H, 10.10.

Capillary GC analysis (column A, oven temperature = 110 °C) revealed that the isolated product consisted of 82% of **20** (t_R = 12.0 min), 2.5% of cis-fused bicyclic isomer (t_R = 13.1 min), and two minor components (10.3%, t_R = 11.6 min and 4.4%, t_R = 12.3 min).[58] Base equilibration (catalytic NaOMe, MeOH, reflux, 35 h) resulted in no change in the relative proportions of the four components.

***Se*-Phenyl 2-[[(1-cyclopentenyl)methoxy]methyl]benzenecarboselenoate (21)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.82 (2 H, m), 2.14 (2 H, m), 2.35 (2 H, m), 3.28 (3 H, s, OCH_3), 5.42 (1 H, s, C*H*OCH_3), 5.58 (1 H, br s, C=CH), 7.39–7.70 (8 H, m, 8 × ArH), 7.82 (1 H, dd, J = 7.4, 0.8 Hz, 1 × ArH); IR (neat)

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ν_{max} 2930, 1696, 1578, 1476, 1440, 1180, 1104, 1086, 870, 738, 690, 668 cm^{-1}; EIMS *m/e* (relative intensity) 215 (63, M^+ – SePh), 183 (base, M^+ – SePh – $HOCH_3$), 165 (73), 155 (37), 128 (24), 115 (24), 105 (18), 91 (21), 77 (41); CIMS (2-methylpropane) *m/e* 373 (M^+ + H), 341 (base, M^+ + H – $HOCH_3$); CIHRMS *m/e* 341.0441 ($C_{19}H_{16}OSe$ requires 341.0444).

***cis*- and *trans*-1,2,3,3a,9,9a-Hexahydro-9-methoxy-4*H*-benz[*f*]inden-4-one (22).** Following the general procedure (method A), **21** (400 mg, 1.07 mmol) afforded, after purification by flash chromatography (SiO_2, 0–10% EtOAc–hexane eluant), 191 mg (231 mg theoretical, 83%) of **22** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10 (2 H, m), 1.44–1.20 (4 H, m), 2.76–3.14 (2 H, overlapping m), 3.19 and 3.41 (3 H, two s, OCH_3), 4.23, 4.28, and 4.56 (1 H, d, *J* = 3.7 Hz; d, *J* = 3.8 Hz and d, *J* = 4.0 Hz, respectively), 7.24–7.86 (4 H, m, 4 × ArH); IR (neat) ν_{max} 2960, 2876, 1686 (C=O), 1600, 1454, 1336, 1288, 1222, 1160, 1120, 1090, 1022, 892, 868, 764 cm^{-1}; CIMS (2-methylpropane) *m/e* 217 (base, M^+ + H), 185 (M^+ + H – $HOCH_3$); CIHRMS *m/e* 217.1226 ($C_{14}H_{16}O_2$ requires 217.1229). Capillary GC analysis (column B: oven temperature 160 °C) indicated the presence of four diastereomers (t_R = 8.6, 8.9, 9.5 and 10.3 min) in a ratio of 14:42:21:23, respectively.

***Se*-Phenyl 2-[*N*,*N*-di(2-propenyl)amino]benzenecarboselenoate (23):** oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.76 (4 H, d, *J* = 6.6 Hz, 2 × NCH_2), 5.20 (4 H, m, 2 × CH=CH_2), 5.97 (2 H, m, 2 × C*H*=CH_2), 7.05–7.64 (3 H, m, 3 × ArH), 7.40 (3 H, m, 3 × ArH), 7.60 (2 H, m, 2 × ArH), 7.64 (1 H, d, *J* = 7.6 Hz, 1 × ArH); IR (neat) ν_{max} 2978, 2840, 1674 (C=O), 1590, 1482, 1444, 1184, 880, 738, 690, 662 cm^{-1}; EIMS *m/e* (relative intensity) 200 (base, M^+ – SePh), 157 (7, $PhSe^+$), 144 (4), 130 (27), 104 (3), 77 (9); CIMS (2-methylpropane) *m/e* 358 (base, M^+ + H); CIHRMS *m/e* 354.0726 ($C_{19}H_{19}NOSe$ requires 354.0737, based on Se^{76}).

2,3-Dihydro-3-methyl-*N*-(2-propenyl)-4-quinolone (24). Following the general procedure (method A), **23** (240 mg, 0.672 mmol) afforded, after purification by flash chromatography (SiO_2, 0–10% EtOAc–hexane eluant), 93 mg (135 mg theoretical, 69%) of **22** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (3 H, d, *J* = 6.9 Hz, C3-CH_3), 2.74 (1 H, m, C3-H), 3.26 (1 H, apparent t, *J* = 11.9 Hz, 1 × C2-H), 3.44 (1 H, dd, *J* = 12.2, 5.4 Hz, 1 × C2-H), 3.89 (2 H, m, NCH_2CH=C), 5.22 (2 H, m, CH=CH_2), 5.83 (1 H, m, C*H*=CH_2), 6.69 (2 H, m, 2 × ArH), 7.34 (1 H, m, 1 × ArH), 7.92 (1 H, dd, *J* = 6.8, 1.2 Hz, C5-H); IR (neat) ν_{max} 2966, 1670 (C=O), 1606, 1562, 1496, 1358, 1232, 752 cm^{-1}; EIMS *m/e* (relative intensity) 201 (base, M^+), 174 (66, M^+ – C_2H_3), 132 (92), 130 (74), 91 (28), 77 (88), 67 (50), 55 (60); CIMS (2-methylpropane) *m/e* 202 (base, M^+ + H); EIHRMS *m/e* 201.1156 ($C_{13}H_{15}NO$ requires 201.1154).

***Se*-Phenyl 2-(2-propenyl)benzenecarboselenoate (25a):** oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.65 (2 H, d, *J* = 4.6 Hz), 4.89–5.21 (2 H, m, CH=CH_2), 5.70–6.23 (1 H, m, C*H*=CH_2), 7.29–7.66 (8 H, m, 8 × ArH), 7.96 (1 H, dd, *J* = 7.8, 1.0 Hz, 1 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 36.4, 114.4, 131.6, 132.2, 134.1, 134.6, 134.9, 136.2, 137.3, 137.6, 138.1, 138.4, 139.0, 195.4; IR (neat) ν_{max} 1701 (C=O), 1641, 993, 908, 765, 740 cm^{-1}; EIMS *m/e* (relative intensity) 302 (21, M^+), 157 (base, $PhSe^+$), 145 (83, M^+ – SePh), 116 (32), 77 (28), 55 (19); CIMS (2-methylpropane) *m/e* 303 (base, M^+ + H); EIHRMS *m/e* 298.0239 ($C_{16}H_{14}OSe$ requires 298.0237, based on Se^{76}).

2,3-Dihydro-2-methyl-1*H*-inden-1-one (26a). Following the general procedure (method A), **25a** (236 mg, 0.780 mmol), afforded, after purification by flash chromatography on (SiO_2, 0–20% Et_2O–hexane eluant), 92 mg (114 mg theoretical, 81%) of **26a** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.28 (3 H, d, *J* = 6.9 Hz, C2-CH_3), 2.48–2.81 (2 H, m, C2-H and C3-H_1), 3.41 (1 H, dd, *J* = 7.9, 17.5 Hz, C3-H_1), 7.25–7.75 (4 H, m, 4 × ArH); IR (neat) ν_{max} 2933, 1711 (C=O), 1611, 1464, 1274, 1212, 1203, 765 cm^{-1}; EIMS *m/e* (relative intensity) 146 (70, M^+), 131 (base, M^+ – CH_3), 115 (46), 103 (42), 91 (31), 65 (30); CIMS (2-methylpropane) *m/e* 147 (base, M^+ + H). All properties were consistent with those previously reported.[77]

***Se*-Phenyl 2-(3-butenyl)benzenecarboselenoate (25b):** oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.34 (2 H, m), 2.90 (2 H, t, *J* = 7.7 Hz, ArCH_2), 4.90–5.10 (2 H, m, CH=CH_2), 5.75–5.90 (1 H, m, C*H*=CH_2), 7.10–7.64 (8 H, m, 8 × ArH), 7.89 (1 H, dd, *J* = 1.3 and 7.7 Hz, 1 × ArH); IR (neat) ν_{max} 1695 (C=O), 1680, 1591, 1462, 1390, 1293, 1266, 739 cm^{-1}; EIMS *m/e* (relative intensity) 159 (base, M^+ – SePh), 131 (93), 115 (18), 91 (54), 77 (22); CIMS (2-methylpropane) *m/e* 317 (base, M^+ + H); CIHRMS *m/e* 313.0465 ($C_{17}H_{16}OSe$ requires 313.0471, based on Se^{76}).

3,4-Dihydro-2-methyl-1(2*H*)-naphthalenone (26b). Following the general procedure (method A), **25b** (214 mg, 0.677 mmol) afforded, after purification by flash chromatography (SiO_2, 0–15% EtOAc–hexane eluant), 82 mg (108 mg theoretical, 76%) of **26b** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (3 H, d, *J* = 6.3 Hz C2-CH_3), 1.50–2.96 (5 H, m), 6.95–7.40 (3 H, m, 3 × ArH), 7.90 (1 H, d, *J* = 7.4 Hz, C8-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.3 (o), 28.7 (e), 31.2 (e), 42.5 (o), 126.4 (o), 127.2 (o), 128.6 (o), 132.2 (e), 132.9 (o), 144.1 (e), 200.6 (e); IR (neat) ν_{max} 2927, 1684 (C=O), 1599, 1453, 1222, 961, 740 cm^{-1}; EIMS *m/e* (relative intensity) 160 (92, M^+), 145 (27), 131 (23), 118 (base, M^+ – C_3H_6), 90 (86), 86 (43); CIMS (2-methylpropane) *m/e* 161 (M^+ + H). All properties were consistent with those reported previously.[77]

Using method B, **25b** (214 mg, 0.677 mmol) afforded 87 mg (108 mg theoretical, 81%) of **26b**.

***Se*-Phenyl 2-(4-pentenyl)benzenecarboselenoate (25c):** oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.69 (2 H, m), 2.07 (2 H, m), 2.80 (2 H, t, *J* = 7.8 Hz, CH_2CO), 4.95–5.10 (2 H, m, CH=CH_2), 5.80 (1 H, m, C*H*=CH_2), 7.30–8.08 (8 H, m, 8 × ArH), 7.85 (1 H, d, *J* = 7.6 Hz, 1 × ArH, C6-H); IR (neat) ν_{max} 2931, 1696 (C=O), 1478, 1431, 1179, 879, 738, 662 cm^{-1}; EIMS *m/e* (relative intensity) 173 (46, M^+ – SePh), 157 (13), 131 (base), 91 (44), 77 (15); CIMS (2-methylpropane) *m/e* 331 (M^+ + H), 174 (base, M^+ + H – SePh); CIHRMS *m/e* 327.0620 ($C_{18}H_{18}OSe$ requires 327.0628, based on Se^{76}).

6,7,8,9-Tetrahydro-6-methyl-5*H*-benzocyclohepten-5-one (26c). Following the general procedure (method A), **25c** (300 mg, 0.909 mmol) afforded, after purification by flash chromatography (SiO_2, 0–10% EtOAc–hexane eluant), 117 mg (158 mg theoretical, 74%) of **26c** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (3 H, d, *J* = 6.7 Hz, C6-CH_3), 1.45–2.05 (4 H, m), 2.67 (2 H, t, *J* = 6.0 Hz, C9-H_2), 2.80–3.05 (1 H, m, C6-H), 7.14 (1 H, d, *J* = 7.6 Hz, C1-H), 7.20 (1 H, t, *J* = 7.6 Hz), 7.36 (1 H, dt, *J* = 7.4, 1.2 Hz), 7.70 (1 H, dd, *J* = 7.4, 1.2 Hz, C4-H); ^{13}C NMR ($CDCl_3$, 75 MHz) 16.0, 25.1, 31.5, 33.2, 43.6, 125.8, 127.9, 129.4, 130.8, 139.2, 141.4, 206.9; IR (neat) ν_{max} 1684 (C=O), 1585, 1426, 1350, 1193, 788, 694, 593 cm^{-1}; EIMS *m/e* (relative intensity) 172 (base, M^+), 157 (70), 144 (48), 132 (37), 91 (51), 77 (31); CIMS (2-methylpropane) *m/e* 173 (M^+ + H). All properties were consistent with those previously reported.[78]

Methyl 4-[2-[(phenylseleno)carbonyl]phenyl]-2-butenoate (25d): oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.69 (3 H, s, OCH_3), 3.72 (2 H, dd, *J* = 6.6, 1.6 Hz, C4-H_2), 5.72 (1 H, dt, *J* = 15.6, 1.6 Hz, C2-H), 7.07 (1 H, dt, *J* = 15.6, 6.6 Hz, C3-H), 7.27 (1 H, dd, *J* = 7.4, 0.9 Hz, 1 × ArH), 7.36–7.65 (7 H, m, 7 × ArH), 7.95 (1 H, dd, *J* = 7.9, 1.4 Hz, 1 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 36.0, 51.4, 122.1, 126.7, 127.2, 127.4, 129.1, 129.4, 131.4, 131.5, 132.5, 135.6, 136.1, 138.4, 146.8, 195.0; IR (neat) ν_{max} 1720 (ester C=O), 1700 (SeC=O), 1655, 1477, 1438, 1274, 1203, 871, 766, 740 cm^{-1}; EIMS *m/e* (relative intensity) 203 (43, M^+ – SePh), 171 (86), 157 (35), 143 (62), 131 (18), 115 (base, $C_9H_7^+$), 77 (56), 59 (32), 51 (33); CIMS (2-methylpropane) *m/e* 361 (M^+ + H), 203 (base, M^+ + H – SePh); CIHRMS *m/e* 357.0378 ($C_{18}H_{16}O_3Se$ requires 357.0370).

Methyl 2-(2-(2,3-Dihydro-1-oxo-1*H*-indenyl))acetate (26d). Following the general procedure (method A), **25d** (200 mg, 0.556 mmol) afforded, after purification by flash chromatography (SiO_2, 0–18% EtOAc–hexane eluant), 99 mg (113 mg theoretical, 88%) of **26d** as a white solid: mp 45–46 °C (ether–hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.59 (1 H, dd, *J* = 17.2, 9.3 Hz, C*H*HCO_2), 2.82–3.02 (3 H, m), 3.44 (1 H, dd, *J* = 17.2, 7.7 Hz, CH*H*CO_2), 3.67 (3 H, s, OCH_3), 7.36 (1 H, t, *J* = 7.4 Hz, 1 × ArH), 7.44 (1 H, d, *J* = 7.7 Hz, C4-H), 7.57 (1 H, t, *J* = 7.4 Hz), 7.75 (1 H, d, *J* = 7.4 Hz, C7-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.8, 34.8, 43.4, 51.6, 123.8, 126.4, 127.3, 134.7, 136.2, 153.1, 172.3, 206.4; IR (neat) ν_{max} 2953, 1737 (ester C=O), 1715 (ketone C=O), 1609, 1437, 1222, 1173, 758 cm^{-1}; EIMS *m/e* (relative intensity) 204 (45, M^+), 172

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(41), 145 (base, M - CO_2CH_3), 130 (45), 115 (93), 91 (18), 59 (14); CIMS (2-methylpropane), *m/e* 205 (base, M^+ + H).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.93. Found: C, 70.22; H, 5.72.

Methyl 5-[2-[(phenylseleno)carbonyl]phenyl]-2-pentenoate (25e): oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.49 (2 H, dt, *J* = 0.9, 7.3 Hz, C4-H_2), 2.94 (2 H, t, *J* = 7.3 Hz, C5-H_2), 3.70 (3 H, s, OCH_3), 5.78 (1 H, d, *J* = 15.6 Hz, C2-H), 6.96 (1 H, dt, *J* = 15.6, 0.9 Hz, C3-H), 7.23–7.60 (8 H, m, 8 × ArH), 7.90 (1 H, d, *J* = 7.6 Hz, 1 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.2, 33.8, 51.4, 121.5, 126.6, 126.9, 129.0, 129.1, 129.4, 131.1, 132.3, 136.0, 138.4, 138.8, 148.1, 166.9, 195.5; IR (neat) ν_{max} 1723 (ester C=O), 1702 (SeC=O), 1657, 1478, 1438, 1272, 1200, 1184, 887, 765, 740 cm^{-1}; EIMS *m/e* (relative intensity) 217 (base, M^+ - SePh), 185 (49), 157 (84), 129 (69), 90 (28), 77 (15), 55 (13); CIMS (2-methylpropane) *m/e* 375 (M^+ + H), 217 (base, M^+ + H - SePh); CIHRMS *m/e* 371.0521 ($C_{19}H_{18}OSe$ requires 371.0526, based on Se^{76}).

Methyl 2-(2-(1,2,3,4-Tetrahydro-1-oxonaphthalenyl))-acetate (26e). Following the general procedure (method A), **25e** (89 mg, 0.239 mmol) afforded, after purification by flash chromatography (SiO_2, 0–15% EtOAc–hexane eluant), 44 mg (52 mg theoretical, 84%) of **26e** as a white solid: mp 52–53 °C (EtOH–H_2O; lit.[79] mp 55–56.5 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.98 (1 H, ddd, *J* = 24.5, 12.8, 4.5 Hz, C3-H_1), 2.26 (1 H, m), 2.44 (1 H, dd, *J* = 15.5, 7.3 Hz, C*H*HCO$_2$), 2.93–3.22 (4 H, m), 3.73 (3 H, s, OCH_3), 7.24 (1 H, d, *J* = 7.5 Hz, C5-H), 7.31 (1 H, t, *J* = 7.5 Hz, C6-H), 7.47 (1 H, td, *J* = 7.5, 1.3 Hz, C7-H), 8.03 (1 H, dd, *J* = 7.5, 1.3 Hz, C8-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.1 (e), 29.2 (e), 34.8 (e), 44.8 (o), 51.7 (o), 126.6 (o), 127.4 (o), 128.7 (o), 132.1 (e), 133.4 (o), 143.9 (e), 173.0 (e), 198.3 (e); IR (KBr) ν_{max} 2950, 1737 (ester C=O), 1684 (ketone C=O), 1601, 1456, 1436, 1355, 1172, 954, 742 cm^{-1}; EIMS *m/e* (relative intensity) 218 (4, M^+), 187 (24), 158 (30), 144 (base, M - $CH_3CO_2CH_3$), 131 (25), 118 (55), 90 (74), 77 (16); CIMS (2-methylpropane) *m/e* 219 (base, M^+ + H).

Methyl 6-[2-[(phenylseleno)carbonyl]phenyl]-2-hexanoate (25f): oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.76 (2 H, m, C5-H_2), 2.22 (2 H, dt, *J* = 7.0, 1.0 Hz, C4-H_2), 2.82 (2 H, t, *J* = 7.6 Hz, C6-H_2), 3.70 (3 H, s, OCH_3), 5.83 (1 H, d, *J* = 15.8 Hz, C2-H), 6.97 (1 H, dt, *J* = 15.8, 1.0 Hz, C3-H), 7.42 (5 H, m, 5 × ArH), 7.61 (3 H, m, 3 × ArH), 7.88 (1 H, d, *J* = 7.5 Hz, 1 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.5, 31.7, 32.8, 51.1, 121.0, 126.3, 126.9, 128.6, 128.8, 129.2, 130.8, 131.9, 135.8, 138.4, 139.6, 148.7, 166.7, 195.2; IR (neat) ν_{max} 1723 (ester C=O), 1702 (SeC=O), 1657, 1438, 1203, 1185, 886, 739 cm^{-1}; EIMS *m/e* (relative intensity) 231 (45, M^+ - SePh), 199 (39), 171 (base, M^+ - SePh - HCO_2CH_3), 149 (45), 131 (40), 91 (79), 77 (47), 55 (31); CIMS (2-methylpropane) *m/e* 389 (M^+ + H), 231 (base, M^+ + H - SePh); CIHRMS *m/e* 385.0682 ($C_{20}H_{20}O_3Se$ requires 385.0682, based on Se^{76}).

Methyl 2-(6-(6,7,8,9-Tetrahydro-5-oxo-5*H*-benzocycloheptenyl))acetate (26f). Following the general procedure (method A), **25f** (230 mg, 0.594 mmol) afforded, after purification by flash chromatography (SiO_2, 20–15% EtOAc–hexane eluant), 127 mg (138 mg theoretical, 92%) of **26f** as a white solid: mp 39–39.5 °C (CH_3OH–H_2O); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60–1.75 (2 H, m), 1.88–1.94 (1 H, m), 2.06–2.18 (1 H, m), 2.48 (1 H, dd, *J* = 16.8, 5.3 Hz, C*H*HCO$_2$), 2.90 and 3.13 (overlapping 2 H, m and 1 H, dd, *J* = 16.8, 8.2 Hz, CH*H*CO$_2$), 3.30–3.52 (1 H, m), 3.65 (3 H, s, OCH_3), 7.21 (1 H, d, *J* = 7.6 Hz, C1-H), 7.27 (1 H, app t, *J* = 7.4 Hz, 1 × ArH), 7.38 (1 H, td, *J* = 7.4, 1.5 Hz, 1 × ArH), 7.70 (1 H, dd, *J* = 7.6, 1.5 Hz, C4-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.4 (e), 29.5 (e), 33.4 (e), 35.9 (e), 45.7 (o), 51.5 (o), 126.4 (o), 128.5 (o), 129.8 (o), 131.4 (o), 139.1 (e), 141.9 (e), 172.6 (e), 205.1 (e); IR (KBr) ν_{max} 2936, 1737 (ester C=O), 1684 (ketone C=O), 1598, 1438, 1175, 739 cm^{-1}; EIMS *m/e* (relative intensity) 232 (45, M^+), 200 (base, M^+ - $HOCH_3$), 172 (24), 144 (61), 131 (77), 118 (26), 104 (40), 91 (65), 77 (29); CIMS (2-methylpropane) *m/e* 233 (base, M^+ + H).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.67; H, 6.97.

***Se*-Phenyl 2-(4-methoxy-3-butenyl)benzenecarboselenoate (25g)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.21 and 2.39 (2 H, two m, *E*- and *Z*-$ArCH_2CH_2$), 2.84 (2 H, t, *J* = 7.5 Hz, $ArCH_2$), 3.46 and 3.57 (3 H, two s, *E*- and *Z*-OCH_3), 4.36 and 4.72 (1 H, two m, *E*- and *Z*-C*H*=CHOCH$_3$), 5.84 and 6.25 (1 H, d, *J* = 6.6 Hz, *Z*-C*H*OCH$_3$ and d, *J* = 12.4 Hz, *E*-C*H*OCH$_3$), 7.20–7.50 (6 H, m, 6 × ArH), 7.61 (2 H, m, 2 × ArH), 7.82 (1 H, t, C6-H); IR (neat) ν_{max} 2932, 1700 (C=O), 1654, 1578, 1478, 1438, 1208, 1186, 1108, 882, 740, 666 cm^{-1}; EIMS *m/e* (relative intensity) 314 (1, M^+ - CH_3OH), 189 (base, M^+ - SePh), 175 (10), 157 (19), 129 (73), 115 (12), 90 (10), 71 (24), 61 (32); CIMS (2-methylpropane) *m/e* 347 (M^+ + H), 189 (base, M^+ + H - HSePh); CIHRMS *m/e* 347.0553 ($C_{18}H_{18}O_2Se$ requires 347.0550).

3,4-Dihydro-2-(methoxymethyl)-1(2*H*)-naphthalenone (26g). Following the general procedure (method A), **25g** (190 mg, 0.549 mmol) afforded, after purification by flash chromatography (SiO_2, 0–12% EtOAc–hexane eluant), 67 mg (104 mg theoretical, 64%) of **26g** as a light tan powder: mp 35–36 °C (hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.94–2.08 (1 H, m, 1 × C3-H), 2.37 (1 H, ddd, *J* = 8.8, 4.4, 4.5 Hz, 1 × C3-H), 2.72–2.84 (1 H, m, C2-H), 3.02 (2 H, dd, *J* = 7.9, 4.3 Hz, C4-H_2), 3.39 (3 H, s, OCH_3), 3.67 (1 H, dd, *J* = 9.6, 7.3 Hz, C*H*HOCH$_3$), 3.87 (1 H, dd, *J* = 9.6, 4.2 Hz, CH*H*OCH$_3$), 7.24 (1 H, d, *J* = 7.7 Hz, C5-H), 7.30 (1 H, t, *J* = 7.8 Hz, C7- or C6-H), 7.46 (1 H, t, *J* = 7.4 Hz, C6- or C7-H), 8.02 (1 H, dd, *J* = 7.7, 1.0 Hz, C8-H); IR (neat) ν_{max} 2930, 1680 (C=O), 1602, 1454, 1226, 1120, 746 cm^{-1}; EIMS *m/e* 190 (16, M^+), 158 (80, M^+ - $HOCH_3$), 145 (40, M^+ - CH_2OCH_3), 130 (base, $C_9H_6O^+$), 115 (31), 90 (19), 45 (51, $CH_3OCH_2^+$); EIHRMS *m/e* 190.0994 ($C_{12}H_{14}O_2$ requires 190.0993).

Methyl 3-[2-[3-oxo-3-(phenylseleno)propyl]phenyl]-2-propenoate (27): oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.97 (2 H, t, *J* = 8.1 Hz, CH_2CO), 3.15 (2 H, t, *J* = 8.1 Hz, $ArCH_2$), 3.83 (3 H, s, OCH_3), 6.39 (1 H, d, *J* = 15.8 Hz, C2-H), 7.23–7.55 (9 H, m, 9 × ArH), 7.96 (1 H, d, *J* = 15.8 Hz, 1 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.4, 48.3, 51.7, 120.0, 126.2, 126.8, 127.2, 128.9, 129.3, 130.0, 130.2, 133.0, 135.7, 136.1, 141.5, 167.1, 199.0; IR (neat) ν_{max} 2949, 1716 (two C=O), 1633, 1478, 1437, 1318, 1275, 1194, 1021, 766, 740 cm^{-1}; EIMS *m/e* (relative intensity) 217 (31, M^+ - SePh), 156 (61), 129 (81), 115 (base), 101 (73), 91 (23), 77 (38), 59 (38); CIMS (2-methylpropane) *m/e* 375 (M^+ + H), 217 (base, M^+ + H - SePh); CIHRMS *m/e* 371.0520 ($C_{19}H_{18}O_3Se$ requires 371.0526, based on Se^{76}).

Methyl 2-(1-(1,2,3,4-Tetrahydro-2-oxonaphthalenyl))-acetate (28). Following the general procedure (method A), **27** (125 mg, 0.334 mmol) afforded, after purification by flash chromatography (SiO_2, 0–20% EtOAc–hexane eluant), 61 mg (73 mg theoretical, 84%) of **28** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 2.45–2.54 (1 H, m, 1 × C3-H), 2.72 (1 H, dt, *J* = 15.6, 5.7 Hz, 1 × C3-H), 3.05 (2 H, dd, *J* = 3.0, 6.0 Hz, C4-H_2), 3.09–3.20 (2 H, m, CH_2CO_2), 3.70 (3 H, s, OCH_3), 3.96 (1 H, t, *J* = 6.0 Hz, C1-H), 7.14 (1 H, m, 1 × ArH), 7.26 (3 H, s, 3 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.0 (o), 28.0 (e), 32.6 (e), 37.1 (e), 48.6 (o), 51.8 (e), 125.2 (o), 126.8 (o), 126.9 (o), 135.2 (e), 137.2 (e), 172.4 (e), 209.7 (e); IR (neat) ν_{max} 2953, 1737 (ester C=O), 1717 (ketone C=O), 1438, 1201, 1166, 746 cm^{-1}; EIMS *m/e* (relative intensity) 219 (59), 186 (base, M^+ - $HOCH_3$), 158 (65), 144 (45), 130 (69), 117 (66), 91 (22); CIMS (2-methylpropane) *m/e* 219 (base M^+ + H).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.48; H, 6.55.

In a separate experiment, cyclization of **27** (348 mg, 0.931 mmol) according to method B afforded 190 mg (203 mg theoretical, 94%) of pure **28**.

Methyl 4-[2-[3-oxo-3-(phenylseleno)propyl]phenyl]-2-butenoate (29): oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.95 (4 H, s), 3.53 (2 H, dd, *J* = 6.2, 1.6 Hz, C4-H_2), 3.71 (3 H, s, OCH_3), 5.72 (1 H, dt, *J* = 15.4, 1.6 Hz, C2-H), 7.05–7.53 (10 H, m, C3-H and 9 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.9, 35.4, 48.2, 51.4, 122.1, 126.2, 127.0, 127.3, 128.9, 129.3, 129.3, 130.2, 135.5, 135.7, 137.8, 147.2, 166.7, 199.3; IR (neat) ν_{max} 1722 (two C=O), 1654, 1438, 1274, 1168, 739 cm^{-1}; EIMS *m/e* (relative intensity) 388 (1, M^+), 314 (66), 234 (18), 199 (38), 157 (base, $PhSe^+$), 129 (50), 77 (62), 51 (28); CIMS (2-methylpropane) *m/e* 389 (M^+ + H); EIHRMS *m/e* 388.0578 ($C_{20}H_{20}SeO_3$ requires 388.0578).

Methyl 2-(6-(6,7,8,9-Tetrahydro-7-oxo-5*H*-benzocycloheptenyl))acetate (30). Following the general procedure (method A), **29** (187 mg, 0.483 mmol) afforded, after purification by flash chromatography (SiO_2, 0–20% EtOAc–hexane eluant), 80 mg (112

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mg theoretical, 71%) of **30** as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.40 (1 H, dd, J = 16.6, 6.0 Hz), 2.54 (1 H, td, J = 12.1, 1.1 Hz), 2.74–3.00 (6 H, m), 3.08 (1 H, m), 3.68 (3 H, s, OCH_3), 7.22 (4 H, s, 4 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.1 (e), 35.4 (e), 36.9 (e), 44.1 (e), 49.0 (o), 51.7 (o), 127.2 (o), 127.3 (o), 129.2 (o), 129.7 (o), 138.8 (e), 140.2 (e), 172.6 (e), 210.7 (e); IR (neat) ν_{max} 2953, 1736 (ester C=O), 1704 (ketone C=O), 1455, 1437, 1180, 766 cm^{-1}; EIMS m/e (relative intensity) 232 (31, M^+), 200 (100, $M^+ - CH_3OH$), 159 (base, $M^+ - CH_2CO_2CH_3$), 129 (93), 115 (91), 104 (26), 91 (61), 77 (36); CIMS (2-methylpropane) m/e 233 (base, $M^+ + H$).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.26; H, 7.19.

Ethyl 2-(methoxyimino)-4-[2-[3-oxo-3-(phenylseleno)propyl]phenyl]-3-butenoate (31): oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.90 (3 H, t, J = 7.1 Hz, OCH_2CH_3), 2.97 (2 H, t, J = 7.7 Hz, CH_2COSe), 3.06 (2 H, t, J = 7.1 Hz, $ArCH_2$), 4.14 (3 H, s, $NOCH_3$), 4.42 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 7.14 (1 H, d, J = 16.6 Hz, CHC=N), 7.20–7.66 (9 H, m, 9 × ArH), 7.90 (1 H, d, J = 16.6 Hz, ArCH=C); IR (neat) ν_{max} 2980, 2938, 1718, 1478, 1458, 1440, 1372, 1334, 1260, 1172, 1048, 932, 740, 690 cm^{-1}; EIMS m/e (relative intensity) 288 (base, M^+ – SePh), 242 (93, M^+ – SePh – HOEt), 184 (66), 157 (40, $PhSe^+$), 142 (14), 129 (15), 115 (43), 77 (7); CIMS (2-methylpropane) m/e 446 (base, $M^+ + H$).

Anal. Calcd for $C_{22}H_{23}NO_4Se$: C, 59.46; H, 5.22; N, 3.15. Found: C, 59.83; H, 5.51; N, 3.35.

Ethyl 2-(Methoxyimino)-3-(1-(1,2,3,4-tetrahydro-2-oxonaphthalenyl))propanoate (32). Following the general procedure (method A), **31** (190 mg, 0.427 mmol) afforded, after purification by flash chromatography (SiO_2, 0–18% EtOAc–hexane eluant), 79 mg (123 mg theoretical, 64%) of **32** as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (3 H, t, J = 7.1 Hz, OCH_2CH_3), 2.51 (1 H, m), 2.65 (1 H, m), 3.04 (3 H, m), 3.21 (1 H, m), 3.82 (1 H, t, J = 7.6 Hz), 4.04 (3 H, s, $NOCH_3$), 4.26 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 7.10–7.30 (4 H, m); EIMS m/e (relative intensity) 289 (1, M^+), 258 (36, $M^+ - OCH_3$), 214 (15), 184 (11), 161 (34), 145 (base, $M^+ - CH_2C(=NOCH_3)CO_2Et$), 133 (42), 115 (34), 99 (21), 91 (10), 77 (9), 71 (17); CIMS (2-methylpropane) m/e 290 ($M^+ + H$).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 65.92; H, 7.15; N, 5.06.

***Se*-Phenyl 2-(4-phenyl-3-butynyl)benzenecarboselenoate (33)**: white solid; mp 106–107 °C (hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.68 (2 H, t, J = 7.2 Hz, $CH_2C\equiv C$), 3.06 (2 H, t, J = 7.2 Hz, $ArCH_2$), 7.29–7.60 (11 H, m, 11 × ArH), 7.64 (2 H, m, 1 × ArH), 7.91 (1 H, d, J = 7.9 Hz, 1 × ArH); IR (KBr) ν_{max} 2228 (w, C≡C), 1704 (C=O), 1566, 1476, 1440, 1184, 890, 756, 742, 692, 666 cm^{-1}; EIMS m/e (relative intensity) 390 (1, M^+), 233 (4, M^+ – SePh), 157 (8, $SePh^+$), 119 (base, $C_9H_{11}^+$), 91 (40, $C_7H_7^+$); CIMS (2-methylpropane) m/e 391 ($M^+ + H$), 233 (base, $M^+ + H$ – HSePh).

Anal. Calcd for $C_{23}H_{18}OSe$: C, 70.95; H, 4.66. Found: C, 71.25; H, 4.60.

2-(4-Phenyl-3-butynyl)benzaldehyde (34). Following the general procedure (method A, in toluene at 110 °C), **33** (161 mg, 0.412 mmol) afforded, after purification by flash chromatography (SiO_2, 0–16% EtOAc–hexane eluant), 59 mg (97 mg theoretical, 61%) of **34** as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.76 (2 H, t, J = 7.1 Hz, $CH_2C\equiv C$), 3.34 (2 H, t, J = 7.1 Hz, $ArCH_2$), 7.25–7.60 (8 H, m, 8 × ArH), 7.86 (1 H, dd, J = 7.4, 0.9 Hz, C6-H), 10.29 (1 H, s, CHO); IR (neat) ν_{max} 2926, 1700 (C=O), 1599, 1576, 1191, 755, 692 cm^{-1}; EIMS m/e (relative intensity) 234 (29, M^+), 233 (36, M^+ – H), 206 (46, M^+ – CO), 115 (base, $C_9H_7^+$), 91 (22), 71 (43); CIMS (2-methylpropane), m/e 235 (base, $M^+ + H$), 207 ($M^+ + H$ – CO); EIHRMS m/e 234.1040 ($C_{17}H_{14}O$ requires 234.1045).

***Se*-Phenyl 2-(2-cyanoethyl)benzenecarboselenoate (35)**: oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.67 (2 H, t, J = 7.1 Hz, CH_2CN), 3.09 (2 H, t, J = 7.1 Hz, $ArCH_2$), 7.35–7.62 (8 H, m, 8 × ArH), 8.01 (1 H, d, J = 7.8 Hz, C6-H); IR (neat) ν_{max} 2937, 2245 (C≡N), 1698 (C=O), 1564, 1452, 1108, 739, 660 cm^{-1}; EIMS m/e (relative intensity) 158 (base, M^+ – SePh), 130 (10, M^+ – COSePh), 103 (13), 89 (5), 77 (13); CIMS (2-methylpropane) m/e 316 ($M^+ + H$); CIHRMS m/e 312.0263 ($C_{16}H_{13}NOSe$ requires 312.0267, based on Se^{76}).

3-(2-Formylphenyl)propionitrile (36). Following the general procedure (method A, in toluene at 110 °C), **35** (105 mg, 0.333 mmol) afforded, after purification by flash chromatography (SiO_2, 0–25% EtOAc–hexane eluant), 41 mg (53 mg theoretical, 77%) of **36** as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.71 (2 H, t, J = 7.1 Hz, CH_2CN), 3.35 (2 H, t, J = 7.1 Hz, $ArCH_2$), 7.39 (1 H, d, J = 7.4 Hz, 1 × ArH), 7.58 (2 H, m, 2 × ArH), 7.83 (1 H, dd, J = 7.3, 1.4 Hz, C6-H), 10.09 (1 H, s, CHO); IR (neat) ν_{max} 2938, 2840, 2750, 2246 (C≡N), 1690 (C=O), 1660, 1576, 1452, 1426, 1196, 760, 660 cm^{-1}; EIMS m/e (relative intensity) 159 (base, M^+), 130 (99, M^+ – CHO), 118 (27), 104 (53), 91 (56), 77 (24), 65 (30); CIMS (2-methylpropane) m/e 160 (base, $M^+ + H$); EIHRMS m/e 159.0684 ($C_{10}H_9NO$ requires 159.0684).

***Se*-Phenyl 2-(cyanomethyl)benzenecarboselenoate (37)**: white needles, mp 109–110.5 °C (hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.03 (2 H, s, CH_2CN), 7.40–7.68 (8 H, m), 8.08 (1 H, d, J = 7.6 Hz, 1 × ArH); IR (KBr) ν_{max} 2240 (C≡N), 1679 (C=O), 1566, 1471, 1434, 1407, 1196, 911, 864, 774, 743, 684, 663, 632 cm^{-1}; EIMS m/e (relative intensity) 157 (4, $PhSe^+$), 144 (base, M^+ – SePh), 116 (28, M^+ – COSePh), 89 (18), 77 (7), 63 (6), 51 (4); CIMS (2-methylpropane) m/e 302 (base, $M^+ + H$).

Anal. Calcd for $C_{15}H_{11}NOSe$: C, 60.01; H, 3.69; N, 4.67. Found: C, 60.33; H, 3.59, N, 4.50.

(2-Formylphenyl)acetonitrile (38). Following the general procedure (method A, in toluene at 110 °C), **37** (301 mg, 1.00 mmol) afforded, after flash chromatography (SiO_2, 0–10% EtOAc–hexane eluant), 123 mg (41%) of recovered **37** and 49 mg (145 mg theoretical, 34%) of **38** as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.06 (2 H, s, CH_2CN), 7.55–7.70 (3 H, m, 3 × ArH), 7.87 (1 H, d, J = 7.0 Hz, 1 × ArH), 10.10 (1 H, s, CHO); IR (neat) ν_{max} 2245 (C≡N), 1701 (C=O), 1185, 1026 cm^{-1}; EIMS m/e (relative intensity) 145 (46, M^+), 118 (base, M^+ – HCN), 90 (65), 89 (42), 63 (19); CIMS (2-methylpropane) m/e 146 ($M^+ + H$); EIHRMS m/e 145.0525 (C_9H_7NO requires 145.0528).

***Se*-Phenyl 3-[2-(cyanomethyl)phenyl]propaneselenoate (39)**: oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.05 (4 H, m, $ArCH_2CH_2CO$), 3.74 (2 H, s, CH_2CN), 7.20–7.55 (9 H, m, 9 × ArH); IR (neat) ν_{max} 2242 (C≡N), 1721 (C=O), 1579, 1492, 1476, 1452, 1440, 1020, 740, 690 cm^{-1}; EIMS m/e (relative intensity) 172 (80, M^+ – SePh), 157 (15, $PhSe^+$), 144 (base, M^+ – COSePh), 130 (68), 117 (98), 103 (34), 91 (13), 77 (58); CIMS (2-methylpropane) m/e (relative intensity) 330 ($M^+ + H$), 172 (base, $M^+ + H$ – HSePh); CIHRMS m/e 330.0393 ($C_{17}H_{15}NOSe$ requires 330.0397).

3-[2-(Cyanomethyl)phenyl]propanal (40). Following the general procedure (method A, in toluene at 110 °C), **39** (188 mg, 0.571 mmol) afforded, after purification by flash chromatography (SiO_2, 0–18% EtOAc–hexane eluant), 23 mg (12%) of recovered **39** and 58 mg (99 mg theoretical, 59%) of **40** as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.71 (2 H, td, J = 7.2, 2.5 Hz, C2-H_2), 3.03 (2 H, t, J = 7.2 Hz, C3-H_2), 3.77 (2 H, s, $CH_2C\equiv N$), 7.20–7.50 (4 H, m, 4 × ArH), 9.85 (1 H, t, J = 2.5 Hz, CHO); IR (neat) ν_{max} 2938, 2245 (C≡N), 1726 (C=O), 1410, 1406, 1291, 1289, 1196, 763 cm^{-1}; EIMS m/e (relative intensity) 173 (12, M^+), 146 (base, M^+ – HCN), 145 (34, M^+ – CO), 112 (18), 90 (47), 77 (25); CIMS (2-methylpropane) m/e 174 ($M^+ + H$); EIHRMS m/e 173.0848 ($C_{11}H_{11}NO$ requires 173.0842).

***Se*-Phenyl 2-[3-(methoxyimino)propyl]benzenecarboselenoate (41)**: oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.50 and 2.62 (2 H, two m, CH_2CHN), 2.99 (2 H, m, $ArCH_2$), 3.79 and 3.82 (3 H, two s, two OCH_3), 6.64 and 7.61 (1 H, two t, J = 4.8 Hz, two CH=N), 7.24–7.57 (8 H, m, 8 × ArH), 7.90 (1 H, d, J = 7.6 Hz, 1 × ArH); IR (neat) ν_{max} 2936, 1702 (C=O, C=N), 1478, 1440, 1186, 1042, 886, 740 cm^{-1}; CIMS (2-methylpropane) m/e 348 (base, $M^+ + H$), 190 ($M^+ + H$ – SePh).

***Se*-Phenyl 3-(1-cyclohexenyl)propaneselenoate (42)**: oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.50–1.70 (4 H, m), 1.95 (4 H, m), 2.31 (2 H, t, J = 7.6 Hz, C3-H_2), 2.80 (2 H, t, J = 7.6 Hz, C2-H_2), 5.45 (1 H, br s, C=CH), 7.20 (3 H, m, 3 × ArH), 7.27 (2 H, m, 2 × ArH); IR (neat) ν_{max} 2926, 1726 (C=O), 1580, 1478, 1440, 1034, 1022, 738, 690 cm^{-1}; EIMS m/e (relative intensity) 294 (1, M^+), 157 (43, $PhSe^+$), 137 (base, M^+ – SePh), 119 (62, M^+ – COSePh), 97 (78), 81 (97), 77 (60), 67 (97, $C_5H_7^+$), 55 (67); CIMS (2-methylpropane) m/e 295 (base, $M^+ + H$); EIHRMS m/e 294.0522 ($C_{15}H_{18}OSe$ requires 294.0523).

3-(1-Cyclohexenyl)propanal (43). Following the general procedure (method A), **42** (150 mg, 0.510 mmol) afforded, after

purification by flash chromatography (SiO_2, 0–20% Et_2O–hexane eluant), 48 mg (70 mg theoretical, 69%) of **43** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.52–1.64 (4 H, m), 1.90–2.04 (4 H, m), 2.27 (2 H, t, J = 6.9 Hz, C3-H_2), 2.51 (2 H, td, J = 6.9, 1.6 Hz, C2-H_2), 5.42 (1 H, br s, C=CH), 9.75 (1 H, t, J = 1.6 Hz, CHO); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.2 (e), 22.6 (e), 24.9 (e), 28.2 (e), 30.0 (e), 41.6 (e), 104.1 (e), 121.6 (o), 202.5 (o); IR (neat) ν_{max} 2930, 1728 (C=O), 1438, 1408, 920 cm^{-1}; EIMS m/e (relative intensity) 138 (8, M^+), 120 (39), 94 (58), 79 (base, $C_6H_7^+$), 75 (40), 67 (62), 55 (29); CIMS (2-methylpropane) m/e 139 (M^+ + H). All properties were consistent with those previously reported.[80]

Methyl 4-[2-[2-oxo-2-(phenylseleno)ethyl]phenyl]-2-butenoate (44): oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.58 (2 H, d, J = 6.3 Hz, C4-H_2), 3.71 (3 H, s, OCH_3), 3.91 (2 H, s, CH_2COSe), 5.74 (1 H, d, J = 15.6 Hz, C2-H), 7.10 (1 H, dt, J = 15.6, 6.3 Hz, C3-H), 7.20–7.45 (9 H, m, 9 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 35.7, 50.9, 51.4, 122.2, 126.4, 127.2, 128.5, 128.7, 129.1, 130.1, 130.2, 131.7, 135.5, 136.9, 146.4, 166.4, 198.4; IR (neat) ν_{max} 1717 (two C=O), 1654, 1438, 1275, 1202, 1170, 1018, 740, 690 cm^{-1}; EIMS m/e (relative intensity) 217 (13), 185 (9), 157 (18), 129 (base, $C_{10}H_9^+$), 115 (14), 101 (14), 77 (14), 59 (9), 51 (8); CIMS (2-methylpropane) m/e 375 (base, M^+ + H).

Anal. Calcd for $C_{19}H_{18}O_3Se$: C, 61.13; H, 4.86. Found: C, 61.12; H, 4.82.

Methyl 2-(2-(1,2,3,4-Tetrahydro-3-oxonaphthalenyl))-acetate (45) and Methyl 2-(2-(2,3-Dihydro-1*H*-indenyl))-acetate (46). Following the general procedure (method A), **44** (216 mg, 0.578 mmol) afforded, after purification by flash chromatography (SiO_2, 0–20% EtOAc–hexane eluant), 47 mg (126 mg theoretical, 37%) of **45** as a white solid, mp 54.5–55.0 °C (CH_3OH–H_2O), and 46 mg (110 mg theoretical, 42%) of **46** as an oil. For **45**: ^1H NMR ($CDCl_3$, 300 MHz) δ 2.56 (1 H, dd, J = 16.0, 5.6 Hz, C*H*HCO$_2$), 2.82–3.16 (4 H, m, C1-H_2, C2-H and CH*H*CO$_2$), 3.68 (2 H, s, C4-H_2), 3.71 (3 H, s, OCH_3), 7.10–7.26 (4 H, m, 4 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.1 (e), 34.4 (e), 44.3 (o), 44.4 (e), 51.8 (o), 126.8 (o), 127.0 (o), 127.8 (o), 128.1 (o), 133.2 (e), 135.6 (e), 172.4 (e), 209.7 (e); IR (KBr) ν_{max} 2952, 1736 (ester C=O), 1717 (ketone C=O), 1494, 1438, 748 cm^{-1}; EIMS m/e (relative intensity) 218 (17, M^+), 186 (84), 144 (base, $M^+ - CH_3CO_2CH_3$), 129 (31), 116 (50), 104 (44), 91 (29), 77 (20); CIMS (2-methylpropane m/e 219 (base, M^+ + H); EIHRMS m/e 218.0938 ($C_{13}H_{14}O_3$ requires 218.0943).

For **46**: ^1H NMR ($CDCl_3$, 300 MHz) δ 2.50 (2 H, d, J = 7.4 Hz), 2.65 (2 H, dd, J = 15.4, 7.1 Hz), 2.89 (1 H, m, C2-H), 3.14 (2 H, dd, J = 15.4, 7.8 Hz), 3.70 (3 H, s, OCH_3), 7.14–7.20 (4 H, m, 4 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.3, 38.9, 39.7, 51.4, 124.4, 126.3, 142.6, 173.3; IR (neat) ν_{max} 2950, 1736 (C=O), 1436, 1273, 1201, 1158, 927, 843, 745 cm^{-1}; EIMS m/e (relative intensity) 190 (23, M^+), 159 (12), 131 (19), 116 (base, $M^+ - CH_3CO_2CH_3$), 91 (14), 74 (5); CIMS (2-methylpropane) m/e 191 (base, M^+ + H); EIHRMS m/e 190.0992 ($C_{12}H_{14}O_2$ requires 190.0993).

***Se*-Phenyl *N*-[(1,2-dimethylethoxy)carbonyl]-*N*-(2-methyl-2,7-octadien-1-yl)-2-aminoethaneselenoate (47b)**: oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.49 (11 H, br s, OtBu and C5′-H_2), 1.59 (3 H, s, C2′-CH_3), 2.06 (4 H, m, C4′-H_2 and C6′-H_2), 3.90–4.06 (4 H, m, CH_2NCH_2), 4.99 (2 H, m, CH=CH_2), 5.22 (1 H, m, C3′-H), 5.75–5.90 (1 H, m, C*H*=CH$_2$), 7.30 (3 H, m, 3 × ArH), 7.51 (2 H, m, 2 × ArH); IR (neat) ν_{max} 2976, 2928, 1706 (C=O), 1478, 1454, 1440, 1418, 1392, 1368, 1242, 1164, 1022, 740, 690 cm^{-1}; EIMS m/e (relative intensity) 252 (1), 224 (9), 196 (12), 152 (15), 123 (12), 81 (20), 71 (44), 57 (base, $C(CH_3)_3^+$); CIMS (2-methylpropane) m/e 438 (M^+ + H, base); CIHRMS m/e 434.1580 ($C_{22}H_{31}NO_3Se$ requires 434.1574, based on Se^{76}).

N-Methyl-1-[[(1,1-dimethylethoxy)carbonyl]amino]-2-methyl-2,7-octadiene (48). Following the general procedure (method A), **47b** (104 mg, 0.238 mmol) afforded, after purification by flash chromatography (SiO_2, 0–10% EtOAc–hexane eluant), 53 mg (60 mg theoretical, 88%) of **48** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.38 (11 H, br s, O*t*Bu and C5-H_2), 1.48 (3 H, s, C2-CH_3), 2.69 (3 H, br s, N-CH_3), 3.65 (2 H, br s, C1-H_2), 4.90 (2 H, m, C8-H_2), 5.15 (1 H, m, C3-H), 5.56–5.80 (1 H, m, C7-H); IR (neat) ν_{max} 2976, 2930, 1700 (C=O), 1480, 1454, 1420, 1392, 1366, 1246, 1176, 1148, 910, 884 cm^{-1}; EIMS m/e (relative intensity) 224 (1), 196 (5, M^+ – tBu), 180 (3), 152 (8), 122 (24), 107 (8), 88 (14), 81 (19), 67 (12), 57 (base, tBu^+); CIMS (2-methylpropane) m/e 254 (M^+ + H), 198 (base, $M^+ - C_4H_8$); CIHRMS m/e 254.2155 ($C_{15}H_{27}NO_2$ requires 254.2151).

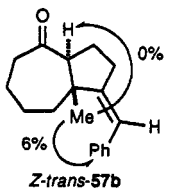
2-(1,1-Dimethyl-3-cyanopropyl)-5-methylcyclohexanone (50). Treatment of **49**[55] (233 mg, 1.00 mmol) with Bu_3SnH in the presence of 4.0 equiv of acrylonitrile according to the general procedure (method A) afforded, after flash chromatography (SiO_2, 0% then 14% EtOAc–hexane eluant), 110 mg (207 mg theoretical, 53%) of **50** as an oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (3 H, s), 0.99 (6 H, overlapping 3 H, s, and 3 H, d, J = 7.3 Hz), 1.25–1.43 (3 H, m), 1.64 (1 H, m), 1.75–2.15 (7 H, m), 2.20 (1 H, apparent t, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.1 (e), 22.1 (o), 23.8 (o), 24.6 (o), 28.0 (e), 34.0 (e), 34.4 (e), 34.6 (e), 36.1 (o), 52.1 (e), 57.2 (o), 120.4 (e), 211.2 (e); IR (neat) ν_{max} 2954, 2246 (C≡N), 1708 (C=O), 1456, 1428, 1390, 1368, 1206, 1122 cm^{-1}; EIMS m/e (relative intensity) 207 (1, M^+), 192 (2), 112 (base, $C_7H_{12}O^+$), 97 (10), 69 (45), 55 (25); CIMS (2-methylpropane) m/e 208 (base, M^+ + H); EIHRMS m/e 207.1622 ($C_{13}H_{21}NO$ requires 207.1623).

General Procedure for the Tandem Free-Radical Rearrangement–Cyclization Reaction: *cis*-Octahydro-7a-methyl-1-(phenylmethylene)-4*H*-inden-4-one (57a). A solution of **56a** (171 mg, 0.538 mmol) in 60 mL of dry C_6H_6 was degassed, treated with AIBN (5 mg), and warmed to reflux. A solution of Bu_3SnH (0.17 mL, 1.88 mg, 0.645 mmol, 1.2 equiv) in 5 mL of dry C_6H_6 was added dropwise over a period of 1.5 h (syringe pump). After an additional 1 h, the solution was cooled to 25 °C and concentrated under reduced pressure. The residue was dissolved in 40 mL of Et_2O and was stirred vigorously at 25 °C with 15 mL of 15% aqueous KF for 15 min. The Et_2O layer was separated, dried ($MgSO_4$), and concentrated. Flash chromatography (SiO_2, 8% EtOAc–hexane eluant) gave 111 mg (129 mg theoretical, 86%) of **57a** (mixture of olefin stereoisomers) as a colorless, viscous oil. Major component: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.12 (3 H, s, CH_3), 1.48–1.72 (3 H, m), 1.78 (2 H, m), 2.18 (2 H, m), 2.34 (2 H, m), 2.60 (2 H, apparent t), 6.44 (1 H, s), 7.11–7.29 (5 H, m, 5 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3 (e), 24.2 (e), 27.4 (o), 33.0 (e), 33.7 (e), 39.3 (e), 50.2 (e), 62.7 (o), 122.3 (o), 126.2 (o), 127.6 (o), 128.7 (o), 138.3 (e), 149.5 (e), 212.9 (e); IR (neat) ν_{max} 2948, 2863, 1711 (C=O), 1602, 1112, 982, 741 cm^{-1}; EIMS m/e (relative intensity) 240 (base, M^+), 225 (39), 197 (26), 169 (16), 141 (19), 128 (18), 115 (27), 107 (18), 91 (63), 77 (16); CIMS (2-methylpropane) m/e 241 (base, M^+ + H); EIHRMS m/e 240.1518 ($C_{17}H_{20}O$ requires 240.1514). Capillary GC analysis (Column A, oven temp 170 °C) indicated the presence of two components (t_R = 7.6 and 7.7 min) in a ratio of 82:18, respectively, identical (GC retention time, ^1H NMR analysis) with samples of authentic material.[26] Base equilibration (cat. NaOMe, MeOH, reflux, 36 h) resulted in no appreciable change (81:19) in the GC ratio of the two components (olefin isomers).

***cis*- and *trans*-Octahydro-8a-methyl-1-(phenylmethylene)azulen-4(1*H*)-one (57b).** Following the general procedure, **56b** (183 mg, 0.551 mmol) afforded 111 mg (139 mg theoretical, 80%) of **57b** as a colorless oil. Capillary GC analysis (Column B, oven temperature 220 °C) indicated the presence of four stereoisomers (t_R = 12.2, 13.3, 15.6, and 17.9 min; ratio = 28:39:16:17, respectively): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91, 0.94, 1.31 and 1.35 (3 H, four s, four CH_3's), 1.18–3.22 (13 H, m), 6.12, 6.17, and 6.45 (1 H, three s, olefinic CH's), 7.15–7.45 (5 H, m, 5 × ArH); IR (neat) ν_{max} 2932, 1700 (C=O), 1492, 1446, 1374, 754, 702 cm^{-1}; EIMS m/e (relative intensity) 254 (75, M^+), 239 (15), 211 (8), 197 (15), 170 (20), 155 (32), 141 (30), 128 (32), 115 (47), 91 (base, $C_7H_7^+$), 77 (20), 55 (49); CIMS (2-methylpropane) m/e 255 (base, M^+ + H); EIHRMS m/e 254.1671 ($C_{18}H_{22}O$ requires 254.1671).

Careful flash chromatography allowed separation of a fraction containing ***Z*-*trans*-57b**:***E*-*trans*-57b** (t_R = 13.3 and 17.9 min, respectively) in a GC ratio of 83:17. The relative stereochemistry of the major component was established by ^1H NMR NOE experiments (see below) and supported by base-catalyzed equilibration (cat. NaOMe, MeOH, reflux, 46 h) of this mixture to a 24:61:4:11 ratio (trans:cis ring fusion ratio 72:28) of the four isomers.

(80) Snider, B. B.; Cartaya-Marin, C. P. *J. Org. Chem.* **1984**, *49*, 1688.

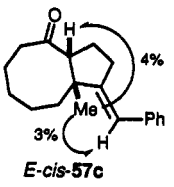


Z-trans-**57b**

As a result, it was found that the isomeric composition of the hydroazulenones **57b** can be readily distinguished by the chemical shifts of the angular methyl singlets in the ^{1}H NMR spectra. Those of the trans-fused isomers (***Z***- and ***E-trans*-57b**) are observed at higher field (0.94 and 0.91 ppm, respectively) than those in the corresponding cis-fused isomers (***Z***- and ***E-cis*-57b**; 1.31 and 1.35 ppm, respectively).

***cis*- and *trans*-Decahydro-9a-methyl-1-(phenylmethylene)-4*H*-cyclopentacycloocten-4-one (57c).** Following the general procedure detailed for the conversion of **56a** to **57a**, **56c** (422 mg, 1.22 mmol) afforded 279 mg (327 mg theoretical, 85%) of **57c** as a mixture of stereoisomers as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05 (2 H, m), 1.06, 1.21, and 1.31 (3 H, three s, C9a-CH_3), 1.29–2.81 (11 H, m), 2.88, 3.17, and 3.19 (1 H, dd, J = 1.5, 15.4 Hz; dd, J = 6.0, 15.2 Hz; m), 2.94 (1 H, m), 6.04, 6.37, and 6.44 (1 H, three s, =CH), 7.09–7.37 (5 H, m, 5 × ArH); IR (neat) ν_{max} 2930, 2868, 1697 (C=O), 1599, 1490, 1458, 1401, 752, 700 cm^{-1}; EIMS m/e (relative intensity) 268 (base, M$^+$), 253 (12), 225 (13), 197 (23), 170 (49), 155 (31), 141 (22), 128 (20), 115 (26), 105 (10), 91 (53), 77 (12), 67 (10), 55 (44); CIMS (2-methylpropane) m/e 269 (base, M$^+$ + H); EIHRMS m/e 268.1835 ($C_{19}H_{24}O$ requires 268.1827).

Capillary GC analysis (column B, oven temperature 220 °C) indicated the presence of four isomers (t_R = 9.4, 9.9, 11.8, and 13.1 min, respectively) in a ratio of 26:40:16:18, respectively (96% purity). Isolation of a sample of **57c** (consisting of ***E-cis*-57c** (t_R = 9.4 min) and ***Z-cis*-57c** (t_R = 11.8 min) in a GC ratio of 82:18 allowed identification of the lowest boiling component (***E-cis*-57c**; t_R = 9.4 min) based on the observation of a positive NOE (4%) between the 3aH and 9a-CH_3 signals in the ^{1}H NMR spectrum (see below). Base-catalyzed equilibration (cat. NaOMe, MeOH, reflux, 72 h), of this sample provided the equilibrium ratio 8:72:2:18 (trans:cis ring fusion ratio 90:10) as determined by capillary GC analysis (column B, oven temperature 220 °C; t_R = 9.4, 9.9, 11.8, and 13.1 min, respectively).



E-cis-**57c**

General Procedure for Ozonolysis of Bicyclic Ketones: *cis*- and *trans*-Octahydro-8a-methyl-1,4-azulenedione (58b). A solution of **57b** (84 mg, 0.33 mmol) in 10 mL of dry CH_2Cl_2 was cooled to −78 °C and treated with a stream of O_3 until a blue color persisted (ca. 4 min). After discharging the blue color with a stream of N_2, the mixture was treated dropwise with Me_2S (1.0 mL, 13.6 mmol, 40 equiv) and allowed to slowly warm to 25 °C overnight. After diluting with 15 mL of CH_2Cl_2 and washing with 5 mL of H_2O, the solution was dried (Na_2SO_4) and concentrated. Flash chromatography (SiO_2, 20% EtOAc–hexane eluant) afforded 44 mg (60 mg theoretical, 73%) of **58b** as a light yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.80 and 1.23 (3 H, two s, *trans*- and *cis*-**8a**-CH_3, respectively), 1.46–2.70 (12 H, m), 3.16 and 3.24 (1 H, dd, J = 3.1, 6.4 Hz and dd, J = 6.5, 11.1 Hz, *cis*- and *trans*-3aH, respectively); IR (neat) ν_{max} 2936, 1736 (C=O), 1700 (C=O), 1458, 1406, 1374, 1166, 1144, 1124, 1058 cm^{-1}; EIMS, m/e (relative intensity) 180 (35, M$^+$), 165 (26), 152 (35), 137 (27), 125 (26), 109 (48), 95 (66), 81 (77), 67 (base, $C_5H_7^+$), 55 (99, $C_4H_7^+$); CIMS (2-methylpropane) m/e 181 (M$^+$ + H); EIHRMS m/e 180.1150 ($C_{11}H_{16}O_3$ requires 180.1150).

Capillary GC analysis (Column B, oven temperature 150 °C) indicated the presence of ***cis*-58b** (t_R = 8.2 min) and ***trans*-58b** (t_R = 9.5 min) in a ratio of 45:55. Base-catalyzed equilibration (catalytic NaOMe, reflux, 38 h), resulted in a GC ratio of 32:68 ***cis*-58b:*trans*-58b**. The assignment of trans ring fusion to the major component from the base-catalyzed epimerization experiment was further supported by MM2 calculations[81] which resulted in a predicted equilibrium ratio of 28:72 ***cis*-58b:*trans*-58b**.

***cis*-Hexahydro-7a-methyl-1*H*-indene-1,4(2*H*)-dione (58a).** A 98-mg (0.41-mmol) sample of ketone **57a** was subjected to ozonolysis (CH_2Cl_2, −78 °C, 3 min; 4 equiv of Me_2S, 25 °C, 14 h), to give 144 mg (68 mg theoretical, 66%) of a single diketone **58a** by GLC analysis (t_R = 6.7 min, oven temperature 170 °C; 96.5% purity), identical in all respects with an authentic sample prepared by an alternative route.[26]

***cis*- and *trans*-Octahydro-9a-methyl-1*H*-cyclopentacyclooctene-1,4(5*H*)-dione (58c).** Following the general procedure, **57c** (242 mg, 0.90 mmol) afforded 112 mg (175 mg theoretical, 64%) of **58c** as an oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79 and 1.22 (3 H, two s, two CH_3), 1.36–2.65 (4 H, m), 3.18 and 3.24 (1 H, dd, J = 6.7, 1.0 Hz, and dd, J = 11.5, 5.9 Hz, respectively); IR (neat) ν_{max} 2936, 1736 (C=O), 1700 (C=O), 1458, 1406, 1374, 1166, 1144, 1124, 1058 cm^{-1}; EIMS m/e (relative intensity) 194 (12, M$^+$), 179 (22), 166 (19), 109 (41), 95 (52), 81 (71), 67 (base, $C_5H_7^+$), 55 (89); CIMS (2-methylpropane) m/e 195 (M$^+$ + H); EIHRMS m/e 194.1315 ($C_{12}H_{18}O_3$ requires 194.1310).

Capillary GC analysis (column A, oven temperature 130 °C) indicated the presence of *cis*-**58c** (t_R = 7.7 min) and *trans*-**58c** (t_R = 8.5 min) in a ratio of 41:59, respectively. Based-catalyzed equilibration (catalytic NaOMe, reflux, 62 h) resulted in a 14:86 GC ratio of *cis*-**58c**:*trans*-**58c**. Prediction of a 10:90 cis:trans ring fusion ratio, based on MM2 calculations[81] of the relative energies of the cis and trans isomers of **58c**, provided further support for the assignments of the relative stereochemistry of the two stereoisomers.

Acknowledgment. The financial support of the National Institutes of Health (CA42056) is gratefully acknowledged.

Supplementary Material Available: Full characterization of **3b–q**, **4**, full details of the preparation of carboxylic acid precursors to phenyl selenoesters **7**, **9**, **11**, **13**, **19**, **21**, **25a–g**, **27**, **29**, **31**, **33**, **35**, **37**, **39**, **42**, **44**, and **47a–b** and the preparation of bromo ketones **56**, and ^{1}H NMR data of **1e**, **1g**, **3a**, **3d–f**, **3h–j**, **3l**, **3o**, **3p–q**, **4**, **9–10**, **12–13**, **15**, **17**, **19**, **21–24**, **25a–g**, **26e**, **26g**, **27**, **29**, **34–36**, **38–42**, **45–46**, **47b**, **48**, **50**, **57b–c**, and **58b–c** (81 pages). This material is contained in many 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.

(81) (a) Still, W. C.; Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T. *Macromodel V2.0*; Department of Chemistry, Columbia University, New York. (b) The conformational searches were performed employing the MM2 force field (Macromodel Version 2.5). Global and close, low lying minima (≤5 kcal) were located by use-directed Monte Carlo sampling of the starting conformations (MCMM = 1000, MCSS = 2) generated by random variations (0–180°) in two to five of the available torsional angles until the global minima were repeatedly (≥30 times) found. See: Chang, G.; Guida, W. C.; Still, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4379.