Supplementary material

**General**: All NMR experiments were conducted on a Varian Unity 400 MHz spectrometer (400 MHz for $^1$H, 100 MHz for $^{13}$C) in CDCl$_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl$_3$. $J$ values are given in Hz using the following abbreviations: s (singlet), br s (broad singlet), t (triplet), q (quartet), pent (pentet) and m (multiplet). Mass spectra were recorded using direct insertion probe on a JMS-SX/SX102A (JEOL, Japan) in EI mode at 70 eV. M$^+$ ions are given for $^{80}$Se. All experiments were carried out in a dry N$_2$-atmosphere. The radical cyclizations were performed at 17°C in a micro photochemical reaction assembly as designed by J. H. Penn and R. D. Orr. Column chromatography was performed on Matrix™ Silica 60A/35-70. The stereochemistry of the products was determined by gNOESY-experiments.

$n$-Bu$_3$SnH was prepared from $n$-Bu$_3$SnCl and distilled before use.$^2$

$\beta$-Allyloxy-alkyl [2-(allyloxy)-cyclohexyl phenyl selenide (1c), 2-(allyloxy)-1-phenylethyl phenyl selenide (3), 2-(allyloxy)-2-$n$-butoxyethyl phenyl selenide (5), 2-(allyloxy)-2-phenylethyl phenyl selenide (6)] and $\beta$-hydroxyalkyl phenyl selenides used were prepared as described in, or, in analogy, with literature.$^3$

2-(Allyloxy)-3-phenylpropyl phenyl selenide (1a). $^1$H NMR (CDCl$_3$) δ 2.96 (dd, $J$ = 13.7, 6.4, 1H), 3.00,(dd, $J$ = 13.7, 5.9, 1H), 3.04 (dd, $J$ = 12.4, 5.8, 1H), 3.10 (dd, $J$ = 12.4, 5.7, 1H), 3.78 (dq, $J$ = 6.5, 5.9, 1H), 3.94 (ddddd, $J$ = 12.5, 5.7, 1.6, 1.2, 1H), 4.02 (ddddd, $J = 12.5$, 5.6, 1.6, 1.2, 1H), 5.14 (ddt, $J$ = 10.3, 1.8, 1.3, 1H), 5.20 (dm, $J$ = 17.2, 1H), 5.83 (ddt, $J$ = 17.1, 10.4, 5.6, 1H), 7.20-7.34 (several peaks, 8H), 7.50 (m, 2H). $^{13}$C NMR (CDCl$_3$) δ 31.8, 40.5, 70.7, 79.6, 116.9, 126.2, 126.7, 128.2, 129.0, 129.5, 130.5, 132.4, 134.7, 138.2. HRMS: calcd for C$_{18}$H$_{20}$OSe, 332.0679, found 332.0685.

2-(Allyloxy)-cyclooctyl phenyl selenide (1d). $^1$H NMR (CDCl$_3$) δ 1.32-1.54 (several peaks, 4H), 1.57-1.97 (several peaks, 7H), 2.06 (m, 1H), 3.62 (m, 2H), 3.92 (ddddd, $J$ = 12.4, 5.7, 1.6, 1.2, 1H), 4.08 (ddddd, $J = 12.4$, 5.7, 1.6, 1.2, 1H), 5.16 (dm, $J$ = 10.3, 1H),
5.27 (dq, \(J = 17.2, 1.6, 1H\)), 5.91 (ddt, \(J = 17.2, 10.3, 5.7, 1H\)), 7.23-7.29 (several peaks, 3H), 7.60 (m, 2H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 24.9, 25.6, 26.1, 26.6, 29.3, 30.0, 50.4, 70.3, 83.0, 116.9, 127.0, 128.7, 130.4, 134.7, 135.1. HRMS: calcd for C\(_{17}\)H\(_{24}\)OSe, 324.0992, found 324.0988.

Spectroscopic data for 2-hydroxy-3-phenylpropyl phenyl selenide,\(^4\) 2-hydroxyhexyl phenyl selenide,\(^5\) 2-hydroxycyclooctyl phenyl selenide,\(^6\) 2-(allyloxy)-hexyl phenyl selenide (1b),\(^4\) were in good agreement with the literature.

**Typical procedure for radical cyclization. 4-Methyl-2-benzyltetrahydrofuran (2a).**
A solution of triethylaluminum in hexanes (1.5 mL, 1.0 M, 1.5 mmol) was added dropwise to a solution of 2-(allyloxy)-2-phenylpropyl phenyl selenide (166 mg, 0.5 mmol), AIBN (6 mg, 0.038 mmol) and tri-\(n\)-butyltin hydride (146 \(\mu\)L, 0.55 mmol) in dry benzene (6 mL). The solution was irradiated over night at 17°C. Water was added and the reaction mixture was extracted with ethyl acetate and dried over MgSO\(_4\). After evaporation of the solvent the crude product was purified by flash chromatography (3% ethyl acetate in pentane), 70 mg (79%) of the title compound was isolated as a mixture of \(cis\) and \(trans\) isomers. \(trans\)-2a \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.03 (d, \(J = 6.8, 3H\)), 1.57 (ddd, \(J = 13.0, 6.7, 6.0, 1H\)), 1.82 (ddd, \(J = 13.0, 8.2, 6.7, 1H\)), 2.32 (m, 1H), 2.75 (dd, \(J = 13.5, 6.7, 1H\)), 2.94 (dd, \(J = 13.5, 6.7, 1H\)), 3.31 (dd, \(J = 8.3, 6.9, 1H\)), 4.05 (dd, \(J = 8.3, 6.8, 1H\)), 4.24 (pent, \(J = 6.7, 1H\)), 7.19-7.36 (several peaks, 5H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 17.7, 34.3, 40.6, 42.3, 74.6, 80.8, 126.1, 128.3, 129.1, 138.9. \(cis\)-2a \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.06 (d, \(J = 6.6, 3H\)), 1.23 (ddd, \(J = 12.2, 9.5, 7.1, 1H\)), 2.11 (dd, \(J = 12.2, 7.2, 5.7, 1H\)), 2.34 (m, 1H), 2.80 (dd, \(J = 13.5, 6.5, 1H\)), 3.00 (dd, \(J = 13.5, 6.5, 1H\)), 3.42 (t, \(J = 7.8, 1H\)), 3.93 (t, \(J = 7.8, 1H\)), 4.15 (dtd, \(J = 9.5, 6.5, 5.7, 1H\)), 7.20-7.36 (several peaks, 5H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 18.0, 33.1, 39.1, 42.3, 75.1, 79.4, 126.1, 128.2, 129.2, 138.9.

The following compounds 2 were similarly prepared. For yields and \(cis\)/\(trans\) (endolexo) ratios, see Tables 1-3.
**cis-11-Methyl-9-oxabicyclo[6.3.0]undecane (2d).** HRMS: calcd for C\(_{11}H_{20}O\), 168.1514, found 168.1488. *exo-2d* \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.99 (d, \(J = 6.5\), 3H), 1.12-1.81 (several peaks, 14H), 3.09 (dd, \(J = 9.7\), 8.1, 1H), 3.88 (dd, \(J = 8.1\), 7.0, 1H), 4.05 (m, 1H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 15.3, 25.6, 25.8, 25.8, 28.4, 29.9, 31.1, 41.6, 50.0, 72.8, 83.4. *endo-2d* \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.96 (d, \(J = 7.1\), 3H), 1.20-1.81 (several peaks, 12H), 2.05 (m, 1H), 2.29 (m, 1H), 3.38 (dd, \(J = 7.9\), 5.0, 1H), 3.66 (dd, \(J = 7.9\), 5.0, 1H), 3.96 (m, 1H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 13.5, 21.8, 25.5, 25.6, 27.3, 30.2, 30.9, 39.5, 45.1, 72.2, 83.1.

Spectroscopic data for *cis/trans-2a*, \(^5\) trans-2b*, \(^5\) *cis-2b*, \(^3\) *exo-2c*, \(^3\) *endo-2c*, \(^3\) *trans-4* and *cis-4*\(^3\) were in good agreement with the literature.