Preparation of 1-Hydroxycyclopentanecarboxylic Acid Derivatives from a Chiral Equivalent of Glycolic Acid

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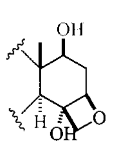
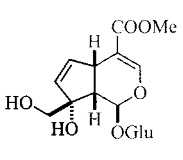
The stereoselective preparation of 1-hydroxycyclopentanecarboxylic acid derivatives is reported. The key reaction is either a radical cyclization or a radical annulation mediated by the transfer of a phenylseleno group. The radical precursors are easily synthesized by two consecutive enolate alkylations. Excellent stereochemical control for the quaternary C(1) stereogenic center has been achieved.

Introduction

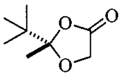
1-Alkoxymethyl and 1-hydroxymethyl-1-cycloalkanol derivatives are widespread among natural products. Two typical examples are shown below: the C ring of taxol[1] and the iridoid monotropein.[2] We are interested in developing a strategy allowing the synthesis of this kind of tertiary alcohol in a diastereo- and enantioselective fashion. In a recent work, we prepared the 1,3-dioxolan-4-one **1**, a chiral equivalent of glycolic acid, from D-mannitol in both enantiomerically pure forms.[3] We have also demonstrated that **1** can be efficiently alkylated via its enolate. In this paper, we show that by a proper combination of enolate alkylation and radical cyclization or annulation,[4] it is possible to prepare substituted 1-hydroxycyclopentanecarboxylic acid derivatives of type **2** from the dioxolanone **1**. For practical purposes, reactions were run with racemic material; extension of this work to optically pure compounds is expected to be straightforward.



C-ring of taxol



monotropeine



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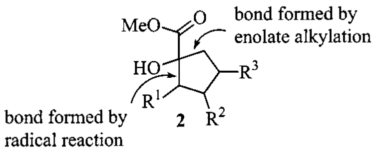

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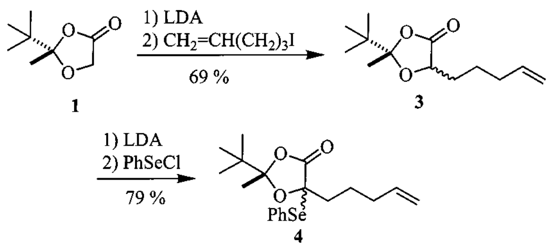
Results

The Radical Cyclization Procedure

Recently, we have demonstrated that intermolecular radical reactions starting from glycolic acid are highly efficient when they are run under phenylseleno transfer conditions.[5] This approach obviates the important problem of direct reduction of the radical intermediate which occurs when standard tin hydride conditions are used. The radical precursor **4** was prepared in two steps from **1**. Alkylation with LDA/1-iodopent-4-ene afforded **3** as a 2.2:1 mixture of diastereomers in 69% yield. The mixture of diastereomers was selenylated with LDA (2 equiv.)/PhSeCl in 79% yield giving the radical precursor **4** as a 3:1 mixture of diastereomers; the relative configurations were not determined since they had no influence on the subsequent radical reaction.[6]



Scheme 1

The cyclization was performed in benzene at different temperatures under irradiation with a 300-W sun lamp (Scheme 2). No initiator is required for this reaction. In all cases, the reaction was finished within 3 h. The temperature has a dramatic influence on the reaction. At temperatures below −30°C, radical dimerization was the main process.[7] At 80°C, the formation of the dimer is fully suppressed and the only isolated products are issued from the cyclization reaction. After optimization, the best results for the cyclization with respect to yield and stereoselectivity, were obtained upon sun lamp irradiation at 40°C. The major product **5** was isolated after flash chromatography in 83% yield as a mixture of the four possible diastereomers (**5a**/**5b**/

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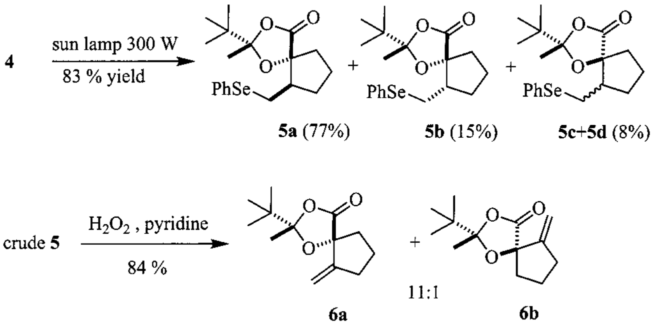
5c+**5d**, 77:15:8).[8] Oxidative elimination of the phenylselenyl group with hydrogen peroxide starting from the crude mixture of diastereomers afforded the methylenecyclopentane derivative **6a**/**6b** in 84% yield as an 11:1 mixture.



Scheme 2

The relative configuration of the major isomer **5a** was determined by X-ray crystal structure analysis (Figure 1). The relative configuration of **5b** was proved by oxidative elimination of a pure sample giving **6a** identical with an authentic sample prepared from **5a**. The inseparable mixture of **5c** and **5d** (approximatively 3:1 mixture based on the crude NMR) gave upon oxidation with hydrogen peroxide a single product **6b**, no attempts to assign the relative configuration at C(6) of **5c** and **5d** was made. The stereoselective formation of the spiro center (*trans*/*cis* = **5a**+**5b**/**5c**+**5d** = **6a**/**6b**, 11:1) is easily explained by steric considerations: reaction occurs *anti* to the large *tert*-butyl group. The moderate stereocontrol of the second center (**5a**/**5b**, 5.1:1) is better than expected for the cyclization of 1,1-disubstituted hexenyl radicals.[9] Interestingly, similar stereochemical outcome have been observed for the cyclization of β-keto esters and β-diesters promoted by manganese(III) acetate. In all these cases, a *cis* relationship between the alkyl chain and the *exo* ester group is observed; however, the stereoselectivities are quite low (≤ 3:1).[10] The four possible transition states, **A**/**A′** and **B**/**B′**, calculated by semiempirical AM1 calculations and leading to **5a** and **5b**, respectively, are depicted in Figure 2.[11] The major isomer **5a** forms from the most stable chair transition state **A** and also from the boat transition state **A′**. In these two transition states, the alkene moiety is oriented *syn* to the ester carbonyl group. This orientation is favored by steric interactions with the methyl group at the acetal center. Indeed, the distance between the nearest hydrogen atom of the alkene and the carbon atom of the methyl group at the acetal center is shorter in **B** (= 3.13 Å) than in **A** (= 3.36 Å) as shown in Figure 2. Similar values are obtained for the boat transition states **A′** and **B′**. Dipole-dipole interactions may also favor the formation of **5a**; however, this hypothesis is not supported by the calculations.

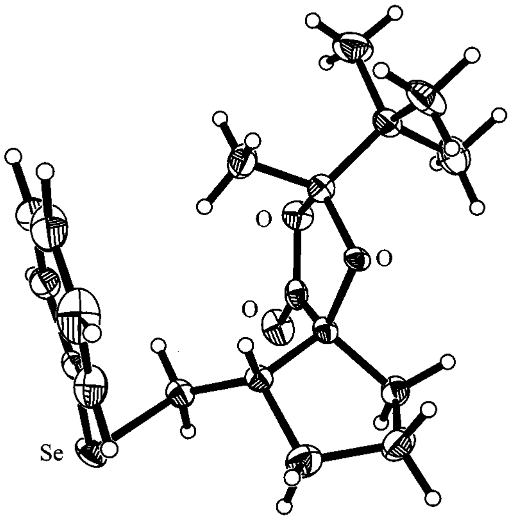


Figure 1. X- Ray crystal structure of **5a**

The Radical Annulation Procedure

A radical-mediated [3+2] annulation procedure based on iodine atom transfer has been developed by Curran.[12] We have already demonstrated that the transfer of a phenylseleno group can be used in similar annulation processes starting from an homopropargylic phenylselenides.[13] Starting from **1**, the preparation of the annulation reagent **8** is straightforward (Scheme 3). The dioxolanone **1** is first selenylated with LDA/PhSeSePh and then propargylated with 3-trimethylsilyl-1-iodopropyne. The selenide **8**, obtained as a 2:1 mixture of diastereomers, is stable and can be chromatographed and stored for several weeks in the refrigerator.

The annulation reactions were conducted by irradiation of **8** with a 300-W sun lamp in benzene at 80°C in the presence of a fourfold excess of the olefin[14] (Scheme 4). Identical results were obtained from both diastereomers of **8**; the reactions were therefore conducted with the mixture of diastereomers. Reaction with methyl acrylate afforded the polysubstituted methylenecyclopentanes **9** in 79% yield as a mixture of four (out of the eight possible) diastereomers in the ratio 3.7:1.8:1:1.8. Treatment of the crude mixture of diastereomers with tetrabutylammonium fluoride (TBAF) furnished the α,β-unsaturated ester **10** as a single diastereomer indicating that the relative configuration at the spiro center is fully controlled during the radical addition step. The relative configuration of **10** has been assessed by measurement of NOE differential spectra. These results were confirmed by measuring similar NOE spectra on **11** obtained by reductive deselenylation of **10**. As expected, the radical addition to methyl acrylate occurrs *anti* to the *tert*-butyl group. The mixture of diastereomers of **9** results from a low diastereoselectivity control of the C(3) center during the cyclization step and from a unselective phenylseleno group transfer giving a mixture of (*E*/*Z*) isomers. Reaction of **8** with *N*-phenylmaleimide was investigated next. The annulation product **12** was isolated in 82% yield. Three contiguous stereogenic centers and a tetrasubstituted double bond are built in this reaction. Four out of the sixteen possible stereoisomers have been observed and isolated by semi-preparative HPLC. Their relative configurations were again proven by NOE difference experiments.

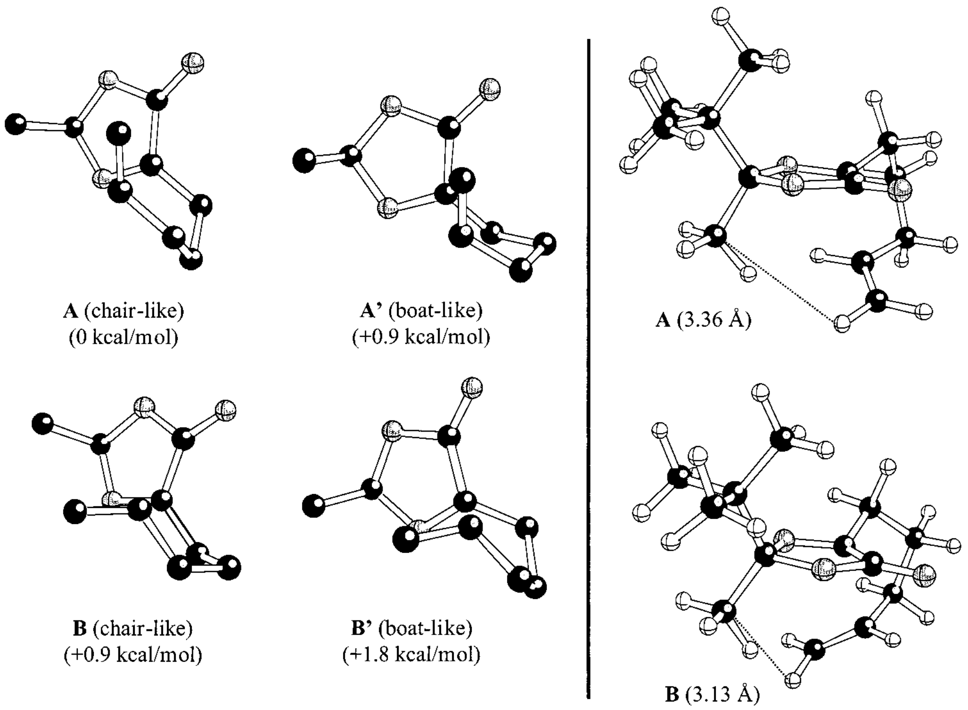
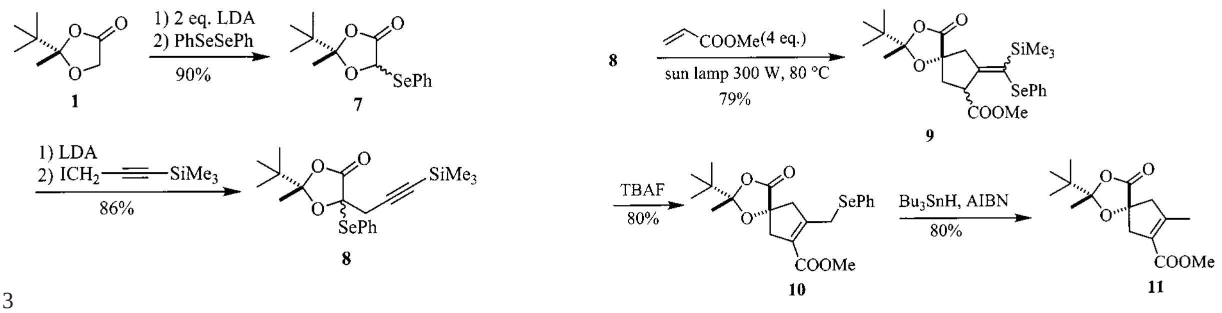


Figure 2. Model for the stereochemical outcome of the radical cyclization and relative heat of formation (hydrogen atoms and the *tert*-butyl group have been omitted for clarity reason)

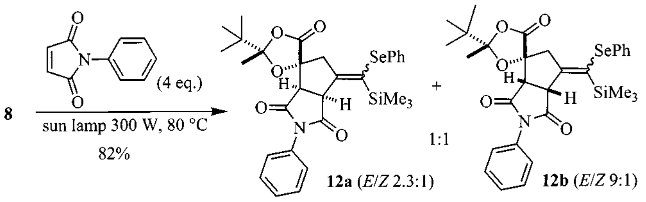


Scheme 3

All four products possess the same relative configuration at the spiro center resulting from radical addition to *N*-phenylmaleimide *anti* to the *tert*-butyl group. The *cis* junction of the fused cycles is fixed by the nature of the substrate. However both isomers **12a**/**12b** are present in a 1:1 ratio indicating that no steroselectivity is observed during the coupling of the prochiral radical with the prochiral olefin.[15]

Preparation of Free 1-Hydroxyesters

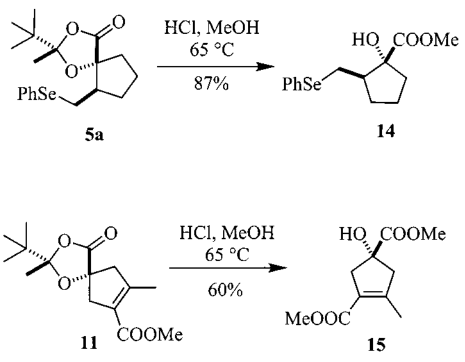
In order to demonstrate the synthetic potential of our approach for the preparation of free 1-hydroxycyclopentanecarboxylate, we have have investigated the solvolysis of the dioxolanone. For instance, compound **5a** and **11** afforded cleanly the methylesters **13** and **14** when treated with methanolic HCl at 65°C (Scheme 5). The tertiary alcohols are stable under these conditions. Moreover, this procedure is compatible with a phenylseleno group (compound **5a**) and with a double bond (compound **11**).



Scheme 4

Conclusions

Combination of enolate and radical chemistry permits a facile synthesis of polysubstituted 1-hydroxycyclopentanecarboxylic acid derivatives. The strong dimerization tendency of captodative radicals can be avoided by running the reactions at temperature higher than 40°C. The stereochemistry at the quaternary center C(1) is efficiently controlled. The control of the other stereogenic centers is satisfactory for cyclization reactions but still problematic for annulations. This last point illustrates an important challenge in radical reactions, i.e. the stereochemical control of the



Scheme 5

intermolecular coupling of a prochiral radical with a prochiral olefinic center. This topic is currently being investigated together with the synthesis of biologically active molecules.

Experimental Section

General: Irradiations were performed using a sun lamp Osram Ultra-Vitalux 300 W. − Flash column chromatography (FC) and filtration: Baker silica gel (0.063−0.200 mm), AcOEt, Et_2O and hexane as eluents. TLC: Baker silica gel 25 UV_{254} anal. plates; detection with UV, I_2, or by spraying with a solution of phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot 4\ H_2O$ (10 g), conc. H_2SO_4 (60 mL), and H_2O (940 mL) with subsequent heating. GC: Carlo Erba HRGC 5300. − IR: Perkin-Elmer 16PC. FT-IR: Mattson Unicam 5000. − NMR: Bruker AM 360 (^1H = 360 MHz ^{13}C = 90.5 MHz), Bruker avance DRX 500 (^1H = 500.13 MHz ^{13}C = 125.7 MHz) and Varian Gemini 200 (^1H = 200 MHz, ^{13}C = 50.3 MHz); chemical shift in ppm relative to tetramethylsilane $\delta = 0$. − MS: Vacuum Generators Micromass VG 70/70E and DS 11-250; CI (NH_3), EI (70 eV); *m/z* (%). The Mass specta of High Resolution were recorded on a FTICR mass spectrometer Bruker 4.7T BioApex II. − Elementary analysis: Ilse Beetz, Microanalytisches Laboratorium, D-8640 Kronach, Germany and Ciba-Geigy, Mikrolabor, CH-1723, Marly, Switzerland.

2-(*tert*-Butyl)-2-methyl-1,3-dioxolan-4-one (1): A solution of bis-trimethylsilylglycolate[16] (7.26 g, 33 mmol) and TMSOTf (0.66 g, 3 mmol) in CH_2Cl_2 (30 mL) was treated at −78°C with pinacolone (3.0 g, 30 mmol). The reaction mixture was allowed to warm to room temp. over 2 h. Sat. $NaHCO_3$ (10 mL) and Et_2O (150 mL) were added, the organic layer was washed with sat. $NaHCO_3$ (5× 15 mL), dried (Na_2SO_4). FC (Et_2O/pentane, 1:10) gave **1** (4.36 g, 92%). − ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.36$ (d, 1 H, $J_{AB} = 14$ Hz, A of AB,); 4.33 (d, 1 H, $J_{AB} = 14$ Hz, B of AB); 1.5 (s, 3 H, Me); 1.02 (s, 9 H, *t*Bu). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.3 (s); 117.7 (s); 64.2 (t); 39.0 (s); 24.2 (q); 20.1 (q). − IR (film): $\tilde{\nu}$ = 3021, 3016, 2360, 2341, 1798, 1211, 745, 738 cm^{-1}. − CI-MS; *m/z* (%): 159 (100) $[M + 1]^+$, 101 (20), 99 (2), 84 (2), 83 (22). − $C_8H_{14}O_3$ (158.20): calcd. C 60.74, H 8.92; found C 60.73, H 9.12.

5-(4-Pentenyl)-2-(*tert*-butyl)-2-methyl-1,3-dioxolan-4-one (3): A 1.6 M BuLi solution in hexane (9.38 mL, 15 mmol) was added to a solution of $(iPr)_2NH$ (2.14 mL, 15 mmol) in THF (50 mL) at −30°C. After cooling at −78°C, a solution of **1** (2.37 g, 15 mmol) in THF (5 mL) was added dropwise. After 15 min, a solution of 4-pentenyl iodide (3.53 g, 18 mmol) in THF (5 mL) was added and the mixture was allowed to warm to room temp. over 2 h. Sat. $NaHCO_3$ (10 mL) and Et_2O (200 mL) were added, the organic layer was washed with sat. $NaHCO_3$ (5× 20 mL) and dried (Na_2SO_4). FC (AcOEt/hexane, 1:20) gave **3** (2.33 g, 69%) as a 2.2:1 mixture of diastereomers. − Major diastereomer: ^1H NMR (200 MHz, $CDCl_3$): δ = 5.81 (m, 1 H, $CH{=}CH_2$); 5.02 (m, 2 H, $CH{=}CH_2$); 4.39 [dd, 1 H, J = 4.5, 7 Hz, H-C(5)]; 2.11 (tq, 2 H, J = 1.5, 7 Hz, CH_2-$CH{=}CH_2$); 1.9 (m, 1 H, CH); 1.68 (m, 3 H); 1.52 (s, 3 H, Me); 1.0 (s, 9 H, *t*Bu). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 173.6 (s); 137.8 (d); 116.2 (s); 115.0 (t); 75.9 (d); 40.2 (s); 33.1 (t); 32.6 (t); 24.5 (q); 22.7 (t); 19.2 (q). − Minor diastereomer: ^1H NMR (360 MHz, $CDCl_3$): δ = 5.8 (m, 1 H, $CH{=}CH_2$); 5.0 (m, 2 H, $CH{=}CH_2$); 4.36 [dd, 1 H, J = 4, 7.6 Hz, H-C(5)]; 2.12 (m, 2 H, CH_2-$CH{=}CH_2$); 1.9 (m, 1 H, CH); 1.65 (m, 3 H); 1.47 (s, 3 H, Me); 1.02 (s, 9 H, *t*Bu). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 173.1 (s); 137.8 (s); 116.1 (s); 115.1 (t); 73.6 (d); 37.9 (s); 33.1 (t); 30.4 (t); 24.4 (q); 24.2 (t); 19.2 (q). − Mixture of diastereomers: IR (film): $\tilde{\nu}$ = 2977, 2965, 1794, 1380, 1254, 1216, 907 cm^{-1}. − CI-MS: 227 (93, $[M+1]^+$), 169 (16), 127 (32), 109 (29), 101 (100), 81 (33), 41 (55). − $C_{13}H_{22}O_3$ (226.32): calcd. C 68.99, H 9.80; found C 68.87, H 9.93.

5-(4-Pentenyl)-2-(*tert*-Butyl)-2-methyl-5-phenylselenyl-1,3-dioxolan-4-one (4): A 1.6 M BuLi solution in hexane (25 mL, 40 mmol) was added to a solution of $(iPr)_2NH$ (5.7 mL, 40 mmol) in THF (150 mL) at −30°C. After cooling at −78°C, a solution of **3** (9.04 g, 40 mmol) in THF (20 mL) was added dropwise. After 15 min, a solution of phenyselenylchloride (9.6 g, 50 mmol) in THF (20 mL) was added and the mixture was allowed to warm at room temp. over 2 h. Sat. $NaHCO_3$ (30 mL) and Et_2O (500 mL) were added, the organic layer was washed with sat. $NaHCO_3$ (5× 20 mL) and dried (Na_2SO_4). FC (AcOEt/hexane, 1:20) gave **4** (12.1 g, 79%) as a 3:1 mixture of diastereomers. − Major diastereomer: ^1H NMR (200 MHz, $CDCl_3$): δ = 7.7 (m, 2 H, arom. H); 7.35 (m, 3 H, arom. H); 5.7 (m, 1 H, $CH{=}CH_2$); 4.92 (m, 2 H, $CH_2{=}CH$); 2.0 (m, 3 H); 1.8 (m, 3 H), 1.67 (s, 3 H, Me); 0.98 (s, 9 H, *t*Bu). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.6 (s); 137.8 (d); 137.2 (d); 129.3 (d); 129.0 (d); 127.7 (s); 115.6 (s); 115.1 (t); 83.7 (s); 39.1 (s); 35.2 (t); 33.1 (t); 24.5 (q); 23.5 (t); 20.2 (q). − Minor diastereomer: ^1H NMR (200 MHz, $CDCl_3$): δ = 7.7 (m, 2 H, arom. H); 7.35 (m, 3 H, arom. H); 5.7 (m, 1 H, $CH{=}CH_2$); 4.9 (m, 2 H, $CH_2{=}CH$); 2.0 (m, 3 H); 1.78 (m, 3 H), 1.5 (s, 3 H, Me); 1.09 (s, 9 H, *t*Bu). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 172.0 (s); 137.6 (d); 137.1 (d); 129.2 (d); 128.9 (d); 127.7 (s); 116.7 (s); 115.1 (t); 83.9 (s); 39.1 (s); 38.4 (t); 37.5 (t); 24.7 (q); 23.8 (t); 20.2 (q). − Mixture of diastereomers: IR (Film): $\tilde{\nu}$ = 2977, 2966, 1788, 1255, 1153, 913, 741, 691 cm^{-1}. − CI-MS: 382 (0.5, $[M+1]^+$), 283 (47), 280 (23), 254 (16), 237 (32), 225 (100), 125 (46), 101 (43). − $C_{19}H_{26}O_3Se$ (381.38): calcd. C 59.84, H 6.87; found C 59.90, H 6.92.

2-(*tert*-Butyl)-2-methyl-6-phenylselenylmethyl-1,3-dioxaspiro[4.4]-nonan-4-one (5): A solution of **4** (400 mg, 1.05 mmol) in benzene (10 mL) was irradiated for 3 h at 40°C. After evaporation, FC (AcOEt/hexane, 1:20) gave **5a**/**5b**/**5c+d** (330 mg, 83%) as a 77:15:8 mixture of diastereomers. − **5a:** ^1H NMR (360 MHz, $CDCl_3$): δ = 7.5 (m, 2 H, arom. H); 7.23 (m, 3 H, arom. H); 3.14 (dd, 1 H, J = 4, 12 Hz, CHH-Se); 2.75 (t, 1 H, J = 12 Hz, CHH-Se); 2.39 (m, 1 H, CH); 2.2 (m, 2 H); 2.0 (m, 1 H); 1.75 (m, 2 H); 1.55 (m, 1 H); 1.35 (s, 3 H, Me); 0.93 (s, 9 H, *t*Bu). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 174.3 (s); 133.0 (d); 129.0 (d); 127.0 (d); 114.0 (s); 88.0 (s); 51.0 (d); 38.7 (s); 38.3 (t); 32.3 (t); 29.4 (t); 24.5 (q); 23.0 (t); 22.4 (q). − **5b:** ^1H NMR (360 MHz, $CDCl_3$): δ = 7.5 (m, 2 H, arom. H); 7.23 (m, 3 H, arom. H); 3.12 (dd, 1 H, J = 4.8, 12 Hz, CHH-Se); 2.75 (dd, 1 H, J = 10.8, 12 Hz, CHH-Se); 2.4 (m, 1 H, CH); 2.15 (m, 2 H); 2.0-1.5 (m, 4 H); 1.42 (s, 3 H, Me); 0.95 (s, 9 H, *t*Bu). − **5c:** ^1H NMR (360 MHz, $CDCl_3$): δ = 7.5 (m, 2 H, arom. H); 7.2 (m, 3 H, arom. H); 3.2 (dd, 1 H, J = 3.1, 12 Hz, CHH-Se); 2.86

(t, 1 H, J = 12 Hz, CH*H*-Se); 2.4 (m, 1 H, CH); 2.15 (m, 1 H); 2.05-1.1 (m, 5 H); 1.46 (s, 3 H, Me); 0.96 (s, 9 H, *t*Bu). − **5d:** ^{1}H NMR (360 MHz, CDCl$_3$): δ = 7.5 (m, 2 H, arom. H); 7.2 (m, 3 H, arom. H); 3.17 (dd, 1 H, J = 4, 12 Hz, C*H*H-Se); 2.8 (t, 1 H, J = 12 Hz, CH*H*-Se); 2.4 (m, 1 H, CH); 2.2 (m, 2 H); 2.06 (m, 1 H); 1.8 (m, 3 H); 1.5 (s, 3 H, Me); 0.99 (s, 9 H, *t*Bu). − Mixture of diastereomers: IR (KBr): $\tilde{\nu}$ = 2962, 2876, 1782, 1479, 1379, 1259, 1150, 923, 741 cm^{-1}. − CI-MS: 381 (29) [M$^+$], 282 (100), 280 (48), 264 (69), 236 (26), 170 (14), 125 (19), 101 (25). − $C_{19}H_{26}O_3Se$ (381.38): calcd. C 59.84, H 6.87; found C 59.96, H 6.90.

2-(*tert*-Butyl)-2-methyl-6-methylene-1,3-dioxaspiro[4.4]nonan-4-one (6): To a solution of crude **5** (266 mg, 0.70 mmol) in CH_2Cl_2 (3 mL) was added pyridine (11 mg, 0.14 mmol) and a 30% solution of H_2O_2 (0.23 mL, 2.1 mmol). After stirring for 2 h at room temp., Et_2O (20 mL) was added. The organic layer was washed with brine and dried (Na_2SO_4). FC (AcOEt/hexane, 1:20) gave **6a** and **6b** (132 mg, 84%) as a 11:1 mixture of diastereomers. − **6a:** ^{1}H NMR (200 MHz, CDCl$_3$): δ = 5.16 (m, 2 H, C*H*$_2$=C); 2.5 (m, 2 H); 2.2 (m, 1 H, CH); 2.07-1.8 (m, 3 H); 1.57 (s, 3 H, Me); 0.99 (s, 9 H, *t*Bu). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 174.1 (s); 151.7 (s); 115.1 (s); 110.4 (t); 86.2 (s); 39.2 (s); 37.7 (t); 30.7 (t); 24.7 (q); 22.7 (t); 21.3 (q). − **6b:** ^{1}H NMR (200 MHz, CDCl$_3$): δ = 5.24 (m, 2 H, C*H*$_2$=C); 2.5 (m, 2 H); 2.2 (m, 1 H, CH); 2.07-1.8 (m, 3 H); 1.53 (s, 3 H, Me); 1.06 (s, 9 H, *t*Bu). − Mixture of diastereomers: IR (film): $\tilde{\nu}$ = 2975, 2879, 1790, 1286, 1153, 930, 734 cm^{-1}. − CI-MS: 224 (100) [M$^+$], 166 (45), 153 (7), 139 (7), 125 (42), 107 (11) 101 (10). − $C_{13}H_{20}O_3$ (224.31): calcd. C 69.61, H 8.99; found C 69.49, H 9.17.

2-(*tert*-Butyl)-2-methyl-5-phenylselenyl-1,3-dioxolan-4-one (7): A 1.6 M BuLi solution in hexane (62.5 mL, 100 mmol) was added to a solution of (*i*Pr)$_2$NH (14.17 mL, 100 mmol) in THF (400 mL) at −30°C. After cooling to −78°C, a solution of **1** (7.9 g, 50 mmol) in THF (20 mL) was added dropwise. After 15 min, a solution of (PhSe)$_2$ (15.6 g, 50 mmol) in THF (15 mL) was added and the solution was stirred for 2 h. Sat. $NaHCO_3$ (10 mL) and Et_2O (200 mL) were added. The organic layer was washed with sat. $NaHCO_3$ (5 × 20 ml) and dried (Na_2SO_4). FC (Et_2O/hexane, 1:20) gave **7** (14.16 g, 90%) as a 1.5:1 mixture of diastereomers. − Major diastereomer: ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.70 (m, 2 H, arom. H); 7.30 (m, 3 H, arom. H); 5.97 (s, 1 H, CHSe); 1.46 (s, 3 H, Me); 0.99 (s, 9 H, *tBu*). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 170.1 (s); 135.9 (d); 129.3 (d); 129.0 (d); 128.7 (d); 126.9 (s); 117.4 (s); 75.4 (d); 39.6 (s); 24.1 (q); 20.6 (q). − Minor diastereomer: ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.7 (m, 2 H, arom. H); 7.3 (m, 3 H, arom. H); 5.93 (s, 1 H, CHSe); 1.31 (s, 3 H, Me); 0.95 (s, 9 H, *t*Bu). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 170.4 (s); 135.3 (d); 129.3 (d); 129.0 (d); 128.7 (d); 127.5 (s); 117.6 (s); 75.2 (d); 38.1 (s); 24.5 (q); 21.0 (q). − Mixture of diastereomers: IR (Film): $\tilde{\nu}$ = 2976, 1793, 1381, 1249, 1215, 1146, 1095, 952, 740 cm^{-1}. − CI-MS: 314 (59) [M+1]$^+$, 158 (25), 101 (100), 83 (49), 57 (26), 43 (57). − $C_{14}H_{18}O_3Se$ (313.26): calcd. C 53.68, H 5.79; found C 54.00, H 6.12.

2-(*tert*-Butyl)-2-methyl-5-phenylselenyl-5-(3-trimethylsilyl-2-propenyl)-1,3-dioxolan-4-one (8): A 1.6 M BuLi solution in hexane (3.13 mL, 5 mmol) was added to a solution of (*i*Pr)$_2$NH (0.71 mL, 5 mmol) in THF (20 mL) at −30°C. After cooling to −78°C, a solution of **7** (1.57 g, 5 mmol) in THF (5 mL) was added dropwise. After 15 min, a solution of 3-iodo-1-propynyl(trimethyl)silane (1.43 g, 6.0 mmol) in THF (5 mL) was added and the solution was allowed to warm to room temp. over 2 h. Sat. $NaHCO_3$ (10 mL) and Et_2O (100 mL) were added. The organic layer was washed with sat. $NaHCO_3$ (5 × 20 mL) and dried (Na_2SO_4). FC (Et_2O/hexane, 1:20) gave **8** (1.83 g, 79%) as a 2:1 mixture of diastereomers. − Major diastereomer: ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.75 (m, 2 H, arom. H); 7.35 (m, 3 H, arom. H); 2.95 (s, 2 H, CH$_2$); 1.76 (s, 3 H, Me); 1.05 (s, 9 H, *t*Bu); 0.14 (s, 9 H, SiMe$_3$). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 170.1 (s); 137.4 (d); 129.6 (d); 127.1 (s); 116.1 (s); 100.1 (s); 89.0 (s); 80.6 (s); 39.2 (s); 30.1 (t); 24.8 (q); 19.8 (q); −0.27 (q). − Minor diastereomer: ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.75 (m, 2 H, arom. H); 7.35 (m, 3 H, arom. H); 2.97 (s, 2 H, CH$_2$); 1.74 (s, 3 H, Me); 1.15 (s, 9 H, *t*Bu); 0.1 (s, 9 H, SiMe$_3$). ^{13}C NMR (50.3 MHz, CDCl$_3$): 171.2 (s); 137.4 (d); 129.6 (d); 129.1 (d); 127.2 (s); 117.6 (s); 101.2 (s); 89.4 (s); 81.3 (s); 38.6 (s); 32.0 (t); 25.3 (q); 22.9 (q); −0.41 (q). − Mixture of diastereomers: IR (Film): $\tilde{\nu}$ = 2964, 2913, 2180, 1793, 1250, 1149, 845 cm^{-1}. − CI-MS: 425 (5) [M+1]$^+$, 324 (42), 296 (18), 266 (20), 172 (29), 139 (72), 125 (76), 101 (100). − $C_{20}H_{28}O_3SeSi$ (423.49): calcd. C 56.72, H 6.66; found C 56.69, H 6.64.

Methyl 2-(*tert*-Butyl)-2-methyl-4-oxo-8-(1-phenylselenyl-1-trimethylsilyl)methylidene-1,3-dioxaspiro[4.4]nonane-7-carboxylate (9): A solution of **8** (802 mg, 1.89 mmol) and methyl acrylate (516 mg, 6 mmol) in benzene (5 mL) was irradiated with a 300-W sun lamp for 3 h at 80°C. After evaporation, FC (AcOEt/hexane, 1:20) gave **9** (762 mg, 79%) as a 4.3:2.6:2.1:1.0 mixture of diastereomers. The diastereomers were separated by column chromatography. − Diastereomer 1: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.4−7.1 (m, 5 H, arom. H); 4.15 (dddd, 1 H, J = 1.8, 6.6, 7.5, 9.1 Hz, CH); 3.64 (s, 3 H, COOMe); 3.12 (d, 1 H, J = 17 Hz, C*H*H); 2.99 (d, 1 H, J = 17 Hz, CH*H*); 2.66 (dt, 1 H, J = 14, 1.8 Hz, C*H*H-CH); 2.52 (m, 1 H, CH*H*-CH); 1.5 (s, 3 H, Me); 1.00 (s, 9 H, *t*Bu); 0.09 (s, 9 H, SiMe$_3$). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ = 174.6 (s); 173.0 (s); 157.5 (s); 133.3 (s); 130.1 (d); 129.7 (d); 125.6 (d); 115.2 (s); 84.2 (s); 52.3 (q); 52.2 (d); 44.1 (t); 42.9 (t); 38.6 (s); 24.5 (q); 22.1 (q); 0.57 (q); − Diastereomer 2: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.4-7.1 (m, 5 H, arom. H); 3.94 (d, 1 H, J = 8.7 Hz, CH); 3.75 (s, 3 H, COOMe); 3.2 (d, 1 H, J = 18.7 Hz, C*H*H); 2.77 (dt, 1 H, J = 18.7, 2.0 Hz, CH*H*); 2.48 (m, 2 H, C*H*$_2$-CH); 1.46 (s, 3 H, Me); 0.82 (s, 9 H, *t*Bu); 0.17 (s, 9 H, SiMe$_3$). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ = 174.1 (s); 172.7 (s); 158.5 (s); 133.3 (s); 130.1 (d); 129.1 (d); 128.7 (d); 128.4 (s); 125.6 (d); 115.2 (s); 83.6 (s); 52.3 (q); 49.2 (d); 48.0 (t); 38.4 (s); 24.4 (q); 21.9 (q); 0.02 (q). − Diastereomer 3: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.35−7.1 (m, 5 H, arom. H); 4.06 (dt, 1 H, J = 2.1, 9.1 Hz, CH); 3.61 (s, 3 H, COOMe); 3.15 (dd, 1 H, J = 2.1, 16 Hz, C*H*H); 2.97 (dd, 1 H, J = 2.1, 16 Hz, CH*H*); 2.51 (m, 2 H, C*H*$_2$-CH); 1.54 (s, 3 H, Me); 1.04 (s, 9 H, *t*Bu); 0.16 (s, 9 H, SiMe$_3$). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ = 174.1 (s); 172.8 (s); 159,6 (s); 133.3 (s); 129.8 (d); 129.1 (d); 129.0 (d); 128.4 (s); 125.6 (d); 115.3 (s); 83.5 (s); 52.4 (q); 48.8 (t); 47.8 (d); 43.3 (t); 38.7 (s); 24.5 (q); 22.5 (q); 0.0 (q). − Diastereomer 4: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.35−7.1 (m, 5 H, arom. H); 4.01 (t, 1 H, J = 8.8 Hz, CH); 3.76 (s, 3 H, COOMe); 3.35 (dd, 1 H, J = 2.0, 17.2 Hz, C*H*H); 2.9 (dd, 1 H, J = 2.0, 17.2 Hz, CH*H*); 2.6 (m, 2 H, C*H*$_2$-CH); 1.52 (s, 3 H, Me); 0.93 (s, 9 H, *t*Bu); 0.16 (s, 9 H, SiMe$_3$). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ = 173.5 (s); 173.3 (s); 159,9 (s); 133.1 (s); 129.1 (d); 129.0 (d); 128.8 (d); 128.4 (s); 125.9 (d); 115.5 (s); 84.9 (s); 52.2 (q); 51.5 (d); 45.2 (t); 41.4 (t); 38.8 (s); 24.5 (q); 22.4 (q); 0.7 (q). − Mixture of diastereomers: IR (Film): $\tilde{\nu}$ = 2962, 1792, 1249, 1153, 1069, 840, 736 cm^{-1}. − CI-MS: 477 (28) [M$^+$], 439 (10), 394 (80), 321 (78), 253 (23), 157 (25), 101 (90). − $C_{24}H_{34}O_5SeSi$ (509.58): calcd. C 56.57, H 6.73; found C 56.43, H 6.93.

Methyl 2-(*tert*-Butyl)-2-methyl-4-oxo-8-(1-phenylselenyl)methyl-1,3-dioxaspiro[4.4]non-7-ene-7-carboxylate (10): To a solution of **9** (mixture of 4 diastereomers) (525 mg, 1.03 mmol) in THF (5 mL) was added dropwise a 1 M solution of TBAF in THF at room temp. and the solution was left overnight. After evaporation, FC (AcOEt/hexane, 1:10) afforded **10** (only one diastereomer) as a pale yellow oil (331 mg, 75%). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.5 (m, 2 H, arom. H); 7.2 (m, 3 H, arom. H); 4.1 (d, 1 H, *J* = 11.4 Hz, C*H*HSePh); 4.0 (d, 1 H, *J* = 11.4, CH*H*SePh); 3.5 (s, 3 H, COOMe); 3.3 (d, 1 H, *J* = 18.5 Hz, C*H*H); 3.2 (d, 1 H, *J* = 17.1 Hz, C*H*H); 3.0 (d, 1 H, *J* = 18.5 Hz, CH*H*); 2.9 (d, 1 H, *J* = 17.1 Hz, CH*H*); 1.5 (s, 3 H, Me); 1.00 (s, 9 H, *t*Bu). NOE diff. ($CDCl_3$): δ = 1.5 (Me)→2.9 (CH*H*CCO$_2$Me, 1.5%); 1.00 (*t*Bu)→3.0 (CH*H*CCH$_2$SePh, 0.55%). − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 175.4 (s); 164.2 (s); 150.5 (s); 135.5 (d); 128.8 (d); 128.1 (d); 124.9 (d); 115.4 (s); 81.9 (s); 51.1 (q); 48.8 (t); 47.2 (t); 38.5 (s); 25.4 (t); 24.4 (q); 22.1 (q). − IR (Film): ṽ = 3056, 2976, 1790, 1713, 1640, 1437, 1379, 1288, 1256, 1153, 1073, 929, 739 cm^{-1}. − CI-MS: 438 (10) [M^{+}], 406 (44), 337 (31), 306 (100), 278 (32), 260 (7), 209 (6), 181 (6), 153 (26), 125 (18), 101 (39), 57 (12). − $C_{21}H_{26}O_5Se$ (437.40): calcd. C 57.67, H 5.99; found C 57.57, H 5.90.

Methyl 2-(*tert*-Butyl)-2-methyl-4-oxo-8-methylidene-1,3-dioxaspiro[4.4]non-7-ene-7-carboxylate (11): A solution of **10** (100 mg, 0.23 mmol) in benzene (4 mL), Bu_3SnH (0.12 mL, 0.46 mmol) and AIBN (10 mg) was irradiated with a 300-W sun lamp for 4 h at room temp. After evaporation, FC (AcOEt/hexane, 1:10) gave **11** as colorless oil (53 mg, 82%). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.7 (s, 3 H, COOMe); 3.3 (d, 1 H, *J* = 16.8 Hz, C*H*H); 3.2 (d, 1 H, *J* = 18.8 Hz, C*H*H); 3.0 (d, 1 H, *J* = 16.8 Hz, CH*H*); 2.8 (d, 1 H, *J* = 18.8 Hz, CH*H*); 2.1 (s, 3 H, Me); 1.5 (s, 3 H, Me); 1.00 (s, 9 H, *t*Bu). NOE diff. ($CDCl_3$): δ = 1.5 (Me)→3.0 (CH*H*CCO$_2$Me, 1.5%); 1.00 (*t*Bu)→2.8 (CH*H*CCH$_3$, 0.5%). − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 176.1 (s); 165.3 (s); 151.9 (s); 123.8 (s); 115.8 (s); 82.4 (s); 52.1 (t); 51.5 (q); 47.6 (t); 38.8 (s); 24.8 (q); 22.4 (q); 16.1 (q). − IR (Film): ṽ = 2976, 2965, 1791, 1719, 1656, 1484, 1436, 1380, 1289, 1247, 1154, 1083, 1046, 930 cm^{-1}. − CI-MS: 282 (42) [M^{+}], 250 (72), 245 (5), 224 (16), 197 (12), 183 (100), 165 (34), 139 (27), 101 (73), 85 (5), 57 (4). − $C_{15}H_{22}O_5$ (282.34): calcd. C 63.81, H 7.85; found C 63.84, H 7.89.

Spiro[2-*tert*-butyl-2-methyl-1,3-dioxolan-4-one-5,4′-2′-phenyl-6′-(1-phenylselenyl-1-trimethylsilylmethylydene)perhydrocyclopentano[*c*]azole-1,3-dione] (12): A solution of **8** (212 mg, 0.5 mmol) and *N*-phenylmaleimide (346 mg, 2 mmol) in benzene (2 mL) was irradiated with a 300-W sun lamp for 4 h at 60°C. After evaporation, FC (AcOEt/hexane, 1:10) gave **12** (244 mg, 82%) as a (*E*)-**12a**/(*Z*)-**12a**/(*E*)-**12b**/(*Z*)-**12b** = 5.2:1.2:3.8:1 mixture of diastereomers. The diastereomers were separated by HPLC (Waters RCM 25x10, *tert*-butyl methyl ether/hexane, 10:90, 5 mL/min); retention time: (*Z*)-**12a** 21.98 min; (*Z*)-**12b** 25.97 min; (*E*)-**12a** 29.94 min; (*E*)-**12b** 34.37 min. − (*E*)-**12a:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52−7.14 (m, 10 H, arom. H); 4.43 (d, 1 H, *J* = 8.3 Hz, C*H*-C=C); 3.74 (d, 1 H, *J* = 8.3 Hz, CH); 3.45 (d, 1 H, *J* = 18 Hz, C*H*H); 2.61 (d, 1 H, *J* = 18 Hz, CH*H*); 1.58 (s, 3 H, Me); 0.87 (s, 9 H, *t*Bu); 0.34 (s, 9 H, SiMe$_3$). NOE diff. ($CDCl_3$): δ = 0.87 (*t*Bu)→3.45 (C*H*H, 0.5%); 0.87 (*t*Bu)→2.61 (CH*H*, 0.5%); 0.34 (SiMe$_3$)→4.43 (COC*H*C=C, 2.2%). − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 174.1 (s); 173.7 (s); 171.7 (s); 151.2 (s); 133.8 (s); 133.3 (s); 132.1 (s); 130.0 (d); 129.7 (d); 129.6 (d); 129.3 (d); 126.7 (d); 126.4 (d); 117.6 (s); 83.2 (s); 52.9 (d); 51.6 (d); 47.1 (t); 39.0 (s); 24.9 (q); 22.6 (q); 0.6 (q). − (*Z*)-**12a:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49−7.18 (m, 10 H, arom. H); 4.96 (d, 1 H, *J* = 8.2 Hz, C*H*-C=C); 3.61 (d, 1 H, *J* = 8.2 Hz, CH); 3.24 (d, 1 H, *J* = 16.3 Hz, C*H*H); 2.91 (d, 1 H, *J* = 16.3 Hz, CH*H*); 1.72 (s, 3 H, Me); 1.05 (s, 9 H, *t*Bu); 0.06 (s, 9 H, SiMe$_3$). NOE diff. ($CDCl_3$): δ = 1.05 (*t*Bu)→3.24 (C*H*H, 0.4%); 0.06 (SiMe$_3$)→3.24 (C*H*H, 0.4%). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 173.9 (s); 173.6 (s); 171.7 (s); 149.5 (s); 134.1 (s); 133.6 (s); 132.1 (s); 131.8 (d); 129.5 (d); 129.3 (d); 129.1 (d); 126.8 (d); 126.6 (d); 117.6 (s); 83.3 (s); 54.9 (d); 50.6 (d); 42.6 (t); 39.2 (s); 24.9 (q); 22.6 (q); 1.3 (q). − (*E*)-**12b:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49−7.13 (m, 10 H, arom. H); 4.50 (d, 1 H, *J* = 8.4 Hz, C*H*-C=C); 3.78 (d, 1 H, *J* = 8.4 Hz, CH); 3.44 (d, 1 H, *J* = 18.3 Hz, C*H*H); 2.87 (d, 1 H, *J* = 18.3 Hz, CH*H*); 1.73 (s, 3 H, Me); 0.95 (s, 9 H, *t*Bu); 0.32 (s, 9 H, SiMe$_3$). NOE diff. ($CDCl_3$): δ = 0.95 (*t*Bu)→3.44 (C*H*H, 0.5%); 0.87 (*t*Bu)→2.61 (CHH, 0.6%); 0.34 (SiMe$_3$)→4.50 (COC*H*C=, 1.7%). − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 173.8 (s); 173.1 (s); 172.2 (s); 154.6 (s); 133.1 (s); 132.1 (s); 131.9 (s); 129.7 (d); 129.6 (d); 129.5 (d); 129.3 (d); 126.8 (d); 126.4 (d); 117.4 (s); 85.6 (s); 58.7 (d); 51.1 (d); 48.3 (t); 38.8 (s); 24.7 (q); 21.8 (q); 0.6 (q). − (*Z*)-**12b:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48-7.20 (m, 10 H, arom. H); 5.00 (d, 1 H, *J* = 8.4 Hz, C*H*-C=C); 3.69 (d, 1 H, *J* = 8.4 Hz, CH); 3.16-3.08 (m, 2 H, CH$_2$); 1.78 (s, 3 H, Me); 1.07 (s, 9 H, *t*Bu); 0.09 (s, 9 H, SiMe$_3$). NOE diff. ($CDCl_3$): δ = 1.07 (*t*Bu)→3.16 (CH$_2$, 0.4%); 0.09 (SiMe$_3$)→3.16 (CH$_2$, 0.6%). For this compound, NOE difference spectra were not conclusive. Better results were obtained after reduction of the phenylseleno group (see below). − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 173.6 (s); 173.1 (s); 172.0 (s); 152.9 (s); 133.7 (s); 132.9 (s); 131.9 (s); 131.3 (d); 129.4 (d); 129.3 (d); 129.1 (d); 126.8 (d); 126.6 (d); 117.5 (s); 86.7 (s); 57.1 (d); 54.9 (d); 44.8 (t); 38.9 (s); 24.8 (q); 21.8 (q); 1.3 (q). − Mixture of diastereomers: IR (KBr): ṽ = 2976, 1789, 1721, 1383, 1152, 926, 841, 733 cm^{-1}. CI-MS: 582 (31) [M^{+}], 498 (10), 470 (12), 454 (14), 442 (19), 174 (35), 158 (46), 101 (100), 83 (19). − $C_{30}H_{35}O_5NSeSi$ (596.66): C 60.39, H 5.91; found C 60.04, H 6.03.

Spiro[2-*tert*-butyl-2-methyl-1,3-dioxolan-4-one-5,4′-2′-phenyl-6′-(1-trimethylsilylmethylydene)perhydrocyclopentano[*c*]azole-1,3-dione]: A solution of *Z*-**12b** (19 mg, 0.03 mmol) in benzene (2 mL), Bu_3SnH (0.008 mL, 0.06 mmol), and AIBN (5 mg) was irradiated with a 300-W sun lamp for 3 h at room temp. After evaporation, FC (AcOEt/hexane, 1:5) gave the reduced derivative as colorless oil (9 mg, 67%). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48−7.44 (m, 2 H, arom. H); 7.40-7.37 (m, 1 H, arom. H); 7.31-7.29 (m, 2 H, arom H); 6.16 (q, 1 H, *J* = 1.9 Hz, CHSi); 4.01 (d, 1 H, *J* = 9.5 Hz, CH-C=C); 3.69 (d, 1 H, *J* = 9.5 Hz, CH); 3.10 (dt, 1 H, *J* = 1.8, 16.4 Hz, C*H*H); 2.91 (dd, 1 H, *J* = 2.4, 16.4 Hz, CH*H*); 1.75 (s, 3 H, Me); 1.60 (s, 9 H, *t*Bu); 0.12 (s, 9 H, SiMe$_3$). NOE diff. ($CDCl_3$): δ = 1.60 (*t*Bu)→3.10 (C*H*H, 0.5%); 0.87 (*t*Bu)→2.91 (CH*H*, 0.5%). − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 174.2 (s); 174.0 (s); 172.8 (s); 146.6 (s); 131.9 (s); 129.5 (d); 129.1 (d); 128.6 (d); 127.0 (d); 117.5 (s); 86.1 (s); 56.0 (d); 51.9 (d); 45.7 (t); 39.1 (s); 24.8 (q); 21.5 (q); −0.1 (q). − HRMS: $C_{24}H_{31}NO_5SiNa$ [M^{+}]: calcd. 464.1863; found: 464.1817. − $C_{24}H_{32}NO_5Si$ [M^{+}]: calcd. 442.2044, found 442.2050.

Methyl 1-Hydroxy-2-phenylselenylmethyl-1-cyclopentanecarboxylate (13): Gaseous HCl was bubbled through a solution of **5a** (42 mg, 0.11 mmol) in abs. MeOH (4 mL) for 2 min. After heating under reflux for 3 h, the solution was cooled and solid $NaCO_3$ (ca. 100 mg) was added. The mixture was stirred for 10 min, filtered, and the solvent was evaporated. H_2O was added to the residue, then extracted with CH_2Cl_2. The combined organic layers were washed with $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated in vacuo. FC (AcOEt/hexane, 3:1) afforded **13** as a yellow oil (30 mg, 87%). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49−7.47 (m, 2 H, arom. H); 7.28−7.23 (m, 3 H, arom. H); 3.80 (s, 3 H, COOMe); 2.96 (dd, 1 H, *J* = 6.2, 11.8 Hz, C*H*HSePh); 2.69 (dd, 1 H, *J* = 9.4, 11.8 Hz, CH*H*SePh); 2.39-2.33 (m, 1 H, CH); 2.23-2.17 (m, 1 H, CH); 2.13-2.07 (m, 1 H, CH); 1.94-1.86 (m, 1 H, CH); 1.85-1.77 (m, 2 H, 2 CH); 1.61-1.52 (m, 2 H, OH, CH). − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 176.6 (s); 132.9 (d); 130.4 (s); 129.5 (d); 127.3 (d); 84.8 (s); 52.9 (d); 52.5 (q); 38.6 (t); 31.9 (t); 28.5 (t); 22.3 (t). −IR (film): ṽ = 3508 (br, OH), 2951, 1724, 1578, 1477, 1436, 1249, 1022, 736 cm^{-1}. − CI-MS: 315 (12), 283 (2), 237 (6), 177 (4), 157

(100), 125 (2), 97 (3). − HRMS: $C_{14}H_{18}O_3SeNa$ [M^+]: calcd. 337.0313; found 337.0314.

Dimethyl 1-Hydroxy-4-methyl-3-cyclopentene-1,3-dicarboxylate (14): Gaseous HCl was bubbled through a solution of **11** (10 mg, 0.040 mmol) in abs. MeOH (2 mL) for 2 min. After heating under reflux for 4 h, the solution was cooled and solid $NaCO_3$ (ca. 100 mg) was added. The mixture was stirred for 10 min, filtered, and the solvent was evaporated. H_2O was added to the residue, and the solution was extracted with CH_2Cl_2. The combined organic layers were washed with $NaHCO_3$, brine, dried ($MgSO_4$), and concentrated in vacuo. FC (AcOEt/hexane, 5:1) afforded **14** as a yellow oil (5 mg, 60%). − ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.82$ (s, 3 H, COOMe); 3.73 (m, 3 H, COOMe); 3.20 (d, 1 H, $J = 16.7$ Hz, C*H*H); 3.15 (d, 1 H, $J = 18.3$ Hz, C*H*H); 2.85 (d, 1 H, $J = 16.7$ Hz, CH*H*); 2.67 (d, 1 H, $J = 18.3$ Hz, CH*H*); 2.15 (s, 3 H, Me). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 176.8$ (s); 165.8 (s); 152.2 (s); 124.2 (s); 77.5 (s); 53.5 (q); 53.4 (t); 51.4 (q); 48.1 (t); 16.3 (q). − IR (Film): $\tilde{\nu} = 3478$ (br, OH), 2954, 1732, 1698, 1557, 1435, 1245, 1098, 765 cm^{-1}. − HRMS: $C_{10}H_{14}O_5Na$ [M^+]: calcd. 237.0733; found 237.0716.

X-Ray Structure Analysis of 5a: Suitable crystals were obtained by slow crystallization from hexane/AcOEt (10:1) at −20°C. Experimental parameters are given in Table 1.

Table 1. Crystal data and structure refinement for **5a**

Empirical formula	$C_{19}H_{26}O_3Se$
Formula weight	381.36
Temperature	110 (2) K
Wavelength	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimension	$a = 10.825(2)$ Å, $\alpha = 90°$ $b = 10.141(2)$ Å, $\beta = 94.88(3)°$ $c = 16.755(3)$ Å, $\gamma = 90°$
Volume	1832.7(6) $Å^3$
Z	4
Density (calculated)	1.382 Mg/m^3
Absorption coefficient	2.061 mm^{-1}
$F(000)$	792
θ range for data collection	2.76 to 28.00°
Index ranges	$-14 \leq h \leq 14, -13 \leq k \leq 13, -21 \leq l \leq 21$
Reflections collected	17003
Independent reflections	4080 ($R_{int} = 0.0329$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4079 / 0 / 313
Goodness-of-fit on F^2	3.783
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0278$, $wR2 = 0.0633$
R indices (all data)	$R1 = 0.0320$, $wR2 = 0.0635$
Largest diff.peak and hole	0.699 and −0.454 $eÅ^{-3}$

Calculations: The semi-empirical calculations were performed with the AM1 hamiltonian using the Spartan 5.0 software (Wavefunction, Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612 USA; © Wavefunction 1997, Inc.).

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[6] Reactions with single diastereomers were investigated; as expected for radical mediated processes, identical reaction times, yields and stereoselectivities were obtained.

[7] The dimerization is stereoselective and is currently being investigated for the preparation of α,α′-dialkylated tartaric acids. Results will be reported separately.

[8] At 80°C, the cyclized products **5a**−**c** (88%) are formed together with a small amount (≤7%) of an unidentified impurity, presumably the product of *6-endo* cyclization.

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