

Supporting Information (Section SI-1)

Oxacycle Synthesis via Intramolecular Reaction of Carbanions and Peroxides

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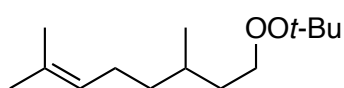
See SI-section 2 for ¹H NMR and ¹³C NMR spectra

I. General Methods

Except where noted, all reactions were conducted under an atmosphere of N₂ in glassware that had been flame dried prior to use. All reagents and solvents were used as supplied commercially, except CH₂Cl₂ (distilled from CaH₂), THF (distilled from Na/benzophenone) and DMF (distilled from CaH₂ under reduced pressure). ¹H NMR and ¹³C NMR spectra were acquired in CDCl₃; the spectrometer frequency is described within individual experimental descriptions. Chemical shifts are reported relative to residual chloroform (7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR). IR spectra were obtained on neat films (ZnSe, ATR mode) with selected absorbances reported in wavenumbers (cm⁻¹). GC/MS was performed using a 30 m DB-5MS column with a 1:200 injector split and 1 mL/min flow of He gas with analysis on an ion trap scanning in EI mode over 50–650 m/z range; the ion source was set at 200 °C. Flash column chromatography was performed on 230-400 μm silica gel. Thin-layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates containing a fluorescent indicator; developed TLC plates were visualized with a hand-held UV lamp or by heating after staining with 1% ceric sulfate/10% ammonium molybdate in 10% H₂SO₄ (general dip) or a peroxide-specific dip composed of a solution of 1.2g of *N,N*-dimethyl-*p*-phenylene diamine dihydrochloride in 1mL acetic acid, 20 mL H₂O, and 100 mL MeOH.¹ Abbreviations throughout: EA = ethyl acetate; Hex = hexane

***tert*-Butyl 3,7-dimethyloct-6-en-1-yl peroxide (1).**

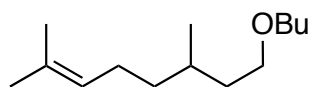
Synthesis of the methanesulfonate precursor: A 0.12M solution of citronellol (467 mg, 3.0 mmol) in methylene chloride at 0 °C was added Et₃N (1.25 mL, 9 mmol) followed by methanesulfonyl chloride (0.35 mL, 0.35 mmol) slowly. The reaction was allowed to warm slowly to room temperature and stirred for 16 h. The reaction was quenched with 25 mL of water and extracted with methylene chloride. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was then purified by column chromatography (25% EA/Hex) to yield 662 mg (94%) of 3,7-dimethyloct-6-en-1-yl methanesulfonate (42602-37-9) as a light yellow oil. R_f: 0.5 (25% EA/Hex). Spectral data matched those previously reported.²



Introduction of the peroxide employed a variant of a known procedure.³ To a suspension of CsOH monohydrate (6.76 g, 40 mmol) in DMF (80 mL) at 0 °C was slowly added *t*-butyl hydroperoxide (8.8 mL, 48 mmol, from a nominally 5.5 M solution

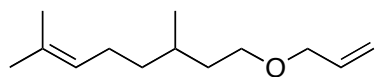
in the mixture was allowed to stir for 30 min, then methanesulfonate 1 (6.3 g, 27 mmol) was added

dropwise in 5 mL of DMF. The reaction was allowed to slowly warm to room temperature. After 5 h, 50 mL of water was added and the resulting mixture was extracted with ether. The combined organic layers were washed with brine and dried with Na₂SO₄. The residue was concentrated under reduced pressure and purified by column chromatography (2.5% EA/Hex) to yield 3.9g (64%) of the peroxide as a colorless oil. R_f: 0.65 (10% EA/Hex). ¹H NMR (400 MHz): δ 0.92 (d, 3H, J= 6.6), 1.18 (m, 1H), 1.26 (s, 9H), 1.30-1.47 (2H, unresolved overlapping signals), 1.50-1.68 (singlet overlapping unresolved signal, 5H), 1.70 (d, 3H, J= 0.9), 1.99 (m, 2H), 3.99 (m, 2H), 5.11 (app. triplet of quintets, 1H, J= 7.2, 1.4). ¹³C NMR (100 MHz): δ 17.6 (CH₃), 19.6 (CH₃), 25.4 (CH₃), 25.7 (CH₂), 26.3 (tBu CH₃'s), 29.7 (CH), 34.6 (CH₂), 37.1 (CH₂), 73.4 (CH₂), 80.0 (C), 124.7 (CH), 131.2 (C). IR: 2975, 2927, 2873, 1456, 1377, 1361, 1241, 1197, 884. HRMS calculated for C₁₄H₂₈O₂Na [M+Na]⁺: 251.1623; found 251.1624.

Butyl 3,7-dimethyloct-6-en-1-yl ether (2)

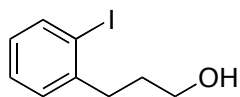
To a 0.2 M solution of peroxide 2 (234 mg, 1.0 mmol) in THF at -78 °C was added nBuLi (2.0 mmol, 0.80 mL of a nominally 2.5 solution in hex) drop wise. After stirring for 10 min, the reaction was allowed to warm to room temperature and after 4 h quenched with water (5 mL) and extracted with ether. The organic layer was dried with Na₂SO₄ and concentrated under reduced pressure. The residue was then purified by column chromatography (2.5% EA/Hex) to yield 138 mg (63%) of the ether as a colorless oil. R_f: 0.5 (10% CH₂Cl₂/Hex). ¹H NMR (400 MHz): δ 0.89-0.97 (s and d overlapping, 6H), 1.18 (m, 1H), 1.30-1.47 (overlapping signals, 4H), 1.52-1.67 (singlet overlapping with 2 other signals, 7H), 1.70 (d, J= 1.0), 2.00 (m, 2H), 3.36-3.51 (overlapping signals, 4H), 5.12 (app. t of q, J= 7.2, 1.3). ¹³C NMR (100 MHz): δ 13.9 (CH₃), 17.6 (CH₂), 19.4 (CH₃), 19.6 (CH₃), 25.5 (CH₂), 25.7 (CH₃), 29.6 (CH), 31.9 (CH₂), 36.7 (CH₂), 37.2 (CH₂), 69.2 (CH₂), 70.7 (CH₂), 124.9 (CH), 131.1 (C). IR: 2959, 2926, 2856, 1256, 1376, 1131, 830, 737. HRMS calculated for C₁₄H₂₈O: 213.2218; found 213.2215.

Allyl 3,7-dimethyloct-6-en-1-yl ether (3)



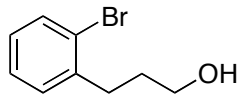
To a 0.2 M solution of peroxide **1** (229 mg, 1.0 mmol) in THF was added allyltributyltin (0.62 mL, 2.0 mmol). The solution was cooled to $-78\text{ }^{\circ}\text{C}$, and *n*BuLi (2.5 mmol, 1.0 mL of a 2.5 M solution in hexane) was added drop wise. After 30 min the reaction was quenched with 10 mL of water and extracted with ether. The combined organic layers were dried with Na_2SO_4 , and concentrated under reduced pressure. The residue was then purified by column chromatography (2.5% EA/Hex) to yield 137 mg (70%) of the allyl ether as a colorless oil. R_f : 0.25 (5% EA/Hex). Spectral details matched those previously reported.⁴

3-(2-Iodophenyl)propanol (4a)



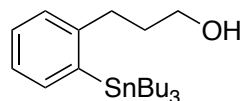
To a 0.42 M solution of commercially available 3-(2-iodophenyl)propionic acid (2.926 g, 10.6 mmol) in a $0\text{ }^{\circ}\text{C}$ solution of THF was added NaBH_4 (825 mg, 21.8 mmol) in one portion. $\text{BF}_3\cdot\text{OEt}_2$ (2.74 mL, 21.8 mmol) was then added drop wise and the reaction stirred for 1 hour. The reaction was quenched with 12 mL MeOH followed by 12 mL of 1M aq. HCl. The mixture was then diluted with EA and the organic layer separated and dried with Na_2SO_4 . The resulting solution was concentrated under reduced pressure and the residue purified by flash chromatography (30% EA/Hex) to yield 2.63g (95%) of the title compound as a light yellow oil. R_f : 0.33 (30% EA/Hex) Spectral details matched those previously reported.⁵

3-(2-Bromophenyl)propanol (4b)



To a 0.5 M solution of commercially available 3-(2-bromophenyl)propionic acid (771 mg, 3.37 mmol) in THF at $0\text{ }^{\circ}\text{C}$ was added NaBH_4 (255 mg, 6.7 mmol) in one portion. $\text{BF}_3\cdot\text{OEt}_2$ (0.842 mL, 6.7 mmol) was then added dropwise and the reaction stirred for 1 hour. The reaction was quenched with methanol (4 mL) followed by 1M HCl (4 mL). The mixture was diluted with EA (15 mL) and the separated organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (30% EA/Hex) to yield 668 mg (92%) of the alcohol as a colorless oil: R_f : 0.33 (30% EA/Hex). Spectral details matched those previously reported.⁶

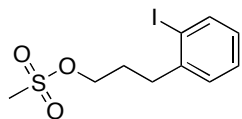
3-(2-(tributylstannyl)phenyl)propan-1-ol (4c)



To a 0.1 M solution of 3-(2-bromophenyl)propan-1-ol **4b** (0.50 mmol, 104 mg) in THF at $-78\text{ }^{\circ}\text{C}$ was added *n*BuLi (nominally 1.6 M in Hex, 1.1 mmol, 0.69 mL) slowly drop wise. The mixture was stirred for 10 minutes at $-78\text{ }^{\circ}\text{C}$, then tributyltin chloride (1.1 mmol, 0.30 mL) was added. The reaction was then allowed to warm slowly to room temperature. After 5 hours the reaction was quenched by sequential addition of small amounts of water and sat. aq. NH_4Cl . The resulting mixture was extracted with ether and the extracts dried with Na_2SO_4 . The mixture was concentrated under reduced pressure and purified via column chromatography (10% EA/Hex) to yield 126 mg (59%) of the title compound as a colorless oil. R_f : 0.40 (20% EA/Hex); $^1\text{H NMR}$ (400 MHz): δ 0.91 (t, 9H, $J=7.3$), 1.10 (m, 6H), 1.35 (m, 6H), 1.53 (m, 6H), 1.90 (m, 2H), 2.70 (m, 2H), 3.76 (dd, 2H,

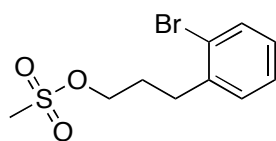
$J=11.3, 6.2$), 7.12-7.50 (m, 5H). ^{13}C NMR (100 MHz): δ 10.4 (CH₃), 13.7 (CH₂), 27.4 (CH₂), 29.2 (CH₂), 35.2 (CH₂), 35.4 (CH₂), 62.7 (CH₂), 125.4 (CH), 128.0 (CH), 128.4 (CH), 136.9 (C), 141.8 (CH), 148.6 (C). HRMS (ESI): calcd for C₂₁H₃₈OSn (M+Na)⁺: 449.1742; found: 449.1845. IR: 3332, 3051, 2953, 2921, 2870, 2851, 1463, 1433, 1417, 1375, 1339, 1291, 1151, 1056, 959, 864, 749, 662, 589.

3-(2-Iodophenyl)propyl methanesulfonate (**5a**)



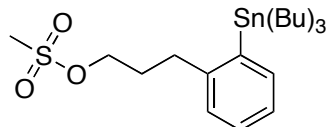
Alcohol **4a** (1.78 g, 5.23 mmol) was converted to the corresponding methanesulfonate (2.14 g, 92%, light yellow oil) by the same procedure employed for compound **5b** (below). R_f: 0.5 (30% EA/Hex). Spectral details matched those previously reported.⁷

3-(2-Bromophenyl)propyl methanesulfonate (**5b**)



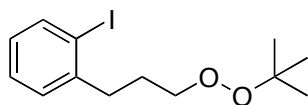
To a 0.2 M solution of alcohol **4b** (1.83 g, 8.51 mmol) in CH₂Cl₂ at 0 °C was added Et₃N (4.7 mL, 34 mmol) followed by methanesulfonyl chloride (0.99 mL, 12.8 mmol, drop wise). The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 20 mL of water and the separated aqueous layer was extracted with additional methylene chloride (2 X 30 mL). The combined organic layers were dried with Na₂SO₄. The crude mixture was concentrated under reduced pressure and purified by flash chromatography (20% EA/Hex) to yield 2.24 g (90%) of the methanesulfonate as a light yellow oil: R_f: 0.45 (20% EA/Hex). Spectral details matched those previously reported.⁸

3-(2-(Tributylstannyl)phenyl)propyl methanesulfonate (**5c**)



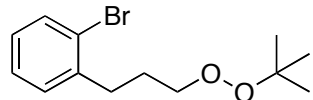
Alcohol **4c** (42.5 mg, 0.10 mmol) was converted to the corresponding methanesulfonate by the same procedure employed for compound **5b** to yield 31.7 mg (63%) of a colorless oil. R_f: 0.6 (30% EA/Hex). ¹H NMR δ 0.91 (t, 9H J= 7.3), 1.10 (m, 6H), 1.36 (quintet, 6H, J= 7.3), 1.53 (m, 6H), 2.07 (tdd, 2H, J= 7.3, 9.8, 6.4), 2.74 (m, 2H), 3.04 (s, 3H), 4.31 (t, 2H, J= 6.5), 7.15-7.35 (m, 4H), 7.35-7.50 (m, 1H). ^{13}C NMR (100 MHz): δ 10.4 (CH₃), 13.7 (CH₂), 27.4 (CH₂), 29.1 (CH₂), 31.5 (CH₂), 34.9 (CH₂), 37.4 (CH₃), 69.2 (CH₂), 125.7 (CH), 127.9 (CH), 128.5 (CH), 137.1 (CH), 141.9 (C), 147.2 (C). HRMS (ESI): calcd for C₂₂H₄₀O₃SSn (M+Na)⁺: 527.1618; found: 527.1619. IR: 2954, 2921, 2870, 2851, 1463, 1355, 1173, 1072, 1000, 959, 921, 873, 833, 806, 751, 730, 667, 591.

3-(2-Iodophenyl)propyl tert-butyl peroxide (**6a**)



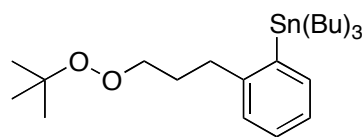
Methanesulfonate **5a** (2.14 g, 6.30 mmol) was converted to the t-butyl peroxide (1.61 g, 77%, light yellow oil) by the same procedure employed for compound **6b** (below). R_f: 0.45 (5% EA/Hex). ¹H NMR (400 MHz): δ 1.23 (s, 9H), 1.94 (tdd, 2H, J= 6.4, 9.0, 6.5), 2.82 (m, 2H), 4.03 (t, 2H, J= 6.4), 6.90 (td, 1H, J=7.4, 1.9), 7.27 (m, 2H), 7.83 (dd, 1H, J= 7.8, 1.1). ^{13}C NMR (100 MHz): δ 26.4 (CH₃), 28.4 (CH₂), 37.4 (CH₂), 74.0 (CH₂), 80.1 (C), 100.6 (C), 127.8 (CH), 128.3 (CH), 129.4 (CH), 139.5 (CH), 144.3 (C). HRMS (ESI): calcd for C₁₃H₁₉IO₂ (M+Na)⁺: 357.0327; found: 357.0315. IR: 2975, 2867, 1562, 1465, 1434, 1361, 1240, 1195, 1079, 1048, 1008, 876, 746, 646.

3-(2-Bromophenyl)propyl tert-butyl peroxide (6b), 897 mg, 42%) was prepared from



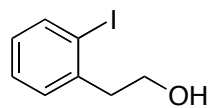
methanesulfonate **5b** (2.29 g, 7.8 mmol) by a similar procedure as for peroxide **1**. R_f : 0.45 (5% EA/Hex) $^1\text{H NMR}$ (400 MHz): δ 1.29 (s, 9H), 1.97 (tdd, 2H, $J = 7.0, 9.7, 6.4$), 2.84 (m, 2H), 4.02 (t, 2H, $J = 6.5$), 7.07 (m, 1H), 7.26 (m, 2H), 7.55 (d, 1H, $J = 7.9$). $^{13}\text{C NMR}$ (100 MHz): δ 26.4 (CH₃), 28.0 (CH₂), 32.8 (CH₂), 74.1 (CH₂), 80.1 (C), 124.5 (C), 127.4 (CH), 127.6 (CH), 130.4 (CH), 132.8 (CH), 141.1 (C). HRMS (ESI): calcd for C₁₃H₁₉BrO₂ (M+Na)⁺: 309.0466; found: 309.0457. IR: 2975, 2869, 2358, 1470, 1438, 1384, 1361, 1240, 1195, 1019, 877, 746, 657.

3-(2-(Tributylstannyl)phenyl)propyl tert-butyl peroxide (6c)



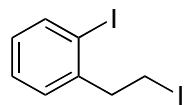
Methanesulfonate **5c** (418 mg, 0.83 mmol) was converted to the peroxide (246 mg, 60%) by the same procedure employed for peroxide **1**. R_f : 0.5 (5% EA/Hex). $^1\text{H NMR}$ (400 MHz): δ 0.91 (t, 9H, $J = 7.3$), 1.1 (m, 6H), 1.29 (s, 9H), 1.36 (quintet, 6H, $J = 7.3$), 1.54 (m, 6H), 1.93 (m, 2H), 2.70 (m, 2H), 4.05 (t, 2H, $J = 6.5$), 7.01-7.33 (m, 3H), 7.41 (m, 1H). $^{13}\text{C NMR}$ (100 MHz): δ 10.4 (CH₃), 13.7 (CH₂), 26.4 (CH₃), 27.4 (CH₂), 29.2 (CH₂), 30.5 (CH₂), 35.9 (CH₂), 74.6 (CH₂), 80.1 (C), 125.3 (CH), 127.9 (CH), 128.4 (CH), 136.8 (CH), 141.8 (C), 148.6 (C). HRMS (ESI): calcd for C₂₅H₄₅O₂Sn (M+Na)⁺: 521.2417; found: 521.2430. IR: 3051, 2955, 2922, 2870, 2852, 2360, 1463, 1434, 1375, 1361, 1241, 1196, 1071, 1020, 959, 875, 750, 667, 592.

2-(2-Iodophenyl)ethanol (7)



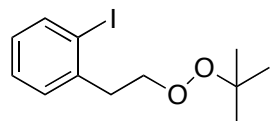
2-(2-Iodophenyl)acetic acid (1.00 g, 3.8 mmol) was converted to the corresponding alcohol (915 mg, 97%, colorless oil) by the same procedure employed for compound **4a**. R_f : 0.25 (20% EA/Hex). Spectral details matched those previously reported.⁷

1-Iodo-2-(2-iodoethyl)benzene (8)

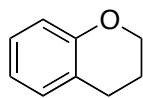


Alcohol **7** (898 mg, 3.62 mmol) was converted to the iodide (**8**, 906 mg, 70%, light yellow oil) using the general procedure described below except that CH₂Cl₂ was used as solvent. R_f : 0.95 (5% EA/Hex). $^1\text{H NMR}$ (400 MHz): δ 3.26-3.41 (overlapping signals, 4H), 6.98 (m, 1H), 7.23-7.38 (overlapping signals, 2H), 7.85 (m, 1H). $^{13}\text{C NMR}$ (100 MHz): δ 3.3 (CH₂), 44.9 (CH₂), 99.9 (C), 128.5 (CH), 128.8 (CH), 129.8 (CH), 139.8 (CH), 143.3 (C). Spectra matched those previously reported.⁷

2-(2-Iodophenyl) ethyl tert-butyl peroxide (9)



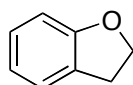
Diiodide **8** (107 mg, 0.30 mmol) was converted to iodoaryl peroxide (21.5 mg, 22%, light yellow oil) using the same procedure as employed for peroxide **1**. The transformation could also be conducted using Ag₂O in THF. R_f : 0.80 (5% EA/Hex). $^1\text{H NMR}$ (400 MHz): δ 1.25 (s, 9H), 3.09 (t, 2H, $J = 7.1$), 4.15 (t, 2H, $J = 7.1$), 6.92 (m, 1H), 7.25-7.33 (overlapping signals, 2H), 7.83 (d, 1H, $J = 7.7$). $^{13}\text{C NMR}$ (100 MHz): δ 26.3 (CH₃), 39.3 (CH₂), 74.1 (CH₂), 80.4 (C), 100.6 (C), 128.2 (CH), 128.3 (CH), 130.3 (CH), 139.5 (CH), 141.2 (CH). HRMS (ESI): calcd for C₁₂H₁₇IO₂ (M+Na)⁺: 343.0171; found: 343.0168.

3,4-dihydro-2H-1-benzopyran (10)

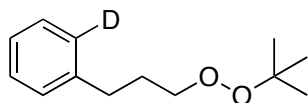
To a 0.2 M solution of 3-(2-iodophenyl)propyl tert-butyl peroxide **6a** (0.344 mg, 2.0 mmol) in THF at -78 °C was dropwise added PhLi (2.2 mmol, 1.4 mL of a nominally 1.6 M solution in Hex). The reaction was allowed to warm to rt and after 1.5 h, was quenched with sat. aq. NH₄Cl. The ether extract was filtered through a plug of silica, diluted with methanol to a standard volume and analyzed for yield by comparison with a standard curve derived using five standardized solutions of reference samples of dihydrobenzopyran, prepared as described below. Following analysis, the solution was concentrated under reduced pressure. Spectra of the residue matched those of the dihydrobenzofuran prepared as described below. R_f: 0.3 (2.5 % EA/Hex).

Preparation of GC standard: Bromophenyl 3-bromopropyl ether was prepared using a variant of a reported procedure.⁹ To a 0.5 M solution of 2-bromophenol (3.46 g, 20 mmol) in DMF was added K₂CO₃ (5.5 g, 40 mmol) followed by 1,3-dibromopropane (10 mL, 100 mmol). The reaction was stirred for 24 h and then quenched with sat. aq. NH₄Cl. The ether extract was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (5% EA/Hex) to yield 4.24 g (72%) of 2-bromophenyl 3-bromopropyl ether as a colorless oil. R_f: 0.45 (5% EA/Hex). The ¹H NMR spectra matched the literature report.⁹

To a 0.2 M solution of 2-bromophenyl 3-bromopropyl ether (588 mg, 2.0 mmol) in THF at -78 °C was dropwise added nBuLi (2.2 mmol, 1.4 mL of a nominally 1.6 M solution in Hex). The reaction was allowed to warm to rt and after 1.5 h, was quenched with sat. aq. NH₄Cl. The ether extract was dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (2.5% EA/Hex) to yield **10** (211 mg, 79%) as a colorless oil. R_f: 0.3 (2.5 % EA/Hex) Spectra matched those previously reported.¹⁰ The product was used to construct a GC/MS response curve in the same manner as described below for 2,3-dihydrobenzofuran.

2,3-Dihydrobenzofuran (11)

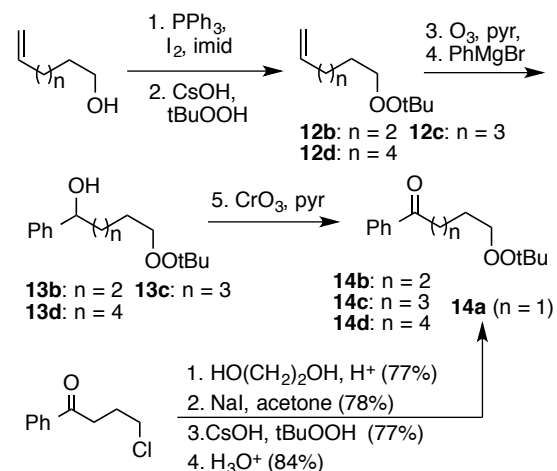
To a -78 °C 0.2M solution of 2-(2-iodophenyl) ethyl *tert*-butylperoxide **9** (0.320 g, 1.0 mmol) in THF was added 1.1 equivalent of nBuLi (nominally 1.6 M in hexane) dropwise under nitrogen. After 5 min, the cooling bath was removed and the reaction was allowed to stir for an additional hour. The reaction was then quenched with a small amount of sat. ammonium chloride. The ether extract was diluted with methanol to a fixed volume and the GC/MS response compared against a standard curve constructed by analysis of commercial **11** (99% grade) to indicate a 90% yield. Alternatively, the ether extract was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography (2.5% EA/Hex) to afford 58% isolated yield of **11**. R_f: 0.3 (2.5 % EA/Hex). The spectra matched those of commercial samples of **11**.

3-(2-Deuterophenyl)propyl tert-butyl peroxide

To a -78 °C solution of peroxide **6a** (66.5 mg, 0.2 mmol) in THF (0.2 M) was dropwise added a nominally 1.6 M solution of nBuLi in hexanes (0.14 mL, 0.22 mmol). The resulting mixture was stirred at -78 °C for five minutes and then quenched with excess CD₃OD (1 mL). The mixture was concentrated under reduced pressure and the residue purified by flash

chromatography (5% EA/Hex) to yield 27.5 mg (66%) of a *t*-butyl phenylpropyl peroxide showing >90% deuterium incorporation at the ortho position based upon the reduction in the integral for the aromatic region in the ¹H NMR. R_f: 0.25 (5% EA/Hex). ¹H NMR (400 MHz): δ 1.29 (s, 9H), 1.97 (tdd, 2H, J= 6.5, 9.4, 6.4), 2.73 (AB dd, 2H), 4.00 (t, 2H, J= 6.5), 7.18-7.35 (m, 4H). ¹³C NMR (100 MHz): δ 26.4 (CH₃), 29.6 (CH₂), 32.4 (CH₂), 74.2 (CH₂), 80.1 (C), 125.8 (C), 128.2 (CH), 128.36 (CH), 128.42 (CH), 141.7 (C). HRMS (ESI): calcd for C₁₃H₁₉DO₂ (M+Na)⁺: 232.1424; found: 232.1420.

General Synthetic Scheme for *n*-peroxyalkylphenones



Syntheses of iodoalkenes employed a reported procedure.¹¹ A flame dried round bottom flask with magnetic stir bar was charged with 1 mmol of the alcohol and THF (substrate concentration 0.2M). The flask was placed in a 0 °C bath and protected from light (foil). The following reagents were added sequentially: imidazole (1.5 mmol), PPh₃ (1.0 mmol) and iodine (1.5 mmol). After the reaction was judged complete (2 h, TLC), it was quenched with sat. aq. Na₂S₂O₃. The organic layer was separated and the aqueous layer was washed with ether/EA (3x). The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography.

6-Iodohept-1-ene [18922-04-6] was prepared (3.30 g, 93%) from 5-hexen-1-ol by the general procedure described above. Spectral details matched those previously reported.¹²

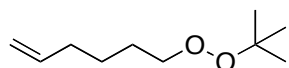
7-Iodohept-1-ene [107175-49-5] was prepared (3.30 g, 95%) from 7-hepten-1-ol by the general procedure described above. Spectral details matched those previously reported.¹³

8-iodooct-1-ene [38380-55-1] was prepared (5.00 g, 94%) from 7-octen-1-ol by the procedure described above. Spectral details matched those previously reported.¹⁴

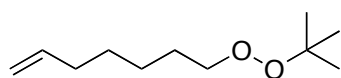
Syntheses of peroxides 12b-d were performed according to an established procedure.³

A flame dried round bottom flask with magnetic stir bar was charged with 1.39 mmol of CsOH, which was dissolved in dry DMF (0.2M). The solution was cooled to 0 °C and the iodoalkene (1.0 mmol) was added, followed by dropwise addition of tert-butyl hydroperoxide (1.4 equiv, nominally 5.5M solution in hex). The reaction was allowed to proceed for 3 hours and then diluted with water. The organic layer was separated and the aqueous layer was washed with EA (3 x). The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (EA/hex).

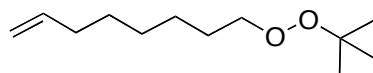
6-(tert-butylperoxy)hex-1-ene (12b) [107671-69-2] was prepared (5.90 g, 70%) from 6-iodohex-1-ene by the procedure described above. Spectral details matched those previously reported.¹⁵



7-(tert-butylperoxy)hept-1-ene (12c) [107671-70-5] was prepared (6.9 g, 79%) from 6-iodohept-1-ene by the procedure described above. Spectral details matched those previously reported.¹⁵



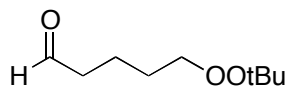
8-(tert-butylperoxy)oct-1-ene (12d) was prepared (5.40 g, 92%) from 8-iodooct-1-ene by the general procedure described above: ¹H NMR (300 MHz): δ 5.82 (ddd, 1H, J=6.7, 16.8), 4.97 (m, 2H), 3.95 (t, 2H, J= 6.7) 2.06 (q, 2H, J=6.2), 1.59 (m, 2H), 1.37 (m, 6H), 1.24 (s, 9H) ¹³C NMR (300 MHz): δ 139.05 (C, H), 114.2 (C, H₂), 80.0 (C), 75.0 (C, H₂), 33.6 (C, H₂), 28.9 (C, H₂), 28.7 (C, H₂), 26.3 (C, H₂), 21.9 (C, H₃). (HRMS) ESI: calcd for C₁₂H₂₄O₃ (M+Na)⁺: 223.1776; found: 223.1672. IR: 2976.1, 2933.9, (m), 1684.0(s). R_f: 0.35 (15% EA/Hex).



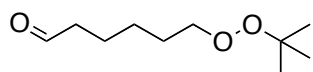
Peroxyalkanals **13b-d** were prepared according to an established procedure.¹⁶

A flame dried round bottom flask with a magnetic stir bar was charged with a 0.2 M solution of alkene (1 mmol) in CH₂Cl₂. The solution was cooled to -78 °C whereupon pyridine (3 mmol) was added. A gas solution of 2% O₃/O₂ (approximately 1 mmol/minute) was introduced for 1 minute. The reaction was warmed to room temperature and diluted with sat. aq NaHCO₃. The organic layer was separated and the aqueous layer was washed with dichloromethane (3x). The combined organic layer were dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography.

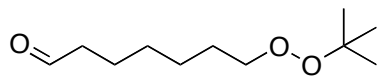
5-(tert-Butylperoxy)pentanal was prepared (5.90 g, 79%) from 6-(tert-butylperoxy)hex-1-ene by the procedure described above. ¹H NMR (400 MHz): δ 9.78 (t, 1H, J=1.5), 3.97 (t, 2H, J= 6.3), 2.49 (ddd, 2H, J= 1.9, 7.3, 14.5), 1.70 (m, 4H), 1.25 (s, 9H). ¹³C NMR (500 MHz): δ 202.3 (CH), 80.1 (C), 74.4 (CH₂), 43.6 (CH₂), 27.4 (CH₂), 26.3 (CH₃), 18.94 (CH₂). HRMS (ESI, NaOAc): calcd for C₉H₁₈O₃ (M+Na)⁺: 199.1310; found: 199.1256. IR: 2939 (n), 1716 (s). R_f: 0.93 (20% EA/Hex).



6-(tert-Butylperoxy)hexanal was prepared (3.90 g, 85%) from 7-(tert-butylperoxy)hept-1-ene by the procedure described above. ¹H NMR (400 MHz): δ 9.78 (s, 1H) 3.95 (t, 2H, J= 7.1), 2.48 (t, 2H, J= 6.5), 2.16 (s, 3H), 1.64 (m, 5H), 1.25 (s, 9H). ¹³C NMR (400 MHz): δ 208.7 (C), 80.3 (C), 74.6 (CH₂), 43.4 (CH₂), 29.9 (CH₂), 27.3 (CH₂), 26.3 (CH₃), 20.5 (CH₂). HREIMS calcd for C₁₀H₂₀O₃ (M+Na)⁺: 211.1412, found: 211.1310. IR: 2977.5 (n), 1715.6 (s). R_f: 0.20 (15 % EA/Hex).



7-(tert-Butylperoxy)heptanal was prepared (5.0 g, 93%) from 8-(tert-butylperoxy)oct-1-ene by the general procedure described above: ^1H NMR (300 MHz): δ 9.75 (s, 1H), 3.92 (t, 2H, $J=6.4$), 2.42 (t, 2H, $J=8.0$), 1.61 (m, 4H), 1.37 (m, 4H), 1.22 (s, 9H). ^{13}C NMR (300 MHz): δ 202.7 (C, H), 80.1 (C), 74.8 (C, H_2), 43.7 (C, H_2), 28.6 (C, H_2), 27.6 (C, H_2), 26.3 (C, H_2), 25.9 (C, H_2), 21.9 (C, H_2). HRESI-MS calcd for $\text{C}_{11}\text{H}_{22}\text{O}_3$ ($\text{M}+\text{Na}$) $^+$: 225.1467; found: 225.1569. IR: 2976.1, 2933.9, (m), 1725.0(s).

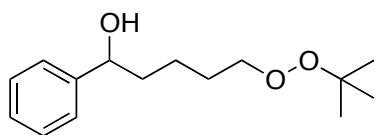


R_f : 0.49 (20% EA/Hex).

Syntheses of 1-phenyl-n-peroxyalkanols **13b-d** employed a reported procedure.¹⁷

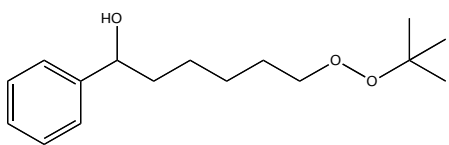
A flame dried round bottom flask with magnetic stir bar was charged with 1 mmol of peroxyaldehyde, which was dissolved in THF (0.2M solution). The solution was cooled to -78°C , whereupon 1.1 mmol of PhMgBr (nominally 1M in THF) was added dropwise. After an hour, the reaction was quenched by dropwise addition of water. The organic layer was separated and the aqueous layer was washed with ether (3x). The resulting solution was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

5-(tert-Butylperoxy)-1-phenylpentan-1-ol (13b) was prepared (3.60 g, 45%) from PhMgBr and 5-(tert-butylperoxy)pentanal by the procedure described above.



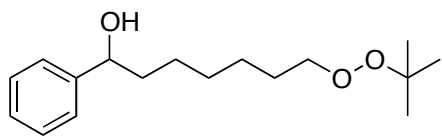
^1H NMR (400 MHz): δ 7.30 (M, 5H), 4.70 (dt, 1H, $J=6.1, 7.5$), 3.94 (t, 2H, $J=6.6$), 1.80 (m, 3H), 1.65 (ddd, 2H, $J=6.6, 7.7, 15.6$), 1.49 (m, 3H), 1.24 (s, 9H). ^{13}C NMR (400 MHz): δ 144.7 (C), 128.5 (CH), 127.6 (CH), 125.9 (CH), 80.1 (C), 74.8 (CH_2), 74.5 (CH_2), 38.9 (CH_2), 27.7 (CH_2), 26.3 (CH_3), 22.5 (CH_2). HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{24}\text{O}_3$ ($\text{M}+\text{Na}$) $^+$: 275.1725; found: 275.1623. IR: 3401.2 (b), 2867.8 (m). R_f : 0.43 (20% EA/Hex).

6-(tert-Butylperoxy)1-phenylhexan-1-ol (13c) was prepared (5.90 g, 85%) from 6-(tert-



butylperoxy)hexanal by the procedure described above: ^1H NMR (300 MHz): δ 7.33 (m, 5H), 4.69 (m, 1H), 3.92 (t, 2H, $J=6.3$), 3.53 (t, 1H, $J=6.5$), 1.78 (m, 4H), 1.40 (m, 4H), 1.24 (s, 9H). ^{13}C NMR (500 MHz): δ 144.8 (C), 128.4 (C, H), 127.5 (C, H), 125.8 (C, H), 80.1 (C), 74.9 (C, H_2), 74.6 (C, H), 38.9 (C, H_2), 27.8 (C, H_2), 26.3 (C, H_2), 26.1 (C, H_2), 25.7 (C, H_2). (HRMS) ESI: calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3$ ($\text{M}+\text{Na}$) $^+$: 289.1882, found: 289.1791. IR: 3401.3 (b), 2933.4 (m). R_f : 0.25 (15% EA/Hex).

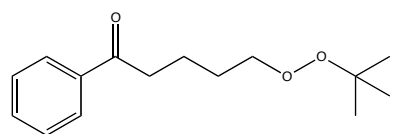
7-(tert-Butylperoxy)1-phenylhexan-1-ol (13d) was prepared (2.70 g, 89%) from 7-(tert-



butylperoxy)heptanal by the procedure described above. ^1H NMR (300 MHz): δ 7.31 (m, 5H), 4.68 (m, 1H), 3.92 (t, 2H, $J=6.3$), 1.77 (m, 4H), 1.38 (m, 6H), 1.24 (s, 9H). ^{13}C NMR (500 MHz): δ 144.8 (C), 128.4 (C, H), 127.5 (C, H), 125.8 (C, H), 80.1 (C), 74.9 (C, H_2), 74.6 (C, H), 38.9 (C, H_2), 27.8 (C, H_2), 26.3 (C, H_2), 26.1 (C, H_2), 25.7 (C, H_2). (HRMS) ESI: calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3$ ($\text{M}+\text{Na}$) $^+$: 303.1584; found: 303.1580. IR: 3401.2 (b), 2976.9, (m). R_f : 0.25 (15% EA/Hex).

Syntheses of peroxyketones **14b-d** employed a reported procedure.¹⁸ A flame dried round bottom flask with magnetic stir bar was charged with a solution of 6 mmol of pyridine in dichloromethane (0.2M). To the stirring solution was added 3 mmol of CrO₃, resulting in a strongly colored (deep burgundy) solution. After the solution had stirred for 15 minutes, a CH₂Cl solution of 0.5 mmol of the alcohol (**13 a-d**) was added. A tarry, black deposit separated immediately. The solution was stirred for an additional 15 min and then decanted from the residue, which was washed with 200 ml of ether. The combined solutions were washed sequentially with 10 mL portions of 5% aq. NaOH (3x), 5% aq. HCl, 5% aq. NaHCO₃, and sat. aq. NaCl. The resulting solution was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography.

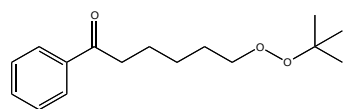
5-(tert-butylperoxy)-1-phenylpentan-1-one (14b) was prepared (2.90 g, 92%) from 5-(tert-butylperoxy)-1-phenylpentan-1-ol (**13b**) by the procedure described above.



¹H NMR (400 MHz): δ 8.00 (d, 2H, J=7.9), 7.58 (t, 1H, J= 7.4), 7.48 (t, 2H, J=7.9) 4.01 (t, 2H, J=6.6), 3.04 (t, 2H, J=7.1), 1.80 (p, 2H, J= 7.8), 1.74 (p, 2H, 7.8), 1.26 (s, 9H). ¹³C NMR (400 MHz): δ 202.3 (C), 137.0 (C, H),

132.9 (C, H), 128.6 (C, H), 128.0 (C, H), 80.1 (C), 75.0 (C, H₂), 38.4 (C, H₂), 27.8 (C, H₂), 26.3 (C, H₂), 26.0 (C, H₃), 24.2 (C, H₂). (HRMS) ESI: calcd for C₁₅H₂₂O₃ (M+Na⁺): 273.1569; found: 273.1457. IR: 2928.4 (m), 1686.5 (s). R_f: 0.23 (15% EA/Hex). R_f: 0.50 (20% EA/Hex).

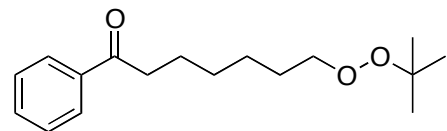
6-(tert-butylperoxy)1-phenylhexan-1-one (14c) was prepared (2.25 g, 90%) from 6-(tert-butylperoxy)1-phenylhexan-1-ol (**13c**) by the procedure described above.



¹H NMR (300 MHz): δ 7.96 (d, 2H, J=7.8), 7.58 (t, 1H, J= 7.3), 7.48 (t, 2H, J=7.5) 3.97 (t, 2H, J=6.8), 3.00 (t, 2H, J=7.5), 1.74 (m, 4H), 1.49 (m, 2H), 1.26 (s, 9H). ¹³C NMR (500 MHz): δ 202.3 (C), 137.0 (C, H), 132.9 (C, H), 128.6 (C, H), 128.0 (C, H), 80.1 (C), 75.0 (C, H₂), 38.4 (C, H₂), 27.8

(C, H₂), 26.3 (C, H₂), 26.1 (C, H₃), 26.0 (C, H₂), 24.2 (C, H₂). (HRMS) ESI: calcd for C₁₆H₂₄O₃ (M+Na⁺): 287.1725; found 287.1633. IR: 2976.1, 2933.9, (m), 1684.0(s). R_f: 0.50 (20% EA/Hex).

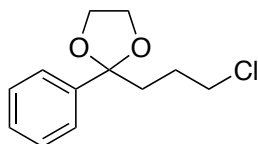
7-(tert-butylperoxy)-1-phenylheptan-1-one (14d) was prepared (2.25 g, 91%) from 7-(tert-butylperoxy)1-phenylhexan-1-ol by the procedure described above.



¹H NMR (300 MHz): δ 7.33 (m, 5H), 4.69 (m, 1H), 3.92 (t, 2H, J=6.3), 3.53 (t, 1H, J=6.5), 1.78 (m, 4H), 1.40 (m, 4H), 1.24 (s, 9H). ¹³C NMR (400 MHz): δ 144.8 (C), 128.4 (C, H), 127.5 (C, H), 125.8 (C, H), 80.1 (C), 74.6 (C, H₂), 39.0 (C, H₂), 29.3 (C, H₂), 27.7 (C, H₂), 26.3 (C, H₂), 26.1 (C,

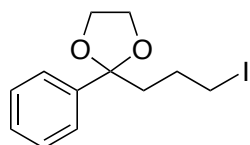
H₃), 26.0 (C, H₂). (HRMS) ESI: calcd for C₁₆H₂₆O₃ (M+Na⁺): 301.1791; found: 301.1882. IR: 2953.1, 2930.9, (m), 1684.0(s). R_f: 0.25 (15% EA/Hex).

2-(3-Chloropropyl)-2-phenyl-1,3-dioxolane was prepared using a modification of a reported procedure.¹⁹ A flame dried round bottom flask with magnetic stir bar and fitted with a Dean-Stark apparatus was charged with commercially available 4-chloro-1-phenylbutan-1-one (0.578 g, 3.0 mmol), ethylene glycol (0.558 g, 3.0 mmol), and p-toluenesulfonic acid monohydrate



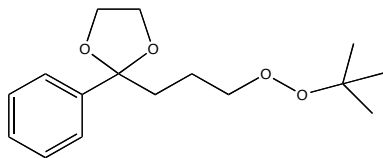
(0.044 g, 0.5 mmol) and toluene (30 mL). The solution was refluxed overnight with azeotropic removal of water and the organic layer was then washed with 5% NaHCO₃. The organic layer was dried over anhydrous Na₂SO₄, and concentrated in vacuo to give 77% (7.7 g) of 2-(3-chloropropyl)-2-phenyl-1,3-dioxolane [3308-98-3]. Spectral details matched those previously reported.²⁰

2-(3-Iodopropyl)-2-phenyl-1,3-dioxolane



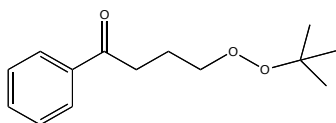
A flame dried round bottom flask with magnetic stir bar was charged with a solution of 2-(3-chloropropyl)-2-phenyl-1,3-dioxolane (5.0 g, 22 mmol), sodium iodide 15.0 g, mmol) and acetone (20 mL). The mixture was stirred and heated under reflux for 30 min, resulting in precipitation of solid sodium tosylate. The reaction was cooled and diluted with water. The lower layer was separated, and the (upper) aqueous layer was extracted with hexane. The combined organic layers were washed sequentially with water and brine and then dried (MgSO₄). The residue obtained upon concentration under reduced pressure was purified by column chromatography to give 5.5 g (78%) of the iodopropyl dioxolane [70969-99-2]. Spectral details matched those previously reported.²¹

2-(3-(*tert*-Butylperoxy)propyl)-2-phenyl-1,3-dioxolane was prepared from the iododioxolane (1.5g, 77%) by a similar procedure as described for peroxide **1**.



¹H NMR (400 MHz): δ 7.74 (m, 2H), 7.33 (m, 3H), 4.03 (ddd, 2H, J=9.9, 14.5, 17.6), 3.93 (t, 2H, J=6.8), 3.79 (ddd, 2H, J=10.8, 14.5, 18.2), 1.98 (m, 2H), 1.69 (m, 2H). ¹³C NMR (400 MHz): δ 142.5 (C), (C, H), 128.1 (C, H), 125.8 (C, H), 125.7 (C, H), 110.2 (C), 80.1 (C), 74.9 (C, H₂), 64.6 (C, H₂), 37.1 (C, H₂), 26.3 (C), 22.3 (C, H₂). HRMS (ESI): calcd for C₁₆H₂₄O₃ (M+Na)⁺: 303.1573; found: 303.1675. IR: 2976 (m).

4-(*tert*-Butylperoxy)-1-phenylbutan-1-one (14a)



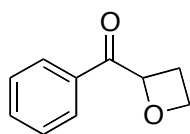
A flame dried round bottom flask with magnetic stir bar was charged with 1.00 mmol (0.280 g) of 2-(3-(*tert*-butylperoxy)propyl)-2-phenyl-1,3-dioxolane in THF (0.2 M). 5% aq. HCl (1.5 mL) was then added and the reaction was allowed to proceed overnight. The organic layer was separated and the aqueous layer was washed with EA (3x). The resulting solution was dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to give 0.200 g (84%) of the ketone. ¹H NMR (400 MHz): δ 8.00 (dt, 2H, J= 2.0, 8.6), 7.45 (tt, 1H, J= 1.3, 2.8), 7.48 (tt, 2H, J=2.0, 3.3), 3.93 (t, 2H, J=6.0), 3.12 (t, 2H, J= 7.1), 2.08 (p, 2H, J = 6-7), 1.26 (s, 9H). ¹³C NMR (400 MHz): δ 199.7 (C), 136.9 (CH), 132.9 (CH), 128.6 (CH), 128.0 (CH), 80.2 (C), 74.0 (CH₂), 35.13 (CH₂), 26.4 (CH₃), 26.1 (CH₂), 22.65 (CH₂). HRMS (ESI): calcd for C₁₄H₂₀O₃ (M+Na)⁺: 259.1412; found: 259.1310. IR: 2976 (m), 2931 (m), 1686 (s). R_f: 0.23 (15% EA/Hex).

Standard Procedure for cyclizations of peroxyketones.

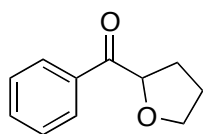
A round bottom flask with a magnetic stir bar was flame-dried, then topped with a septum and placed under vacuum until the flask cooled. The flask was filled with nitrogen and charged with

1-1.5 mmol of potassium *tert*-butoxide. The flask was again evacuated and then flushed with nitrogen. THF was added to dissolve the base (final concentration, 0.2 M) whereupon a 0.2M THF solution of the peroxyketone (**14a-d**, 1.00 mmol) was added dropwise to the stirring solution, resulting in a clear reddish-brown solution. Upon disappearance of starting material (TLC), the reaction was quenched by dropwise addition of excess water. The organic phase was separated and the aqueous phase was washed 3x with ether/EA. The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to give the cyclic ethers **15a-c**.

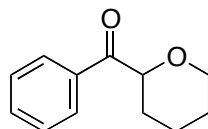
Oxetan-2-yl(phenyl)methanone (15a) was prepared (2.25 g, 70%) from 4-(*tert*-butylperoxy)-1-phenylbutan-1-one **14a** by the procedure described above. ¹H NMR (400 MHz): δ 7.93 (d, 2H, J=8.7), 7.55 (t, 1H, J=7.3), 7.49 (t, 2H, J=7.8) 5.94 (dd, 1H, J=7.1, 8.6), 4.84 (q, 1H, J=7.5), 4.67 (dt, 1H, J=6.4, 15.2), 3.03 (m, 2H). ¹³C NMR (500 MHz): δ 199.8 (C), 133.7 (C, H₂), 128.8 (C, H), 128.5 (C, H₂), 82.3 (CH), 69.5 (CH₂), 25.8 (CH₂). HRMS (HREI): calcd for C₁₀H₁₀O₂ (M+Na)⁺: 185.0681; found: 185.0580. IR: 2976 (m), 1683 (s). R_f: 0.23 (15% EA/Hex).



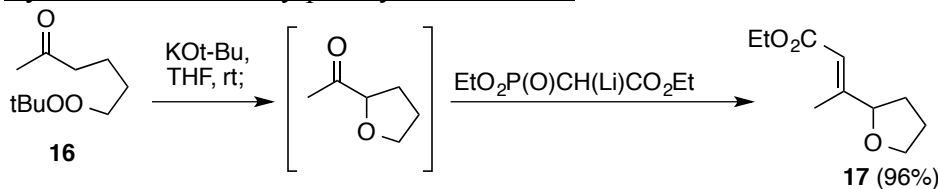
Phenyl(tetrahydrofuran-2-yl)methanone (15b, [141957-79-1]) was prepared (0.168 g, 99% yield) from 5-(*tert*-butylperoxy)-1-phenylpentanone-1-one **14b** using the procedure described above. R_f: 0.25 (15% EA/Hex). Spectral details matched those previously reported.²²



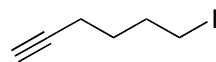
Phenyl(tetrahydro-2H-pyran-2-yl)methanone (15c) [73504-72-0] was prepared (0.138 g, 80% yield) from peroxyhexanone **14c** using the procedure described above. R_f: 0.27 (15% EA/Hex). Spectral details matched those previously reported.²³



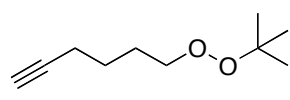
Cyclization of 6-*t*-butylperoxy-hexan-2-one:



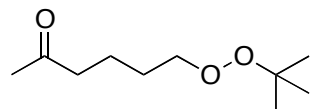
6-iodohex-1-yne was prepared (10.0 g, 92%) from commercially available 5-hexynyl iodide by a route similar to that described for **8**. Spectral details matched those previously reported.²⁴



6-(*tert*-butylperoxy)hex-1-yne [184941-42-2] was prepared (2.61 g, 78%) from 6-iodohex-1-yne by a procedure similar to that described for **1**. Spectral details matched those previously reported.²⁵

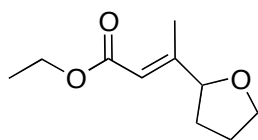


6-(*tert*-butylperoxy)hexan-2-one (16) was prepared from peroxyalkyne by an adaptation of a reported procedure.²⁶ A flame dried round bottom flask with magnetic stir bar was charged with the peroxyalkyne (6.0 mmol (0.340 mg) of



the peroxyalkyne, 1 mL H₂O, and 10mL MeOH. AuCl (0.027g) was added. Following disappearance of starting material (TLC), the majority of solvent was removed under reduced pressure and the remaining suspension was diluted with ether and washed with a 1:1 mixture of brine/aq. NH₄Cl. The separated aqueous layer was washed with ether (3x) and the combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography to afford the peroxyketone (1.03 g, 93%). ¹H NMR (300 MHz): δ 3.96 (t, 2H, J=6.3), 2.27 (t, 2H, J= 6.3), 1.7 (s, 3H, J), **1.65** (m, 4H), 1.24 (s, 9H). ¹³C NMR (400 MHz): δ 208.7 (C), 80.0 (C), 74.6 (C, H₂), 43.4 (C, H₂), 29.8 (C, H₂), 27.3 (C, H₂), 26.0 (C, H₂), 20.2 (C, H₂). (HRMS) ESI: calcd for C₁₆H₂₄O₃ (M+Na)⁺: 287.1725; found 287.1633. IR: 2976, 2933, (m), 1684 (s). R_f: 0.50 (20% EA/Hex).

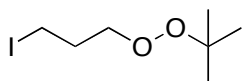
(E)-Ethyl 3-(tetrahydrofuran-2-yl)but-2-enoate (17)



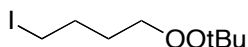
A round bottom flask with a magnetic stir bar was flame-dried and then cooled under vacuum. The flask was flushed with N₂ and then charged with (0.045 g, mmol) of potassium *tert*-butoxide. The flask was again evacuated and then backfilled with nitrogen. Sufficient THF was added to bring the base to 0.2M and the mixture was stirred until the base dissolved. A solution of 0.5 mmol of compound 6-(*tert*-butylperoxy)hexan-2-one in THF (3 mL) was then added dropwise to the stirring solution. Following disappearance of starting material, reaction was monitored via TLC, upon disappearance of starting material 1.00 mmol of triethyl phosphonoacetate (.244g, 1mmol) was added to the reaction. After two hours, brine was added. The organic phase was separated and the aqueous phase was washed 3x with ether/EA. The combined organic layers were dried over Na₂SO₄ and the residue obtained upon concentration purified by chromatography to afford 0.080 g (96%) of the enoate (two steps). R_f: 0.18 (20% EA/Hex) ¹H NMR (400 MHz): δ 3.71 (ddd, 1H, J=4.4, 3.0, 11.7), 3.34 (ddd, 1H, J= 3.3, 11.2, 2.8), 2.71 (ddd, 1H, J= 5.5, 12.2, 5.7) 2.22 (ddd, 1H, J=1.2, 4.1, 12.0), 2.01 (m, 4H), 1.61 (m, 7H), 1.24 (ddd, 1H, J= 4.6, 1.6, 16.4). ¹³C NMR (500 MHz): δ 215.3 (C), 80.3 (C), 64.7 (CH₂), 41.6 (CH₂), 39.1 (CH₂), 30.8 (CH₂), 29.1 (CH₂), 25.67 (CH₂), 20.4 (CH₂) and 19.7 (CH₂). HRMS (HREI): calcd for C₁₀H₁₆O₃ (M+ Na): 207.1099; found: 207.0997. IR: 2939 (n), 1716 (s).

Synthesis of 1,*n*- iodoperoxides employed a modification of a reported procedure.³ A flame dried round bottom flask with a magnetic stir bar was charged with 0.2M solution of CsOH•H₂O (1.2 mmol) in DMF, followed by the 1,*n*-diiodide (1.00 mmol) and then *tert*-butyl peroxide (1.2mmol), added dropwise. Upon disappearance of starting material (TLC, ~ 3 h), the reaction was quenched with an equal volume of water. The separated aqueous layer was washed with hexane and dried over MgSO₄. The residue obtained after concentration was purified by filtration through silica gel (hexane).

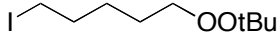
1-(*tert*-butylperoxy)-3-iodopropane (18a) [101860-37-1] was prepared (0.540 g, 70% yield) from *t*-butyl hydroperoxide and 1,3-diiodopropane using the procedure described above. Spectral details matched those previously reported.²⁷



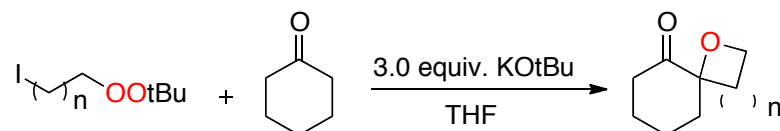
1-(*tert*-butylperoxy)-4-iodobutane (18b) was prepared (0.240 g, 72% yield) from 1,4-diiodobutane using the procedure described above. ¹H NMR (400 MHz): δ



3.98 (t, 2H, J=6.34), 3.23 (t, 3H, J= 6.87), 1.95 (p, 2H, J= 7.05), 1.72 (m, 2H), 126 (s, 9H). ¹³C NMR (300 MHz): δ 80.2 (C), 73.6 (CH₂), 30.3 (CH₂), 28.9 (CH₂), 26.3 (CH₃), 6.5 (CH₂). HRMS (HREI): calcd for C₈H₁₇O₂I: 272.0300; found: 272.0273. IR: 2939 (m). R_f: 0.19 (10% EA/Hex).

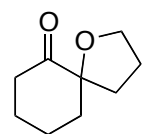
 **1-(tert-butylperoxy)-5-iodopentane (18c)** was prepared (0.789 g, 64% yield) from 1,5-diiodopentane by the procedure described above. ¹H NMR (400 MHz): δ 3.95 (t, 2H, J=6.14), 3.21 (t, 3H, J= 6.55), 1.87 (p, 2H, J= 7.25), 1.72 (m, 2H), 1.66 (m, 2H), 1.64 (m, 2H), 1.24 (s, 9H). ¹³C NMR (300 MHz): δ 80.0 (C), 74.8 (CH₂), 33.3 (CH₂), 27.7 (CH₂), 26.3 (CH₃), 22.9 (CH₂), 6.5 (CH₂). HRMS (HREI): calcd for C₉H₁₉O₂ (M⁺): 286.0400; found: 286. IR: 286.0430 (m). R_f: 0.20 (15% EA/Hex).

General Procedure for annelation of spirocyclic ethers onto cyclohexanone. Illustrated for **1-oxaspiro[5.5]undecan-7-one (19b)**



Potassium tert-butoxide (3.00 mmol, 0.336 g) was weighed into a flame dried round bottom flask with a magnetic stir bar. A septum was placed into the round bottom flask, and the atmosphere was removed and replaced with N₂ (3 x). The base was dissolved into THF (15 mL). A solution of cyclohexanone (3.00 mL, 0.294 g) in THF (15 mL, 0.2M) was added dropwise and the reaction stirred for 15 minutes, whereupon a solution of 1-(tert-butylperoxy)-4-iodobutane (**18b**, 1 mmol, 0.272 g) in THF (5 mL, 0.2 M) was added dropwise, resulting in development of slight opacity and yellow-orange coloration. After disappearance of starting material (TLC), the reaction was quenched via drop wise addition of water. The organic phase was separated and the aqueous phase was washed 3x with ether/EA. The combined organic phases were dried with Na₂SO₄ and the solvent was removed *in vacuo*. The residue was purified on silica (5% EA/hex) to furnish 0.430 g (87%) of the oxaspiroundecanone **19b**. ¹H NMR (400 MHz): δ 3.71 (ddd, 1H, J=4.4, 3.0, 11.7), 3.34 (ddd, 1H, J= 3.3, 11.2, 2.8), 2.71 (ddd, 1H, J= 5.5, 12.2, 5.7) 2.22 (ddd, 1H, J=1.2, 4.1, 12.0), 2.01 (m, 4H), 1.61 (m, 7H), 1.24 (ddd, 1H, J= 4.6, 1.6, 16.4). ¹³C NMR (500 MHz): δ 215.3 (C), 80.3 (C), 64.7 (CH₂), 41.6 (CH₂), 39.1 (CH₂), 30.8 (CH₂), 29.1 (CH₂), 25.67 (CH₂), 20.4 (CH₂) and 19.7 (CH₂). HRMS (HREI): calcd for C₁₀H₁₆O₂ (M⁺): 168.112; found: 168.115. IR: 2939 (n), 1716 (s). R_f: 0.23 (15% EA/Hex).

1-oxaspiro[4.5]decan-6-one [19a, 129529-81-3] was prepared (0.134 g, 86% yield) from the reaction of cyclohexanone with *t*-butyl 3-iodopropyl peroxide **18a** using the procedure described above. Spectral details matched those previously reported.²⁸



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