Supplementary Methods.

All reactions were conducted under an oxygen atmosphere and used oven-dried glass wares. All reactions were conducted using 100 W Hg lamp as a light source without any filter or blue-LED lights (30 lamps, power density: 40 mW cm\(^{-2}\)). All solvents were dried according to known methods and distilled prior to use. Starting materials at the highest commercial quality were purchased and purified by distillation or passing through an activated alumina column. Photosensitizers were used as received without further purification. NMR spectra were recorded using CDCl\(_3\). \(^1\)H NMR were recorded at 400 or 600 MHz, and \(^13\)C NMR at 100 or 150 MHz. Data reported as: s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet, and b= broad. Specific optical rotation was obtained using JASCO p-2000 polarimeter (serial no: A060361232) with a sodium lamp and is reported as follows: [\(\alpha\)]\(_D\) (c= 10 mg/1mL, solvent: CHCl\(_3\)). Chiral Gas Chromatography analysis were carried out using a GC-2014 SHIMADZU gas-chromatograph (serial no: C11484301285SA) equipped with a FID detector and suitable for operation with fused silica capillary column. The carrier gas was high purity grade nitrogen (N\(_2\)).

**General procedure for C-H bond functionalization of cyclic and linear ether:** A dry test tube (20 mL) with rubber septum and magnetic stirrer bar was charged with aliphatic ether (1 mL). The test tube was purged with dry oxygen for 10 minutes and then added 1 x 10\(^{-5}\) M of photosensitizer (typically meso-TPP or rosebengal) and again purged with dry oxygen for 5 minutes. Finally, it was added 10 mol% of Lewis acid (\(\gamma\)-Al\(_2\)O\(_3\)). The solution was then irradiated using 100 W Hg lamp or a blue-LEDs array for 8 h at room temperature under an 1 atm oxygen atmosphere. The unreacted starting material was evaporated using a rotary evaporator, and the residue products were submitted for NMR analysis.

**General procedure for Aromatic ethers:** A dry test tube (20 mL) with rubber septum and magnetic stirrer bar was charged with aromatic ether (1 mmol). The test tube was purged with dry oxygen for 10 minutes, added 1 x 10\(^{-5}\) M of photosensitizer (typically meso-TPP or rose bengal) and again purged with dry oxygen for 5 minutes. Finally, it was added 10 mol% of Lewis acid (\(\gamma\)-Al\(_2\)O\(_3\)). The solution was irradiated using a 100 W Hg lamp or a blue-LEDs array for 12 h at room temperature under an 1 atm oxygen atmosphere. The unreacted starting material was removed via a silica column using hexane and ethyl acetate as eluent.
Selective oxidative alpha ethereal C-H functionalization of pitofenone. A dry test tube (20 mL) with rubber septum and magnetic stirrer bar was charged with pitofenone 1t (1 mmol), and then bubbled with dry oxygen for 10 minutes before addition of 1 x 10⁻⁵ M of photosensitizer (meso-TPP) and 10 mol% of Lewis acid (γ-Al₂O₃). The solution was then irradiated using a blue-LEDs array at room temperature (25-28 °C) under an 1 atm oxygen atmosphere for 20 h. The reaction mixture was diluted with ethyl acetate-hexane (4:6 volume ratio), and stirred for 10 min. The mixture was filtered through celite, silica gel pads, and washed with ethyl acetate. The filtrate was concentrated using a rotary evaporator. The residue products were purified by column chromatography on silica gel and collected as pasty form. The collected product was dissolved in ether, followed by slow addition of HCl in ether under stirring for 2 h at room temperature. Finally, the solid product (3t) was collected by filtration.

Kinetic isotope labeling experiments by THF-d₈. THF-d₈ was used as a starting material to react with singlet oxygen, which leads to the production of THF-d₈ peroxide in 8% yield after 15 h irradiation using a 100 W Hg lamp. The yield (8%) of THF-d₈ hydroperoxide is significant lower than that (35%) of the THF-H₈ hydroperoxide under the same condition, which is due to the stronger C-D bond than the C-H bond and is consistent with the expected kinetic isotope effect.
Spectroscopic Data.

**Hydroperoxy-tetrahydrofuran (2a)**\(^1\,^2\) (CAS Registry No: 4676-82-8)

![Image of (2a)]

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 9.1\) (s, 1H), 5.58-5.56 (m, 1H), 3.95-3.93 (m, 2H), 2.04-1.82 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 107.9, 67.6, 29.0,\) and 23.8.

NMR data of (2a) was identical with that in the literature\(^1\,^2\).

**Dihydrofuran-2(3H)-one (3a)** (CAS NO: 96-48-0)

![Image of (3a)]

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 4.33-4.30\) (t, 2H), 2.48-2.45 (t, 2H), 2.26-2.22 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 178.1, 68.8, 27.9,\) and 22.5.

*NMR data (3a) is in agreement with authentic commercially available sample.*

**2-hydroperoxytetrahydro-2H-pyran (2b)**\(^3\) (CAS Registry No: 4676-84-0)

![Image of (2b)]

Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.16\) (s, 1H), 5.10-5.08 (t, 1H), 3.99-3.94 (m, 2H), 3.66-3.62 (m, 1H), 1.77-1.54 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 102.4, 62.7, 27.2, 25.0\) and 19.4. NMR data of (2b) was identical with that in the literature\(^3\).

**2-tetrahydro-2H-pyran-2-one (3b)** (CAS NO: 542-28-9)

![Image of (3b)]
Colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl$_3$): δ 8.16 (s, 1 H), 4.34-4.31 (t, 2H), 2.58-2.48 (t, 2H), 1.89-1.56 (m, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): δ 172.2, 69.8, 30.1, 22.8, and 19.2.
NMR data is in agreement with authentic commercially available sample.

2-hydroperoxyoxepane (2c)³ (CAS Registry No: 366817-95-0)

![2-hydroperoxyoxepane (2c)](image)

Colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl$_3$): δ 8.74 (s, 1H), 5.21-5.17 (m, 1H), 3.81-3.62 (m, 2H), 2.04-1.61 (m, 8H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): δ 106.2, 62.8, 30.7, 30.6, 29.2 and 22.8.
NMR data of (2c) was identical with that in the literature³.

Oxepan-2-one (3c) (CAS NO: 502-44-3)

![Oxepan-2-one (3c)](image)

Colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl$_3$): δ 4.17-4.12 (m, 2H), 2.57-2.53 (q, 2H), 1.78-1.67 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): δ 176.0, 69.0, 34.3, 29.0, 28.6, and 22.7.
NMR data is in agreement with authentic commercially available sample.

2-hydroperoxy-1, 3-dioxolane (2d)⁴ (CAS Registry No: 5771-94-8)

![2-hydroperoxy-1, 3-dioxolane (2d)](image)

Colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl$_3$): δ 9.13 (s, 1H), 6.09-6.01 (s, 1H), 4.17-4.09 (m, 2H), 3.98-3.95 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): δ 116.7 and 65.0.
NMR data of (2d) was identical with that in the literature⁴.

1, 3-dioxolan-2-one (3d) (CAS NO: 96-49-1)
Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 4.5 (s, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.4 and 64.5. NMR data is in agreement with authentic commercially available sample.

**2-hydroperoxy-1, 4-dioxane (2e)** (CAS Registry No: 4722-59-2)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.41 (s, 1H), 5.02 (s, 1H), 4.18-4.11 (m, 1H), 3.80-3.60 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 98.9, 66.1, 65.9 and 61.15. IR (neat, cm$^{-1}$) 3450, 1265, 1184; HRMS calcd for C$_4$H$_8$O$_4$: (M+H): 105.0.

**1,4-dioxan-2-one (3e)**$^5$ (CAS NO: 3041-16-5)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.41 (s, 1H), 5.02 (s, 1H), 4.18-4.11 (m, 1H), 3.80-3.60 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 98.9, 66.1, 65.9 and 61.15. NMR data of (3e) was identical with that in the literature.$^5$

**2-hydroperoxy-2-methyltetrahydrofuran (2f)** (CAS Registry No: 23277-12-5)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.0 (s, 1H), 3.97-3.94 (m, 2H), 2.04-1.84 (m, 4H), 1.51 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 113.1, 68.7, 34.7, 25.0, and 21.6. IR (neat, cm$^{-1}$) 3342, 1119; HRMS calcd for C$_5$H$_{10}$O$_3$: (M+H): 119.0.
2-hydroperoxy-2-(methoxymethyl)tetrahydrofuran (2g)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.21-4.20 (m, 1H), 3.65-3.64 (m, 1H), 3.38-3.36 (m, 5H), 2.48-2.44 (m, 1H), 1.91-1.78 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 108.25, 75.0, 66.2, 59.2, 31.8, and 28.7.

2-(chloromethyl)-2-hydroperoxytetrahydrofuran (2h)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.05-3.90 (m, 2H), 3.83-3.55 (m, 3H), 2.09-1.87 (m, 4H), 1.45; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 112.3, 69.8, 69.4, 44.6, 44.4, 32.5, 32.3, 24.9 and 24.6.

2-hydroperoxy-2,5-dimethyltetrahydrofuran (2i) (CAS Registry No: 25258-70-2)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.11, 9.07 (s, 1H), 4.26-4.16 (m, 1H), 2.16-1.64 (m, 4H), 1.45, 1.417 (s, 3H), 1.27-1.19 (dd 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 112.9, 112.8, 77.4, 76.1, 35.9, 34.7, 32.6, 32.5, 22.4, 22.1, 21.7 and 20.5.

2-hydroperoxy-2, 5-dimethoxytetrahydrofuran (2j)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.80-5.77(m, 1H), 3.64(s, 3H), 3.37(s, 3 H), 2.64-2.61(m, 1H) 2.40-2.37 (m, 2H), 2.06-1.97 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 130.8, 128.7, 107.4, 106.8, 56.84, 56.82, 29.43, 28.96, 28.94, 28.3.
2-hydroperoxy-2, isopropoxypropane \(^{6,7}\) (2k)

![Structure of 2-hydroperoxy-2, isopropoxypropane](image)

Colorless oil; \(^1\H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.85(s, 1H), 4.09-3.98(m, 2H), 1.35(s, 6H), 1.97-1.81(d, 6H); \(^{13}\C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 120.3, 67.3, 23.0, and 22.7.

NMR data of (2k) was identical with that in the literature\(^{6,7}\).

2-phenyl butyrate (3l)\(^8\)

![Structure of 2-phenyl butyrate](image)

Colorless oil; \(^1\H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.39-7.36 (m, 2H), 7.24-7.22 (m, 1H), 7.09-7.07(d, 2H), 2.56-2.53 (t, 2H), 1.82-1.66 (q, 2H), 1.09-1.05 (t, 3H); \(^{13}\C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 173.3, 152.3, 130.2, 125.0, 122.0, 36.3, 19.0, 14.2.

NMR data of (3l) was identical with that in the literature\(^8\).

2-hydroperoxy-2, methoxymethyl)tetrahydrofuran \(^{9}\) (3m) (CAS NO: 2315-68-6)

![Structure of 2-hydroperoxy-2, methoxymethyl)tetrahydrofuran](image)

Colorless oil; \(^1\H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.05-8.03 (t, 2 H), 7.55-7.43 (m, 1 H), 7.41-7.33 (m, 2 H), 4.34-4.31 (t, 2 H), 1.77-1.72 (t, 2 H), 1.58-1.47 (m, 2 H), 1.04-0.83 (t, 3 H); \(^{13}\C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 166.9, 134.0, 130.5, 129.4, 128.5, 65.0, 31.3, 18.6, 14.0.

NMR data of (3m) was identical with commercially available authentic material and with that in the literature\(^9\).

1-hydroperoxy-1-hydroperoxyisochroman \(^{510}\) (CAS Registry No: 2734-00-1)
Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.35 (s, 1H), 7.44-7.36 (m, 1H), 7.30-7.21 (m, 2H), 7.15-7.13 (d, 1H), 6.36, 6.20 (s, 1H), 4.46-4.28 (t, 1H), 4.06-3.98 (m, 1H), 3.11-3.02 (m, 1H), 2.65-2.60 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 135.6, 135.2, 129.6, 129.3, 128.95, 128.93, 128.6, 128.5, 128.4, 128.3, 126.28, 126.23, 100.9, 99.0, 58.3, 58.0, 27.7 and 27.5.

NMR data of (2n) was identical with that in the literature$^{10}$.

**Isochroman-1-one (3n)$^{11}$** (CAS NO: 4702-34-5)

Pale white pasty oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.05-8.03 (d, 1H), 7.51-7.47 (m, 1H), 7.36-7.32 (m, 1H), 7.23-7.21 (d, 1H), 4.50-4.47 (t, 2H), 3.03-3.00 (t, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.0, 139.4, 133.5, 130.2, 127.5, 127.1, 125.1, 67.1 and 27.6.

NMR data of (3n) was identical with commercially available authentic material and with that in the literature$^{11}$.

**Benzofuran-3(2H)-one (3o)$^{12}$** (CAS NO: 7169-34-8)

Pale white solid; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.66-7.64 (m, 1H), 7.61-7.57 (t, 1H), 4.60 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 199.8, 173.9, 137.8, 124.0, 121.9, 121.1, 113.6, and 74.6.

NMR data of (3o) was identical with commercially available authentic material and with that in the literature$^{12}$.

**1-hydroperoxy-1,3-dihydroisobenzofuran (2p)$^{13}$** (CAS Registry No: 4676-81-7)
Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.52 (s, 1H), 7.44-7.22 (m, 4H), 6.62, 6.21 (s, 1H), 5.28-5.04 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 140.3, 133.4, 129.9, 127.7, 123.5, 120.9, 110.3, and 72.8.

NMR data of (2p) was identical with that in the literature$^{13}$.

Isobenzofuran-1(3H)-one (3p)$^{11}$ (CAS NO: 87-41-2)

White solid; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.87-7.85 (d, 1H), 7.86-7.62 (t, 1H), 7.51-7.45 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.0, 146.4, 133.9, 128.9, 125.5, 122.06, 122.05, and 69.5. NMR data of (3p) was identical with commercially available authentic material and with that in the literature$^{11}$.

4-bromoisobenzofuran-1(3H)-one (3q)$^{14}$ (CAS NO: 102308-43-0)

White solid; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.78-7.76 (d, 1H), 7.73-7.71 (d, 1H), 7.40-7.36 (t, 1H), 5.13 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 169.7, 146.4, 136.5, 130.7, 127.7, 124.3, 116.3, and 69.6. NMR data of (3q) was identical with commercially available authentic material and with that in the literature$^{14}$.

4-hydroperoxy-2,3-dihydrobenzo[b][1,4]dioxine (2r)
Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 6.89-6.87 (m, 4H), 5.54, 5.53 (s, 1H), 4.13-4.04 (m, 2H), 3.56 (b, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.72, 140.93, 122.38, 121.9, 117.71, 117.18, 88.9, and 66.6.

(3aR,5aS,9aS)-3a,6,6,9a-tetramethyldecahyronaphtho[2,1-b]furan-2(3aH)-one (3s)$^{15}$ (CAS NO: 102308-43-0)

White solid; $^1$H NMR (400 MHz, CDCl$_3$): δ 2.40-2.32 (q, 1H), 2.21-2.15(q, 1H), 2.04-2.00 (m, 1H), (1.95-1.89 (d, 1H), 1.85-1.81 (m, 1H), 1.67-1.59 (m, 2H), 1.43-1.40 (m, 3H),1.28 (s, 3H), 1.209-1.13 (m, 2H), 1.03-0.97 (m, 2H), 0.87 (s, 3H), 0.81(s, 3H), 0.77 (s, 3H) ; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 176.7, 86.2, 59.0, 56.5, 42.0, 39.4, 36.2, 38.6, 35.9, 33.0, 33.01, 29.5, 28.6,21.4, 20.8, 20.4, 17.9, 14.9. IR (KBr, cm$^{-1}$) 2997, 2867, 2845, 1776, 1456, 1198, 1126, 950; HRMS calcd for C$_{16}$H$_{26}$O$_2$: 250.1933, found: 250.1930.

1-(2-(4-(2-(methoxycarbonyl)benzoyl)phenoxy)-2-oxoethyl)piperidin-1-iium chloride (3t)
Brown solid; ¹H NMR (600 MHz, CDCl₃): δ 8.01 (d, J= 12.0 Hz, 1H) 7.73 (d, J= 12.0 Hz, 2H), 7.64-7.53 (m, 2 H), 7.33 (d, J= 12.0 Hz, 1H), 7.27 (d, J= 6.0 Hz, 2H), 4.30 (s, 2H), 3.74 (b, 2H), 3.62 (s, 3H), 3.38 (broad, 2H), 2.18 (broad, 2H), 1.90 (broad, 3H), 1.54 (b, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 195.6, 166.1, 162.7, 152.8, 141.1, 135.5, 132.5, 130.8, 130.1, 129.8, 128.8, 127.4, 121.6, 55.7, 53.8, 52.3, 22.8 and 21.0; EI-MS calcd for C₂₂H₂₄NO₅⁺ (M⁺): 382.1649, found: 382.1650.

**Preparation of pitofenone starting material (It)**

The synthetic route for preparation of pitofenone starting material (It) was listed below.

1-methyl 2-(4-(2-(piperidin-1-yl)ethoxy)benzoyl)benzoate (It)

Brown solid; ¹H NMR (600 MHz, CDCl₃): δ 7.97 (d, J=6.0 Hz, 1H), 7.65 (d, J=6.0 Hz, 2H), 7.57-7.47 (m, 2H), 7.32 (d, J=6.0 Hz, 1H), 6.85 (d, J=6.0 Hz, 2H), 4.10 (t, J=6.0 Hz, 2H), 3.59 (s, 3H), 2.73 (t, J=6.0 Hz, 2H), 2.45 (s, 4H), 1.57-1.53 (m, 4H), 1.40 (t, J=6.0 Hz, 2H); ¹³C NMR
Preparation method of (S)-2-methyltetrahydrofuran (1v)\textsuperscript{17,18}. 80 Miligram of CBS catalyst was combined with 1.5 mL of THF-BH\textsubscript{3} at 15-20 degree, to this of 2.0 g of 4-chloro-2-pentanone in 7 mL of dry THF solution and 7 mL of THF-BH\textsubscript{3} solution were added simultaneously via syringe. The reaction was stirred for 10 minutes at 15-20 degree and the reaction mixture was quenched by dilute acetic water, the product (1u) was separated by layer separation.

2.0 Gram of (S)-5-chloropentan-2-ol (1u) was dissolved in diethyl ether and cooled to 10 degree, slowly added 1.3 eqv. of t-BuOK at 10 degree. And then the reaction mixture was maintained at 20-25 degree for 3 hrs. After 3 hrs, the (S)-2-methyltetrahydrofuran (1v) was collected under atmospheric distillation.

(S)-5-chloropentan-2-ol (1u)\textsuperscript{17,18} (CAS NO: 99212-19-8)

Pale brown oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 3.83-3.78\) (m, 1 H), 3.56-3.52 (t, 2 H), 1.91-1.76 (m, 2 H), 1.61-1.50 (m, 3 H), 1.19-1.17 (d, 3 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta 67.4, 45.1, 36.2, 28.8,\) and 23.6. SOR: \([\alpha]_D +15.165^\circ\) in CHCl\textsubscript{3} (10 mg/1 mL CHCl\textsubscript{3}).

Spectroscopic data of (1u) was identical with that in the literature\textsuperscript{17,18}

(S)-2-methyltetrahydrofuran (1v)\textsuperscript{18}
Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 3.92-3.82 (m, 2 H), 3.69-3.65 (m, 1 H), 1.96-1.81 (m, 3 H), 1.39-1.34 (m, 1 H), 1.19-1.18 (d, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 75.1, 67.6, 33.0, 25.8, and 20.9. SOR: $[\alpha]_D^{\circ} +19.400$° in CHCl$_3$ (10 mg/1ml CHCl$_3$) Spectroscopic data of (1v) was identical with that in the literature$^{18}$.

(R)-2-hydroperoxy-2-methyltetrahydrofuran (2v)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.1(s, 1 H), 3.97-3.94 (t, 3 H), 2.04-1.84 (m, 4 H), 1.52 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 113.1, 68.7, 34.7, 25.0, and 21.6. SOR: $[\alpha]_D^{\circ} -12.626$° in CHCl$_3$ (10 mg/1 mL CHCl$_3$).

Measurements of enantiomeric excess (ee) by chiral gas chromatography.

Instrumentation: Gas Chromatography analysis were carried out using GC-2014 SHIMADZU gas-chromatograph (serial no: C11484301285SA) equipped with a FID detector and a fused silica capillary column. The carrier gas was high purity grade nitrogen (N$_2$).

Column: Fused silica tubing (undeactivated, untreated) with 60 m x 0.53 mm (serial no: 1406465) was purchased from RESTEK GC Columns. Prior to use, the column was washed with n-hexane, chloroform (purified by basic alumina), acetone, and water. The cleaning procedure was repeated once in a reverse order.

Coating of column: In a typical coating procedure, 15.1 mg of nickel(II) bis[(1R)-3-(heptfluorobutryl)camphorates] and 200 mg of squalane (purchased from Alfa Aesar) were dissolved in 3.5 mL acid-free, high purity grade chloroform, and mixed well by sonication A 60 m x 0.53 mm fused silica capillary column was coated with this solution at 0.6 atm. of N$_2$ (over pressure) at 30 °C. The N$_2$ pressure was maintained for 5 hr after the coating solution was injected through the column. The column was connected to the gas chromatograph and conditioned at
0.3 atm. (overpressure) N\textsubscript{2} with the column temperature being raised from 30 to 100 °C and then maintained there for 12 h with the exit end left open.

**Analysis condition:** Column temperature: 80 °C, injection temperature: 150 °C, injection split ratio was 1:50, injection volume: 1.0 µL, column flow: the over pressure of the carrier gas was 0.3-0.5 atm. n-Octane was used as a non-coordinating reference standard.

**Preparation of chiral Nickel(II) bis[(1R)-3-(hepta-fluorobutyryl)camphorates]-complex\textsuperscript{19}: sodium (1R)-3-(Heptafluorobutyryl)camphorate.** 0.3 Gram sample of 80% sodium hydride suspension in paraffin (1 0 mmol of NaH) was washed under nitrogen with dry benzene until the paraffin was completely removed. The residue was suspended in benzene and transferred into the reaction flask. 2.5 Gram (7.2 mmol) of (1R)-3-(heptafluorobutyryl) camphor was dissolved in 80 mL of dry benzene, and then added to the suspension of sodium hydride in benzene. The mixture was stirred for 3 h under nitrogen at 30-35 °C, and then concentrated in vacuum using rotary evaporator. The residue was dissolved in warm chloroform, and the solution was filtered. The filtrate was diluted (1:1) with dry ether with vigorous mixing by stirring. The mixture was allowed to cool down to 5 °C, leading to gradual formation of precipitates. The solid was isolated by filtration and re-precipitated from chloroform/ether. The final product was dried at high vacuum, yielding 2.45 g of product which is equivalent to a 92% yield.

Nickel(II) bis[(1R)-3-(heptafluorobutyryl)camphorate]. 2 Gram (5.4 mmol) sample of sodium (1R)-3-(heptafluorobutyryl)camphorate was dissolved in 50 mL of dry ethanol. Then 0.37 g (2.85 mmol) of anhydrous powdered nickel(II) chloride was added, followed by refluxing the mixture for 12 h. The green solution was filtered to remove sodium chloride as a by-product, then concentrated the filtrate, and the residue was dried at high vacuum. Yield: 1.3 g (32%) of a pale green glassy powder.

Since the molar optical rotational angle value of the as-produced chiral 2-hydroperoxyl-2-methyl-THF is not available. We have followed a procedure from the literature\textsuperscript{S19} to determine the enantiomeric excess (ee) of the chiral 2-hydroperoxyl-2-methyl-THF (2v) by using a chiral gas chromatography (GC) (chiral Ni-complex coated with column). From the enantiomeric resolution by chiral GC, we have calculated the enantiomeric excess (ee) for (R)-1-methyl-THF-hydroperoxide is to be a 96.44%.
Supplementary Figure 1. NMR spectra of compound 2a, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 2. NMR spectra of compound 2b, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 3. NMR spectra of compound 2c, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 4. NMR spectra of compound 2d, (a) \(^1\)H NMR, and (b) \(^{13}\)C NMR spectra.
Supplementary Figure 5. NMR spectra of compound 3d, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 6. NMR spectra of compound 2e, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 7. NMR spectra of compound 2f, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 8. NMR spectra of compound 2g, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 9. NMR spectra of compound 2h, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 10. NMR spectra of compound 2i, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 11. NMR spectra of compound 2j, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra
Supplementary Figure 12. NMR spectra of compound 2n, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra
Supplementary Figure 13. NMR spectra of compound 3n, (a) $^1$H NMR of compound 3n, and (b) $^{13}$C NMR of compound 3n.
Supplementary Figure 14. NMR spectra of compounds 3o, (a) $^1$H NMR of compound 3o, and (b) $^{13}$C NMR of compound 3o.
Supplementary Figure 15. NMR spectra of compound 2p, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra
Supplementary Figure 16. NMR spectra of compound 3p. (a) $^1$H NMR, and (b) $^{13}$C NMR spectra
Supplementary Figure 17. NMR spectra of compound 3q. (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 18. NMR spectra of compound 2r, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 19. $^1$H NMR spectrum of compound 2s.
Supplementary Figure 20. NMR spectra of compound 3s, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 21. $^{13}$C NMR spectra of compound 3s.
Supplementary Figure 22. NMR spectra of compound 3t, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 23. HRMS spectrum of compound 3t.
Supplementary Figure 24. NMR spectra of compound 1t, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 25. NMR spectra of compound 1v, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 26. NMR spectra of compound 2v, (a) $^1$H NMR, and (b) $^{13}$C NMR spectra.
Supplementary Figure 27. $^1$H NMR spectra of (a) THF-d$_8$, and (b) THF-d$_8$-hydroperoxide.
Supplementary Figure 28. $^1$H NMR spectrum of compound THF-hydroperoxide and THF-lactone.

Supplementary Figure 29. ORTEP diagram of compound (3aR,5aS,9aS)-3a,6,6,9a tetramethyl decahydronaphtho[2,1-b]furan-2(3aH)-one (3s).
**Supplementary Table 1.** Crystal data and structure refinement for 120421LT_0m.

| Parameter                                      | Value                              |
|------------------------------------------------|------------------------------------|
| Identification code                            | 120421lt_0m                        |
| Empirical formula                             | C16 H26 O2                         |
| Formula weight                                 | 250.37                             |
| Temperature                                    | 100(2) K                           |
| Wavelength                                     | 0.71073 Å                          |
| Crystal system                                 | Monoclinic                         |
| Space group                                    | P 1 2 1 1                          |
| Unit cell dimensions                           |                                     |
| a                                              | 7.4988(5) Å                       |
| α                                              | 90°                                |
| b                                              | 10.6861(7) Å                      |
| β                                              | 110.507(3)°                       |
| c                                              | 9.4162(7) Å                       |
| γ                                              | 90°                                |
| Volume                                         | 706.73(8) Å                        |
| Z                                              | 2                                  |
| Density (calculated)                           | 1.177 Mg/m³                        |
| Absorption coefficient                         | 0.075 mm⁻¹                         |
| F(000)                                         | 276                                |
| Crystal size                                   | 0.15 x 0.03 x 0.03 mm³             |
| Theta range for data collection                | 2.31 to 26.40°                     |
| Index ranges                                   | -9<=h<=9, -8<=k<=13, -11<=l<=11     |
| Reflections collected                          | 6262                               |
| Independent reflections                        | 2329 [R(int) = 0.0307]             |
| Completeness to theta = 26.40°                 | 99.8 %                             |
| Absorption correction                          | Semi-empirical from equivalents    |
| Max. and min. transmission                     | 0.9486 and 0.7138                  |
| Refinement method                              | Full-matrix least-squares on F²    |
| Data / restraints / parameters                  | 2329 / 1 / 167                     |
| Goodness-of-fit on F²                           | 1.056                              |
| Final R indices [I>2sigma(I)]                  | R1 = 0.0340, wR2 = 0.0771          |
| R indices (all data)                           | R1 = 0.0399, wR2 = 0.0801          |
| Absolute structure parameter                   | -1.5(12)                           |
| Largest diff. peak and hole                     | 0.143 and -0.191 eÅ⁻³              |
**Supplementary Table 2.** Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 120421LT_0m. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| O(1) | -4674(2) | 6625(1) | 4264(2) | 41(1) |
| O(2) | -1614(2) | 6088(1) | 4919(1) | 26(1) |
| C(1) | 3520(3)  | 2213(2) | 10056(2) | 34(1) |
| C(2) | 2873(2)  | 3507(2) | 10358(2) | 25(1) |
| C(3) | 1671(2)  | 4230(2) | 8910(2)  | 19(1) |
| C(4) | -413(2)  | 3740(2) | 8087(2)  | 20(1) |
| C(5) | -1320(2) | 4777(2) | 6945(2)  | 20(1) |
| C(6) | -3435(2) | 4844(2) | 5971(2)  | 27(1) |
| C(7) | -3410(2) | 5924(2) | 4950(2)  | 30(1) |
| C(8) | -385(2)  | 5050(2) | 5765(2)  | 22(1) |
| C(9) | -577(2)  | 2456(2) | 7331(2)  | 26(1) |
| C(10)| 4671(3)  | 4269(2) | 11222(2) | 35(1) |
| C(11)| 1690(3)  | 3433(2) | 11408(2) | 29(1) |
| C(12)| -321(2)  | 2935(2) | 10654(2) | 29(1) |
| C(13)| -1423(2) | 3695(2) | 9257(2)  | 26(1) |
| C(14)| 2685(2)  | 4492(2) | 7772(2)  | 22(1) |
| C(15)| 1648(2)  | 5486(2) | 6583(2)  | 24(1) |
| C(16)| -475(3)  | 4070(2) | 4580(2)  | 29(1) |
| Bond                  | Distance [Å] |
|-----------------------|--------------|
| O(1)-C(7)             | 1.203(2)     |
| O(2)-C(7)             | 1.3680(19)   |
| O(2)-C(8)             | 1.483(2)     |
| C(1)-C(2)             | 1.524(3)     |
| C(1)-H(1A)            | 0.9800       |
| C(1)-H(1B)            | 0.9800       |
| C(1)-H(1C)            | 0.9800       |
| C(2)-C(10)            | 1.541(2)     |
| C(2)-C(11)            | 1.545(2)     |
| C(2)-C(3)             | 1.552(2)     |
| C(3)-C(14)            | 1.541(2)     |
| C(3)-C(4)             | 1.571(2)     |
| C(3)-H(3)             | 1.0000       |
| C(4)-C(5)             | 1.529(2)     |
| C(4)-C(9)             | 1.531(3)     |
| C(4)-C(13)            | 1.540(2)     |
| C(5)-C(6)             | 1.531(2)     |
| C(5)-C(8)             | 1.535(2)     |
| C(5)-H(5)             | 1.0000       |
| C(6)-C(7)             | 1.506(3)     |
| C(6)-H(6A)            | 0.9900       |
| C(6)-H(6B)            | 0.9900       |
| C(8)-C(16)            | 1.515(3)     |
| C(8)-C(15)            | 1.521(2)     |
| C(9)-H(9A)            | 0.9800       |
| C(9)-H(9B)            | 0.9800       |
| C(9)-H(9C)            | 0.9800       |
| C(10)-H(10A)          | 0.9800       |
| C(10)-H(10B)          | 0.9800       |
| C(10)-H(10C)          | 0.9800       |
| C(11)-C(12)           | 1.520(3)     |
| C(11)-H(11A)          | 0.9900       |
| C(11)-H(11B)          | 0.9900       |
| C(12)-C(13)           | 1.520(3)     |
| C(12)-H(12A)          | 0.9900       |
| C(12)-H(12B)          | 0.9900       |
C(13)-H(13A)  0.9900
C(13)-H(13B)  0.9900
C(14)-C(15)   1.542(2)
C(14)-H(14A)  0.9900
C(14)-H(14B)  0.9900
C(15)-H(15A)  0.9900
C(15)-H(15B)  0.9900
C(16)-H(16A)  0.9800
C(16)-H(16B)  0.9800
C(16)-H(16C)  0.9800
C(7)-O(2)-C(8) 108.90(13)
C(2)-C(1)-H(1A) 109.5
C(2)-C(1)-H(1B) 109.5
H(1A)-C(1)-H(1B) 109.5
C(2)-C(1)-H(1C) 109.5
H(1A)-C(1)-H(1C) 109.5
H(1B)-C(1)-H(1C) 109.5
C(1)-C(2)-C(10) 107.52(15)
C(1)-C(2)-C(11) 111.38(16)
C(10)-C(2)-C(11) 106.34(15)
C(1)-C(2)-C(3) 114.38(15)
C(10)-C(2)-C(3) 109.40(15)
C(11)-C(2)-C(3) 107.51(13)
C(14)-C(3)-C(2) 115.14(13)
C(14)-C(3)-C(4) 111.47(13)
C(2)-C(3)-C(4) 115.99(14)
C(14)-C(3)-H(3) 104.2
C(2)-C(3)-H(3) 104.2
C(4)-C(3)-H(3) 104.2
C(5)-C(4)-C(9) 112.29(14)
C(5)-C(4)-C(13) 108.47(13)
C(9)-C(4)-C(13) 108.99(14)
C(5)-C(4)-C(3) 103.03(13)
C(9)-C(4)-C(3) 115.59(13)
C(13)-C(4)-C(3) 108.14(13)
C(4)-C(5)-C(6) 124.59(14)
C(4)-C(5)-C(8) 116.36(13)
C(6)-C(5)-C(8) 101.41(13)
C(4)-C(5)-H(5) 104.1
C(6)-C(5)-H(5) 104.1
C(8)-C(5)-H(5) 104.1
C(7)-C(6)-C(5) 100.14(14)
C(7)-C(6)-H(6A) 111.7
C(5)-C(6)-H(6A) 111.7
C(7)-C(6)-H(6B) 111.7
C(5)-C(6)-H(6B) 111.7
H(6A)-C(6)-H(6B) 109.5
O(1)-C(7)-O(2) 120.35(18)
O(1)-C(7)-C(6) 129.46(16)
O(2)-C(7)-C(6) 110.14(14)
O(2)-C(8)-C(16) 105.22(13)
O(2)-C(8)-C(15) 111.58(14)
C(16)-C(8)-C(15) 111.25(14)
O(2)-C(8)-C(5) 100.12(12)
C(16)-C(8)-C(5) 119.20(15)
C(15)-C(8)-C(5) 108.83(14)
C(4)-C(9)-H(9A) 109.5
C(4)-C(9)-H(9B) 109.5
H(9A)-C(9)-H(9B) 109.5
C(4)-C(9)-H(9C) 109.5
H(9A)-C(9)-H(9C) 109.5
H(9B)-C(9)-H(9C) 109.5
C(2)-C(10)-H(10A) 109.5
C(2)-C(10)-H(10B) 109.5
H(10A)-C(10)-H(10B) 109.5
C(2)-C(10)-H(10C) 109.5
H(10A)-C(10)-H(10C) 109.5
H(10B)-C(10)-H(10C) 109.5
C(12)-C(11)-C(2) 114.66(14)
C(12)-C(11)-H(11A) 108.6
C(2)-C(11)-H(11A) 108.6
C(12)-C(11)-H(11B) 108.6
C(2)-C(11)-H(11B) 108.6
H(11A)-C(11)-H(11B) 107.6
| Bond                  | Angle (degrees) |
|----------------------|-----------------|
| C(13)-C(12)-C(11)    | 111.54(15)      |
| C(13)-C(12)-H(12A)   | 109.3           |
| C(11)-C(12)-H(12A)   | 109.3           |
| C(13)-C(12)-H(12B)   | 109.3           |
| C(11)-C(12)-H(12B)   | 109.3           |
| H(12A)-C(12)-H(12B)  | 108.0           |
| C(12)-C(13)-C(4)     | 112.38(14)      |
| C(12)-C(13)-H(13A)   | 109.1           |
| C(4)-C(13)-H(13A)    | 109.1           |
| C(12)-C(13)-H(13B)   | 109.1           |
| C(4)-C(13)-H(13B)    | 109.1           |
| H(13A)-C(13)-H(13B)  | 107.9           |
| C(3)-C(14)-C(15)     | 112.53(13)      |
| C(3)-C(14)-H(14A)    | 109.1           |
| C(15)-C(14)-H(14A)   | 109.1           |
| C(3)-C(14)-H(14B)    | 109.1           |
| C(15)-C(14)-H(14B)   | 109.1           |
| H(14A)-C(14)-H(14B)  | 107.8           |
| C(8)-C(15)-C(14)     | 108.57(14)      |
| C(8)-C(15)-H(15A)    | 110.0           |
| C(14)-C(15)-H(15A)   | 110.0           |
| C(8)-C(15)-H(15B)    | 110.0           |
| C(14)-C(15)-H(15B)   | 110.0           |
| H(15A)-C(15)-H(15B)  | 108.4           |
| C(8)-C(16)-H(16A)    | 109.5           |
| C(8)-C(16)-H(16B)    | 109.5           |
| H(16A)-C(16)-H(16B)  | 109.5           |
| C(8)-C(16)-H(16C)    | 109.5           |
| H(16A)-C(16)-H(16C)  | 109.5           |
| H(16B)-C(16)-H(16C)  | 109.5           |
Supplementary Figure 30. ORTEP diagram of compound Isobenzofuran-1(3H)-one (3p)

**Supplementary Table 4.** Crystal data and structure refinement for 110813_0m.

| Parameter                                    | Value                               |
|----------------------------------------------|-------------------------------------|
| Identification code                          | 110813_0m                           |
| Empirical formula                           | C8 H6 O2                             |
| Formula weight                               | 134.13                              |
| Temperature                                  | 296(2) K                            |
| Wavelength                                   | 0.71073 Å                           |
| Crystal system                               | Monoclinic                          |
| Space group                                  | P 1 21/c 1                          |
| Unit cell dimensions                         |                                      |
| a                                             | 7.7471(7) Å                         |
| β                                             | 112.208(4)°                         |
| c                                             | 8.1277(9) Å                         |
| Volume                                       | 632.04(11) Å³                       |
| Z                                             | 4                                   |
| Density (calculated)                         | 1.410 Mg/m³                         |
| Absorption coefficient                       | 0.102 mm⁻¹                          |
| F(000)                                       | 280                                 |
| Crystal size                                 | 0.20 x 0.17 x 0.15 mm³              |
| Theta range for data collection              | 2.84 to 26.43°                      |
| Index ranges                                 | -6≤h≤9, -13≤k≤12, -10≤l≤10           |
| Reflections collected                        | 5345                                |
| Independent reflections                      | 1293 [R(int) = 0.0338]              |
| Completeness to theta = 26.43°               | 99.4 %                              |
| Absorption correction                        | Semi-empirical from equivalents     |
| Max. and min. transmission                   | 0.9486 and 0.8358                   |
| Refinement method                            | Full-matrix least-squares on F²     |
| Data / restraints / parameters                | 1293 / 0 / 91                       |
| Goodness-of-fit on F²                         | 1.180                               |
Final R indices [I>2σ(I)]
R1 = 0.0405, wR2 = 0.1125
R indices (all data)
R1 = 0.0662, wR2 = 0.1431
Largest diff. peak and hole
0.173 and -0.236 e Å⁻³

**Supplementary Table 5.** Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for 110813_0m. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| O(1) | 13257(2) | 7538(1) | 6052(2) | 77(1) |
| O(2) | 13760(2) | 5928(1) | 7876(2) | 52(1) |
| C(1) | 12631(2) | 6742(2) | 6691(2) | 50(1) |
| C(2) | 10699(2) | 6454(2) | 6429(2) | 41(1) |
| C(3) | 10699(2) | 5478(2) | 7500(2) | 40(1) |
| C(4) | 9038(2)  | 5029(2) | 7531(2) | 49(1) |
| C(5) | 7412(2)  | 5593(2) | 6465(2) | 56(1) |
| C(6) | 12676(2) | 5102(2) | 8496(2) | 48(1) |
| C(7) | 9051(2)  | 7013(2) | 5329(2) | 53(1) |
| C(8) | 7407(2)  | 6572(2) | 5368(2) | 58(1) |

**Supplementary Table 6.** Bond lengths [Å] and angles [°] for 110813_0m.

| Bond          | Length  |
|---------------|---------|
| O(1)-C(1)     | 1.201(2) |
| O(2)-C(1)     | 1.354(2) |
| O(2)-C(6)     | 1.443(2) |
| C(1)-C(2)     | 1.463(2) |
| C(2)-C(3)     | 1.371(2) |
| C(2)-C(7)     | 1.391(2) |
| C(3)-C(4)     | 1.385(2) |
| C(3)-C(6)     | 1.494(2) |
| C(4)-C(5)     | 1.374(3) |
| C(4)-H(4)     | 0.9300  |
| C(5)-C(8)     | 1.385(3) |
| Bond/Angle | Distance/Value |
|------------|---------------|
| C(5)-H(5)  | 0.9300        |
| C(6)-H(6A) | 0.9700        |
| C(6)-H(6B) | 0.9700        |
| C(7)-C(8)  | 1.372(3)      |
| C(7)-H(7)  | 0.9300        |
| C(8)-H(8)  | 0.9300        |
| C(1)-O(2)-C(6) | 110.35(13) |
| O(1)-C(1)-O(2)   | 121.20(16)  |
| O(1)-C(1)-C(2)   | 130.43(17)   |
| O(2)-C(1)-C(2)   | 108.37(15)   |
| C(3)-C(2)-C(7)   | 121.60(16)   |
| C(3)-C(2)-C(1)   | 108.55(13)   |
| C(7)-C(2)-C(1)   | 129.85(17)   |
| C(2)-C(3)-C(4)   | 120.43(15)   |
| C(2)-C(3)-C(6)   | 107.97(14)   |
| C(4)-C(3)-C(6)   | 131.59(17)   |
| C(5)-C(4)-C(3)   | 117.96(18)   |
| C(5)-C(4)-H(4)   | 121.0        |
| C(3)-C(4)-H(4)   | 121.0        |
| C(4)-C(5)-C(8)   | 121.73(17)   |
| C(4)-C(5)-H(5)   | 119.1        |
| C(8)-C(5)-H(5)   | 119.1        |
| O(2)-C(6)-C(3)   | 104.74(13)   |
| O(2)-C(6)-H(6A)  | 110.8        |
| C(3)-C(6)-H(6A)  | 110.8        |
| O(2)-C(6)-H(6B)  | 110.8        |
| C(3)-C(6)-H(6B)  | 110.8        |
| H(6A)-C(6)-H(6B) | 108.9        |
| C(8)-C(7)-C(2)   | 117.89(18)   |
| C(8)-C(7)-H(7)   | 121.1        |
| C(2)-C(7)-H(7)   | 121.1        |
| C(7)-C(8)-C(5)   | 120.37(16)   |
| C(7)-C(8)-H(8)   | 119.8        |
| C(5)-C(8)-H(8)   | 119.8        |

Symmetry transformations used to generate equivalent atoms:
**Supplementary Table 7.** Anisotropic displacement parameters ($\AA^2 \times 10^3$) for 110813_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} ]$

|   | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{23}$  | $U_{13}$  | $U_{12}$  |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| O(1) | 66(1)    | 76(1)    | 96(1)    | 20(1)    | 41(1)    | -8(1)    |
| O(2) | 36(1)    | 64(1)    | 58(1)    | 4(1)     | 18(1)    | 5(1)     |
| C(1) | 46(1)    | 54(1)    | 50(1)    | -1(1)    | 20(1)    | -1(1)    |
| C(2) | 37(1)    | 44(1)    | 39(1)    | -5(1)    | 11(1)    | 1(1)     |
| C(3) | 38(1)    | 43(1)    | 37(1)    | -6(1)    | 13(1)    | 1(1)     |
| C(4) | 45(1)    | 55(1)    | 48(1)    | -6(1)    | 18(1)    | -6(1)    |
| C(5) | 38(1)    | 71(1)    | 59(1)    | -20(1)   | 19(1)    | -9(1)    |
| C(6) | 42(1)    | 53(1)    | 49(1)    | 4(1)     | 16(1)    | 6(1)     |
| C(7) | 48(1)    | 52(1)    | 49(1)    | 4(1)     | 8(1)     | 6(1)     |
| C(8) | 37(1)    | 69(1)    | 56(1)    | -10(1)   | 3(1)     | 10(1)    |

**Supplementary Table 8.** Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) for 110813_0m.

|   | x    | y    | z    | U(eq) |
|---|------|------|------|-------|
| H(4) | 9024 | 4366 | 8252 | 59    |
| H(5) | 6284 | 5310 | 6480 | 67    |
| H(6A) | 13008 | 5191 | 9767 | 58    |
| H(6B) | 12873 | 4251 | 8240 | 58    |
| H(7) | 9062 | 7666 | 4591 | 64    |
| H(8) | 6283 | 6932 | 4654 | 70    |
### (S)-2-methyltetrahydrofuran (1v) (1.0 M in CHCl$_3$)

| No. | Sample Name | Measurement Date | PMT Voltage[V] | Temperature[°C] | Optical Rotation Monitor | Specific O.R. | Path Length[mm] | Concentration[%] | S.D. | C.V. | Comment |
|-----|-------------|------------------|----------------|----------------|---------------------------|--------------|----------------|----------------|-----|-----|---------|
| 1   | Blank       |                  | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 2   | Blank-1     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 3   | Blank-2     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 4   | Blank-3     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 5   | Blank-4     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 6   | Blank-5     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 7   | Blank-6     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 8   | Blank-7     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 9   | Blank-8     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 10  | Blank-9     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 11  | Blank-10    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 12  | Blank-11    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 13  | Blank-12    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 14  | Blank-13    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 15  | Blank-14    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |

### (R)-2-hydroperoxy-2-methyltetrahydrofuran (2v) (1.0 M in CHCl$_3$)

| No. | Sample Name | Measurement Date | PMT Voltage[V] | Temperature[°C] | Optical Rotation Monitor | Specific O.R. | Path Length[mm] | Concentration[%] | S.D. | C.V. | Comment |
|-----|-------------|------------------|----------------|----------------|---------------------------|--------------|----------------|----------------|-----|-----|---------|
| 1   | Blank       |                  | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 2   | Blank-1     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 3   | Blank-2     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 4   | Blank-3     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 5   | Blank-4     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 6   | Blank-5     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 7   | Blank-6     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 8   | Blank-7     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 9   | Blank-8     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 10  | Blank-9     | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 11  | Blank-10    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 12  | Blank-11    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 13  | Blank-12    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 14  | Blank-13    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 15  | Blank-14    | 2015/02/02 T=0.1 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |

| No. | Sample Name | Measurement Date | PMT Voltage[V] | Temperature[°C] | Optical Rotation Monitor | Specific O.R. | Path Length[mm] | Concentration[%] | S.D. | C.V. | Comment |
|-----|-------------|------------------|----------------|----------------|---------------------------|--------------|----------------|----------------|-----|-----|---------|
| 16  | PEROXIDEPRODUCT 1.0M-1 | 2015/02/02 T=5.0 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 17  | PEROXIDEPRODUCT 1.0M-2 | 2015/02/02 T=5.0 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 18  | PEROXIDEPRODUCT 1.0M-3 | 2015/02/02 T=5.0 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 19  | PEROXIDEPRODUCT 1.0M-4 | 2015/02/02 T=5.0 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
| 20  | PEROXIDEPRODUCT 1.0M-5 | 2015/02/02 T=5.0 | 5.00           | 0.00           | -                         | 0.00         |                | 1.91           | 0.05 | 100 |         |
(R)-2-hydroperoxy-2-methyltetrahydrofuran (2v) (0.75 M in CHCl₃)

| No. | Sample Name | Measurement Date | PMT Voltage[V] | Temperature[°C] | Optical Rotation Monitor | Specific O.R. | Path Length[mm] |
|-----|-------------|------------------|----------------|----------------|--------------------------|--------------|----------------|
| 1.  | Blank       | 2015/06/29 4:53:54 | 283            | 53.48          | 0.048                    |              |                |
| 2.  | Blank-1     | 2015/06/29 4:53:54 | 283            | 53.31          | 0.039                    |              |                |
| 3.  | Blank-2     | 2015/06/29 4:53:54 | 283            | 53.23          | 0.032                    |              |                |
| 4.  | Blank-3     | 2015/06/29 4:53:54 | 283            | 53.77          | 0.057                    |              |                |
| 5.  | Blank-4     | 2015/06/29 4:53:54 | 283            | 53.80          | 0.059                    |              |                |
| 6.  | Blank-5     | 2015/06/29 4:53:54 | 283            | 53.84          | 0.058                    | +13.0295     | 50             |
| 7.  | Blank-6     | 2015/06/29 4:53:54 | 283            | 53.87          | 0.058                    | +13.0297     | 50             |
| 8.  | Blank-7     | 2015/06/29 4:53:54 | 283            | 53.87          | 0.058                    | +13.0293     | 50             |
| 9.  | 2.0000      | 0.0215 0.2560     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 10. | 2.0000      | 0.0215 0.2560     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 11. | 2.0000      | 0.0215 0.2560     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 12. | 2.0000      | 0.0215 0.2560     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |

(R)-2-hydroperoxy-2-methyltetrahydrofuran (2v) (0.25 M in CHCl₃)

| No. | Sample Name | Measurement Date | PMT Voltage[V] | Temperature[°C] | Optical Rotation Monitor | Specific O.R. | Path Length[mm] |
|-----|-------------|------------------|----------------|----------------|--------------------------|--------------|----------------|
| 1.  | Blank       | 2015/06/29 4:53:54 | 283            | 53.48          | 0.048                    |              |                |
| 2.  | Blank-1     | 2015/06/29 4:53:54 | 283            | 53.31          | 0.039                    |              |                |
| 3.  | Blank-2     | 2015/06/29 4:53:54 | 283            | 53.23          | 0.032                    |              |                |
| 4.  | Blank-3     | 2015/06/29 4:53:54 | 283            | 53.77          | 0.057                    |              |                |
| 5.  | Blank-4     | 2015/06/29 4:53:54 | 283            | 53.80          | 0.059                    |              |                |
| 6.  | Blank-5     | 2015/06/29 4:53:54 | 283            | 53.84          | 0.058                    | -13.0295     | 50             |
| 7.  | Blank-6     | 2015/06/29 4:53:54 | 283            | 53.87          | 0.058                    | -13.0297     | 50             |
| 8.  | Blank-7     | 2015/06/29 4:53:54 | 283            | 53.87          | 0.058                    | -13.0293     | 50             |
| 9.  | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 10. | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 11. | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 12. | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |

(R)-2-hydroperoxy-2-methyltetrahydrofuran (2v) (2.0 M in CHCl₃)

| No. | Sample Name | Measurement Date | PMT Voltage[V] | Temperature[°C] | Optical Rotation Monitor | Specific O.R. | Path Length[mm] |
|-----|-------------|------------------|----------------|----------------|--------------------------|--------------|----------------|
| 1.  | Blank       | 2015/06/29 4:53:54 | 283            | 53.48          | 0.048                    |              |                |
| 2.  | Blank-1     | 2015/06/29 4:53:54 | 283            | 53.31          | 0.039                    |              |                |
| 3.  | Blank-2     | 2015/06/29 4:53:54 | 283            | 53.23          | 0.032                    |              |                |
| 4.  | Blank-3     | 2015/06/29 4:53:54 | 283            | 53.77          | 0.057                    |              |                |
| 5.  | Blank-4     | 2015/06/29 4:53:54 | 283            | 53.80          | 0.059                    |              |                |
| 6.  | Blank-5     | 2015/06/29 4:53:54 | 283            | 53.84          | 0.058                    | -13.0295     | 50             |
| 7.  | Blank-6     | 2015/06/29 4:53:54 | 283            | 53.87          | 0.058                    | -13.0297     | 50             |
| 8.  | Blank-7     | 2015/06/29 4:53:54 | 283            | 53.87          | 0.058                    | -13.0293     | 50             |
| 9.  | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 10. | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 11. | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |
| 12. | 2.0000      | 0.0215 0.1129     | 283            | 53.85          | 0.059                    | -13.0233     | 50             |

Supplementary Figure 31. Specific optical rotation (SOR)
Supplementary Figure 32. GC chromatograph of n-octane (as a reference standard).

Supplementary Figure 33. Chiral GC chromatograph of racemic 2-hydroperoxyl-2-methyl-THF (2f).
Supplementary Figure 34. Chiral GC chromatograph of (R)-2-hydroperoxyl-2-methyl-THF (2v).
Supplementary Figure 35. Simulated peak fitting by Origin: Chiral GC chromatograph of (R)-2-hydroperoxyl-2-methyl-THF-peroxides.

**Supplementary Discussion**

*Determination of singlet O\(_2\) reaction rate with THF.* To measure the chemical reaction rate of THF with singlet O\(_2\), a competition reaction was carried out using 1-methylcyclohexene (MCH) as a competing reactant (Supplementary Figure 36a). 1-Methylcyclohexene is known to react with singlet O\(_2\) to generate allyl peroxides with a reaction rate of 0.16 x 10\(^6\) M\(^{-1}\) s\(^{-1}\). In the presence of MCH, the amount of the THF product 2a decreases gradually at higher MCH concentrations in accompany with the formation of MCH oxidation products 2u, 2u’, and 2u”. The amounts of THF product, 2a, and the MCH products, 2u, 2u’, and 2u”, can be determined using \(^1\)H NMR in the presence of known amount of an internal standard, namely, 1,4-dicyanobenzene (Supplementary Figure 36b for the \(^1\)H NMR assignments of all products). From the slope of the Supplementary Figure 36c, the chemical reaction rate of singlet O\(_2\) with THF was determined to be ~3.84 x 10\(^3\) M\(^{-1}\)s\(^{-1}\) (see detailed calculation procedure).
(a) 

\[
\begin{align*}
\text{(THF)} & \quad 1a \\
\text{O}_2, \text{h} & \quad \text{TPP-Meso} \\
\text{2 h, RT} & \quad \text{MCH} \\
\text{100 W Hg lamp} & \quad \text{THF product} \\
\text{THF product} & \quad 2a \\
\text{MCH products} & \quad 2u + 2u' + 2u''
\end{align*}
\]

(b) 

0.91 M of 1-methylcyclohexene in THF

(c) 

Equation: \( y = a + b \times \frac{[\text{THF}]}{[\text{MCH}]} \)

| Value   | Standard Value |
|---------|----------------|
| 0.02    | 0.05978        |
| 0.024   | 0.00135        |

Yield ratio of [THF-pdt]/[MCH-pdt] vs Conc. ratio, [THF]/[MCH]
Supplementary Figure 36. Competition of 1-methylcyclohexene (MCH) with THF to react with singlet O$_2$.  (a) Photo-irradiation of a THF (12.36 M) solution containing different concentrations of MCH.  (b) $^1$H NMR spectrum and assignments of all reaction products of 1-methylcyclohexene (0.9 M) in THF with singlet O$_2$.  (c) The plot of [THF-product]/[MCH-products] vs. [THF]/[MCH].  The slope is equal to $k_1/k_2$, where $k_1$ is the reaction rate of THF with singlet O$_2$, and $k_2$ the reaction rate of MCH with singlet O$_2$.

From Supplementary Figure 36(c), one can obtain a slope value of 0.024, which is equal to the $k_1/k_2$, where $k_1$ is the intrinsic chemical reaction rate of THF with singlet oxygen, and $k_2 = 0.36 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, the intrinsic chemical reaction rate of 1-methylcyclohexene with THF (see the chemical equations derived below). Therefore, one can obtain the chemical reaction rate of THF with singlet O$_2$ to be $3.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$. Consequently, the lifetime of singlet O$_2$ in neat THF is 21.06 $\mu$s, which is the reciprocal of the apparent rate in neat THF (12.36 M).

\begin{align}
^1\text{O}_2 & \xrightarrow{k_0} \text{O}_2 + \text{hv} \\
^1\text{O}_2 & \xrightarrow{k_{1}[\text{THF}]} \text{THF-pdt} \\
^1\text{O}_2 & \xrightarrow{k_{2}[\text{MCH}]} \text{MCH-pdt= 2u+2u'+2u''} \\
\end{align}

\( \text{case a), in neat THF} \)

\[ k_{\text{Total}} = k_0 + k_1[\text{THF}] \]

\[ \Phi_{\text{THF-pdt}} = \frac{k_1[\text{THF}]}{k_0 + k_1[\text{THF}]} \]
Quantum yield measurement of singlet oxygen chemical reaction with THF. The chemical quantum yield of singlet O\(_2\) in THF, by definition, can be obtained via two methods: either the ratio of “moles of THF-singlet oxygen reaction products” vs. “the moles of singlet oxygen formed”; or the observed apparent chemical reaction rate (k\(_1\)[THF]) of singlet oxygen with THF divided by the total rates (k\(_0\) + k\(_1\)[THF]) of all physical (k\(_0\)) and chemical (k\(_1\)[THF]) deactivation channels (see the chemical equation shown below).
In CCl$_4$, the physical deactivation rate, $k_0$ value, is $1/(900 \, \mu s) = 1.1 \times 10^3 \, s^{-1}$. In neat THF, the $k_0$ value is assumed to be $(13/4 = 3.25)$ times faster than for CCl$_4$, since THF has 13 (C-H, C-C or C-O) single bonds when compared to 4 C-Cl single bonds for CCl$_4$. To the first approximation, this assumption is valid since solvent nuclear vibrational motion is the main exit channel responsible for the physical deactivation (via electronic-vibrational coupling) of singlet O$_2$. Therefore, the $k_0$ value for THF is tentatively assumed to be approximately $1.1 \times 10^3 \, s^{-1} \times 3.25 = 3.6 \times 10^3 \, s^{-1}$. From the competition reaction with 1-methylcyclohexene, we obtained the chemical reaction rate of singlet O$_2$ in THF to be $3.8 \times 10^3 \, M^{-1} \, s^{-1}$. Neat THF has a THF concentration of 12.35 M. Therefore, the chemical quantum yield of product formation for singlet O$_2$ chemical reaction with THF can be obtained by the Supplementary Equation (6):

$$
\Phi_{\text{THF,pdt}} = \frac{k_1[\text{THF}]}{k_0 + k_1[\text{THF}]}
$$

In CCl$_4$, the physical deactivation rate of singlet O$_2$ in THF adopted in the above calculation may not be accurate. Nevertheless, the physical deactivation rate is at least one order slower than the chemical reaction rate of singlet O$_2$ in THF. Small variation in the physical deactivation rate will not change significantly the chemical quantum yield value (here, 0.93) of singlet O$_2$ in THF.
Supplementary Figure 37. Check CIF PDF files for compound 3p.

**checkCIF/PLATON report**

Structure factors have been supplied for datablock(s) I

*THIS REPORT IS FOR GUIDANCE ONLY IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.*

No syntax errors found. CIF dictionary Interpreting this report

**Datablock: I**

| Bond precision: | C-C = 0.0021 Å | Wavelength=0.71073 |
|-----------------|----------------|---------------------|
| Cell:           | a=7.7471(7) b=10.8420(11) c=8.1277(9) |
|                 | alpha=90 beta=112.208(4) gamma=90 |
| Temperature:    | 296 K |
| Volume          | Calculated: 632.04(11) | Reported: 632.04(11) |
| Space group     | P 21/c | P 1 21/c 1 |
| Hall group      | -P 2ybc | -P 2ybc |
| Moiety formula  | C8 H6 O2 | ? |
| Sum formula     | C8 H6 O2 | C8 H6 O2 |
| Mr              | 134.13 | 134.13 |
| Dx,g cm\(^{-3}\) | 1.410 | 1.410 |
| Z               | 4 | 4 |
| Mu (mm\(^{-1}\)) | 0.102 | 0.102 |
| F000            | 280.0 | 280.0 |
| F000'           | 280.16 | |
| h,k,lmax        | 9,13,10 | 9,13,10 |
| Nref            | 1301 | 1293 |
| Tmin,Tmax       | 0.980,0.985 | 0.836,0.949 |
| Tmin'           | 0.980 |

Correction method= # Reported T Limits: Tmin=0.836 Tmax=0.949
AbsCorr = MULTI-SCAN

Data completeness = 0.994 Theta(max)= 26.430
R(reflections) = 0.0405( 947) wR2(reflections) = 0.1431( 1293)
S = 1.180 Npar= 91

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
Supplementary Figure 38. Check CIF PDF file for compound 3s.

**checkCIF/PLATON report**

Structure factors have been supplied for datablock(s) I

**THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.**

No syntax errors found. CIF dictionary Interpreting this report

**Datablock: I**

Bond precision: C-C = 0.0025 A Wavelength=0.71073

| Cell: | a=7.4988(5) | b=10.681(7) | c=9.4162(7) |
|------|-------------|-------------|-------------|
| alpha=90 | beta=110.507(3) | gamma=90 |

Temperature: 100 K

| Calculated | Reported |
|------------|----------|
| Volume | 706.73(9) | 706.73(8) |
| Space group | P 21 | P 1 2 1 |
| Hall group | P 2yb | P 2yb |
| Moiety formula | C16 H26 O2 | ? |
| Sum formula | C16 H26 O2 | C16 H26 O2 |
| Mr | 250.37 | 250.37 |
| Dx,g cm-3 | 1.176 | 1.177 |
| Z | 2 | 2 |
| M | 0.075 | 0.075 |
| F000 | 276.0 | 276.0 |
| F000' | 276.12 | |
| h,k,lmax | 9,13,11 | 9,13,11 |
| Nref | 2901[ 1533] | 2329 |
| Tmin,Tmax | 0.997,0.998 | 0.714,0.949 |
| Tmin' | 0.989 | |

Correction method= # Reported T Limits: Tmin=0.714 Tmax=0.949
AbsCorr = MULTI-SCAN

Data completeness= 1.52/0.80 Theta(max)= 26.400

R(reflections) = 0.0340( 2080) wR2(reflections) = 0.0801( 2329)

\[ S = 1.056 \quad Npar = 167 \]

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
**Purification of starting materials.** Starting materials were purchased at the highest commercial quality and further purification by distillation process or activated alumina column chromatography. Low boiling liquid starting materials (1a-1k) were purified by distillation process (distillation procedure followed by known literature methods). Aromatic Starting materials (1l-1r) were purified by passing through activated alumina column chromatography under N₂ atmosphere. As requested by one of the reviewer, we have attached the \(^1\)H-NMR of purified starting materials (See Supplementary Figures 39-53).

Supplementary Figure 39. \(^1\)H NMR spectrum of compound 1a.
Supplementary Figure 40. $^1$H NMR spectrum of compound 1b.

Supplementary Figure 41. $^1$H NMR spectrum of compound 1c
Supplementary Figure 42. $^1$H NMR spectrum of compound 1d

Supplementary Figure 43. $^1$H NMR spectrum of compound 1e.
Supplementary Figure 44. $^1$H NMR spectrum of compound 1f.

Supplementary Figure 45. $^1$H NMR spectrum of compound 1h.
Supplementary Figure 46. $^1$H NMR spectrum of compound 1k

Supplementary Figure 47. $^1$H NMR spectrum of compound 1i
Supplementary Figure 48. $^1$H NMR spectrum of compound 1j.

Supplementary Figure 49. $^1$H NMR spectrum of compound 1m.
Supplementary Figure 50. $^1$H NMR spectrum of compound 1n.

Supplementary Figure 51. $^1$H NMR spectrum of compound 1o.
Supplementary Figure 52. $^1$H NMR spectrum of compound 1p.

Supplementary Figure 53. $^1$H NMR spectrum of compound 1r.
Supplementary References:

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