Copper Catalyzed Rearrangement of Vinyl Oxiranes

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Supporting Information

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General Information: Commercial reagents were purchased and used without further purification. All glassware was flame dried and reactions were performed under a nitrogen atmosphere, unless otherwise stated. Toluene, dichloromethane, diethyl ether, and THF were dried over a column of alumina. Flash chromatography was done with MP Silitech 32-63D 60Å silica, and thin layer chromatography (TLC) was performed with EMD 250 µm silica gel 60-F₂₅₄ plates. ¹H and ¹³C NMR data was acquired on a Varian Inova 400, 500, or 600 (400, 500 or 600 MHz) spectrometer and referenced to residual protic solvent. IR spectroscopy was done on a Nicolet Avatar 370 OTGS spectrometer. High-resolution mass spectrometry was performed at the University of Illinois at Urbana-Champaign facility.

Representative Procedure for the Rearrangement of Vinyl Oxiranes to 2,5-Dihydrofurans:

Stock solutions of the epoxide (0.792 mmol) in toluene (2.75 mL, total volume) and the catalyst (0.0429 mmol, 5 mol% loading) in toluene (3.00 mL) were prepared. To a 13x100 mm threaded culture tube was added 0.50 mL of the substrate solution, followed by 0.50 mL of the catalyst solution. The septum was replaced with a cap, and the seal was reinforced with Teflon tape. The tube was put in a 150°C oil bath. At the end of the reaction, the tube was cooled to room temperature, and the solvent was removed *in vacuo*. The crude product mixture was analyzed by NMR spectroscopy on a Varian Inova 600 where d1 was set to 60 seconds. Ratios reported in Tables 1 and 2 were determined by integration of the crude ¹H spectrum and are the average of 3-5 experiments.

Alternatively, Cu(hfacac)₂ was removed by filtration through a plug of type II alumina (30% Et₂O/pentane) to afford the dihydrofuran product with no other purification necessary, in most cases. Cu(tfacac)₂ was removed by adding a few drops of 8 M NaOH to the concentrated crude product. The mixture was allowed to stir for about 10 minutes and a precipitate was observed. The mixture was then dissolved in 30% Et₂O/pentane and filtered through a plug of type II alumina. Cu(dbm)₂ and Cu(ptfm)₂ are not soluble in toluene at room temperature, so

reactions were performed on a scale using approximately 10 mg of catalyst. The reactions for the yields reported in Table 2 were performed on at least a 0.10 g scale.

In the rearrangement of substrates **14** and **17**, flash chromatography was required in order to isolate pure products. The dihydrofuran product was most easily isolated by first reducing any carbonyl by-products with NaBH₄ (0.5 eq in methanol).

Control Experiments

All substrates are thermally stable under the reaction conditions in the absence of catalyst.

The following compounds lead to the partial or complete conversion to aldehyde as the major product when present at a 5 mol% loading in toluene at 150°C for 15 hours.

Magnesium bromide
 Iron (III) bromide
 [1,2-Bis(diphenylphosphino)ethane]dichloronickel(II)
 Ruthenium(III) chloride hydrate
 Ruthenium(II) chloride 1,5-cyclooctadiene
 Chlorocyclopentadienylbis(triphenylphosphine)ruthenium(II)
 Ruthenium(III) acetylacetonate
 Rhodium(II) acetate dimer
 Palladium(II) hexafluoroacetylacetonate
 Palladium(II) acetate
 Indium(III) chloride
 Tin(II) chloride

The following compounds did not react with substrate **5** when present at a 5 mol% loading in toluene at 150°C for 15 hours.

Potassium iodide (30 mol%)
 Manganese(II) acetylacetonate
 Iron(II) acetylacetonate
 Iron(III) acetylacetonate
 Cobalt(II) acetylacetonate
 Nickel(II) acetylacetonate
 Zinc acetylacetonate hydrate
 Palladium(II) acetylacetonate
 Silver trifluoroacetate
 Silver acetate
 Dichloro(ethylenediamine)platinum(II)
 Gold(I) chloride
 Hexafluoroacetylacetone

The following compounds lead to a complex mixture of products when present at a 5 mol% loading in toluene at 150°C for 15 hours.

Manganese(II) hexafluoroacetylacetonate trihydrate
 Iron (II) hexafluoroacetylacetonate
 Cobalt(II) hexafluoroacetylacetonate hydrate

Nickel(II) hexafluoroacetylacetonate hydrate
 Zinc hexafluoroacetylacetonate dihydrate
 Tetrakis(triphenylphosphine)palladium(0)
 Gold(III) chloride

Several protic acids (HCl, TFA, pTSA, and CSA) were briefly explored. Only in the case of (±)-Camphor-10-sulfonic acid was any 2,5-dihydrofuran observed (<10%).

Temperature and Solvent Experiments

For substrate **5**, the rearrangement was found to proceed well in a variety of solvents, including benzene, toluene, *m*-xylene, ethyl acetate, 1,2-dichloroethane, acetone, and 1,4-dioxane. When dimethylsulfoxide was used as the solvent, **5** was cleanly converted to aldehyde (**7**). The rearrangement has also been found to proceed at temperatures as low as 100°C for substrate **5**. Specifically, the reaction was run for 12 hours with a 5 mol% loading of Cu(hfacac)₂ to give a product ratio of 16:1 2,5-dihydrofuran:aldehyde.

Synthesis of substrates

1,2-Epoxy-3-hexyl-3-butene (5): Prepared in one step from 2-hexylacrolein¹ (9.53 g, 61.9 mmol) through a modification of a known method² where the reaction was allowed to warm to room temperature after consumption of the aldehyde and monitored for the consumption of the chlorohydrin. The product was obtained as a yellow oil (7.27g, 69% yield) after chromatography (5% Et₂O/pentane). ¹H-NMR (500 MHz, CDCl₃) δ 5.12 (s, 1H), 4.93 (app q, 1H, *J* = 1.3 Hz), 3.33-3.30 (m, 1H), 2.86 (dd, 1H, *J* = 4.3, 5.8 Hz), 2.62 (dd, 1H, *J* = 2.8, 5.3 Hz), 2.01-1.87 (m, 2H), 1.50-1.36 (m, 2H), 1.34-1.21 (m, 6H), 0.87 (t, 3H, *J* = 6.8 Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 145.9, 112.1, 54.0, 48.1, 31.9, 31.0, 29.2, 28.3, 22.8, 14.3; IR (neat) 2957, 2928, 2858, 1644, 1467, 1379, 1249, 1025, 900 cm⁻¹; HRMS (EI⁺) *m/z* 154.1358 [calculated mass for C₁₀H₁₈O (M⁺) 154.1358].

¹ Nakatsuji, Y.; Nakamura, T.; Yonetani, M.; Yuya, H.; Okahara, M. *J. Am. Chem. Soc.* **1988**, *110*, 531-538.

² Lautens, M.; Maddess, M. L.; Sauer, E. L. O.; Ouellet, S. G. *Org. Lett.* **2002**, *4*, 83-86.

3-Hexyl-2,5-dihydrofuran (6): $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 5.49-5.42 (m, 1H), 4.68-4.57 (m, 2H), 4.56-4.45 (m, 2H), 2.07 (t, 2H, $J = 7.0$ Hz), 1.51-1.40 (m, 2H), 1.37-1.22 (m, 6H), 0.88 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 140.9, 118.8, 77.3, 76.2, 31.9, 29.3, 27.8, 27.3, 22.8, 14.3; IR (neat) 2956, 2927, 2856, 1662, 1466, 1379, 1340, 1071, 1004, 959, 900 cm^{-1} ; HRMS (EI^+) m/z 154.1355 [calculated mass for $\text{C}_{10}\text{H}_{18}\text{O}$ (M^+) 154.1358].

1-Nonen-3-ol (12): To a flask at 0°C containing THF (400 mL) and vinylmagnesium bromide (1.0 M in THF, 100 mL) was added heptaldehyde (11.42 g, 100.0 mmol). The reaction was monitored by TLC and quenched with 1 M HCl after 1 hour. The solvent was concentrated *in vacuo* and the resulting crude mixture was extracted with dichloromethane. The layers were separated and the aqueous layer was extracted with dichloromethane (2x), washed with saturated sodium bicarbonate, water and dried over Na_2SO_4 . Solvent was removed *in vacuo* to give a yellow oil (11.80 g, 82% yield) that was carried forward without further purification. Characterization data is previously reported in the literature.³

1-Nonen-3-one (13): To a solution of **12** (11.80 g, 83.10 mmol) in acetone (250 mL) at 0°C was added Jones reagent⁴ (32mL). After twenty minutes, the reaction was quenched with isopropanol. Water and dichloromethane were added, and the layers were separated. The

³ Bourland, T. C.; Carter, R. G.; Yokochi, A. F. T. *Org. Biomol. Chem.* **2004**, 2, 1315-1329.

⁴ Hassner, A.; Stumer, C. *Organic Syntheses Based on Name Reactions and Unnamed Reactions*. New York: Elsevier Science Inc., 1994, volume 11, p 192.

aqueous layer was extracted (3x) with dichloromethane then washed with a saturated solution of NaHCO_3 (2x) and brine. It was dried over Na_2SO_4 , and the solvent was removed *in vacuo* to give a slightly green oil (9.29 g, 80%) that was carried forward without further purification. It was not necessary to use flame-dried glassware and work under an N_2 atmosphere. Characterization data is previously reported in the literature.⁵

1,2-Epoxy-2-hexyl-3-butene (14): Prepared from **13** (3.99 g, 28.50 mmol) in a modified version of a known procedure⁶, where the reaction was allowed to warm to room temperature upon consumption of the ketone. The product was obtained as a yellow oil (2.13 g, 49% yield) after chromatography (5% Et_2O /pentane). ^1H NMR (500 MHz, C_6D_6) δ 5.66 (dd, 1H, $J = 10.5$, 17.5 Hz), 5.32 (dd, 1H, $J = 1.5$, 17.5 Hz), 5.02 (dd, 1H, $J = 1.5$, 10.5 Hz), 2.42 (d, 1H, $J = 5.5$ Hz), 2.34 (d, 1H, $J = 5.5$ Hz), 1.61-1.54 (m, 1H), 1.49-1.41 (m, 1H), 1.40-1.11 (m, 8H), 0.86 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 138.8, 116.0, 58.7, 55.1, 34.2, 32.4, 30.1, 25.7, 23.3, 14.6; IR (neat) 3091, 3039, 2956, 2931, 2859, 1641, 1467, 1412, 1379, 1142, 1105, 988, 922 cm^{-1} ; HRMS (EI^+) m/z 155.1435 [calculated mass for $\text{C}_{10}\text{H}_{19}\text{O}$ ($\text{M}+\text{H}$) $^+$ 155.1436].

(E)-1-Chloro-3-undecen-2-ol (15): Prepared from *trans*-2-decenal² (5.08 g, 32.93 mmol) to give a yellow oil (6.01g, 89% yield) after chromatography (15% EtOAc /hexane). ^1H -NMR (500 MHz, CDCl_3) δ 5.85-5.77 (m, 1H), 5.49-5.42 (m, 1H), 4.30 (dt, 1H, $J = 4.0$, 6.3 Hz), 3.61 (dd, 1H, $J = 3.5$, 11.5 Hz), 3.49 (dd, 1H, $J = 7.5$, 11.0 Hz), 2.18 (s, 1H), 2.05 (q, 2H, $J = 7.2$ Hz), 1.42-1.19 (m, 10H), 0.88 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 135.5, 128.0, 72.6, 50.2, 32.5, 32.0, 29.3, 29.3, 29.1, 22.9, 14.3; IR (neat) 3356, 2956, 2925, 2855, 1670, 1466, 1430, 1379, 1302, 1250, 1060, 967, 758, 724 cm^{-1} ; HRMS (EI^+) m/z 204.1281 [calculated mass for $\text{C}_{11}\text{H}_{21}\text{ClO}$ (M^+) 204.1281].

⁵ Nakahira, H.; Ryu, I.; Ikebe, M.; Oku, Y.; Ogawa, A.; Kambe, N.; Sonoda, N; Murai, S. *J. Org. Chem.* **1992**, 57, 17-28.

⁶ Gu, H.; Xu, W. M.; Kinstle, T. H. *Tetrahedron Letters* **2005**, 46, 6449-6451.

***trans*-1,2-Epoxy-3-undecene (10):** Prepared from **15**² (4.95 g, 24.21 mmol) to give an orange oil (4.01 g, 99% yield). ¹H NMR (500 MHz, C₆D₆) δ 5.71 (td, 1H, *J* = 6.9, 15.3 Hz), 5.10-5.03 (m, 1H), 3.05 (ddd, 1H, *J* = 2.6, 3.8, 7.9 Hz), 2.51 (dd, 1H, *J* = 4.3, 5.3 Hz), 2.27 (dd, 1H, *J* = 2.8, 5.8 Hz), 1.92-1.86 (m, 2H), 1.31-1.13 (m, 10H), 0.89 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (125 MHz, C₆D₆) δ 137.7, 127.6, 52.8, 49.1, 32.6, 32.0, 29.4, 29.3, 29.1, 22.9, 14.3 cm⁻¹; IR (neat) 2956, 2925, 2855, 1670, 1466, 1396, 1379, 1246, 1130, 964, 933, 842 cm⁻¹; HRMS (EI⁺) *m/z* 168.1515 [calculated mass for C₁₁H₂₀O (M⁺) 168.1514].

2-Heptyl-2,5-dihydrofuran (11): ¹H-NMR (500 MHz, C₆D₆) δ 5.52-5.45 (m, 2H), 4.85-4.79 (m, 1H), 4.56-4.46 (m, 2H), 1.60-1.16 (m, 12H), 0.88 (t, 3H, *J* = 7.5 Hz); ¹³C NMR (125 MHz, C₆D₆) 130.7, 127.1, 86.6, 75.4, 37.0, 32.6, 30.5, 30.1, 26.2, 23.4, 14.7; IR (neat) 2956, 2926, 2854, 1466, 1353, 1118, 1078, 1019 cm⁻¹; HRMS (EI⁺) *m/z* 168.1510 [calculated mass for C₁₁H₂₀O (M⁺) 168.1514].

(3*E*)-1,3-undecadiene (16): To freshly azeotroped methyl triphenylphosphonium bromide (35.34 g, 98.9 mmol) in THF (500 mL) at 0°C was added *n*-BuLi (65 mL, 1.6 M in hexane). The reaction was allowed to stir at 0°C for an hour, at which point *trans*-2-decenal (10.20 g, 66.13 mmol) was added. After 30 minutes, the reaction mixture was quenched with water. The THF was removed *in vacuo*, and the resulting mixture extracted (2x) with dichloromethane. The combined organic layers were washed with a saturated brine solution and dried over Na₂SO₄. The organic layers were concentrated *in vacuo*, until the solid began to precipitate out. At this point, hexane was added to further precipitate the solid. The mixture was filtered and the

remaining solvent was removed. The product was obtained as a clear oil (8.91 g, 87% yield) after chromatography (5% Et₂O/pentane). ¹H NMR (500 MHz, CDCl₃) δ 6.36-6.27 (m, 1H), 6.09-6.01 (m, 1H), 5.75-5.67 (m, 1H), 5.09 (ddd, 1H, *J* = 0.5, 1.0, 17.0 Hz), 4.95 (ddd, 1H, *J* = 0.5, 1.0, 10.3 Hz), 2.08 (q, 2H, *J* = 7.3 Hz), 1.44-1.21 (m, 10H), 0.89 (t, 3H, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 137.6, 135.8, 131.1, 114.7, 32.8, 32.1, 29.4, 29.4, 29.4, 22.9, 14.3; HRMS (EI⁺) *m/z* 152.1561 [calculated mass for C₁₁H₂₀ (M⁺) 152.1565].

trans-3,4-Epoxy-1-undecene (17): To a dichloromethane (120 mL) solution of **16** (2.04 g, 13.42 mmol) was added Na₂HPO₄ (3.26 g) and *m*-CPBA (77% purity, 3.26 g, 14.48 mmol). After 3.5 hours, the reaction was cooled to 0°C, filtered through celite, washed with saturated NaHCO₃ (4x), saturated brine and then dried over Na₂SO₄. The solvent was removed *in vacuo*, and after chromatography (5% Et₂O/pentane), a clear oil was obtained (0.67 g, 30% yield). ¹H NMR (500 MHz, CDCl₃) δ 5.62-5.53 (m, 1H), 5.45 (dd, 1H, *J* = 1.5, 17.0 Hz), 5.25 (dd, 1H, *J* = 1.5, 10.3 Hz), 3.09 (dd, 1H, *J* = 2.3, 7.8 Hz), 2.82 (dt, 1H, *J* = 2.2, 5.6 Hz), 1.61-1.53 (m, 2H), 1.52-1.21 (m, 10H), 0.88 (t, 3H, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 136.2, 119.1, 60.7, 59.0, 32.2, 32.0, 29.6, 29.4, 26.1, 22.9, 14.3; IR (neat) 2957, 2927, 2857, 1643, 1460, 1406, 1378, 985, 918, 879 cm⁻¹; HRMS (EI⁺) *m/z* 168.1516 [calculated mass for C₁₁H₂₀O (M⁺) 168.1514].

1-(*p*-Tolyl)prop-2-en-1-ol (18): Prepared from *p*-tolualdehyde (7.59 g, 63.2 mmol) in the same way as **12** to give a yellow oil (9.25, 99% yield) that was carried forward without further purification. Characterization data is previously reported in the literature.⁷

⁷ Lehmann, J.; Lloyd-Jones, G. C. *Tetrahedron* **1995**, 51, 8863-8874.

1-(*p*-Tolyl)-2-propen-1-one (19): Prepared from **18** (13.10 g, 88.5 mmol) in the same way as **13** to give a yellow oil (11.76 g, 91%) that was carried forward without further purification. Characterization data is previously reported in the literature.⁸

2,3-Epoxy-1-(*p*-tolyl)-1-propanone (20): Prepared from **19** (8.64 g, 59.18 mmol) using a previously published procedure⁹ with a modified work-up. Upon consumption of the starting material, water was added, and the layers were separated. The organic layer was washed with saturated brine (3x), saturated Na₂SO₃ (2x), and dried over MgSO₄. The solvent was removed *in vacuo* to give a yellow oil (8.45 g, 88% yield) that was carried forward without further purification. It was not necessary to use flame-dried glassware and work under an N₂ atmosphere. ¹H-NMR (400 MHz, CDCl₃) δ 7.90 (d, 2H, *J* = 8.0 Hz), 7.25 (d, 2H, *J* = 8.0 Hz), 4.21-4.16 (m, 1H), 3.09-3.03 (m, 1H), 2.93-2.87 (m, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 194.2, 145.1, 133.0, 129.6, 128.5, 51.0, 47.6, 21.8; IR (neat) 3072, 3031, 3003, 2924, 2854, 1932, 1682, 1607, 1573, 1412, 1389, 1302, 1235, 1214, 1186, 1154, 1084, 1038, 955, 885, 832, 734, 689 cm⁻¹; HRMS (EI⁺) *m/z* 162.0684 [calculated mass for C₁₀H₁₀O₂ (M⁺) 162.0681].

1,2-Epoxy-3-(*p*-tolyl)-3-butene (21): Prepared from **20** (1.00 g, 6.17 mmol) in the same way as **16** to give a yellow oil (0.47 g, 47% yield). ¹H-NMR (400 MHz, C₆D₆) δ 7.29-7.23 (m, 2H), 6.98-6.93 (m, 2H), 5.41-5.38 (m, 1H), 5.32 (d, 1H, *J* = 1.6 Hz), 3.40-3.35 (m, 1H), 2.49 (dd, 1H,

⁸ Bodwell, G. J.; Li, J.; Miller, D. O. *Tetrahedron* **1999**, 55, 12939-12956.

⁹ Wipf, P.; Jung, J.-K. *J. Org. Chem.* **2000**, 65, 6319-6337.

$J = 4.0, 6.4$ Hz), 2.27 (dd, 1H, $J = 2.6, 6.2$ Hz), 2.10 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) 144.6, 138.1, 135.3, 129.3, 126.2, 112.0, 52.6, 49.8, 21.4; IR (neat) 3086, 3051, 3028, 2988, 2920, 2868, 1628, 1514, 1396, 1290, 1246, 1188, 1121, 1019, 918, 825 cm^{-1} ; HRMS (EI^+) m/z 160.0892 [calculated mass for $\text{C}_{11}\text{H}_{12}\text{O}$ (M^+) 160.0888].

3-(p-tolyl)-2,5-Dihydrofuran (22): ^1H NMR (500 MHz, CDCl_3) δ 7.28 (d, 2H, $J = 7.0$ Hz), 7.19 (d, 2H, $J = 8.0$ Hz), 6.22-6.19 (m, 1H), 5.04-5.00 (m, 2H), 4.89-4.85 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 138.5, 138.1, 129.9, 129.5, 125.9, 119.6, 77.0, 75.6, 21.5; IR (neat) 3086, 3028, 2951, 2918, 2874, 2843, 1657, 1606, 1513, 1477, 1344, 1311, 1275, 1244, 1079, 1005, 972, 901, 789 cm^{-1} ; HRMS (EI^+) m/z 160.0890 [calculated mass for $\text{C}_{11}\text{H}_{12}\text{O}$ (M^+) 160.0888].

Ethyl 3-butyl-2-heptenoate (23): To a solution of NaH (60% in mineral oil, 1.77 g, 44.29 mmol) in THF (180 mL) at 0°C was slowly added triethylphosphonoacetate (8.4 mL, 42.18 mmol). The mixture was allowed to warm to room temperature and stir for an hour, at which point 5-nonanone (3.04 g, 21.37 mmol) was added, and the reaction was refluxed. After 24 hours, the reaction was quenched with water. The layers were separated, and the aqueous layer was extracted with Et_2O (2x). The combined organic layers were washed with a saturated brine solution and dried over Na_2SO_4 . After chromatography (50% DCM/pentane), a clear oil was obtained (4.33 g, 97% yield). ^1H NMR (500 MHz, CDCl_3) δ 5.61 (s, 1H), 4.13 (q, 2H, $J = 7.2$ Hz), 2.62-2.56 (m, 2H), 2.16-2.10 (m, 2H), 1.49-1.29 (m, 8H), 1.27 (t, 3H, $J = 7.3$ Hz), 0.92 (t, 3H, $J = 7.0$), 0.91 (t, 3H, $J = 7.3$); ^{13}C NMR (125 MHz, CDCl_3) δ 166.8, 165.2, 115.2, 59.6, 38.3, 32.1, 31.1, 30.0, 23.3, 22.7, 14.6, 14.2, 14.2; IR (neat) 2958, 2932, 2862, 1716, 1642, 1466, 1378, 1232, 1189, 1146, 1117, 1039, 862, 733 cm^{-1} ; HRMS (EI^+) m/z 212.1772 [calculated mass for $\text{C}_{13}\text{H}_{24}\text{O}_2$ (M^+) 212.1776].

3-Butyl-2-hepten-1-ol (24): To a solution of LiAlH_4 (0.45 g, 11.97 mmol) in Et_2O (25 mL) at 0°C was slowly added a solution of **23** (4.23 g, 19.95 mmol, in 5 mL Et_2O). After an hour, the reaction was quenched with water then 1 M HCl and filtered through celite. The organic layer was separated and dried over Na_2SO_4 . Solvent was removed *in vacuo* to give a clear oil (3.33 g, 96% yield) that was carried forward without further purification. ^1H NMR (500 MHz, CDCl_3) δ 5.38 (t, 1H, $J = 7.0$ Hz), 4.15 (d, 2H, $J = 7.0$ Hz), 2.08-1.97 (m, 4H), 1.43-1.17 (m, 9H), 0.90 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (500 MHz, CDCl_3) δ 144.8, 123.4, 59.4, 36.7, 31.3, 30.4, 30.3, 23.0, 22.7, 14.2, 14.2; IR (neat) 3318, 2957, 2929, 2872, 2860, 1663, 1466, 1378, 1340, 1300, 1237, 1071, 1011, 734 cm^{-1} ; HRMS (EI^+) m/z 170.1667 [calculated mass for $\text{C}_{11}\text{H}_{22}\text{O}$ (M^+) 170.1671].

3-Butyl-2-heptenal (25): To a solution of **24** (3.23 g, 19.0 mmol) in dichloromethane (350 mL) was added activated MnO_2 (24.79 g, 285 mmol). After 48 hours, the crude reaction mixture was filtered through celite, and the solvent was removed *in vacuo* to give a yellow oil (2.97 g, 93% yield) that was used without further purification. Characterization data is previously reported in the literature¹⁰.

4-butyl-1,3-octadiene (26): Prepared from **25** (2.87 g, 16.9 mmol) in the same way as **16**. The product (2.54 g, 91% yield) was carried forward without chromatography. Spectral data matched that previously reported in the literature¹¹.

¹⁰ Bonete, P.; Nájera, C. *Tetrahedron* **1996**, 52, 4111-4122.

¹¹ Deagostino, A.; Prandi, C.; Zavattaro, C.; Venturello, P. *Eur. J. Org. Chem.* **2003**, 2612-2616.

4-butyl-3,4-epoxy-1-octene (27): Prepared from **26** (1.14 g, 6.87 mmol) in the same way as **17** to give a yellow oil (0.49 g, 39% yield) after chromatography (2.5%-5% Et₂O/pentane). ¹H NMR (500 MHz, CDCl₃) δ 5.76 (ddd, 1H, *J* = 7.3, 10.8, 17.5 Hz), 5.43 (ddd, 1H, *J* = 0.9, 1.5, 17.2 Hz), 5.31 (ddd, 1H, *J* = 0.8, 1.6, 10.5 Hz), 3.18 (d, 1H, *J* = 7.2 Hz), 1.65-1.50 (m, 4H), 1.49-1.24 (m, 8H), 0.91 (t, 3H, *J* = 7.2 Hz), 0.90 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 133.7, 120.0, 65.7, 63.7, 35.0, 30.0, 27.6, 27.1, 23.2, 23.1, 14.3, 14.2; IR (neat) 2957, 2932, 2863, 1730, 1641, 1467, 1379, 1342, 1286, 1255, 1161, 1119, 985, 920 cm⁻¹; HRMS (EI⁺) *m/z* 182.1666 [calculated mass for C₁₂H₂₂O (M⁺) 182.1671].

2,2-dibutyl-2,5-dihydrofuran (28): ¹H NMR (500 MHz, CDCl₃) δ 5.83 (dt, 1H, *J* = 1.5, 6.2 Hz), 5.60 (dt, 1H, *J* = 2.5, 6.2 Hz), 4.61-4.59 (m, 2H), 1.62-1.47 (m, 4H), 1.35-1.14 (m, 8H), 0.88 (t, 6H, *J* = 7.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 132.5, 126.1, 93.3, 75.7, 39.9, 26.5, 23.4, 14.4; IR (neat) 2956, 2932, 2861, 1467, 1378, 1349, 1081, 1063, 1034, 1019, 984, 920, 812, 717 cm⁻¹; HRMS (EI⁺) *m/z* 182.1660 [calculated mass for C₁₂H₂₂O (M⁺) 182.1671].

4-butyl-1-chloro-3-octen-2-ol (29): Prepared from **25**² (0.99 g, 5.89 mmol) to give a yellow oil (0.80 g, 63% yield) after chromatography (20% Et₂O/pentane). ¹H NMR (500 MHz, C₆D₆) δ 5.10 (d, 1H, *J* = 8.4 Hz), 4.44-4.34 (m, 1H), 3.24 (s, 1H), 3.22 (d, 1H, *J* = 1.7 Hz), 1.93-1.82 (m, 4H), 1.66 (s, 1H), 1.32-1.10 (m, 8H), 0.86 (t, 3H, *J* = 7.2 Hz), 0.84 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (125 MHz, C₆D₆) δ 145.8, 124.4, 68.8, 50.5, 36.9, 31.5, 31.2, 30.7, 23.4, 23.1, 14.6, 14.5; IR (neat) 3361, 2957, 2931, 2872, 2860, 1662, 1466, 1427, 1378, 1339, 1251, 1058, 1007, 845, 734 cm⁻¹; HRMS (EI⁺) *m/z* 218.1432 [calculated mass for C₁₂H₂₃ClO (M⁺) 218.1437].

4-Butyl-1,2-epoxy-3-octene (30): Prepared from **29**² (0.80 g, 3.66 mmol) to give an orange oil (0.66 g, 99% yield). ¹H-NMR (500 MHz, C₆D₆) δ 4.86 (d, 1H, *J* = 8.7 Hz), 3.41 (ddd, 1H, *J* = 2.6, 4.0, 8.7 Hz), 2.60 (dd, 1H, *J* = 4.1, 5.6 Hz), 2.34 (dd, 1H, *J* = 2.6, 5.6 Hz), 2.10-1.99 (m, 2H), 1.94-1.88 (m, 2H), 1.41-1.14 (m, 8H), 0.85 (t, 6H, *J* = 7.3 Hz); ¹³C NMR (125 MHz, C₆D₆) δ 147.8, 123.8, 48.8, 48.6, 37.3, 31.7, 31.1, 30.7, 23.3, 23.2, 14.5, 14.5; IR (neat) 3041, 2957, 2929, 2872, 2860, 1664, 1466, 1378, 1252, 1136, 1109, 948, 931 cm⁻¹; HRMS (EI⁺) *m/z* 182.1672 [calculated mass for C₁₂H₂₂O (M⁺) 182.1671].

2,3-Dimethyl-1,2-epoxy-3-butene (31): To a solution of 2,3-dimethyl-1,3-butadiene (4.13 mL, 36.5 mmol) in dichloromethane (360 mL) at 0°C was added *m*-CPBA (77% purity, 6.93 g, 40 mmol). The reaction was quenched with Na₂SO₃ after 1 hour. The layers were separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with NaHCO₃ and dried over MgSO₄. The organic layer was concentrated and distilled to give a clear liquid (0.70 g, 20% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.05 (dd, 1H, *J* = 0.8, 1.6 Hz), 4.92 (p, 1H, *J* = 1.5 Hz), 2.76 (dd, 1H, *J* = 0.7, 5.4 Hz), 2.70 (d, 1H, *J* = 5.3 Hz), 1.71 (dd, 3H, *J* = 0.9, 1.4 Hz), 1.45 (d, 3H, *J* = 0.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 112.7, 58.1, 54.2, 20.8, 18.6; IR (neat) 3095, 3045, 2976, 2933, 1646, 1445, 1379, 1348, 1319, 1289, 1173, 1140, 1111, 1069, 1008, 902, 861 cm⁻¹; HRMS (EI⁺) *m/z* 98.0732 [calculated mass for C₆H₁₀O (M⁺) 98.0732].

2,5-Dihydro-3,4-dimethylfuran (32): ¹H NMR (500 MHz, C₆D₆) δ 4.48 (s, 4H), 1.26 (s, 6H); ¹³C NMR (125 MHz, C₆D₆) δ 127.48, 80.09, 9.66. Other characterization data is previously reported in the literature.¹²

¹² Ripoll, J. *Tetrahedron Letters* **1974**, 18, 1665-1666.

(E)-4-Dodecen-3-ol (33): To a solution of EtMgBr (100 mL, 1 M in THF) in THF (500 mL) at 0°C was added *trans*-2-decenal (15.2 g, 98.5 mmol). The reaction was monitored by TLC, and after 2.5 hours, the reaction was quenched with a saturated NH₄Cl solution. The layers were separated, and the aqueous layer was extracted with Et₂O (2x). The combined organic layers were washed with a saturated brine solution and dried over Na₂SO₄. The solvent was removed *in vacuo* to give a clear oil (11.70 g, 64% yield). ¹H NMR (500 MHz, C₆D₆) δ 5.56-5.48 (m, 1H), 5.44-5.37 (m, 1H), 3.82 (q, 1H, *J* = 6.4 Hz), 1.95 (q, 2H, *J* = 7.0 Hz), 1.57-1.38 (m, 2H), 1.36-1.17 (m, 10H), 1.02 (s, 1H), 0.89 (t, 3H, *J* = 7.0), 0.88 (t, 3H, *J* = 7.5); ¹³C NMR (125 MHz, C₆D₆) δ 134.3, 131.6, 74.5, 33.0, 32.6, 31.1, 30.1, 30.0, 29.9, 23.4, 14.7, 10.4; IR (neat) 3346, 2959, 2925, 2855, 1670, 1463, 1378, 1121, 1060, 965 cm⁻¹; HRMS (EI⁺) *m/z* 184.1823 [calculated mass for C₁₂H₂₄O (M⁺) 184.1827].

(E)-4-dodecen-3-one (34): Prepared from **33** (11.70 g, 63.5 mmol) in the same way as **13** to give a yellow oil (10.98 g, 95% yield) which was carried on to the next step without further purification. ¹H NMR (400 MHz, CDCl₃) δ 6.82 (td, 1H, *J* = 6.9, 15.9 Hz), 6.08 (td, 1H, *J* = 1.5, 15.9 Hz), 2.55 (q, 2H, *J* = 7.4 Hz), 2.23-2.15 (m, 2H), 1.51-1.39 (m, 2H), 1.36-1.18 (m, 8H), 1.08 (t, 3H, *J* = 7.3 Hz), 0.87 (t, 3H, *J* = 7.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 147.4, 130.2, 33.4, 32.7, 31.9, 29.3, 29.3, 28.3, 22.8, 14.3, 8.4; IR (neat) 2957, 2927, 2856, 1700, 1675, 1631, 1460, 1377, 1357, 1202, 1117, 978 cm⁻¹; HRMS (EI⁺) *m/z* 182.1672 [calculated mass for C₁₂H₂₂O (M⁺) 182.1671].

***trans*-4,5-epoxy-3-dodecanone (35):** Prepared from **34** (15.0 g, 80.2 mmol) in the same way as **20** to give a clear oil (10.0 g, 63% yield) after chromatography. ¹H NMR (400 MHz, CDCl₃) δ 3.18 (d, 1H, *J* = 1.9 Hz), 3.00 (ddd, 1H, *J* = 2.0, 5.1, 6.9 Hz), 2.49-2.36 (m, 1H), 2.36-2.19 (m, 1H), 1.67-1.48 (m, 2H), 1.48-1.35 (m, 2H), 1.35-1.16 (m, 8H), 1.01 (t, 3H, *J* = 7.3 Hz), 0.84 (t, 3H, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 208.3, 59.6, 58.6, 32.0, 31.8, 30.6, 29.3, 29.2,

25.9, 22.7, 14.1, 7.1; IR (neat) 2928, 2857, 1712, 1460, 1434, 1409, 1379, 1358, 1227, 1181, 1121, 1086 cm^{-1} ; HRMS (EI^+) m/z 198.1623 [calculated mass for $\text{C}_{12}\text{H}_{22}\text{O}_2$ (M^+) 198.1620].

trans-3,4-Epoxy-2-ethyl-1-undecene (36): Prepared from **35** (5.0 g, 25.2 mmol) in the same way **16** was made to give a yellow oil (2.73 g, 55% yield). ^1H NMR (500 MHz, C_6D_6) δ 5.21 (qd, 1H, $J = 0.9, 1.8$ Hz), 4.87 (q, 1H, $J = 1.6$ Hz), 2.98 (d, 1H, $J = 2.0$ Hz), 2.68 (ddd, 1H, $J = 2.1, 4.9, 6.1$ Hz), 2.00-1.90 (m, 1H), 1.89-1.78 (m, 1H), 1.49-1.13 (m, 12H), 0.95 (t, 3H, $J = 7.5$ Hz), 0.89 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 148.5, 110.5, 60.3, 60.0, 33.0, 32.5, 30.1, 30.0, 26.7, 24.9, 23.4, 14.7, 13.0; IR (neat) 3090, 2962, 2928, 2857, 1649, 1458, 1378, 899, 880 cm^{-1} ; HRMS (EI^+) m/z 196.1828 [calculated mass for $\text{C}_{13}\text{H}_{24}\text{O}$ (M^+) 196.1827].

4-Ethyl-2-heptyl-2,5-dihydrofuran (37): ^1H NMR (500 MHz, C_6D_6) δ 5.24-5.21 (m, 1H), 4.95-4.88 (m, 1H), 4.55-4.44 (m, 2H), 1.80-1.71 (m, 2H), 1.68-1.16 (m, 12H), 0.88 (t, 3H, $J = 7.0$ Hz), 0.88 (t, 3H, $J = 7.5$); ^{13}C NMR (125 MHz, C_6D_6) δ 143.1, 122.8, 87.2, 77.1, 37.5, 32.6, 30.6, 30.2, 26.3, 23.4, 20.7, 14.7, 12.6; IR (neat) 2958, 2927, 2854, 1664, 1461, 1377, 1360, 1171, 1117, 1074, 1050 cm^{-1} ; HRMS (EI^+) m/z 196.1825 [calculated mass for $\text{C}_{13}\text{H}_{24}\text{O}$ (M^+) 196.1827].

8-oxa-bicyclo[3.2.1]-6-octene (38): ^1H NMR (500 MHz, C_6D_6) δ 5.74 (s, 2H), 4.54 (d, 2H, $J = 3.4$ Hz), 4.25 (methylene chloride), 1.76-1.68 (m, 2H), 1.64-1.51 (m, 1H), 1.33-1.20 (m, 1H), 0.94-0.83 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 131.0, 79.5, 25.6, 16.6.

9-oxa-bicyclo[4.2.1]-7-nonene (39): ^1H NMR (500 MHz, C_6D_6) δ 5.44 (s, 2H), 4.91 (dd, 2H, J = 1.1, 6.5 Hz), 1.83-1.73 (m, 2H), 1.65-1.56 (m, 2H), 1.51-1.42 (m, 2H), 1.26-1.16 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 131.5, 83.4, 34.6, 25.1; HRMS (EI^+) m/z 124.0891 [calculated mass for $\text{C}_8\text{H}_{12}\text{O}$ (M^+) 124.0888].

1,3-bis[4-(trifluoromethyl)phenyl]propane-1,3-dione (40): Prepared from 4-(trifluoromethyl)acetophenone (0.53 g, 2.82 mmol) and methyl 4-(trifluoromethyl)benzoate (1.15 g, 5.64 mmol) according to a previously reported procedure¹³ to give an orange solid (0.59 g, 67% yield) after chromatography (50% hexane/toluene). ^1H NMR (enol form, 500 MHz, CDCl_3) δ 16.61 (s, 1H), 8.12-8.08 (m, 4H, J = 8.2 Hz), 7.79-7.75 (m, 4H, J = 8.2 Hz), 6.88 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) 184.9, 138.6, 138.5, 134.7-133.9 (q, $J_{\text{C-F}}$ = 32.8 Hz), 127.8, 127.1-120.6 (q, $J_{\text{C-F}}$ = 273.3 Hz), 126.0-126.0 (q, $J_{\text{C-F}}$ = 3.8 Hz), 94.3; IR (neat) 1604, 1534, 1317, 1163, 1130, 1115, 1076, 1065, 1014, 860, 846, 795, 748 cm^{-1} ; HRMS (EI^+) m/z 360.0586 [calculated mass for $\text{C}_{17}\text{H}_{10}\text{F}_6\text{O}_2$ (M^+) 360.0585].

¹³ Popic, V. V.; Korneev, S. M.; Nikolaev, V. A.; Korobitsyna, I. K. *Synthesis* **1991**, 195-198.

Copper (II) 1,3-bis(4-trifluoromethylphenyl)-1,3-propanedionate (41): A minimal amount of Et₂O was used to dissolve **40** (1.19 g, 3.31 mmol), and then NaOAc (0.271 g, 3.30 mmol) was added. In a separate flask, Cu(OAc)₂ (0.300 g, 1.64 mmol) in 70 mL MeOH was sonicated. The Cu(OAc)₂ solution was added to the ligand solution and left to stir at room temperature for 18 hours. At this point, the solution was concentrated *in vacuo* and filtered. The green solid was recrystallized in toluene (0.91 g, 71% yield). HRMS (EI⁺) *m/z* 781.0312 [calculated mass for C₃₄H₁₈F₁₂O₄Cu (M⁺) 781.0309].

Bis(2-acetylcyclohexanonato)copper (II): Previously reported in the literature.¹⁴

Bis[2-(trifluoroacetyl)cyclohexanonato]copper (II): Previously reported in the literature.¹⁵

¹⁴ King, N. J., Jr.; Ferguson, L. N. *J. Org. Chem.* **1967**, 32, 1691-1692

¹⁵ Ebraheem, K. A. K.; Hamdi, S. T.; Khalaf, M. N. *Canadian Journal of Spectroscopy* **1983**, 28, 9-13; Hamdi, S. T. *Monatsh. Chem.* **1992**, 123 1081-1087.

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Crystal Structure Data for Copper (II) 1,3-bis(4-trifluoromethylphenyl)-1,3-propanedionate (41**).**

Figure S1. Crystal structure of **41** where hydrogens have been omitted.

Table S1. Crystal data and structure refinement for **41**.

Empirical formula	$C_{51}H_{27}Cu_{1.50}F_{18}O_6$	
Formula weight	1173.04	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1008(4) Å	$\alpha = 76.251(2)^\circ$.
	b = 14.5074(5) Å	$\beta = 81.606(2)^\circ$.
	c = 16.1862(5) Å	$\gamma = 73.170(2)^\circ$.
Volume	2415.18(14) Å ³	
Z	2	
Density (calculated)	1.613 Mg/m ³	
Absorption coefficient	0.786 mm ⁻¹	
F(000)	1173	
Crystal size	0.60 x 0.40 x 0.30 mm ³	
Theta range for data collection	1.50 to 30.51°.	
Index ranges	-15 ≤ h ≤ 15, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23	
Reflections collected	72539	
Independent reflections	14642 [R(int) = 0.0282]	
Completeness to theta = 30.51°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7983 and 0.6498	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14642 / 0 / 730	
Goodness-of-fit on F ²	1.275	
Final R indices [I > 2σ(I)]	R1 = 0.0443, wR2 = 0.1504	
R indices (all data)	R1 = 0.0514, wR2 = 0.1551	
Largest diff. peak and hole	0.918 and -0.760 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **41**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1A)	5000	0	10000	22(1)
F(1A)	6769(4)	2725(11)	4612(3)	93(4)
F(2A)	5229(10)	3925(4)	4739(3)	77(2)
F(1A')	6539(8)	2135(7)	4628(3)	90(2)
F(2A')	6117(16)	3614(10)	4683(2)	128(6)
F(3A)	4778(2)	2805(2)	4589(1)	88(1)
F(4A)	6844(2)	4064(1)	12571(1)	72(1)
F(5A)	4856(2)	4397(1)	12898(1)	65(1)
F(6A)	5630(2)	5287(1)	11835(1)	50(1)
O(1A)	4805(1)	824(1)	8880(1)	25(1)
O(2A)	5039(1)	1058(1)	10492(1)	25(1)
C(1A)	5168(1)	1619(1)	8635(1)	20(1)
C(2A)	5414(2)	2139(1)	9185(1)	23(1)
C(3A)	5286(1)	1854(1)	10080(1)	20(1)
C(4A)	5316(1)	1972(1)	7686(1)	21(1)
C(5A)	5020(2)	1443(1)	7162(1)	27(1)
C(6A)	5139(2)	1744(1)	6281(1)	31(1)
C(7A)	5555(2)	2577(1)	5918(1)	30(1)
C(8A)	5865(2)	3102(2)	6425(1)	34(1)
C(9A)	5749(2)	2800(1)	7308(1)	29(1)
C(10A)	5433(1)	2510(1)	10623(1)	20(1)
C(11A)	5666(2)	3423(1)	10282(1)	29(1)
C(12A)	5762(2)	4020(1)	10810(1)	31(1)
C(13A)	5615(2)	3711(1)	11686(1)	24(1)
C(14A)	5391(2)	2801(1)	12040(1)	32(1)
C(15A)	5304(2)	2205(1)	11507(1)	29(1)
C(16A)	5679(2)	2905(2)	4963(1)	44(1)
C(17A)	5724(2)	4353(1)	12253(1)	30(1)
Cu(1)	2301(1)	1193(1)	8981(1)	24(1)
O(1)	2401(1)	404(1)	10116(1)	29(1)
O(2)	2102(1)	149(1)	8522(1)	28(1)
O(3)	2141(1)	1995(1)	7866(1)	27(1)
O(4)	2151(1)	2274(1)	9503(1)	26(1)
F(1)	-502(2)	-866(2)	14201(1)	76(1)
F(2)	1307(2)	-792(2)	14468(1)	77(1)
F(3)	1015(2)	-2149(1)	14384(1)	70(1)
F(4)	-1076(8)	-2613(8)	7081(6)	79(3)
F(4')	-937(9)	-2427(7)	6737(12)	132(4)
F(5)	661(13)	-2723(9)	6184(3)	122(3)
F(5')	1112(11)	-3072(12)	6345(11)	57(4)
F(6)	351(2)	-3737(1)	7338(1)	73(1)
F(7)	2165(2)	5336(1)	3771(1)	83(1)
F(8)	598(1)	4717(2)	3860(1)	72(1)
F(9)	2427(2)	3906(1)	3569(1)	61(1)
F(10)	2696(1)	5776(1)	11620(1)	62(1)
F(11)	1006(2)	6723(1)	11047(1)	71(1)
F(12)	901(1)	5556(1)	12100(1)	48(1)
C(1)	1911(1)	-324(1)	10383(1)	22(1)

C(2)	1579(2)	-825(1)	9854(1)	24(1)
C(3)	1693(1)	-570(1)	8959(1)	21(1)
C(4)	2142(1)	2904(1)	7652(1)	22(1)
C(5)	2146(2)	3488(1)	8225(1)	25(1)
C(6)	2108(1)	3157(1)	9107(1)	21(1)
C(7)	1676(1)	-602(1)	11332(1)	22(1)
C(8)	1971(2)	-54(1)	11836(1)	27(1)
C(9)	1684(2)	-247(1)	12715(1)	31(1)
C(10)	1119(2)	-998(2)	13093(1)	32(1)
C(11)	833(2)	-1556(2)	12604(1)	39(1)
C(12)	1109(2)	-1355(1)	11726(1)	34(1)
C(13)	1317(1)	-1164(1)	8451(1)	22(1)
C(14)	555(2)	-1798(1)	8814(1)	26(1)
C(15)	203(2)	-2320(1)	8323(1)	29(1)
C(16)	612(2)	-2221(1)	7464(1)	28(1)
C(17)	1358(2)	-1588(2)	7089(1)	33(1)
C(18)	1700(2)	-1058(1)	7582(1)	29(1)
C(19)	2093(2)	3343(1)	6717(1)	23(1)
C(20)	1757(2)	2834(1)	6198(1)	30(1)
C(21)	1652(2)	3227(2)	5337(1)	34(1)
C(22)	1907(2)	4126(1)	4986(1)	30(1)
C(23)	2263(2)	4629(1)	5490(1)	34(1)
C(24)	2353(2)	4244(1)	6356(1)	30(1)
C(25)	1984(1)	3867(1)	9673(1)	21(1)
C(26)	1536(2)	4876(1)	9398(1)	28(1)
C(27)	1397(2)	5506(1)	9953(1)	30(1)
C(28)	1730(2)	5124(1)	10781(1)	25(1)
C(29)	2184(2)	4111(1)	11069(1)	26(1)
C(30)	2303(2)	3488(1)	10516(1)	24(1)
C(31)	751(2)	-1191(2)	14034(1)	44(1)
C(32)	190(2)	-2791(2)	6952(1)	40(1)
C(33)	1770(2)	4542(2)	4054(1)	38(1)
C(34)	1583(2)	5789(1)	11387(1)	33(1)

Table S3. Bond lengths [Å] and angles [°] for **41**.

Cu(1A)-O(2A)#1	1.9029(12)
Cu(1A)-O(2A)	1.9029(12)
Cu(1A)-O(1A)	1.9223(11)
Cu(1A)-O(1A)#1	1.9224(11)
F(1A)-C(16A)	1.243(5)
F(2A)-C(16A)	1.394(6)
F(1A')-C(16A)	1.405(5)
F(2A')-C(16A)	1.227(5)
F(3A)-C(16A)	1.299(3)
F(4A)-C(17A)	1.331(2)
F(5A)-C(17A)	1.313(2)
F(6A)-C(17A)	1.345(2)
O(1A)-C(1A)	1.2870(18)
O(2A)-C(3A)	1.2719(18)
C(1A)-C(2A)	1.394(2)
C(1A)-C(4A)	1.500(2)
C(2A)-C(3A)	1.407(2)
C(3A)-C(10A)	1.495(2)
C(4A)-C(5A)	1.397(2)
C(4A)-C(9A)	1.396(2)
C(5A)-C(6A)	1.387(2)
C(6A)-C(7A)	1.388(3)
C(7A)-C(8A)	1.380(2)
C(7A)-C(16A)	1.504(2)
C(8A)-C(9A)	1.391(2)
C(10A)-C(15A)	1.392(2)
C(10A)-C(11A)	1.391(2)
C(11A)-C(12A)	1.387(2)
C(12A)-C(13A)	1.382(2)
C(13A)-C(14A)	1.386(2)
C(13A)-C(17A)	1.494(2)
C(14A)-C(15A)	1.388(2)
Cu(1)-O(3)	1.9035(12)
Cu(1)-O(4)	1.9085(12)
Cu(1)-O(2)	1.9161(12)
Cu(1)-O(1)	1.9181(12)
O(1)-C(1)	1.2827(19)
O(2)-C(3)	1.2735(19)
O(3)-C(4)	1.2808(19)
O(4)-C(6)	1.2791(18)
F(1)-C(31)	1.342(3)
F(2)-C(31)	1.318(3)
F(3)-C(31)	1.332(3)
F(4)-C(32)	1.347(8)
F(4')-C(32)	1.274(5)
F(5)-C(32)	1.269(4)
F(5')-C(32)	1.354(12)
F(6)-C(32)	1.337(3)
F(7)-C(33)	1.309(3)
F(8)-C(33)	1.321(2)
F(9)-C(33)	1.337(3)
F(10)-C(34)	1.337(2)
F(11)-C(34)	1.340(2)
F(12)-C(34)	1.314(2)

C(1)-C(2)	1.394(2)
C(1)-C(7)	1.495(2)
C(2)-C(3)	1.403(2)
C(3)-C(13)	1.496(2)
C(4)-C(5)	1.398(2)
C(4)-C(19)	1.499(2)
C(5)-C(6)	1.393(2)
C(6)-C(25)	1.499(2)
C(7)-C(12)	1.394(2)
C(7)-C(8)	1.394(2)
C(8)-C(9)	1.391(2)
C(9)-C(10)	1.386(3)
C(10)-C(11)	1.382(3)
C(10)-C(31)	1.499(2)
C(11)-C(12)	1.388(2)
C(13)-C(18)	1.394(2)
C(13)-C(14)	1.398(2)
C(14)-C(15)	1.382(2)
C(15)-C(16)	1.385(2)
C(16)-C(17)	1.388(2)
C(16)-C(32)	1.500(2)
C(17)-C(18)	1.386(2)
C(19)-C(24)	1.393(2)
C(19)-C(20)	1.392(2)
C(20)-C(21)	1.381(2)
C(21)-C(22)	1.384(3)
C(22)-C(23)	1.378(2)
C(22)-C(33)	1.498(2)
C(23)-C(24)	1.387(2)
C(25)-C(26)	1.387(2)
C(25)-C(30)	1.401(2)
C(26)-C(27)	1.390(2)
C(27)-C(28)	1.383(2)
C(28)-C(29)	1.394(2)
C(28)-C(34)	1.494(2)
C(29)-C(30)	1.385(2)

O(2A)#1-Cu(1A)-O(2A)	180.0
O(2A)#1-Cu(1A)-O(1A)	87.33(5)
O(2A)-Cu(1A)-O(1A)	92.67(5)
O(2A)#1-Cu(1A)-O(1A)#1	92.67(5)
O(2A)-Cu(1A)-O(1A)#1	87.33(5)
O(1A)-Cu(1A)-O(1A)#1	180.00(8)
C(1A)-O(1A)-Cu(1A)	123.75(10)
C(3A)-O(2A)-Cu(1A)	125.16(10)
O(1A)-C(1A)-C(2A)	124.46(14)
O(1A)-C(1A)-C(4A)	114.87(13)
C(2A)-C(1A)-C(4A)	120.67(14)
C(1A)-C(2A)-C(3A)	123.66(14)
O(2A)-C(3A)-C(2A)	125.01(14)
O(2A)-C(3A)-C(10A)	114.80(13)
C(2A)-C(3A)-C(10A)	120.18(13)
C(5A)-C(4A)-C(9A)	118.91(14)
C(5A)-C(4A)-C(1A)	118.56(14)
C(9A)-C(4A)-C(1A)	122.52(14)
C(6A)-C(5A)-C(4A)	120.57(16)

C(7A)-C(6A)-C(5A)	119.65(15)
C(6A)-C(7A)-C(8A)	120.59(15)
C(6A)-C(7A)-C(16A)	119.66(16)
C(8A)-C(7A)-C(16A)	119.75(17)
C(7A)-C(8A)-C(9A)	119.82(17)
C(8A)-C(9A)-C(4A)	120.45(15)
C(15A)-C(10A)-C(11A)	118.60(14)
C(15A)-C(10A)-C(3A)	118.72(14)
C(11A)-C(10A)-C(3A)	122.66(13)
C(12A)-C(11A)-C(10A)	120.80(15)
C(13A)-C(12A)-C(11A)	119.79(15)
C(12A)-C(13A)-C(14A)	120.39(15)
C(12A)-C(13A)-C(17A)	119.72(15)
C(14A)-C(13A)-C(17A)	119.88(15)
C(15A)-C(14A)-C(13A)	119.45(15)
C(14A)-C(15A)-C(10A)	120.97(15)
F(2A')-C(16A)-F(1A)	63.9(4)
F(2A')-C(16A)-F(3A)	119.6(6)
F(1A)-C(16A)-F(3A)	118.5(6)
F(2A')-C(16A)-F(2A)	42.3(6)
F(1A)-C(16A)-F(2A)	104.3(5)
F(3A)-C(16A)-F(2A)	90.2(4)
F(2A')-C(16A)-F(1A')	104.3(5)
F(1A)-C(16A)-F(1A')	41.8(4)
F(3A)-C(16A)-F(1A')	90.2(4)
F(2A)-C(16A)-F(1A')	138.6(3)
F(2A')-C(16A)-C(7A)	116.3(3)
F(1A)-C(16A)-C(7A)	116.2(3)
F(3A)-C(16A)-C(7A)	113.65(17)
F(2A)-C(16A)-C(7A)	109.7(3)
F(1A')-C(16A)-C(7A)	107.9(3)
F(5A)-C(17A)-F(4A)	107.58(17)
F(5A)-C(17A)-F(6A)	106.28(16)
F(4A)-C(17A)-F(6A)	104.37(16)
F(5A)-C(17A)-C(13A)	113.33(15)
F(4A)-C(17A)-C(13A)	112.21(15)
F(6A)-C(17A)-C(13A)	112.47(14)
O(3)-Cu(1)-O(4)	93.54(5)
O(3)-Cu(1)-O(2)	87.74(5)
O(4)-Cu(1)-O(2)	168.65(6)
O(3)-Cu(1)-O(1)	177.96(5)
O(4)-Cu(1)-O(1)	85.81(5)
O(2)-Cu(1)-O(1)	92.52(5)
C(1)-O(1)-Cu(1)	123.93(10)
C(3)-O(2)-Cu(1)	124.32(11)
C(4)-O(3)-Cu(1)	126.12(10)
C(6)-O(4)-Cu(1)	125.54(10)
O(1)-C(1)-C(2)	124.31(14)
O(1)-C(1)-C(7)	115.02(13)
C(2)-C(1)-C(7)	120.65(14)
C(1)-C(2)-C(3)	124.15(15)
O(2)-C(3)-C(2)	124.93(14)
O(2)-C(3)-C(13)	115.38(13)
C(2)-C(3)-C(13)	119.69(14)
O(3)-C(4)-C(5)	124.77(14)
O(3)-C(4)-C(19)	115.21(13)

C(5)-C(4)-C(19)	120.00(14)
C(6)-C(5)-C(4)	123.71(15)
O(4)-C(6)-C(5)	125.59(14)
O(4)-C(6)-C(25)	114.70(13)
C(5)-C(6)-C(25)	119.71(14)
C(12)-C(7)-C(8)	118.86(15)
C(12)-C(7)-C(1)	122.29(14)
C(8)-C(7)-C(1)	118.75(14)
C(9)-C(8)-C(7)	120.33(16)
C(10)-C(9)-C(8)	119.82(16)
C(9)-C(10)-C(11)	120.62(16)
C(9)-C(10)-C(31)	120.74(17)
C(11)-C(10)-C(31)	118.59(18)
C(12)-C(11)-C(10)	119.40(18)
C(11)-C(12)-C(7)	120.96(16)
C(18)-C(13)-C(14)	118.83(14)
C(18)-C(13)-C(3)	119.10(14)
C(14)-C(13)-C(3)	122.04(14)
C(15)-C(14)-C(13)	120.55(15)
C(14)-C(15)-C(16)	119.94(15)
C(17)-C(16)-C(15)	120.36(15)
C(17)-C(16)-C(32)	121.54(16)
C(15)-C(16)-C(32)	118.07(16)
C(18)-C(17)-C(16)	119.58(16)
C(17)-C(18)-C(13)	120.72(15)
C(24)-C(19)-C(20)	119.26(15)
C(24)-C(19)-C(4)	122.31(14)
C(20)-C(19)-C(4)	118.42(14)
C(21)-C(20)-C(19)	120.53(16)
C(20)-C(21)-C(22)	119.71(16)
C(23)-C(22)-C(21)	120.36(15)
C(23)-C(22)-C(33)	120.98(17)
C(21)-C(22)-C(33)	118.65(16)
C(22)-C(23)-C(24)	120.17(16)
C(23)-C(24)-C(19)	119.95(15)
C(26)-C(25)-C(30)	119.22(14)
C(26)-C(25)-C(6)	122.45(14)
C(30)-C(25)-C(6)	118.31(14)
C(25)-C(26)-C(27)	120.48(15)
C(28)-C(27)-C(26)	119.78(16)
C(27)-C(28)-C(29)	120.58(15)
C(27)-C(28)-C(34)	120.49(15)
C(29)-C(28)-C(34)	118.91(15)
C(30)-C(29)-C(28)	119.30(14)
C(29)-C(30)-C(25)	120.62(15)
F(2)-C(31)-F(3)	106.5(2)
F(2)-C(31)-F(1)	108.0(2)
F(3)-C(31)-F(1)	104.3(2)
F(2)-C(31)-C(10)	113.75(19)
F(3)-C(31)-C(10)	112.46(19)
F(1)-C(31)-C(10)	111.32(18)
F(5)-C(32)-F(4')	93.1(11)
F(5)-C(32)-F(6)	110.2(6)
F(4')-C(32)-F(6)	109.6(7)
F(5)-C(32)-F(5')	27.8(7)
F(4')-C(32)-F(5')	118.0(10)

F(6)-C(32)-F(5')	89.1(8)
F(5)-C(32)-F(4)	116.7(7)
F(4')-C(32)-F(4)	25.3(8)
F(6)-C(32)-F(4)	91.8(5)
F(5')-C(32)-F(4)	137.9(6)
F(5)-C(32)-C(16)	115.2(2)
F(4')-C(32)-C(16)	114.8(3)
F(6)-C(32)-C(16)	112.32(17)
F(5')-C(32)-C(16)	110.1(6)
F(4)-C(32)-C(16)	108.3(4)
F(8)-C(33)-F(7)	109.6(2)
F(8)-C(33)-F(9)	103.06(18)
F(7)-C(33)-F(9)	105.62(17)
F(8)-C(33)-C(22)	112.05(16)
F(7)-C(33)-C(22)	113.46(17)
F(9)-C(33)-C(22)	112.33(18)
F(12)-C(34)-F(11)	105.60(17)
F(12)-C(34)-F(10)	105.86(16)
F(11)-C(34)-F(10)	107.73(17)
F(12)-C(34)-C(28)	113.54(16)
F(11)-C(34)-C(28)	111.71(15)
F(10)-C(34)-C(28)	111.94(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **41**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1A)	34(1)	15(1)	19(1)	-2(1)	-8(1)	-9(1)
F(1A)	37(2)	166(10)	29(2)	22(4)	10(1)	4(3)
F(2A)	137(6)	52(2)	24(2)	10(1)	-3(2)	-14(3)
F(1A')	108(4)	97(4)	32(2)	-13(2)	20(2)	9(3)
F(2A')	269(15)	153(9)	26(2)	-4(3)	9(4)	-180(11)
F(3A)	99(1)	147(2)	31(1)	11(1)	-22(1)	-68(1)
F(4A)	66(1)	63(1)	104(1)	-50(1)	-54(1)	7(1)
F(5A)	95(1)	79(1)	44(1)	-41(1)	30(1)	-56(1)
F(6A)	84(1)	30(1)	43(1)	-15(1)	-6(1)	-22(1)
O(1A)	39(1)	19(1)	21(1)	-1(1)	-9(1)	-13(1)
O(2A)	40(1)	18(1)	22(1)	-3(1)	-6(1)	-12(1)
C(1A)	23(1)	16(1)	20(1)	-3(1)	-5(1)	-5(1)
C(2A)	30(1)	20(1)	21(1)	-5(1)	-3(1)	-10(1)
C(3A)	23(1)	17(1)	21(1)	-4(1)	-5(1)	-6(1)
C(4A)	24(1)	20(1)	20(1)	-5(1)	-2(1)	-6(1)
C(5A)	35(1)	25(1)	24(1)	-7(1)	-4(1)	-11(1)
C(6A)	39(1)	36(1)	23(1)	-10(1)	-5(1)	-14(1)
C(7A)	33(1)	40(1)	20(1)	-6(1)	0(1)	-12(1)
C(8A)	45(1)	38(1)	23(1)	-3(1)	2(1)	-22(1)
C(9A)	43(1)	29(1)	21(1)	-6(1)	0(1)	-18(1)
C(10A)	23(1)	18(1)	21(1)	-6(1)	-4(1)	-6(1)
C(11A)	46(1)	27(1)	21(1)	-6(1)	-1(1)	-20(1)
C(12A)	47(1)	26(1)	26(1)	-8(1)	1(1)	-20(1)
C(13A)	27(1)	24(1)	25(1)	-9(1)	-5(1)	-8(1)
C(14A)	53(1)	26(1)	20(1)	-4(1)	-7(1)	-15(1)
C(15A)	48(1)	21(1)	22(1)	-2(1)	-7(1)	-14(1)
C(16A)	47(1)	66(2)	21(1)	-7(1)	0(1)	-23(1)
C(17A)	37(1)	29(1)	30(1)	-12(1)	-6(1)	-10(1)
Cu(1)	35(1)	17(1)	22(1)	-2(1)	-7(1)	-10(1)
O(1)	48(1)	23(1)	23(1)	-1(1)	-9(1)	-18(1)
O(2)	44(1)	21(1)	24(1)	-3(1)	-6(1)	-15(1)
O(3)	40(1)	19(1)	24(1)	-3(1)	-7(1)	-12(1)
O(4)	39(1)	17(1)	23(1)	-2(1)	-5(1)	-9(1)
F(1)	48(1)	125(2)	40(1)	-19(1)	16(1)	-6(1)
F(2)	106(1)	120(2)	31(1)	-26(1)	4(1)	-67(1)
F(3)	102(1)	68(1)	30(1)	4(1)	1(1)	-24(1)
F(4)	72(4)	134(7)	70(5)	-35(4)	-18(3)	-68(6)
F(4')	98(4)	105(4)	220(9)	-113(5)	-127(5)	53(3)
F(5)	232(7)	178(5)	27(1)	-32(3)	20(3)	-173(5)
F(5')	56(7)	84(8)	52(7)	-57(7)	-1(4)	-17(7)
F(6)	124(2)	50(1)	66(1)	-14(1)	-29(1)	-41(1)
F(7)	162(2)	77(1)	32(1)	11(1)	-21(1)	-77(1)
F(8)	47(1)	123(2)	34(1)	4(1)	-13(1)	-16(1)
F(9)	75(1)	75(1)	29(1)	-14(1)	1(1)	-14(1)
F(10)	55(1)	91(1)	63(1)	-48(1)	1(1)	-35(1)
F(11)	142(2)	25(1)	44(1)	-12(1)	-25(1)	-9(1)
F(12)	60(1)	55(1)	33(1)	-21(1)	9(1)	-17(1)
C(1)	26(1)	16(1)	23(1)	-3(1)	-4(1)	-4(1)
C(2)	31(1)	21(1)	24(1)	-5(1)	-2(1)	-10(1)
C(3)	24(1)	16(1)	24(1)	-4(1)	-4(1)	-4(1)

C(4)	25(1)	20(1)	23(1)	-3(1)	-3(1)	-9(1)
C(5)	35(1)	19(1)	22(1)	-1(1)	-5(1)	-10(1)
C(6)	23(1)	18(1)	23(1)	-3(1)	-3(1)	-7(1)
C(7)	24(1)	19(1)	22(1)	-6(1)	-2(1)	-3(1)
C(8)	32(1)	27(1)	26(1)	-6(1)	-6(1)	-10(1)
C(9)	32(1)	36(1)	27(1)	-13(1)	-5(1)	-8(1)
C(10)	33(1)	38(1)	23(1)	-9(1)	0(1)	-6(1)
C(11)	52(1)	42(1)	28(1)	-9(1)	7(1)	-25(1)
C(12)	52(1)	30(1)	25(1)	-9(1)	3(1)	-20(1)
C(13)	25(1)	17(1)	24(1)	-4(1)	-5(1)	-5(1)
C(14)	31(1)	25(1)	24(1)	-3(1)	-4(1)	-11(1)
C(15)	35(1)	26(1)	29(1)	-3(1)	-8(1)	-15(1)
C(16)	33(1)	25(1)	29(1)	-8(1)	-9(1)	-9(1)
C(17)	43(1)	39(1)	25(1)	-10(1)	-2(1)	-18(1)
C(18)	36(1)	31(1)	25(1)	-7(1)	-1(1)	-17(1)
C(19)	26(1)	22(1)	22(1)	-4(1)	-3(1)	-9(1)
C(20)	42(1)	30(1)	23(1)	-5(1)	-4(1)	-18(1)
C(21)	46(1)	39(1)	24(1)	-8(1)	-6(1)	-20(1)
C(22)	32(1)	37(1)	21(1)	-4(1)	-3(1)	-13(1)
C(23)	48(1)	31(1)	25(1)	1(1)	-6(1)	-20(1)
C(24)	43(1)	27(1)	24(1)	-3(1)	-6(1)	-18(1)
C(25)	24(1)	19(1)	21(1)	-4(1)	-2(1)	-7(1)
C(26)	41(1)	20(1)	21(1)	-1(1)	-8(1)	-6(1)
C(27)	46(1)	18(1)	26(1)	-3(1)	-7(1)	-7(1)
C(28)	32(1)	21(1)	23(1)	-5(1)	-2(1)	-8(1)
C(29)	33(1)	23(1)	21(1)	-2(1)	-5(1)	-7(1)
C(30)	28(1)	20(1)	23(1)	-1(1)	-4(1)	-7(1)
C(31)	44(1)	63(2)	27(1)	-14(1)	3(1)	-15(1)
C(32)	50(1)	41(1)	39(1)	-12(1)	-13(1)	-19(1)
C(33)	42(1)	52(1)	22(1)	-3(1)	-3(1)	-19(1)
C(34)	47(1)	28(1)	27(1)	-9(1)	-2(1)	-11(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **41**.

	x	y	z	U(eq)
H(2AA)	5682	2718	8941	27
H(5AA)	4735	873	7411	32
H(6AA)	4936	1381	5928	37
H(8AA)	6157	3667	6172	41
H(9AA)	5966	3160	7657	35
H(11B)	5760	3640	9680	35
H(12B)	5928	4640	10570	37
H(14B)	5298	2587	12642	38
H(15B)	5154	1580	11749	35
H(2A)	1255	-1373	10114	29
H(5A)	2176	4149	7999	30
H(8A)	2370	454	11578	33
H(9A)	1876	134	13056	37
H(11A)	452	-2073	12866	47
H(12A)	909	-1735	11388	40
H(14A)	278	-1870	9404	31
H(15A)	-319	-2746	8574	35
H(17A)	1632	-1518	6499	40
H(18A)	2201	-617	7325	35
H(20A)	1597	2212	6437	36
H(21A)	1407	2882	4988	40
H(23A)	2447	5241	5243	40
H(24A)	2591	4595	6703	36
H(26A)	1322	5140	8826	34
H(27A)	1073	6195	9765	36
H(29A)	2409	3851	11639	31
H(30A)	2604	2797	10710	29