

Supporting Information
(Experimental Section, Figures S1 – S18)

**Oxidative Cyclization of 1,5-Dienes with
Hydrogen Peroxide Catalyzed by an Osmium(III)
Complex: Synthesis of *cis*-Tetrahydrofurans**

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■ EXPERIMENTAL SECTION

Complexes **1**, **2**, and $[\text{Os}^{\text{III}}(\text{OTf})(\text{bpy})_2]\text{OTf}$ were synthesized by following the literature.¹⁻³

Synthesis and Characterization of Complex

$[\text{Os}^{\text{III}}(\text{OH})(\text{H}_2\text{O})(\text{bpy})_2](\text{OTf})_2$ (**9**). $[\text{Os}^{\text{III}}(\text{OTf})(\text{bpy})_2]\text{OTf}$ (10 mg, 11 μmol) was dissolved in non-dehydrate acetone and recrystallized three times (acetone/diethyl ether). Then, red crystals precipitated. The crystals were collected by filtration, washed with diethyl ether, and dried in vacuo. (3.1 mg, 34 %).

X-ray Crystallography. A single crystal of **9** was obtained by vapor diffusion of diethyl ether into an acetone solution of **9**. The single crystal was mounted on a loop, and all measurements were made on a Rigaku R-Axis RAPID diffractometer using multi-layer mirror monochromated Mo-K α radiation at -165°C . The structures were solved by direct methods (SIR2011) and refined anisotropically by full-matrix least squares on F^2 .⁴ The hydrogen atoms were attached at idealized positions on carbon atoms and were not refined. All structures in the final stages of refinement showed no movement in the atom positions. The calculations were performed using the Single-Crystal Structure Analysis Software, version 3.8.⁵

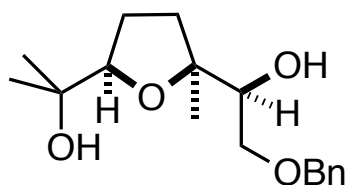
Catalytic Oxidative Cyclization. A solution of **1** (4.0 mg, 5 μmol) in H_2O -*t*-BuOH (1:1 v/v, 5 mL) was degassed by bubbling an Ar gas for 30 min. Then, a 1,5-diene (500 μmol) was added to the solution and 2 equivalents of H_2O_2 (105.2 μL , 1000 μmol) was slowly introduced into the solution through a septum cap by using a syringe pump over the reaction time. After the catalytic reaction, the organic products were extracted with 15 mL portion of ethyl acetate three times, and the combined organic layer was concentrated by a rotary evaporator. The products were identified by ^1H -NMR and NOESY spectra. The yields of products were determined from the ^1H -NMR spectra, where integral ratios of the protons were compared with the integration ratio of the protons (Cl-CH-) of 1,1,2,2-tetrachloroethane as an internal standard (500 μmol). The catalytic experiments were performed at least three times per one substrate and the averaged yields have been reported. The NMR data are given in the Supporting Information (Figures S1 – S17).

Synthesis of 3b. A solution of **1** (4.0 mg, 5 μmol) in H_2O -*t*-BuOH (1:1 v/v, 5 mL) was degassed by bubbling an Ar gas for 30 min. Then, **3a** (122.2 mg, 500 μmol) was added to the solution and 2 equivalents of H_2O_2 (105.2 μL , 1000 μmol) was slowly introduced into the solution through a septum cap by using a syringe pump over the reaction time. After 5 hours stirring, the organic products were extracted with 15 mL portion of ethyl acetate three times, and the combined organic layer was concentrated by a rotary evaporator to give a pale yellow oil. **3b** was purified by a column chromatography (Merk, silica gel 60) using a hexane-acetone (4 : 1)

mixed solvent as an eluent ($R_f = 0.11$). The solvent containing **3b** was removed by a rotary evaporator to give a colorless oil. Yield, 63.3 mg (215 μmol , 43%). The ^1H and ^{13}C NMR spectra are given in Figures S1 and S2.

Direct reaction of 2 with 3. A H_2O - t -BuOH mixed solvent (1.5 mL-3.5 mL) containing **2** (50 mmol) and **3** (500 mmol) was stirred for 5 h at 70 $^\circ\text{C}$. The organic product was extracted with 5 mL portions of diethyl ether three times. The combined organic layer was dried over Na_2SO_4 , and Na_2SO_4 was filtered off. The filtrate was removed by a rotary evaporator to give a oil. The yield of **3b** was determined to be 30% from the ^1H -NMR spectrum using 1,1,2,2-tetrachloroethane as an internal standard.

- (1) Sugimoto, H.; Kitayama, K.; Mori, S.; Itoh, S. *J. Am. Chem. Soc.* **2012**, *134*, 19270.
- (2) Sugimoto, H.; Ashikari, K.; Itoh, S. *Chem. Asian. J.* **2013**, *8*, 2154.
- (3) Taube, H, *Inorg. Synth.* **1986**, *24*, 291.
- (4) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **2012**, *45*, 357.
- (5) Crystal Structure 3.8: Crystal Structure Analysis Package, Rigaku Corporation (2000-2006). 9009 New Trails Dr. The Woodlands TX 77381 USA.

**3b**

^1H -NMR (400 MHz, CDCl_3/TMS) Δ = 7.39-7.29 (m, 5H, ArCH), 4.60 (d, J = 12.0 Hz, 2H, OCH_2Ph), 3.85 (t, J = 7.2 Hz, 1H, THF CH), 3.75 (dd, J = 3.2, 8.4 Hz, 1H, CH_2OBn), 3.67 (dd, J = 3.2, 9.7 Hz, 1H, CH_2OBn), 3.58 (t, J = 8.4, 9.2 Hz, 1H, C-CH-OH) 2.24 (m, 1H, $\text{CH}_2\text{-CH}_2$), 2.06-1.87 (m, 2H, $\text{CH}_2\text{-CH}_2$), 1.62 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.23 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.10 (s, 3H, CH_3) ppm

^{13}C -NMR (125 MHz, CDCl_3/TMS) 137.9, 142.0, 128.5, 127.8, 85.8, 83.9, 75.4, 73.5, 71.8, 71.6, 35.2, 29.3, 27.8, 26.3, 25.0, 24.4

HRMS (CI^+) calcd for $\text{C}_{17}\text{H}_{27}\text{O}_4$ $[\text{M}+\text{H}]^+$ 295.1909 found 295.1910.

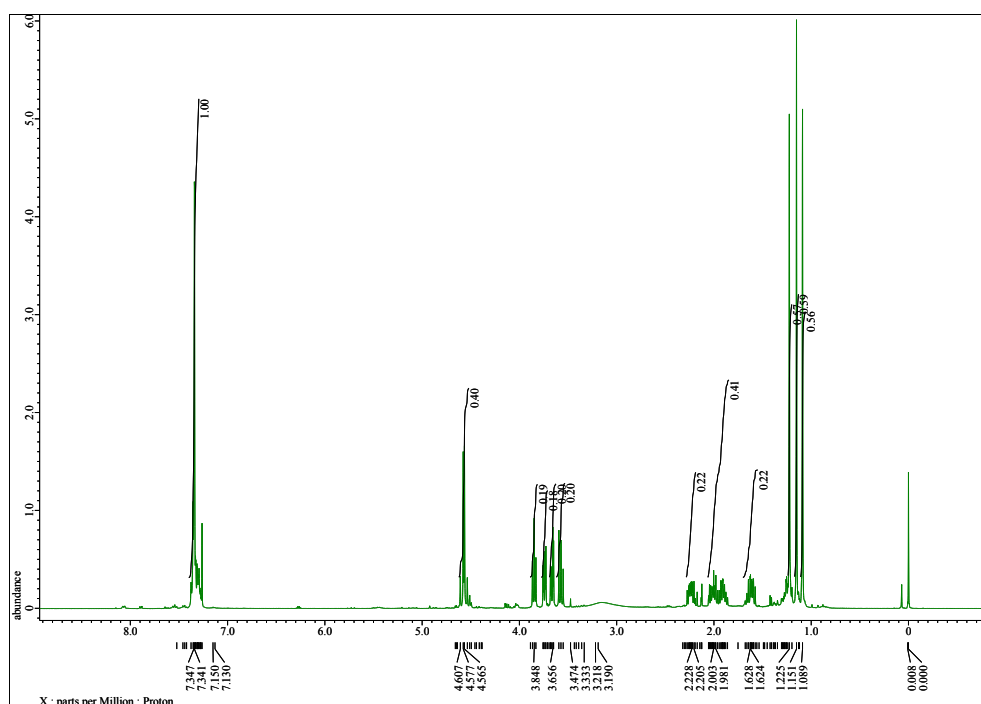


Figure S1. ^1H NMR spectrum of **3b**.

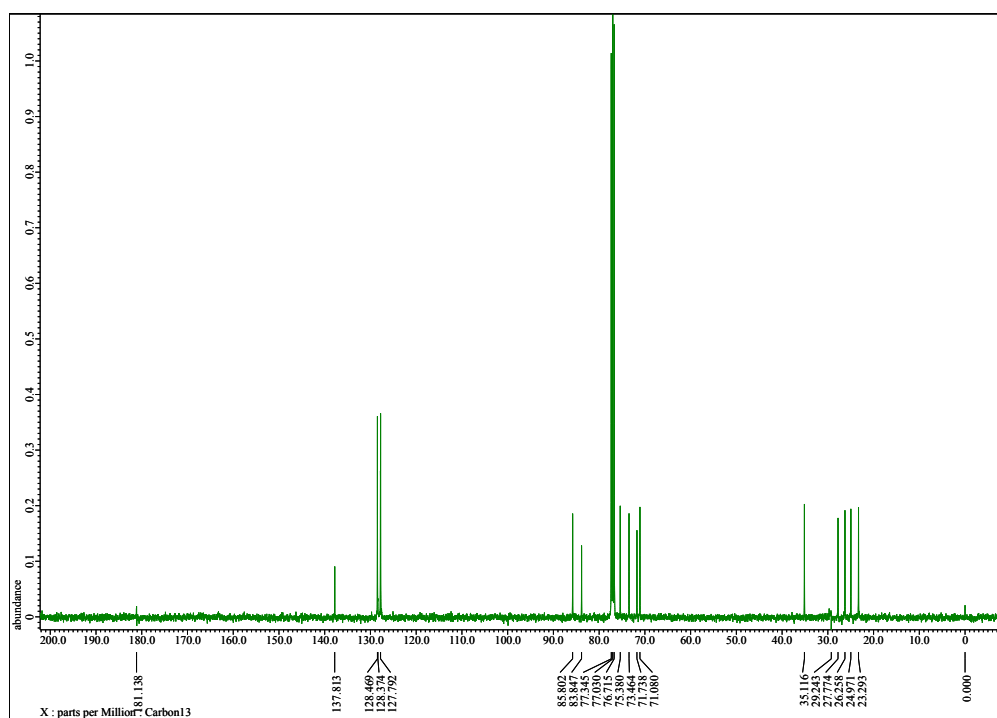


Figure S2. ^{13}C NMR spectrum of **3b**.

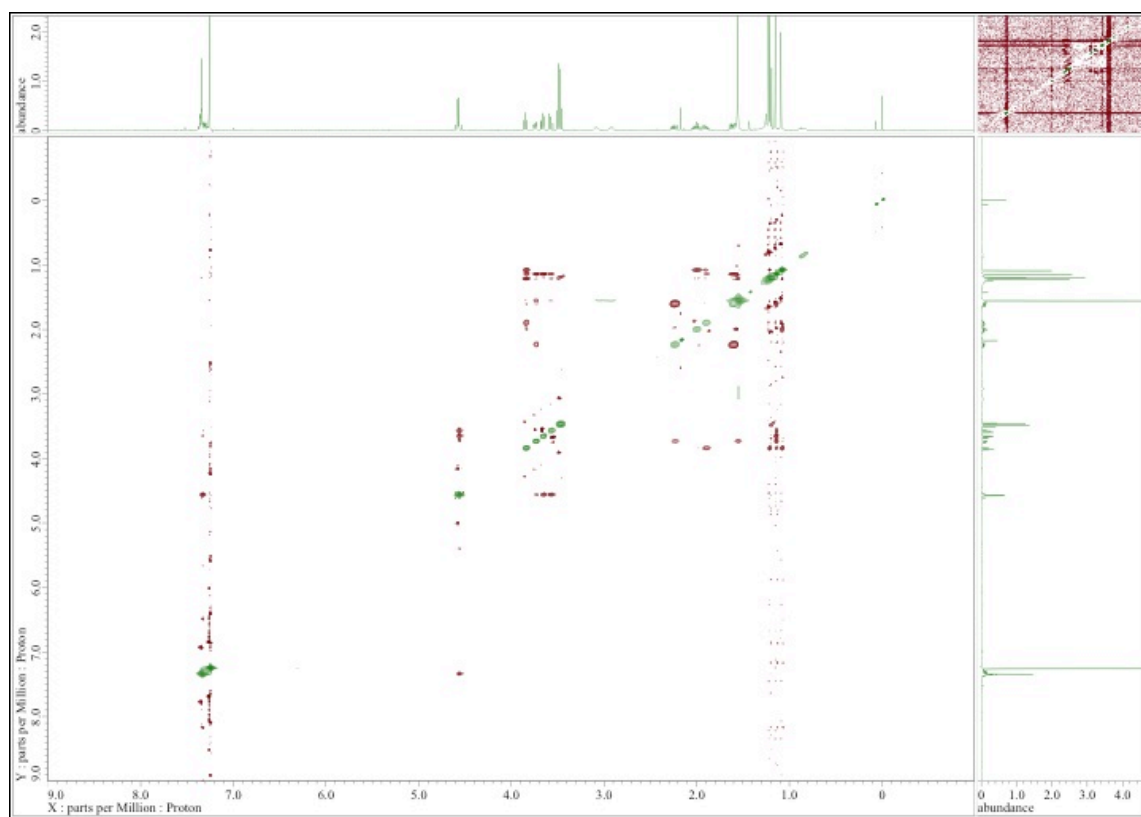
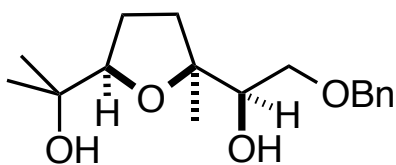


Figure S3. NOESY NMR spectrum of **3b**.

**4b**

^1H -NMR (400 MHz, CDCl_3/TMS) δ = 7.39-7.29 (m, 5H, ArCH), 4.57 (s, 2H, OCH_2Ph), 3.85 (t, J = 3.2, 8.0 1H, CHOH), 3.82 (t, J = 6.8 1H, THF CH), 3.63 (dd, J = 3.2, 10.0 1H, CH_2OBn), 3.42 (dd, J = 8.0, 10.0 1H, CH_2OBn) 2.24 (m, 1H, $\text{CH}_2\text{-CH}_2$), 2.03-1.87 (m, 2H, $\text{CH}_2\text{-CH}_2$), 1.54 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.25 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.10 (s, 3H, CH_3) ppm

^{13}C -NMR (125 MHz, CDCl_3/TMS) 137.7, 128.4, 128.3, 128.1, 84.9, 84.4, 76.7, 73.4, 71.9, 71.7, 71.2, 32.7, 27.6, 26.5, 25.0, 23.5,

HRMS (CI^+) calcd for $\text{C}_{17}\text{H}_{27}\text{O}_4$ $[\text{M}+\text{H}]^+$ 295.1909 found 295.1908.

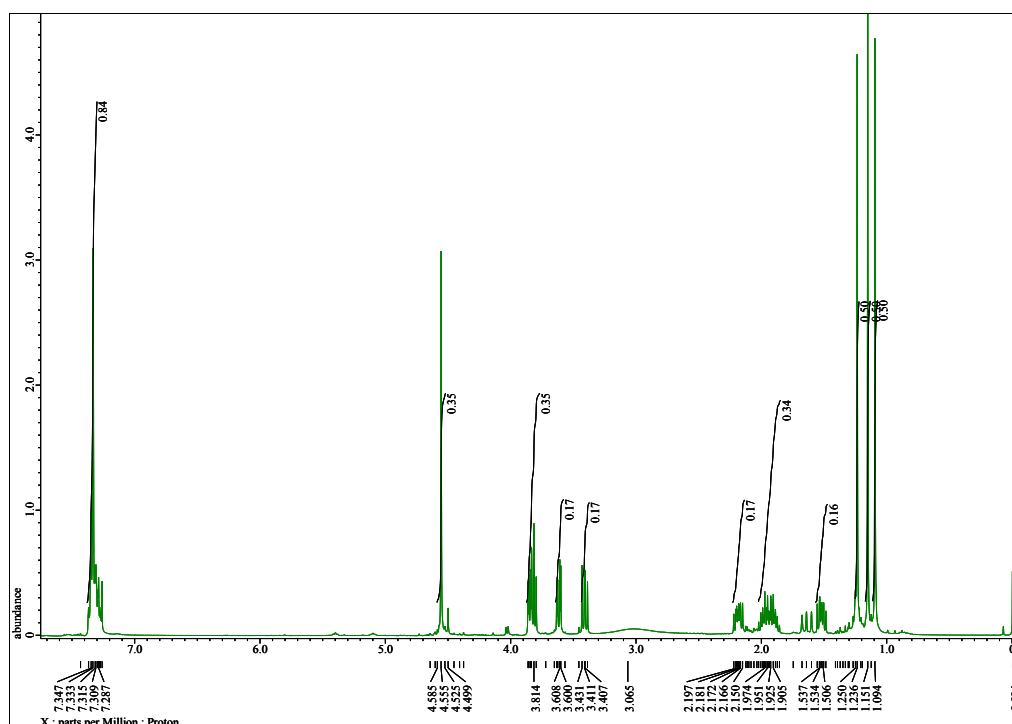


Figure S4. ^1H NMR spectrum of **4b**.

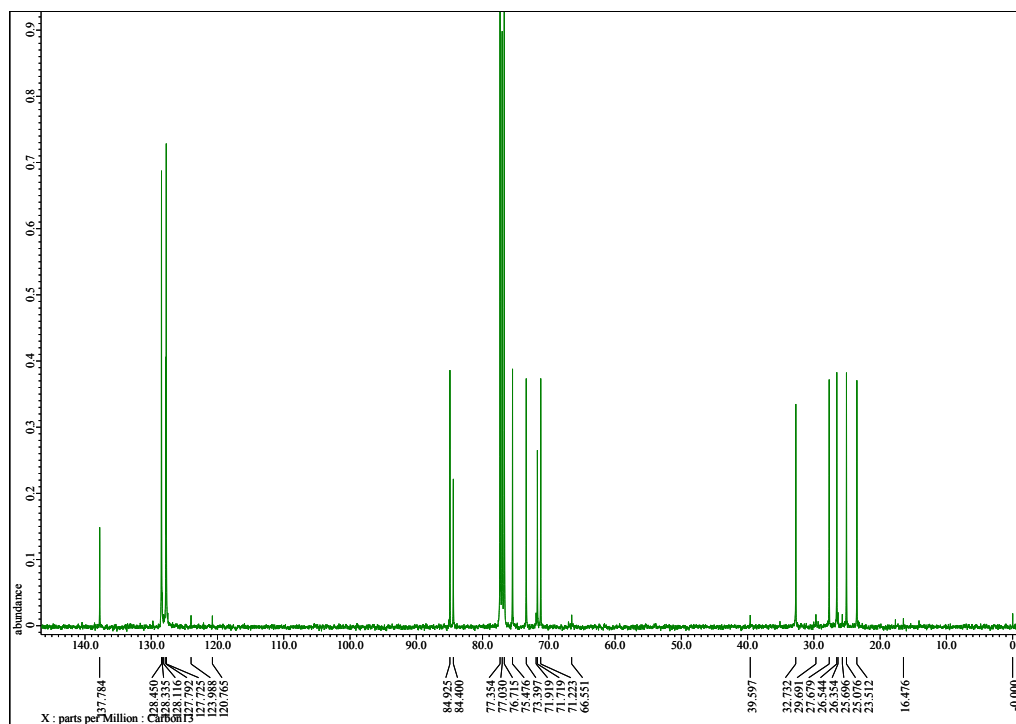
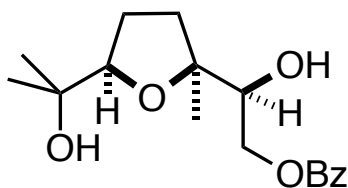


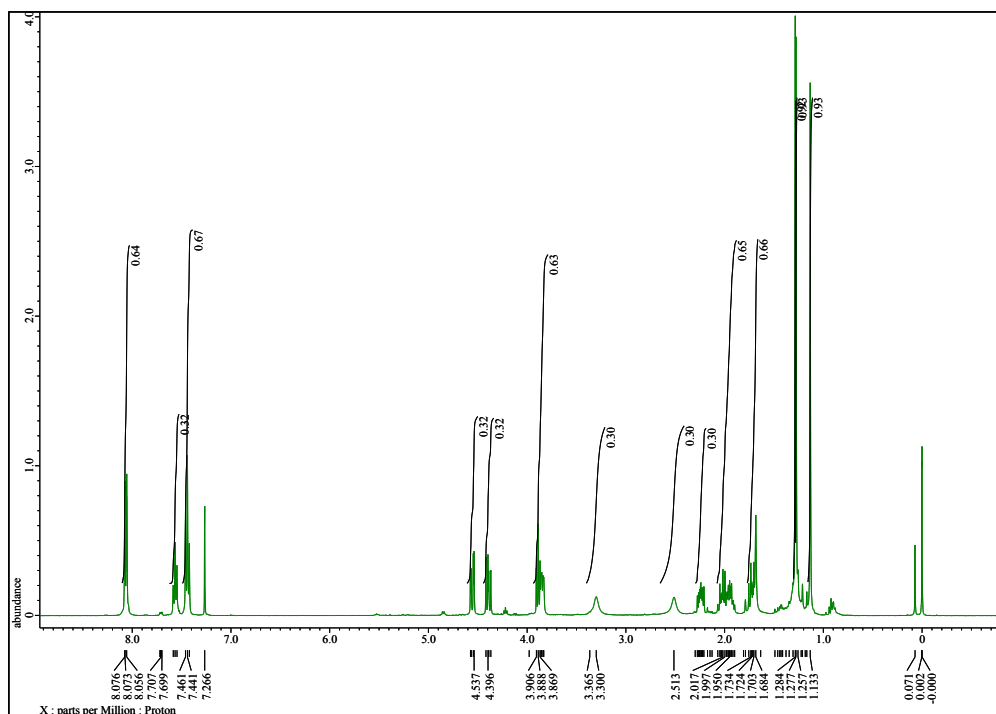
Figure S5. ^{13}C NMR spectrum of **4b**.

**5b**

^1H -NMR (400 MHz, CDCl_3/TMS) δ = 8.07 (d, J = 7.79 Hz, 1H, ArCH), 7.56 (t, J = 7.33 Hz, 2H, ArCH), 7.44 (t, J = 7.79 Hz, 2H, ArCH), 4.55 (dd, J = 3.21, 11.45 Hz, 1H, CH_2OBz), 4.39 (dd, J = 8.24, 11.5 Hz, 1H, CH_2OBz), 3.84 (t, J = 7.33, 1H, THF CH), 3.82 (dd, J = 2.29, 7.79 Hz, 1H, CHOH), 2.29-2.2 (m, 1H, $\text{CH}_2\text{-CH}_2$), 2.07-1.98 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.98-1.89 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.78-1.70 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.28 (s, 3H, CH_3), 1.13 (s, 3H, CH_3) ppm

^{13}C -NMR (125 MHz, CDCl_3/TMS) 166.9, 133.1, 129.9, 129.7, 128.3, 85.6, 84.2, 75.4, 71.8, 66.5, 35.6, 27.6, 26.5, 25.2, 23.0

HRMS (CI^+) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5$ $[\text{M}+\text{H}]^+$ 309.1701 found 309.1701.

**Figure S6.** ^1H NMR spectrum of **5b**.

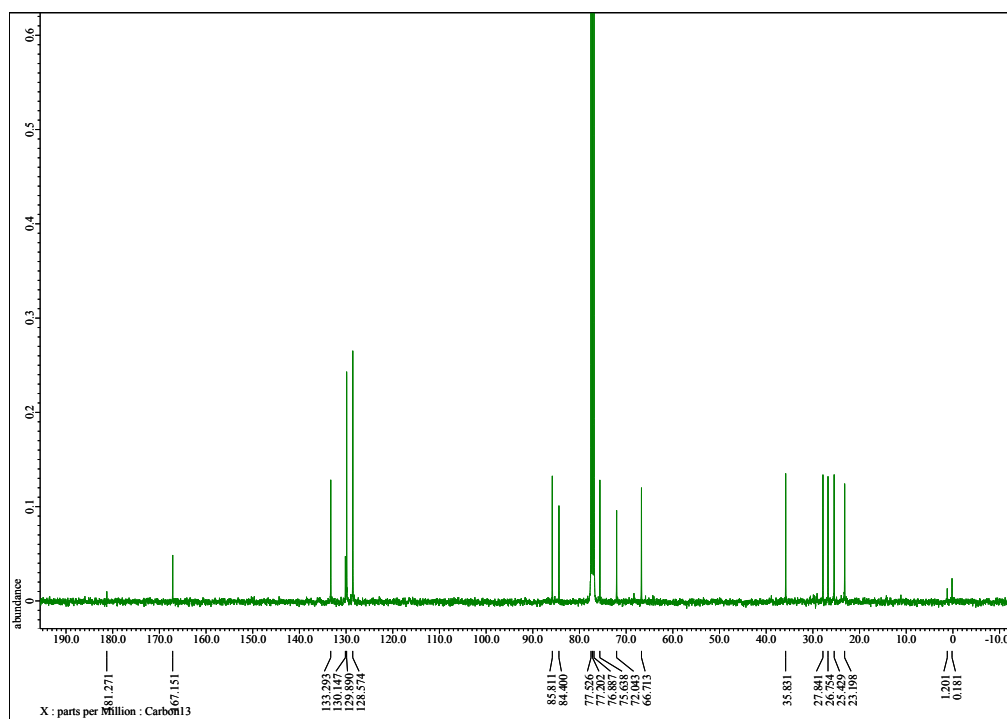
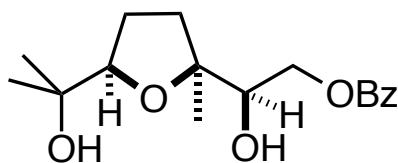


Figure S7. ^{13}C NMR spectrum of **5b**.

**6b**

^1H -NMR (400 MHz, CDCl_3/TMS) δ = 8.07 (d, J = 7.73 Hz, 1H, ArCH), 7.57 (t, J = 7.33 Hz, 2H, ArCH), 7.45 (t, J = 7.79 Hz, 2H, ArCH), 4.65 (dd, J = 2.75, 11.91 Hz, 1H, CH_2OBz), 4.23 (dd, J = 7.79, 11.5 Hz, 1H, CH_2OBz), 3.96 (dd, J = 2.29, 7.79 Hz, 1H, THF CH), 3.86 (t, J = 7.73 Hz, 1H, CHOH), 2.31-2.24 (m, 1H, $\text{CH}_2\text{-CH}_2$), 2.07-1.97 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.96-1.88 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.65-1.58 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.27 (s, 3H, CH_3), 1.13 (s, 3H, CH_3) ppm

^{13}C -NMR (125 MHz, CDCl_3/TMS) 167.0, 133.2, 129.7, 128.4, 85.1, 84.4, 75.2, 71.6, 66.7, 33.1, 29.7, 27.7, 26.5, 25.3, 23.1

HRMS (CI^+) calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5$ $[\text{M}+\text{H}]^+$ 309.1701 found 309.1700.

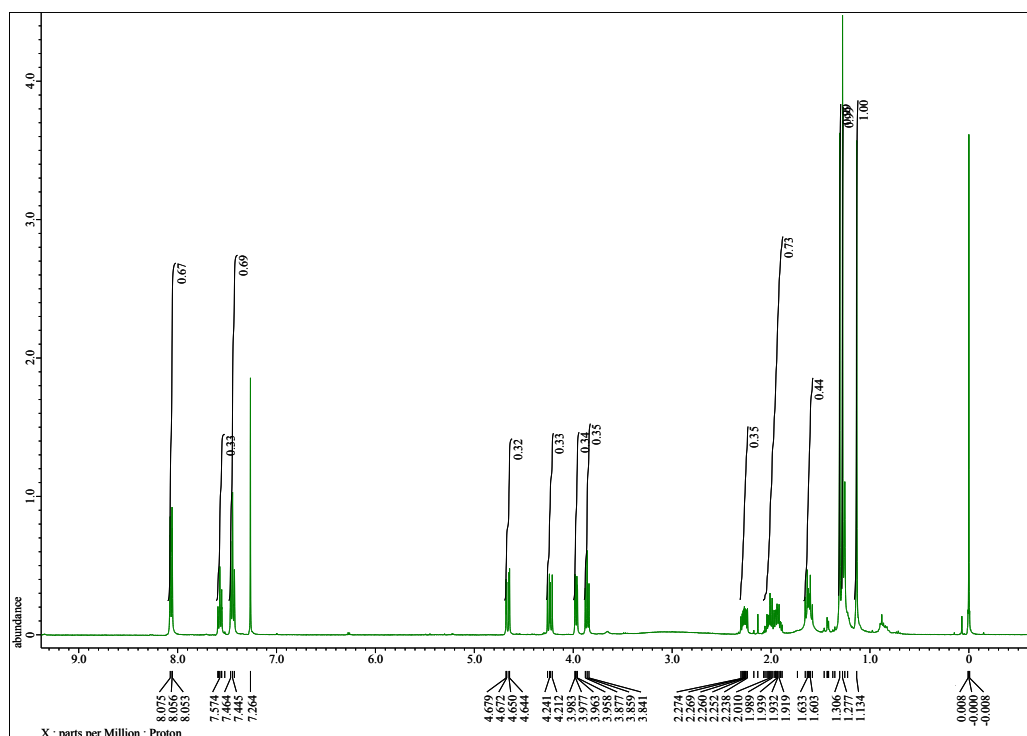


Figure S8. ^1H NMR spectrum of **6b**.

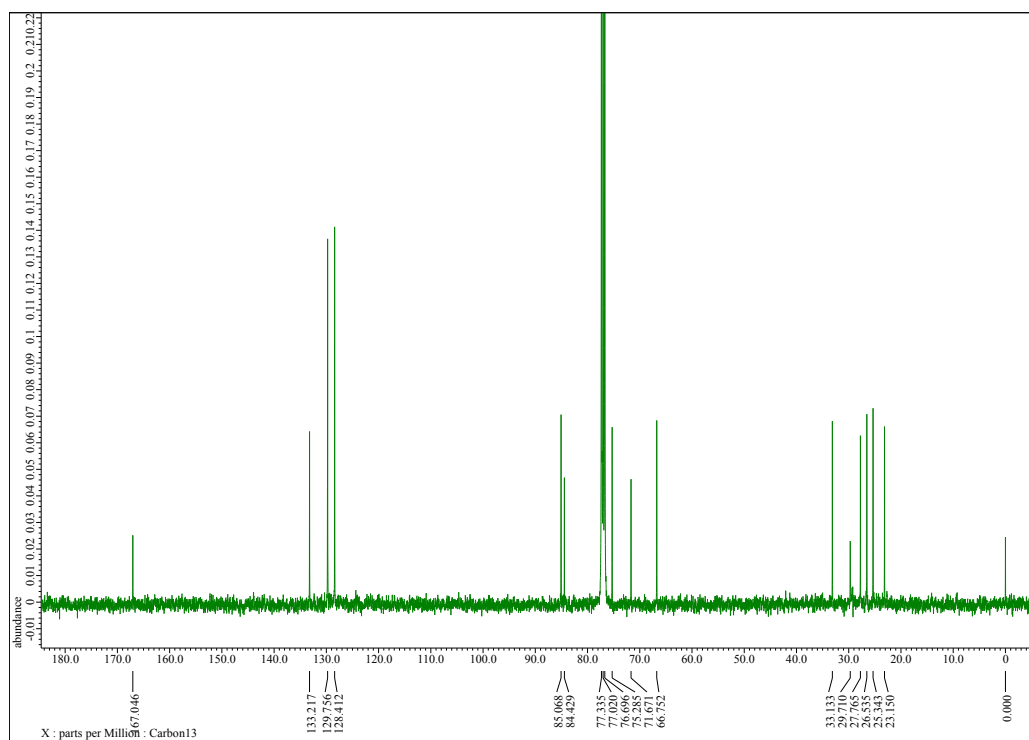
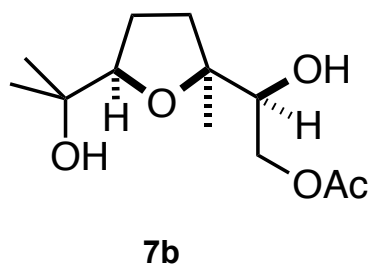


Figure S9. ¹³C NMR spectrum of **6b**.



^1H -NMR (400 MHz, CDCl_3/TMS) δ 4.31 (dd, $J = 2.75, 11.5$ Hz, 1H, CH_2OAc), 4.11 (dd, $J = 8.70, 11.45$ Hz, 1H, CH_2OAc), 3.87 (t, $J = 7.33$ Hz, 1H, THF CH), 3.70 (dd, $J = 2.75, 8.70$ Hz, 1H, CHOH), 2.21-2.15 (m, 1H, $\text{CH}_2\text{-CH}_2$), 2.1 (s, 3H, OCOCH_3), 2.01-1.87 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.72-1.63 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.50-1.37 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.27 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.12 (s, 3H, CH_3) ppm

^{13}C -NMR (125 MHz, CDCl_3/TMS) 171.3, 85.6, 84.0, 76.7, 71.8, 66.0, 35.5, 27.7, 26.5, 25.2, 22.8, 21.0

HRMS (CI^+) calcd for $\text{C}_{12}\text{H}_{23}\text{O}_5$ $[\text{M}+\text{H}]^+$ 247.1545 found 247.1543

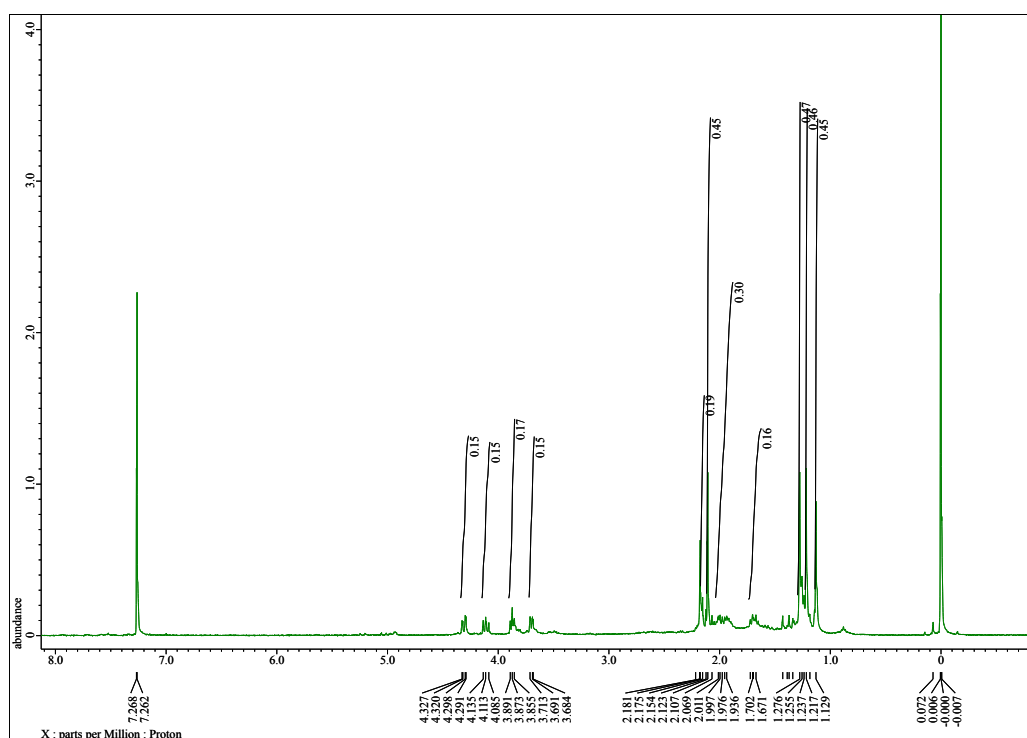


Figure S10. ^1H NMR spectrum of **7b**.

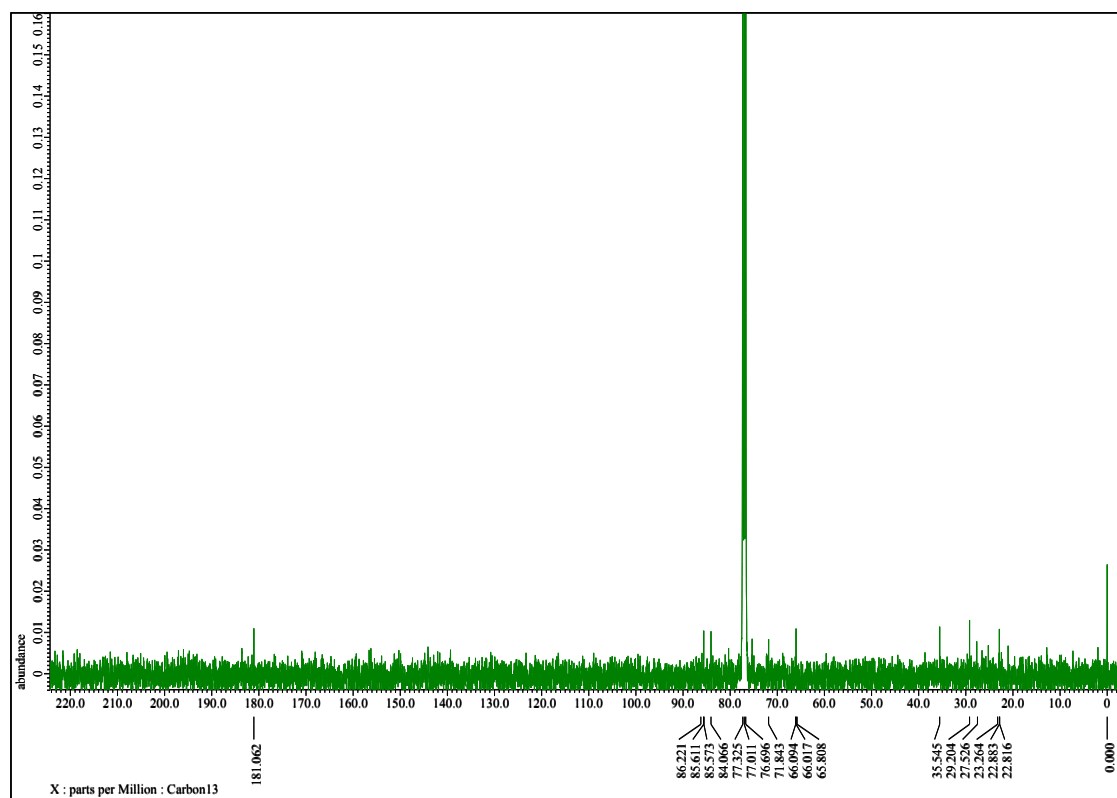
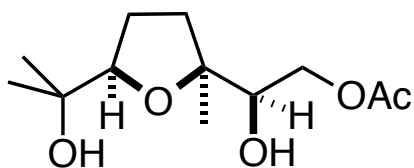


Figure S11. ¹³C NMR spectrum of **7b**.

**8b**

^1H -NMR (400 MHz, CDCl_3/TMS) δ = 4.39 (dd, J = 2.29, 11.45 Hz, 1H, CH_2OAc), 3.96 (dd, J = 8.24, 11.45 Hz, 1H, CH_2OAc), 3.83 (m, 2H, THF H, CH-OH), 2.23-2.16 (m, 1H, $\text{CH}_2\text{-CH}_2$), 2.11 (s, 3H, OCOCH_3), 2.02-1.85 (m, 2H, $\text{CH}_2\text{-CH}_2$), 1.61-1.54 (m, 1H, $\text{CH}_2\text{-CH}_2$), 1.27 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.12 (s, 3H, CH_3) ppm

^{13}C -NMR (125 MHz, CDCl_3/TMS) 171.8, 85.2, 84.5, 75.4, 71.9, 66.5, 33.2, 28.0, 26.8, 25.6, 23.4, 21.2

HRMS (CI^+) calcd for $\text{C}_{12}\text{H}_{23}\text{O}_5$ $[\text{M}+\text{H}]^+$ 247.1545 found 247.1543

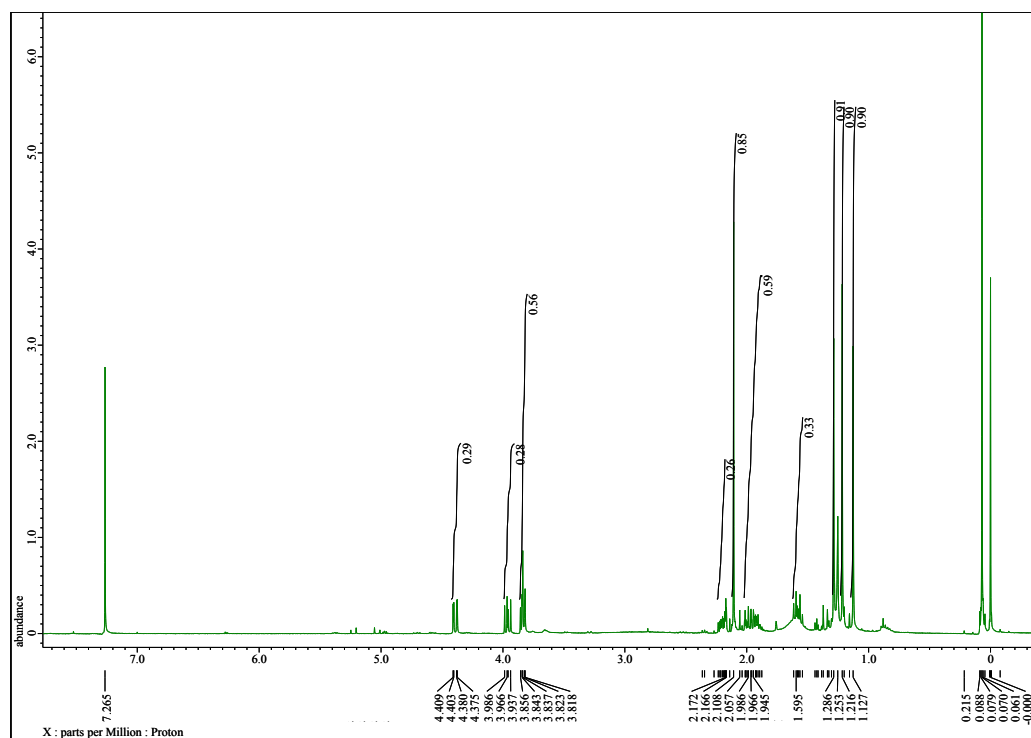


Figure S12. ^1H NMR spectrum of **8b**.

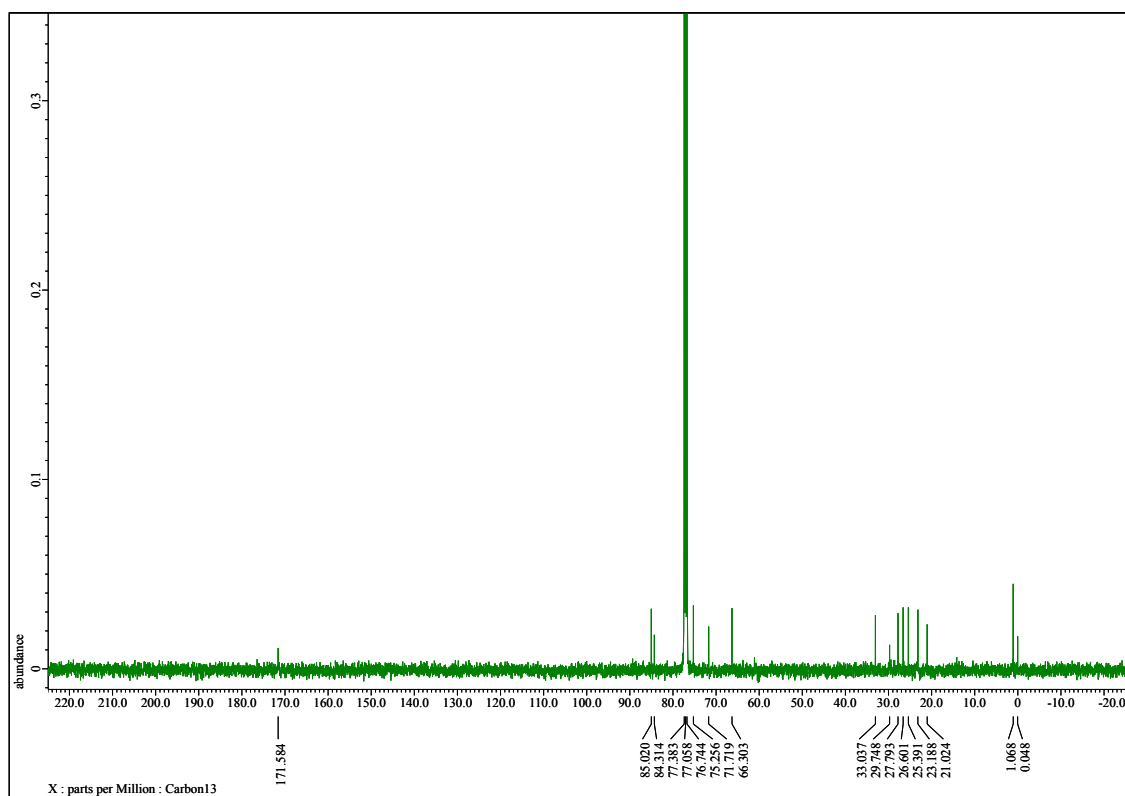
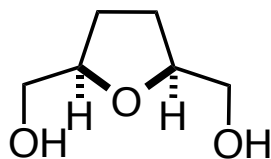


Figure S13. ¹³C NMR spectrum of **8b**.

**9b**

¹H-NMR (400 MHz, CDCl₃/TMS) ¹ = 4.14-4.07 (m, 2H, THF *H*), 3.80 (dd, *J* = 2.75, 11.9 Hz, 2H, OHCH₂C), 3.45 (dd, *J* = 5.04, 11.45 Hz, 2H, OHCH₂C), 2.64 (s, 2H, OH), 1.97-1.92 (m, 1H, CH₂-CH₂), 1.85-1.78 (m, 1H, CH₂-CH₂) ppm

¹³C-NMR (125 MHz, CDCl₃/TMS) 80.2, 64.9, 27.3

HRMS (CI⁺) calcd for C₆H₁₃O₃ [M+H]⁺ 133.0864 found 133.0864.

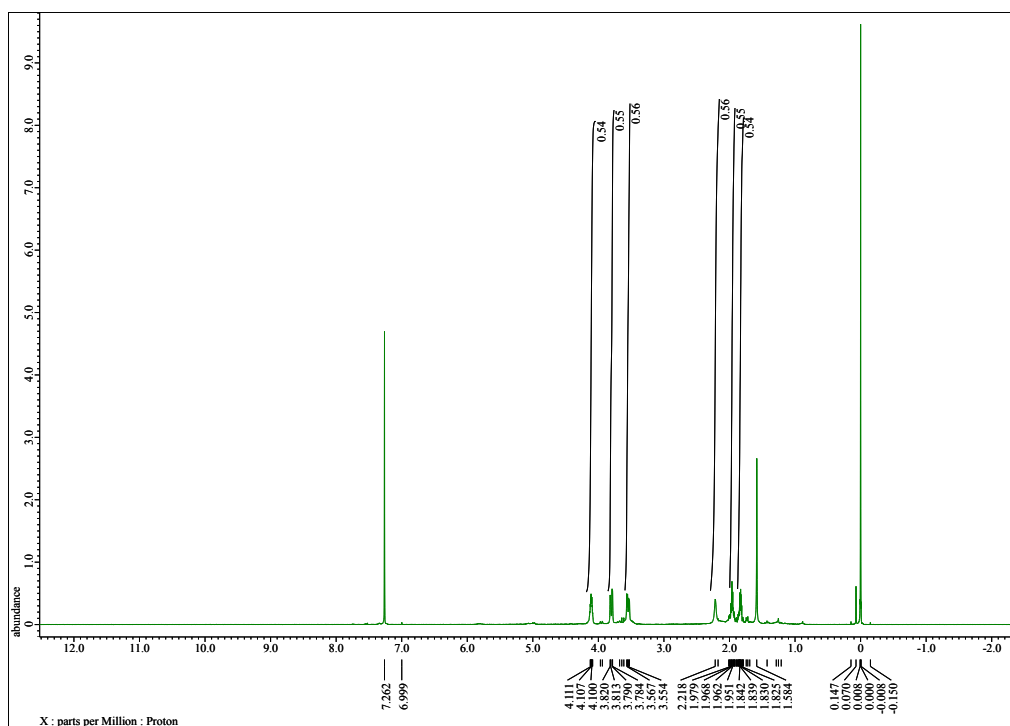


Figure S14. ¹H NMR spectrum of **9b**.

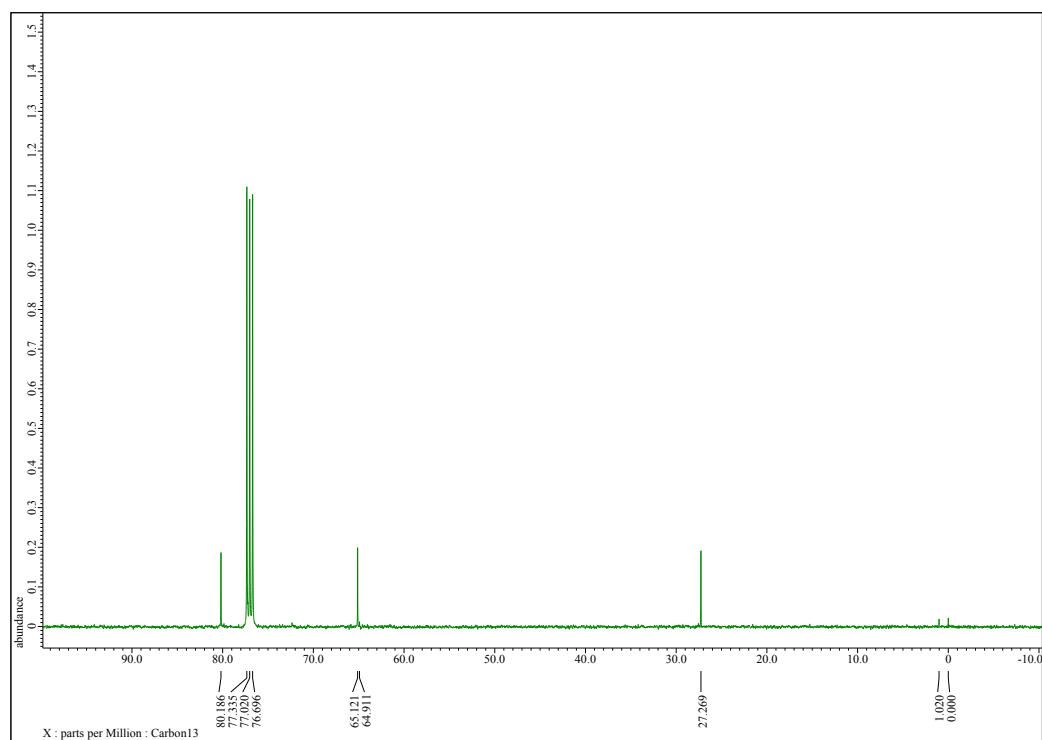
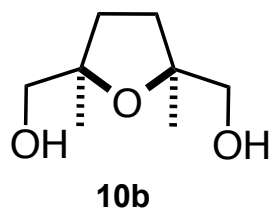


Figure S15. ^{13}C NMR spectrum of **9b**.



^1H -NMR (400 MHz, CDCl_3/TMS) δ = 3.58 (d, J = 11.0 Hz, OHCH_2C), 3.48 (d, J = 11.0 Hz, OHCH_2C), 2.21 (q, J = 6.41, 12.82 Hz, 2H, $\text{CH}_2\text{-CH}_2$), 1.78 (q, J = 6.87, 12.36 Hz, 2H, $\text{CH}_2\text{-CH}_2$) 1.21 (s, 6H, THF CH_3) ppm

^{13}C -NMR (125 MHz, CDCl_3/TMS) δ = 84.3, 69.3, 34.1, 25.4

HRMS (CI^+) calcd for $\text{C}_8\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$ 161.1777 found 161.11

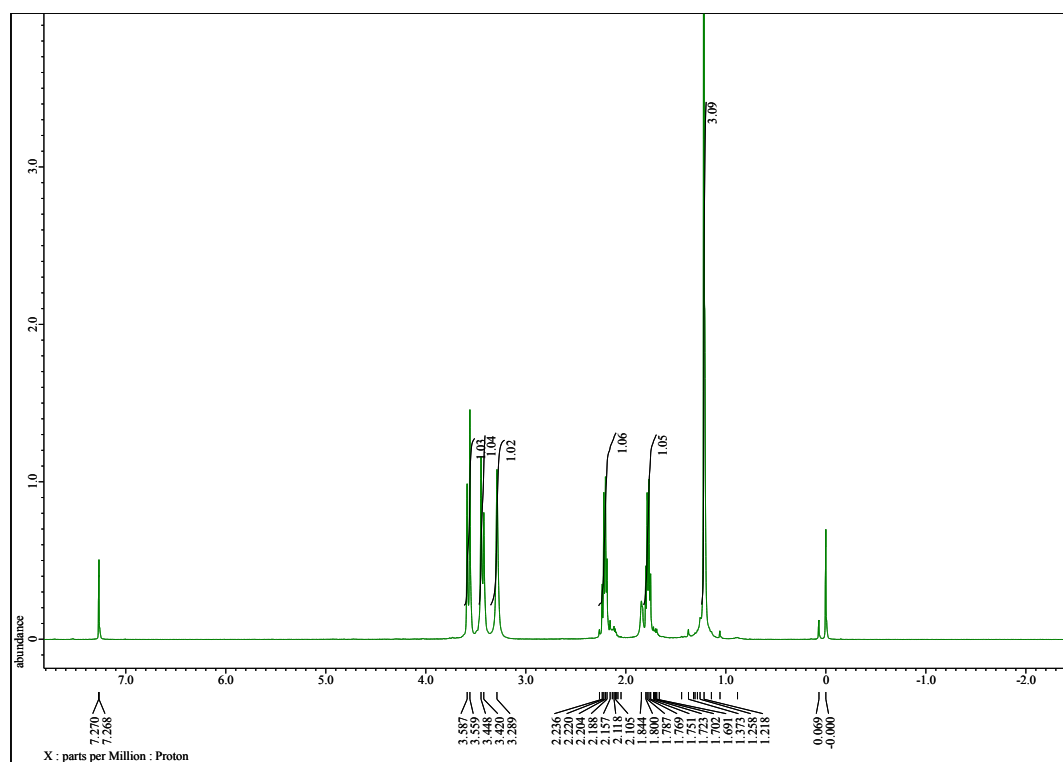


Figure S16. ^1H NMR spectrum of **10b**.

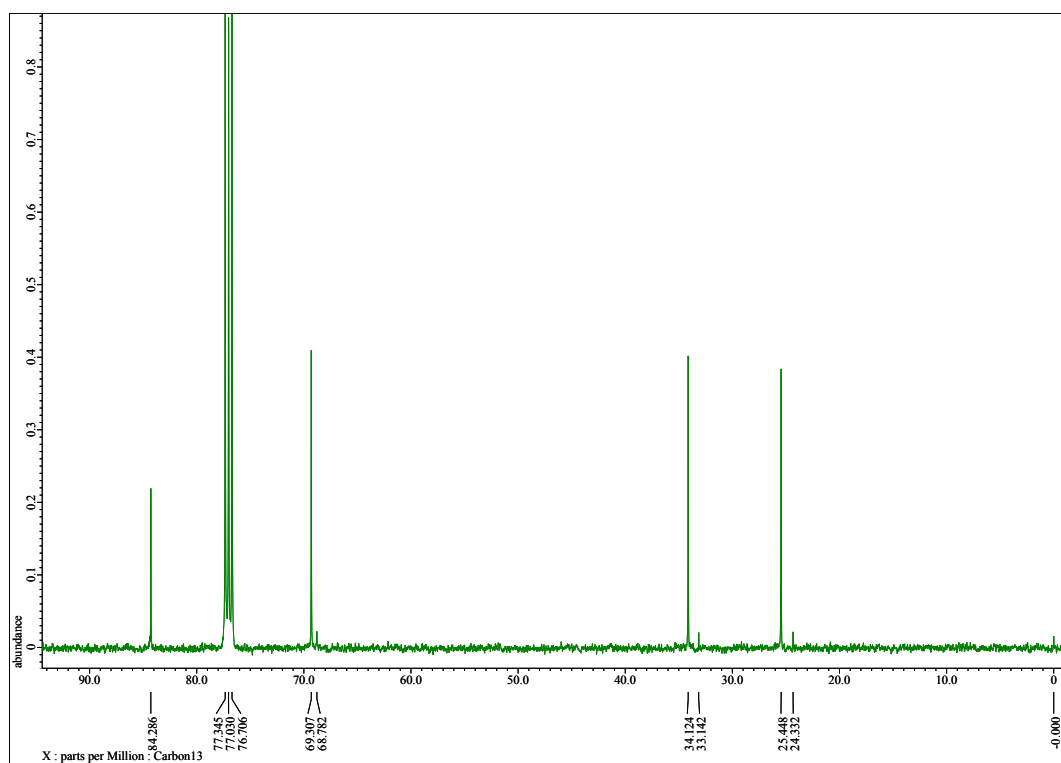


Figure S17. ¹³C NMR spectrum of **10b**.

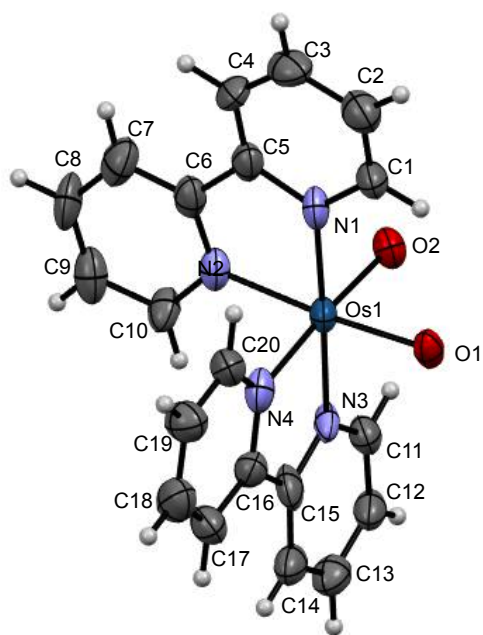


Figure S18. Crystal structure of the cationic part of [Os^{III}(OH)(H₂O)(bpy)₂](CF₃SO₃)₂ (**9**). The triflate anions are omitted for clarity.