Supporting Information

Efficient Piancatelli rearrangements of HMF derivatives under microwave activation or subcritical water conditions to produce functionalized hydroxylated cyclopentenones

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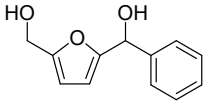
I. General information

All non-aqueous reactions were run under an inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds. Anhydrous THF was obtained by filtration through drying columns. All reagent-grade chemicals and other solvents were obtained from commercial suppliers and were used as received. Reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel (60 F_{254}) plates (Merck) and visualized using UV light (254 and 312 nm) and developed by heating the plate after spraying with an aqueous solution of sulfomolybdic acid. When necessary, the crude was filtered on Supelco celite 545 (particle size 0.02-0.1 mm). Flash column chromatography was conducted on Merck silica gel 60 (40-63 µm) or on Combiflash Companion using Interchim silica columns. Proton magnetic resonance ^{1}H NMR spectra (500.1 MHz) and carbon magnetic resonance ^{13}C NMR spectra (125.8 MHz) were recorded on Bruker Avance spectrometer. Analyses were acquired in acetone-d_6 (δ_H 2.05 ppm; δ_C 29.84 and 206.66 ppm). The following abbreviations are used for the proton spectra multiplicities : s: singulet, d: doublet, t: triplet, q: quadruplet, m: multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Infrared spectra (IR) were obtained on a Perkin-Elmer Spectrum 100 model instrument and are reported in reciprocal centimeters (cm^{-1}). High-resolution mass spectra (HRMS) were recorded with a Micromass LCT Premier XE instrument (Waters) and were determined by electrospray ionization (ESI) coupled with a time of flight analyser (TOF).

II. Addition of arylboronic acids to HMF

Table 1, entry 3, named later as Conditions A.

5-(hydroxymethyl)furan-2-yl)(phenyl)methanol 3a.



3a

A solution of rhodium(II) heptafluorobutyrate dimer $[Rh(pfb)_2]_2$ (32 mg, 3 mol%) in *t*-amylalcohol (5 mL) was stirred at room temperature for 5 minutes. Then, benzeneboronic acid (245 mg, 2.0 mmol, 2.0 eq.), 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride (13 mg, 3 mol%), *t*-BuOK (224 mg, 2.0 mmol, 2.0 eq.) and 5-hydroxymethylfurfural (126 mg, 1.0 mmol, 1.0 eq.) were added respectively. The mixture was stirred for 1.5 h at 55 °C. After filtration on celite and concentration under vaccum, the residue was purified by flash chromatography using EtOAc/*n*-heptane (10:90 to 70:30) to afford compound **3a** (54 mg, 26% yield) which was obtained as a pale white powder with an Rf = 0.25 (EtOAc/*n*-heptane 1:1).

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.5, 15.1 Hz, 2H), 7.27 (t, *J* = 7.4, 14.8 Hz, 1H), 6.18 (d, *J* = 3.1 Hz, 1H), 6.05 (d, *J* = 2.9 Hz, 1H), 5.77 (d, *J* = 4.3 Hz, 1H), 5.06 (d, *J* = 4.7 Hz, 1H), 4.45 (d, *J* = 4.7 Hz, 2H), 4.32 (t, *J* = 5.2, 10.5 Hz, 2H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ 157.8 (C), 155.9 (C), 143.4 (C), 128.9 (2xCH), 128.2 (C), 127.6 (2xCH), 108.3 (CH), 108.1 (CH), 70.3 (CH), 57.4 (CH_2).

IR (neat) ν_{max}: 3327, 2927, 2869, 1662, 1557, 1494, 1452, 1411, 1242, 1188, 1011,791, 744, 691 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{12}H_{11}O_3$ $[M-H]^-$ 203.0714, found 203.0702.

Table 1, entry 4, named later as Conditions B.

A solution of rhodium(II) acetate dimer $[Rh(OAc)_2]_2$ (13 mg, 3 mol%) in a mixture of DME/water (5:1) (6 mL) was stirred at room temperature for 5 minutes. Then, benzeneboronic acid (245 mg, 2.0 mmol, 2.0 eq.), 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride (13 mg, 3 mol%), *t*-BuOK (224 mg, 2.0 mmol, 2.0 eq.) and 5-hydroxymethylfurfural (126 mg, 1.0 mmol, 1.0 eq.) were added respectively. The mixture was stirred for 0.5 h at 90 °C. After filtration on celite and concentration under vaccum, the residue was purified by flash chromatography using EtOAc/*n*-heptane (EtOAc/*n*-heptane 70:30) to afford the catalyst dirhodium tetraacetate **$[Rh_2(OAc)_4](IPr)$** (18 mg, 70% yield) as purple needles suitable for X-ray structure analysis with an Rf = 0.8 (EtOAc/*n*-heptane 1:1) and the compound **3a** (200 mg, 98% yield) as a pale white powder with an Rf = 0.25 (EtOAc/*n*-heptane 1:1).

$[Rh_2(OAc)_4](IPr)$

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.51 (s, 2H), 7.37 (t, *J* = 7, 15 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 4H), 3.29 (m, 4H), 1.26 (br, 12H), 1.23 (d, *J* = 7 Hz, 12H), 1.05 (d, *J* = 7 Hz, 12H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ188.9, 146.6, 139.3, 129.6, 126.0, 123.7, 28.9, 25.6, 23.4, 22.9.

IR (neat) ν_{max}: 2966, 2869, 1702, 1590, 1427, 1400, 1152, 939, 805, 761, 688 cm^{-1}.

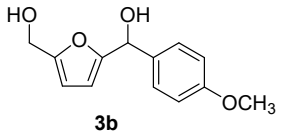
HRMS (ESI): *m/z* calcd. for $C_{37}H_{54}N_2NaO_8Rh_2$ $[M+Na]^+$ 883.1882, found 883.1718.

Table 1, entry 6, named later as Conditions C.

To a mixture of palladium chloride $PdCl_2$ (18 mg, 5 mol%), tris(1-naphthyl)phosphine (42 mg, 5 mol%), benzeneboronic acid (245 mg, 2.0 mmol, 2.0 eq.), K_2CO_3 (414 mg, 3.0 mmol, 3.0 eq.) and 5-hydroxymethylfurfural (126 mg, 1.0 mmol, 1.0 eq.) was added anhydrous THF (10 mL). The mixture was stirred for 16 h at 65 °C. After filtration on celite and concentration under vaccum, the residue was purified by flash chromatography using EtOAc/*n*-heptane (20:80 to 80:20) to afford compound **3a** (147 mg, 72% yield) which was obtained as a pale white powder with an Rf = 0.25 (EtOAc/*n*-heptane 1:1).

Table 2, entry 1, Conditions A.

(5-(Hydroxymethyl)furan-2-yl)(4-methoxyphenyl)methanol 3b.



3b

Following the **Conditions A**, the reaction was performed on HMF (250 mg, 2.0 mmol) and 4-methoxy-phenylboronic acid (602 mg, 4.0 mmol) to produce compound **3b** (89 mg, 19% yield) which was obtained as a pale yellow oil with an Rf = 0.4 (EtOAc/*n*-heptane 1:1).

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.36 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.16 (d, *J* = 3.1 Hz, 1H), 6.02 (d, *J* = 3.1 Hz, 1H), 5.70 (d, *J* = 4.9 Hz, 1H), 4.81 (d, *J* = 4.9 Hz, 1H), 4.45 (d, *J* = 5.9 Hz, 2H), 4.16 (t, *J* = 5.9 Hz, 1H), 3.78 (s, 3H)

^{13}C NMR (125.8 MHz, acetone-d_6) δ 160.1 (C), 158.2 (C), 155.8 (C), 135.6 (C), 128.8 (2xCH), 114.3 (2xCH), 108.2 (CH), 107.7 (CH), 70.0 (CH), 57.4 (CH_2), 55.5 (CH_3).

IR (neat) ν_{max}: 3413, 2932, 2326, 1610, 1512, 1304, 1249, 1174, 1034, 797 cm^{-1}.

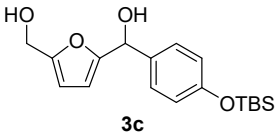
HRMS (ESI): *m/z* calcd. for $C_{13}H_{13}O_4$ $[M-H]^-$ 233.0819, found 233.0808.

Table 2, entry 2, Conditions B.

Following the **Conditions B**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-methoxy-phenylboronic acid (303 mg, 2.0 mmol) to produce compound **3b** (176 mg, 55% yield).

Table 2, entry 4, Conditions A.

(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)(5-(hydroxymethyl)furan-2-yl)methanol 3c.



3c

Following the **Conditions A**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-(*tert*-butyldimethylsiloxy)phenylboronic acid (504 mg, 2.0 mmol) to produce compound **3c** (184 mg, 55% yield) which was obtained as a pale yellow oil with an Rf = 0.6 (EtOAc/*n*-heptane 7:3).

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.33 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.15 (d, *J* = 3.4 Hz, 1H), 6.02 (d, *J* = 3.2 Hz, 1H), 5.69 (d, *J* = 4.5 Hz, 1H), 4.84 (d, *J* = 5.3 Hz, 1H), 4.45 (d, *J* = 5.7 Hz, 2H), 4.18 (t, *J* = 6.1, 12.3 Hz, 1H), 0.99 (s, 9H), 0.21 (s, 6H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ 158.88 (C), 156.65 (C), 137.30 (C), 129.64 (CH_2), 121.19 (CH_2), 108.99 (CH), 108.61 (CH), 70.79 (CH), 58.20 (CH_2), 26.89 (CH_3), 19.60 (C), -3.43 (CH_3).

IR (neat) ν_{max}: 3330, 2956, 2930, 2886, 2858, 1608, 1509, 1472, 1254, 1167, 1010, 915, 838, 800, 708, 665 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{25}O_3Si$ $[M-H_2O+H]^+$ 317.1567, found 317.1565.

Table 2, entry 5, Conditions B.

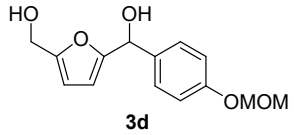
Following the **Conditions B**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-(*t*-butyldimethylsiloxy)phenylboronic acid (504 mg, 2.0 mmol) to produce compound **3c** (41 mg, 12% yield).

Table 2, entry 6, Conditions C.

Following the **Conditions C**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-(*t*-butyldimethylsiloxy)phenylboronic acid (504 mg, 2.0 mmol) to produce compound **3c** (181 mg, 54% yield).

Table 2, entry 7, Conditions A.

(5-(hydroxymethyl)furan-2-yl)(4-(methoxymethyl)phenyl)methanol 3d.



3d

Following the **Conditions A**, the reaction was performed on HMF (252 mg, 2.0 mmol) and 4-(methoxymethyl)phenylboronic acid (724 mg, 4.0 mmol) to produce compound **3d** (100 mg, 20% yield) which was obtained as a pale yellow oil with an Rf = 0.5 (EtOAc/*n*-heptane 1:1).

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.18 (d, *J* = 3.8 Hz, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 5.72 (d, *J* = 4.7 Hz, 1H), 5.19 (s, 2H), 4.89 (d, *J* = 4.8, 1H), 4.45 (d, *J* = 5.9, 2H), 4.22 (t, *J* = 6, 11.9, 1H), 3.43 (s, 3H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ 158 (C), 157.7 (C), 155.9 (C), 136.8 (C), 128.8 (CH), 116.7 (CH), 108.2 (2xCH), 107.8 (2xCH), 95.139 (CH_2), 69.99 (CH), 57.38 (CH_2), 56.04 (CH_3)

IR (neat) ν_{max}: 3434, 2901, 1679, 1609, 1509, 1312, 1235, 1151, 1077, 999, 800 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{14}H_{17}O_5$ $[M+H]^+$ 265.1071, found 265.1070.

Table 2, entry 8, Conditions B.

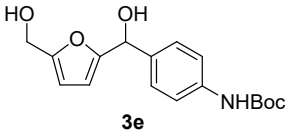
Following the **Conditions B**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-(methoxymethyl)phenylboronic acid (362 mg, 2.0 mmol) to produce compound **3d** (214 mg, 82% yield).

Table 2, entry 9, Conditions C.

Following the **Conditions C**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-(methoxymethyl)phenylboronic acid (362 mg, 2.0 mmol) to produce compound **3d** (120 mg, 45% yield).

Table 2, entry 11, Conditions B.

***tert*-butyl (4-(hydroxy(5-(hydroxymethyl)furan-2-yl)methyl)phenyl) carbamate 3e.**



3e

Following the **Conditions B**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-Boc-aminophenylboronic acid (474 mg, 2.0 mmol) to produce compound **3e** (45 mg, 14% yield) as a pale yellow oil with an Rf = 0.2 (EtOAc/*n*-heptane 1:1).

^{1}H NMR (500.1 MHz, acetone-d_6) δ δ 8.41 (s, 1H), 7.49-7.54 (m, 2H), 7.33-7.37 (m, 2H), 6.16 (d, *J* = 3.1 Hz, 1H), 6.03 (d, *J* = 3.1 Hz, 1H), 5.70 (d, *J* = 4.8 Hz, 1H), 4.87 (d, *J* = 4.9 Hz, 1H), 4.45 (d, *J* = 6.0 Hz, 2H), 4.20 (t, *J* = 6.0 Hz, 1H), 1.48 (s, 9H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ 158.0 (C), 155.8 (C), 153.7 (C), 139.8 (C), 137.3 (C), 127.9 (4xCH), 118.7 (CH), 108.1 (CH), 107.7 (CH), 70.0 (CH), 57.3 (CH_2), 28.5 (3xCH_3).

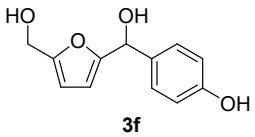
IR (neat) ν_{max}: 3328, 1702, 1597, 1526, 1413, 1367, 1316, 1240, 1182, 1054, 1016, 846, 775 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{20}NO_5$ $[M-H]^-$ 318.13470, found 318.1245; *m/z* calcd. for $C_{17}H_{21}NNaO_5$ $[M+Na]^+$ 342.13119, found 342.1313

Table 2, entry 12, Conditions C.

Following the **Conditions C**, the reaction was performed on HMF (126 mg, 1.0 mmol) and 4-Boc-aminophenylboronic acid (474 mg, 2.0 mmol) to produce compound **3e** (185 mg, 58% yield).

4-(Hydroxy(5-(hydroxymethyl)furan-2-yl)methyl)phenol 3f



3f

Following the **Conditions C**, the reaction was performed on HMF (150 mg, 1.19 mmol) and (4-hydroxyphenyl)boronic acid (328 mg, 2.38 mmol) to produce compound **3f** (103 mg, 40% yield) which was obtained as a pale yellow oil with an Rf = 0.2 (EtOAc/petroleum ether 7:3).

^{1}H NMR (500.1 MHz, acetone-d_6) δ 8.28 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.8 (d, *J* = 8.4 Hz, 2H), 6.16 (d, *J* = 3.2 Hz, 1H), 6.01 (d, *J* = 3.2 Hz, 1H), 5.66 (d, *J* = 4.8 Hz, 1H), 4.74 (d, *J* = 4.8 Hz, 1H), 4.45 (d, *J* = 6.0 Hz, 2H), 4.16 (t, *J* = 6.0 Hz, 1H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ 158.34 (C), 157.67 (C), 155.7543 (C), 134.46 (C), 128.87 (2xCH), 115.66 (2xCH), 108.15 (CH), 107.60 (CH), 70.11 (CH), 57.35 (CH_2)

IR (neat) ν_{max}: 3311, 1688, 1613, 1598, 1513, 1448, 1361, 1258, 1232, 1170, 1011, 963, 840, 804.

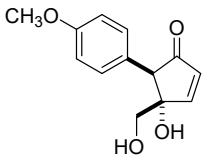
HRMS (ESI): *m/z* calcd. for $C_{12}H_{11}O_3$ ($[M-H_2O+H]^+$) 203.0703, found 203.0702.

III. Piancatelli rearrangements

MW-100: general procedure for Piancatelli rearrangements performed under microwave activation. To a solution of subtrate **3b-e** (1 eq.) in a mixture of *t*-BuOH/water 5:1 (0.05 *M*) was added $DyCl_3$ (10 mol %). The reaction mixture was heated under MW irradiation for 1.5 h at 100 °C. After cooling to room temperature, the mixture quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were then washed with brine, dried over magnesium sulfate (Mg_2SO_4), filtered and concetrated to dryness under vaccum. The crude product was purified by flash chromatography to afford the cyclopentanone derivatives **4b-e**.

Zippertex: general procedure for Piancatelli rearrangements performed under subcritical water conditions (100 °C and 100 bars) using the Zippertex technology.
To a solution of subtrate **3b-e** (1 eq.) in *t*-BuOH/water 1:5 (1 *M*) was placed in Zippertex® bowl, then nitrogen/air pressure (100 bars) was applied and the mixture was heated in 5-10 min to 100 °C for 2 hours. After cooling to room temperature in 30-40 min, the cell was depressurized and the mixture was concentrated under reduced pressure. The crude product was purified by flash chromatography to afford the cyclopentanone derivatives **4b-e**.

Table 3, entry 1, Conditions MW-100.
4-Hydroxy-4-(hydroxymethyl)-5-(4-methoxyphenyl)cyclopent-2-en-1-one 4b.



4b

Following the conditions **MW-100**, the reaction was performed on **3b** (70 mg, 0.3 mmol) to produce compound **4b** (32 mg, 46% yield, d.r. > 95:5) as a pale yellow solid with an Rf = 0.3 (EtOAc/*n*-heptane, 7:3). Mp: 134 - 136 °C.

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.60 (d, *J* = 6.0 Hz, 1H), 7.13-7.17 (m, 2H), 6.85-6.88 (m, 2H), 6.29 (d, *J* = 6.0 Hz, 1H), 4.70 (s, 1H), 3.76-3.79 (s, 4H), 3.70 (s, 1H), 3.27 (dd, *J* = 10.6 Hz, 3.7 Hz, 1H), 3.17 (dd, *J* = 10.6 Hz, 6.2 Hz, 1H).

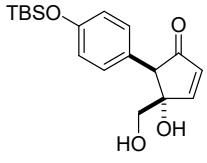
^{13}C NMR (125.8 MHz, acetone-d_6) δ 205.0 (C), 164.0 (CH), 159.6 (C), 134.0 (CH), 132.2 (2xCH), 127.8 (C), 114.1 (2xCH), 83.2 (C), 66.7 (CH), 63.8 (CH_2), 55.4 (CH_3).

IR (neat) ν_{max}: 3397, 2934, 1696, 1612, 1512, 1247, 1179, 1040, 836, 812, *769*, 692 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{13}H_{15}O_4$ $[M+H]^+$ 235.0965, found 235.0979.

Table 3, entry 2, Conditions Zippertex.
Following the conditions **Zippertex**, the reaction was performed on **3b** (2.81 g, 12.0 mmol) to produce compound **4b** (2.30 g, 82% yield, d.r. = 90:10).

Table 3, entry 3, Conditions MW-100.
(4S,5R)-5-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-4-hydroxy-4-(hydroxymethyl)cyclopent-2-en-1-one 4c.



4c

Following the conditions **MW-100**, the reaction was performed on **3c** (103 mg, 0.3 mmol) to produce compound **4c** (32.5 mg, 32% yield, d.r. > 95:5) as a pale yellow oil with an Rf = 0.3 (EtOAc/*n*-heptane, 7:3).

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.63 (d, 1H, *J* = 6.0 Hz), 7.16 (d, 2H, *J* = 8.5 Hz), 6.86 (d, 2H, *J* = 8.6 Hz), 6.33 (d, 1H, *J* = 6.0 Hz), 4.76 (s, 1H), 3.80 (s, 1H), 3.74 (s, 1H), 3.26 (dd, 2H, *J* = 10.6, 19.3 Hz), 1.03 (s, 9H), 0.25 (s, 6H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ 164.8 (CH), 134.7 (CH), 132.9 (2x CH), 121.1 (2x CH), 67.5 (CH_2), 64.5 (CH), 26.8 (2x CH_2), -3.6 (2x CH_3).

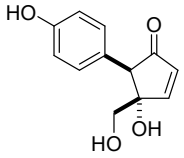
IR (neat) ν_{max}: 3383, 2930, 2857, 1699, 1609, 1511, 1404, 1264, 1173, 1035, 914, 840, 782 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{27}O_4Si$ $[M+H]^+$ 335.1673, found 335.1501.

Table 3, entry 4, Conditions MW-100.
Following the conditions **MW-100**, the reaction was performed on **3c** (214 mg, 0.6 mmol) to produce compound **4c** (41 mg, 19% yield, d.r. > 95:5).

Table 3, entry 5, Conditions Zippertex.
Following the conditions **Zippertex**, the reaction was performed on **3c** (470 mg, 1.4 mmol) to produce compound **4c** (141 mg, 30% yield, d.r. > 95:5) and compound **5** (16 mg, 5% yield, d.r. > 95:5) as a pale yellow oil with an Rf = 0.2 (EtOAc/*n*-heptane, 7:3).

(4S,5R)-4-hydroxy-4-(hydroxymethyl)-5-(4-hydroxyphenyl)cyclopent-2-en-1-one 5.



5

^{1}H NMR (500.1 MHz, acetone-d_6) δ 8.25 (s, 1H), 7.61 (d, *J* = 5.9 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.29 (d, *J* = 5.9 Hz, 1H), 4.68 (s, 1H), 3.74 (t, *J* = 5.9, 11.2 Hz, 1H), 3.68 (s, 1H), 3.24 (ddd, *J* = 4.0, 4.3, 30.8, 52.1 Hz, 2H).

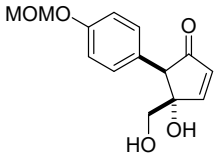
^{13}C NMR (125.8 MHz, acetone-d_6) δ 205.6 (CO), 164.2 (CH), 157.2 (C), 134.1 (CH), 132.2 (2xCH), 126.5 (C), 115.7 (2xCH), 83.2 (C), 66.9 (CH_2), 63.8 (CH).

IR (neat) ν_{max}: 3460, 2926, 1702, 1622, 1514, 1260, 1052, 1033, 688 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{12}H_{11}O_4$ $[M-H]^-$ 219.0663, found 219.0627.

Table 3, entry 6, Conditions Zippertex.
Following the conditions **Zippertex**, the reaction was performed on **3c** (550 mg, 1.64 mmol) with $Na_2S_2O_4$ (22 mg, 4 wt%) to produce compound **4c** (88 mg, 16% yield, d.r. > 95:5) and compound **5** (150 mg, 41% yield, d.r. > 95:5).

Table 3, entry 7, Conditions MW-100.
(4S,5R)-4-hydroxy-4-(hydroxymethyl)-5-(4-(methoxymethyl)phenyl)cyclopent-2-en-1-one 4d.
Following the conditions **MW-100**, the reaction was performed on **3d** (80 mg, 0.3 mmol) to produce compound **4d** (8 mg, 10% yield, d.r. > 95:5) as a pale yellow oil with an Rf = 0.35 (EtOAc/*n*-heptane, 7:3).



4d

^{1}H NMR (500.1 MHz, acetone-d_6) δ 7.58 (d, *J* = 5.9 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.29 (d, *J* = 5.8 Hz, 1H), 5.17 (d, *J* = 0.8 Hz, 2H), 4.83 (s, 1H), 3.87 (dd, *J* = 2.12, 4.7 Hz, 1H), 3.71 (s, 1H), 3.42 (s, 3H), 3.22 (m, 2H).

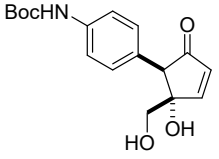
^{13}C NMR (125.8 MHz, acetone-d_6) δ 205.4 (C), 164.4 (CH), 157.2 (C), 134.0 (CH), 132.3 (2x CH), 129.1 (C), 116.5 (2x CH), 95.1 (CH_2), 83.3 (C), 66.5 (CH_2), 63.9 (CH), 56.1 (CH_3).

IR (neat) ν_{max}: 3408, 2930, 1698, 1611, 1511, 1338, 1235, 1150, 1077, 996, 920, 840, 812, 769 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{14}H_{17}O_5$ $[M+H]^+$ 265.1071, found 265.1071.

Table 3, entry 8, Conditions Zippertex.
Following the conditions **Zippertex**, the reaction was performed on **3d** (510 mg, 1.9 mmol) with $Na_2S_2O_4$ (21 mg, 4 wt%) to produce compound **4d** (340 mg, 66% yield, d.r. = 92:8) and compound **5** (43 mg, 10% yield, d.r. > 95:5).

Table 3, entry 9, Conditions MW-100.
***tert*-butyl (4-((1R,2S)-2-hydroxy-2-(hydroxymethyl)-5-oxocyclopent-3-en-1-yl)phenyl)carbamate 4e.**
Following the conditions **MW-100**, the reaction was performed on **3e** (100 mg, 0.3 mmol) to produce compound **4e** (60 mg, 60% yield, d.r. = 90:10) as a pale yellow oil with an Rf = 0.1 (EtOAc/*n*-heptane, 1:1).



4e

^{1}H NMR (500.1 MHz, acetone-d_6) δ 8.41 (s, 1H), 7.59 (d, *J* = 5.6 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.29 (d, *J* = 6.0 Hz, 1H), 4.80 (s, 1H), 3.85 (dd, *J* = 1.6, 4.6 Hz, 1H), 3.70 (s, 1H), 3.23 (m, 2H), 1.5 (s, 9H).

^{13}C NMR (125.8 MHz, acetone-d_6) δ 205.0 (C), 164.9 (C), 164.1 (CH), 139.4 (C), 134.0 (2xCH), 131.5 (CH), 129.7 (C), 118.5 (2x CH), 83.3 (C), 79.9 (C), 66.7 (CH_2), 63.9 (CH), 28.5 (3xCH_3).

IR (neat) ν_{max}: 3330, 2979, 2930, 1698, 1596, 1524, 1414, 1367, 1319, 1299, 1175, 1054, 773 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{21}NNaO_5$ $[M+Na]^+$ 342.1312, found 342.1294.

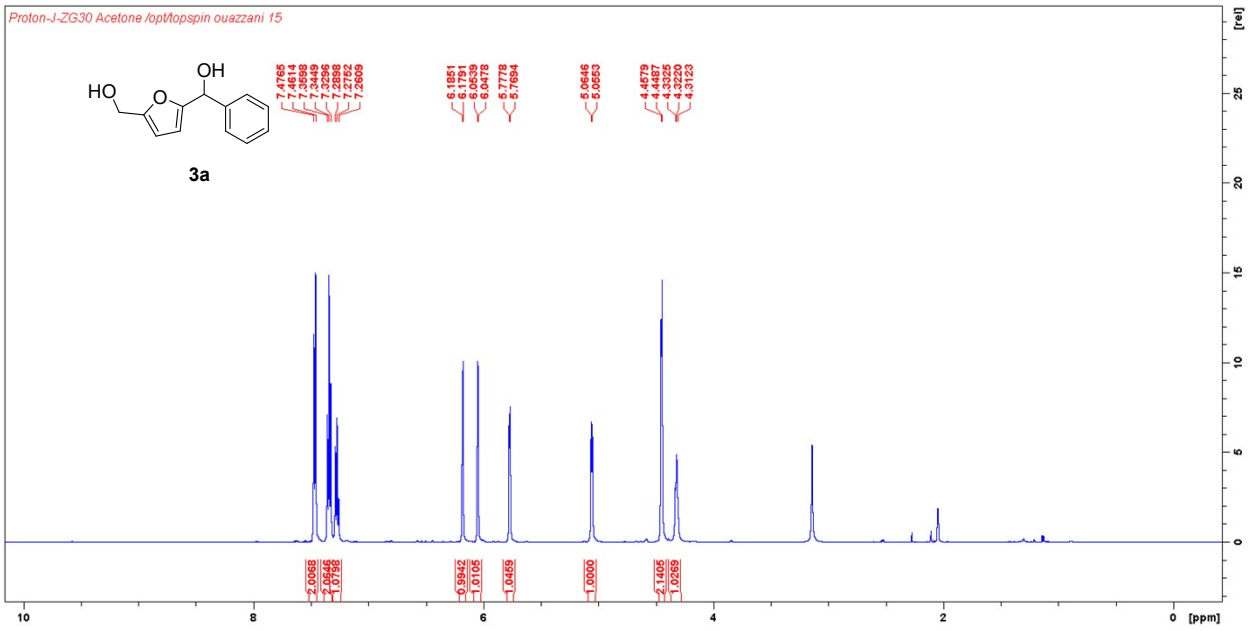
Scheme 1, Conditions MW-100.
The reaction was performed on 4-(*t*-butyldimethylsilyloxy)biphenyl (100 mg, 0.35 mmol) following the general procedure **MW-100** which led to any reaction and the starting material was cleanly recovered unchanged.

Scheme 1, Conditions Zippertex.
The reaction was performed on 4-(*t*-butyldimethylsilyloxy)biphenyl (500 mg, 1.76 mmol) with $Na_2S_2O_4$ (20 mg, 4 wt%) following the general procedure **Zippertex** which led to any reaction and the starting material was cleanly recovered unchanged.

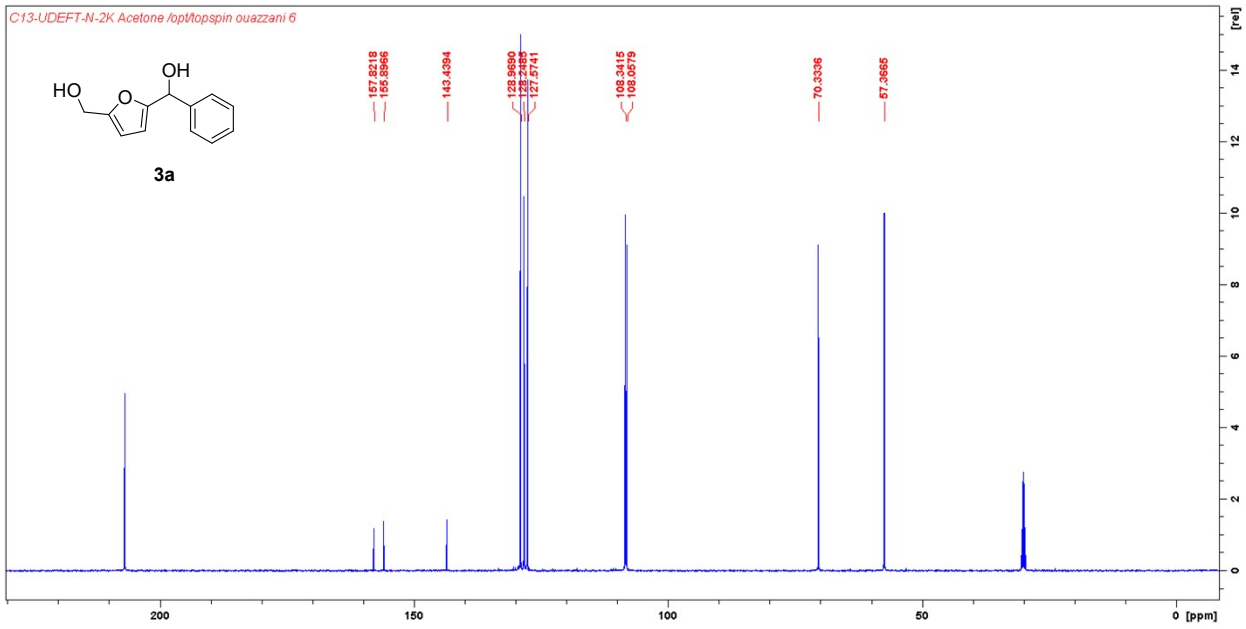
Attempt of Piancatelli rearrangement on substrate 3f.
Following the conditions **MW-100**, the reaction was performed on **3f** (46 mg, 0.2 mmol). Full conversion of the substrate **3f** was observed by NMR, but only degradation of the substrate and no traces of the expected compound **5** were observed.

IV. NMR Spectra

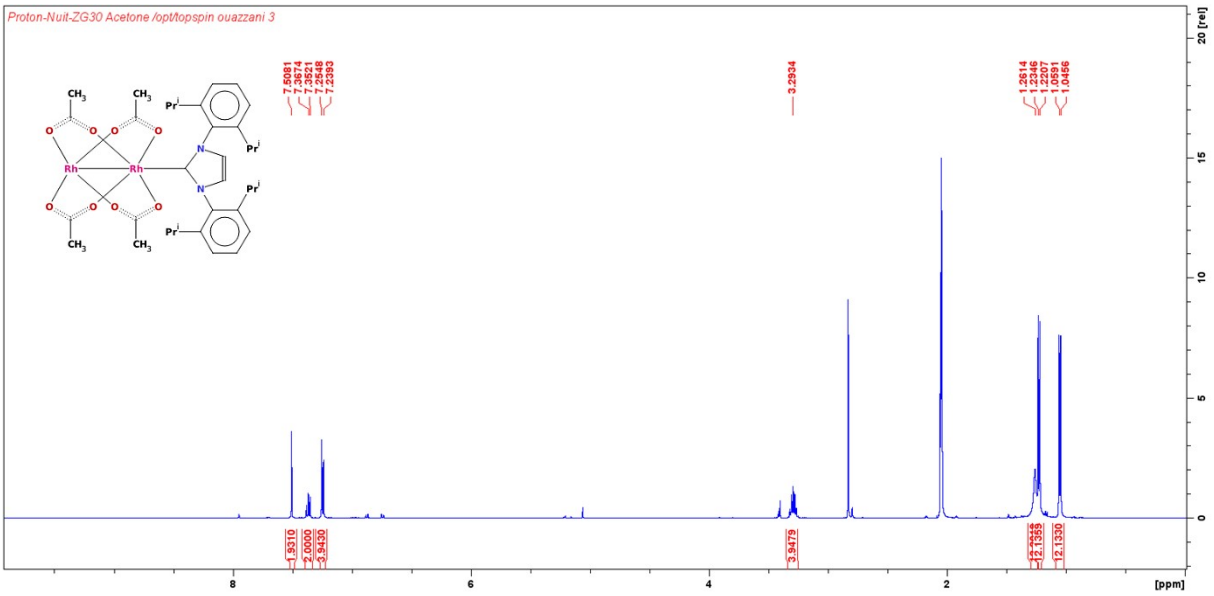
^{1}H NMR (500.1 MHz, acetone-d_6) of 5-(hydroxymethyl)furan-2-yl)(phenyl)methanol, 3a



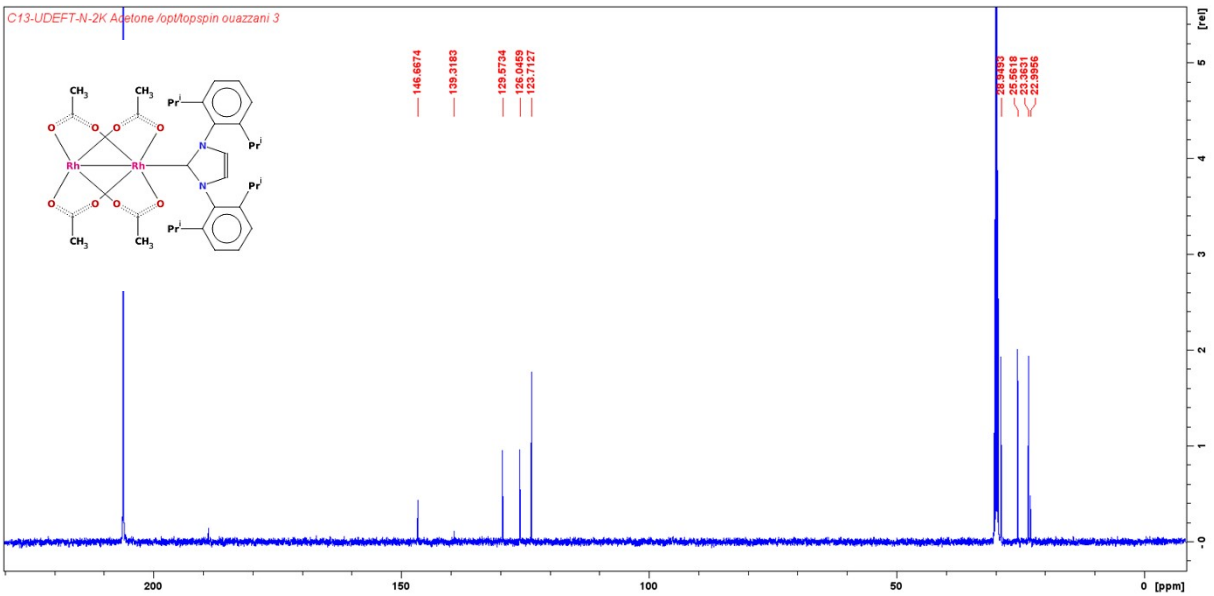
^{13}C NMR (125.8 MHz, acetone-d_6) of 5-(hydroxymethyl)furan-2-yl)(phenyl)methanol, 3a



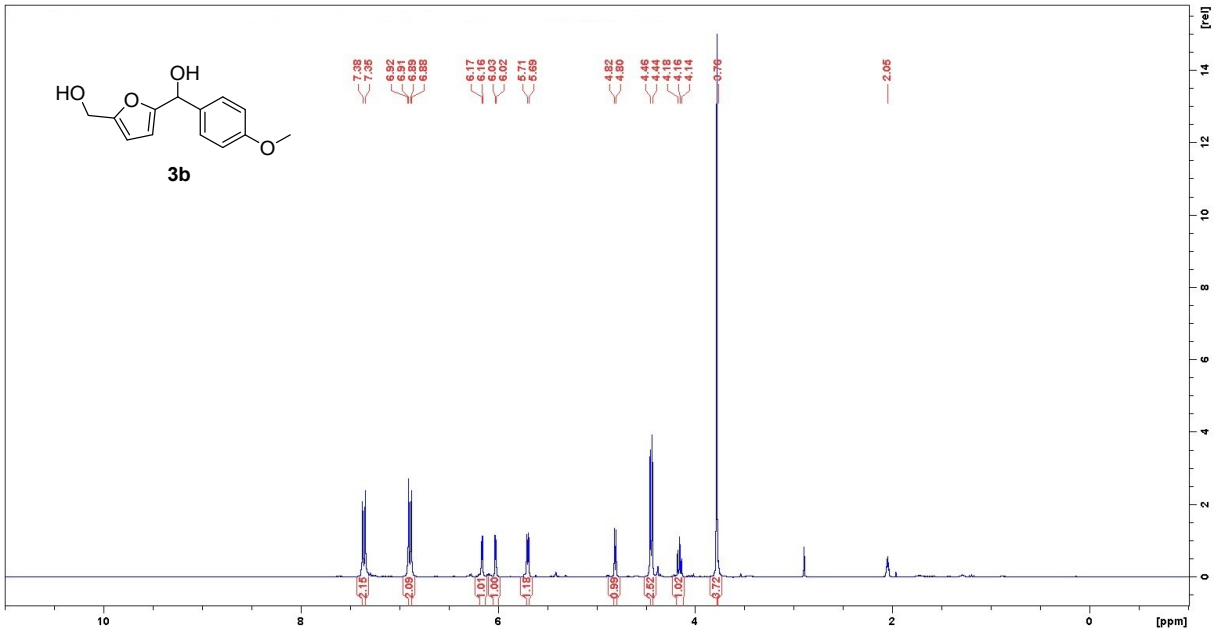
^{1}H NMR (500.1 MHz, acetone-d_6) $[Rh_2(OAc)_4](IPr)$



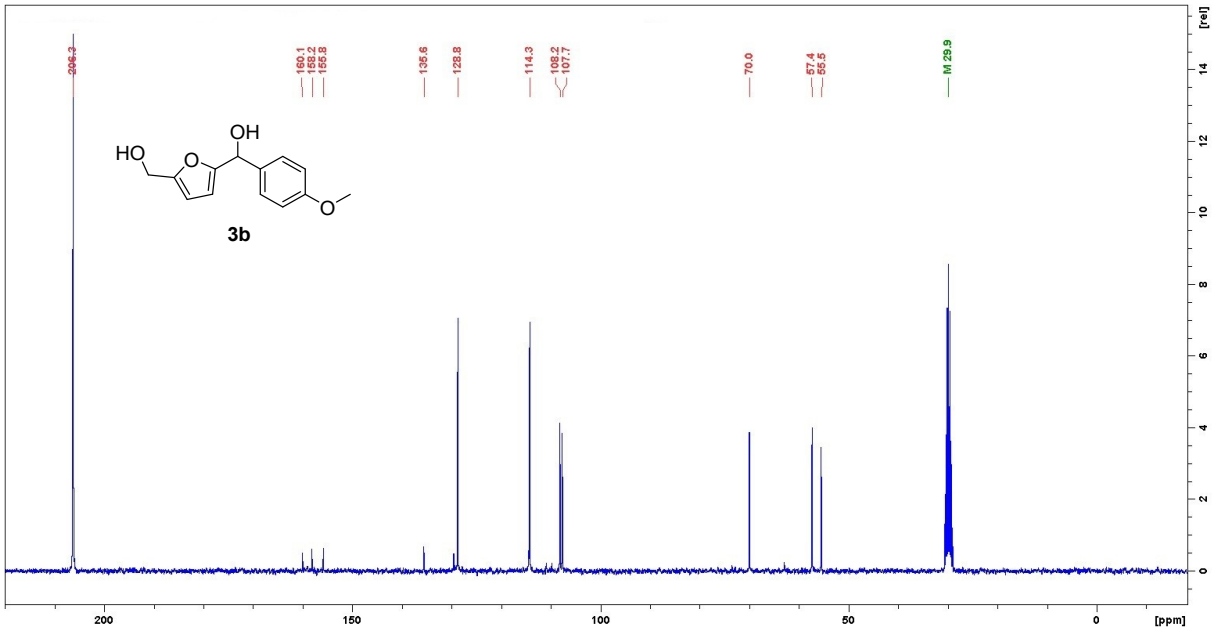
^{13}C NMR (125.8 MHz, acetone-d_6) $[Rh_2(OAc)_4](IPr)$



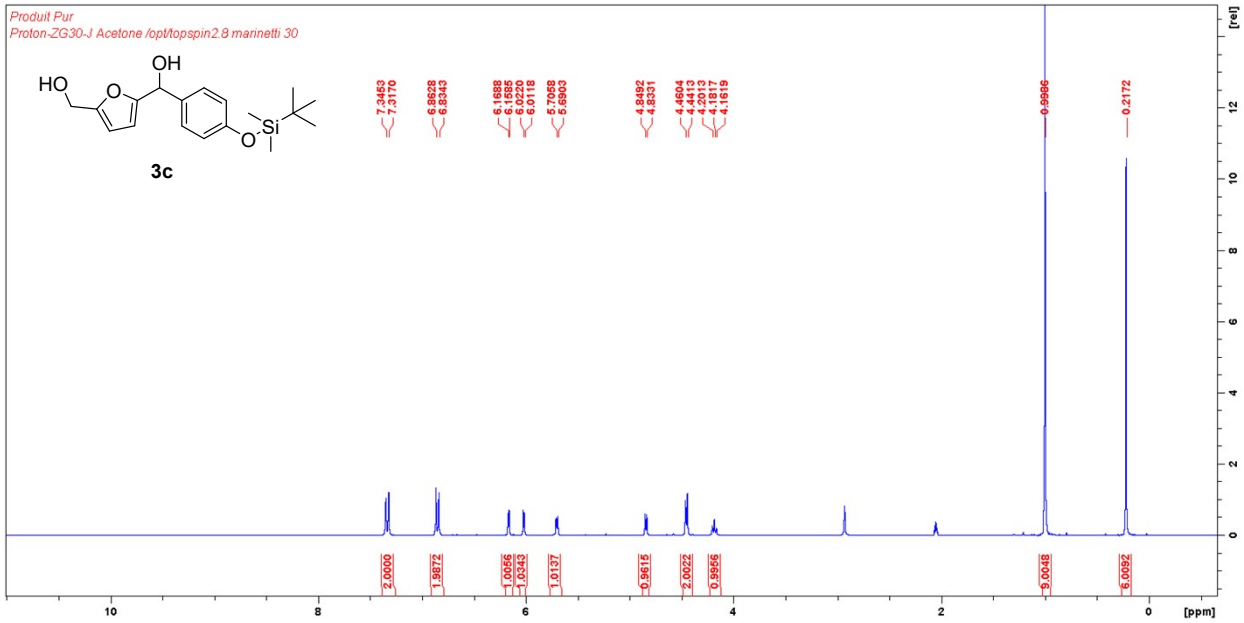
^{1}H NMR (500.1 MHz, acetone-d_6) of (5-(Hydroxymethyl)furan-2-yl)(4-methoxyphenyl)methanol, 3b



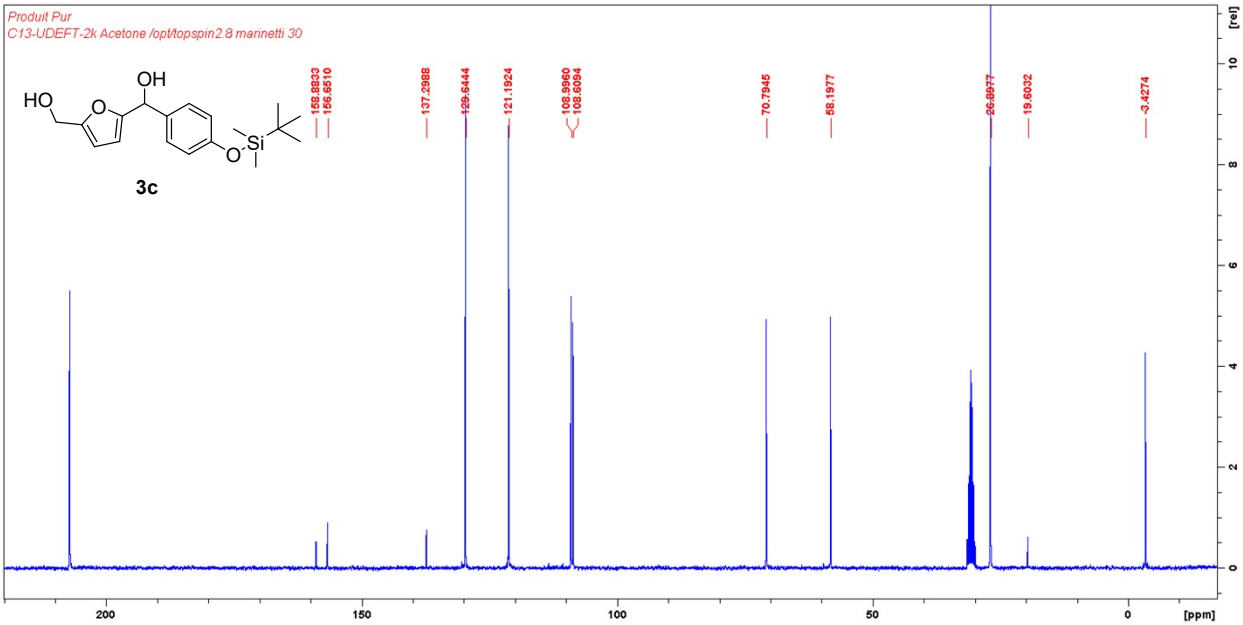
^{13}C NMR (125.8 MHz, acetone-d_6) of (5-(Hydroxymethyl)furan-2-yl)(4-methoxyphenyl)methanol, 3b



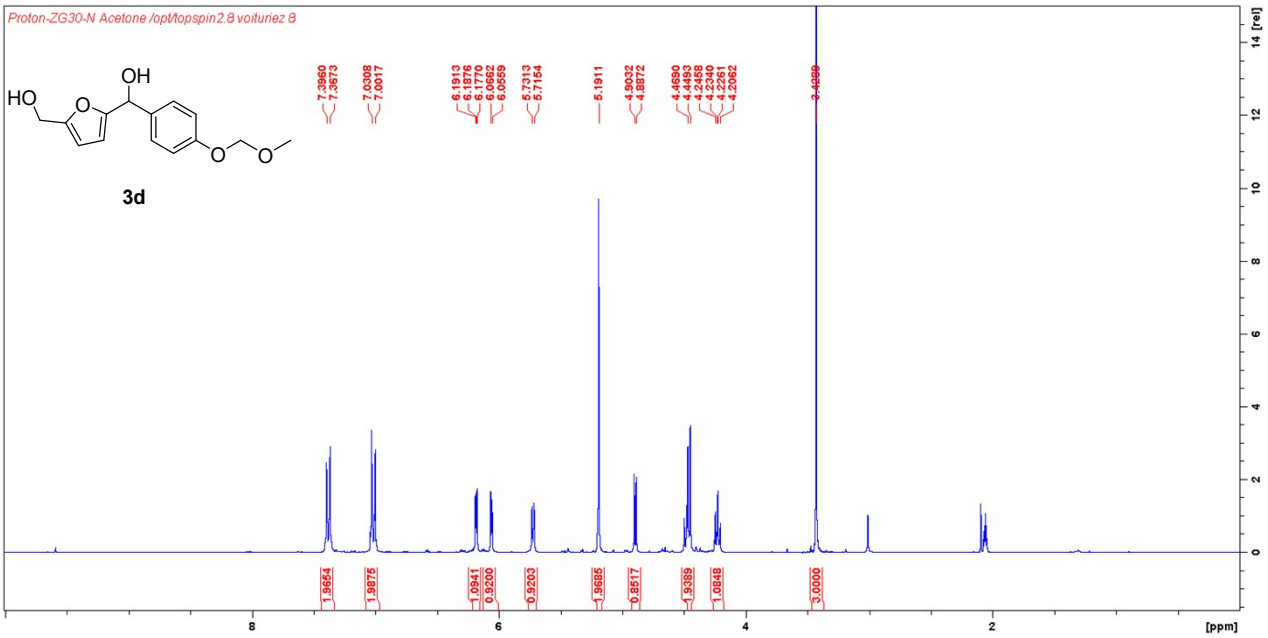
^{1}H NMR (500.1 MHz, acetone-d_6) of (4-((*tert*-butyldimethylsilyl)oxy)phenyl)(5-(hydroxymethyl)furan-2-yl)methanol, 3c



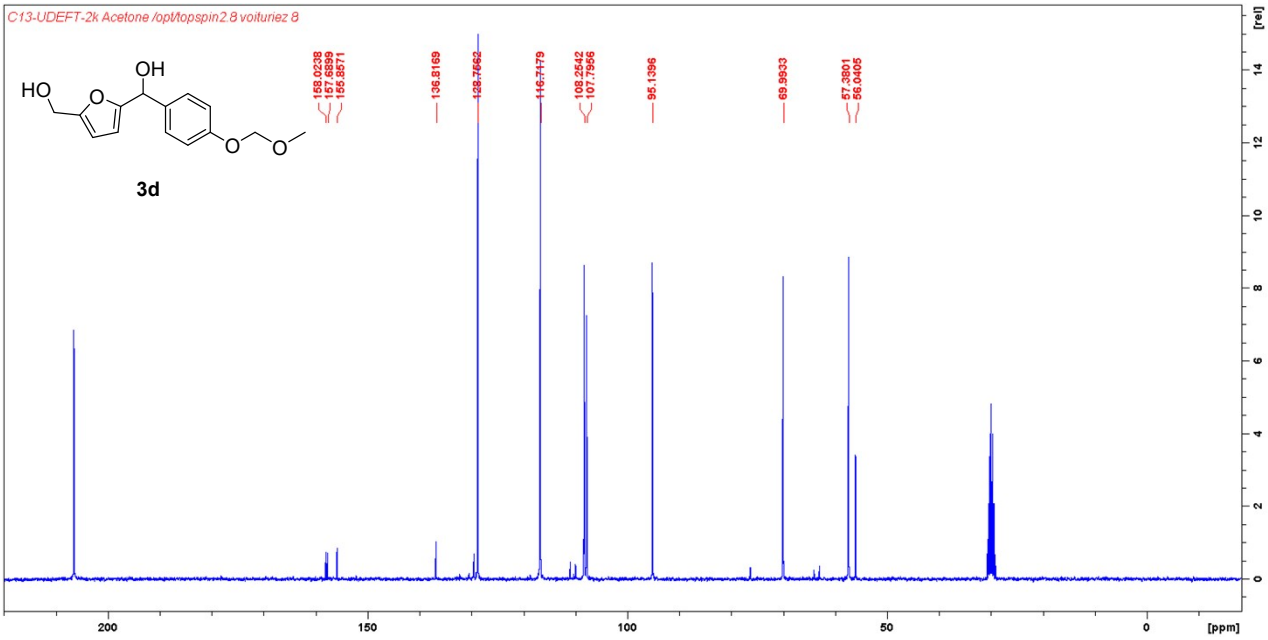
^{13}C NMR (125.8 MHz, acetone-d_6) of (4-((*tert*-butyldimethylsilyl)oxy)phenyl)(5-(hydroxymethyl)furan-2-yl)methanol, 3c



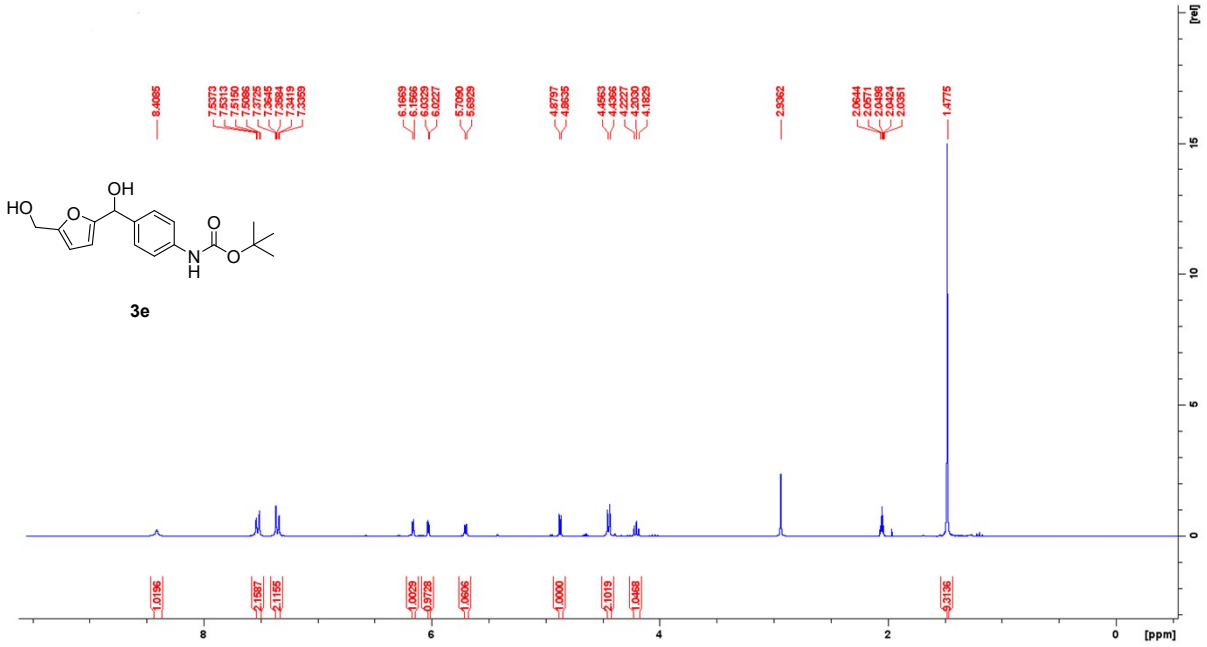
^{1}H NMR (500.1 MHz, acetone-d_6) of (5-(hydroxymethyl)furan-2-yl)(4-(methoxymethyl)phenyl)methanol, 3d



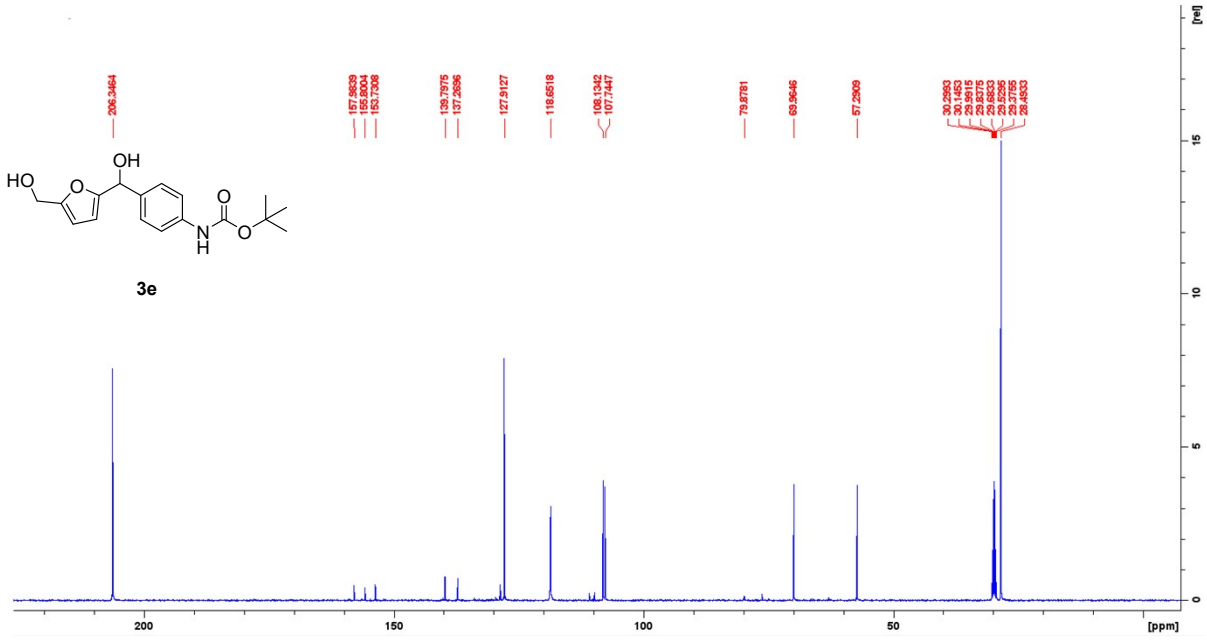
^{13}C NMR (125.8 MHz, acetone-d_6) of (5-(hydroxymethyl)furan-2-yl)(4-(methoxymethyl)phenyl)methanol, 3d



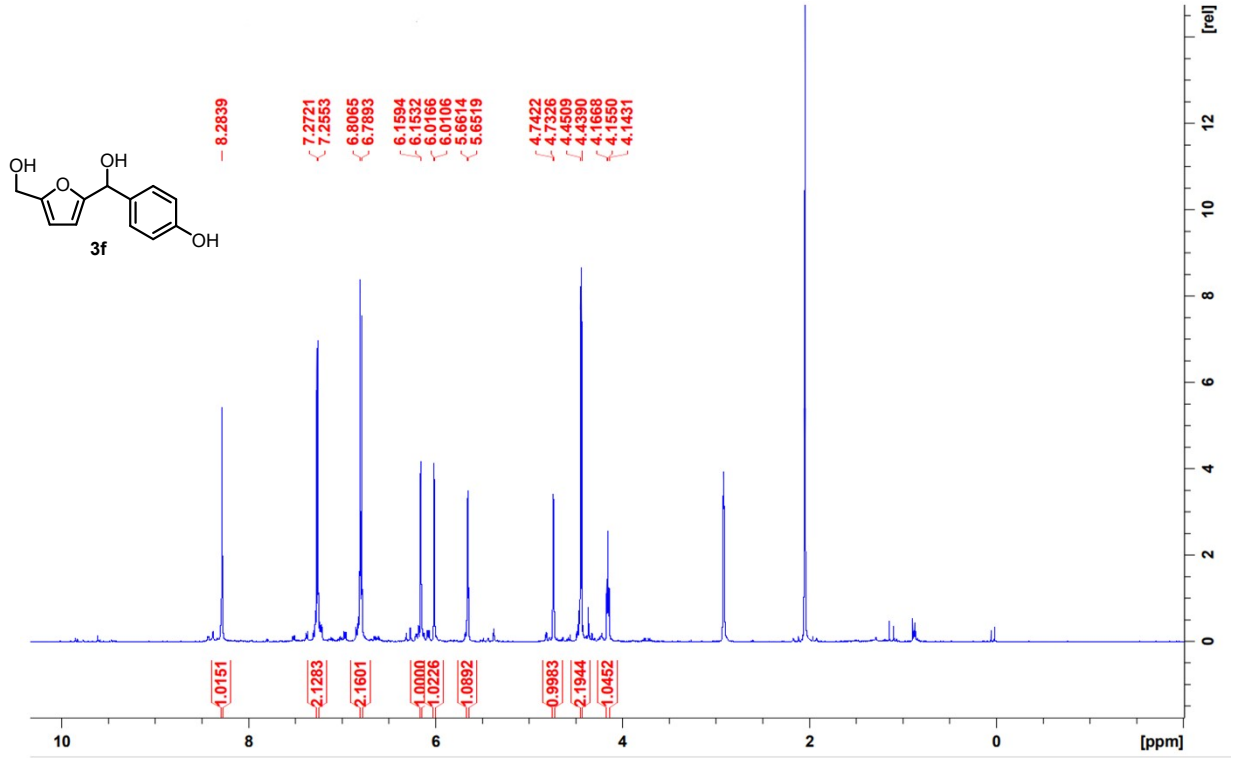
^{1}H NMR (500.1 MHz, acetone-d_6) of *tert*-butyl (4-(hydroxy(5-(hydroxymethyl)furan-2-yl)methyl)phenyl) carbamate, 3e



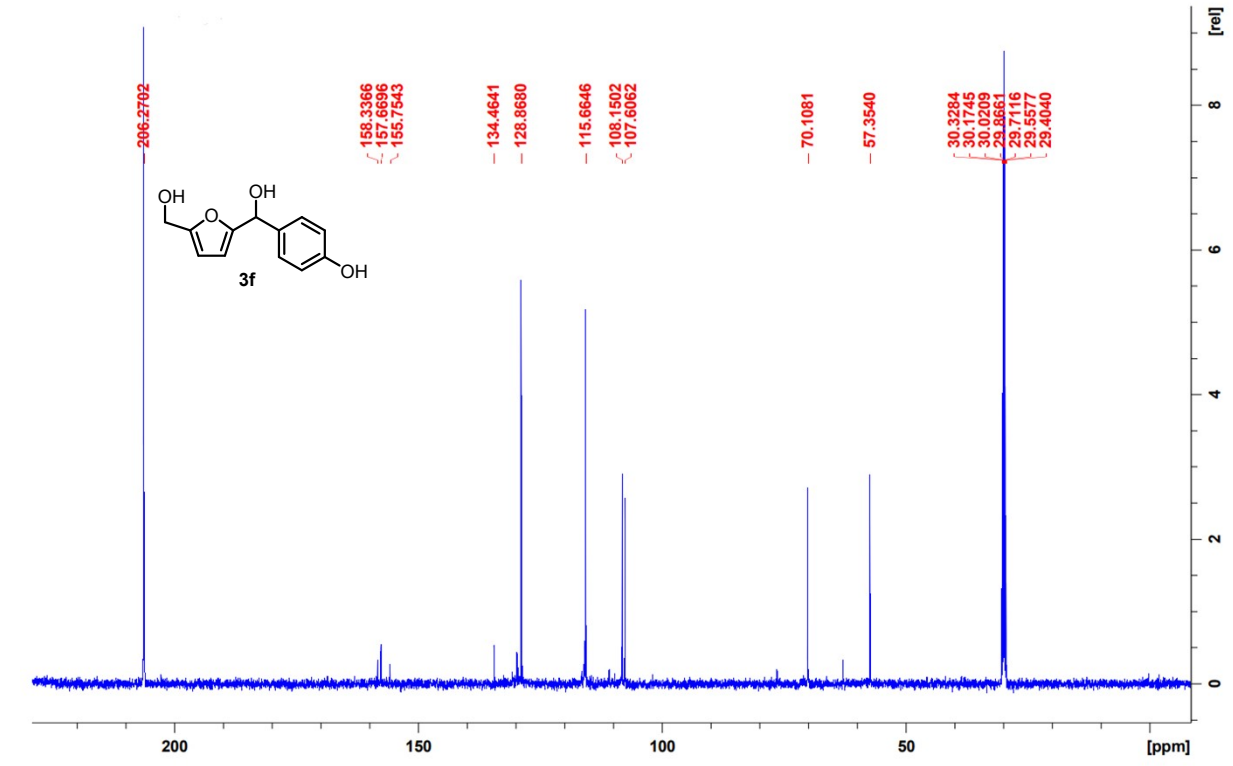
^{13}C NMR (125.8 MHz, acetone-d_6) of *tert*-butyl (4-(hydroxy(5-(hydroxymethyl)furan-2-yl)methyl)phenyl) carbamate, 3e



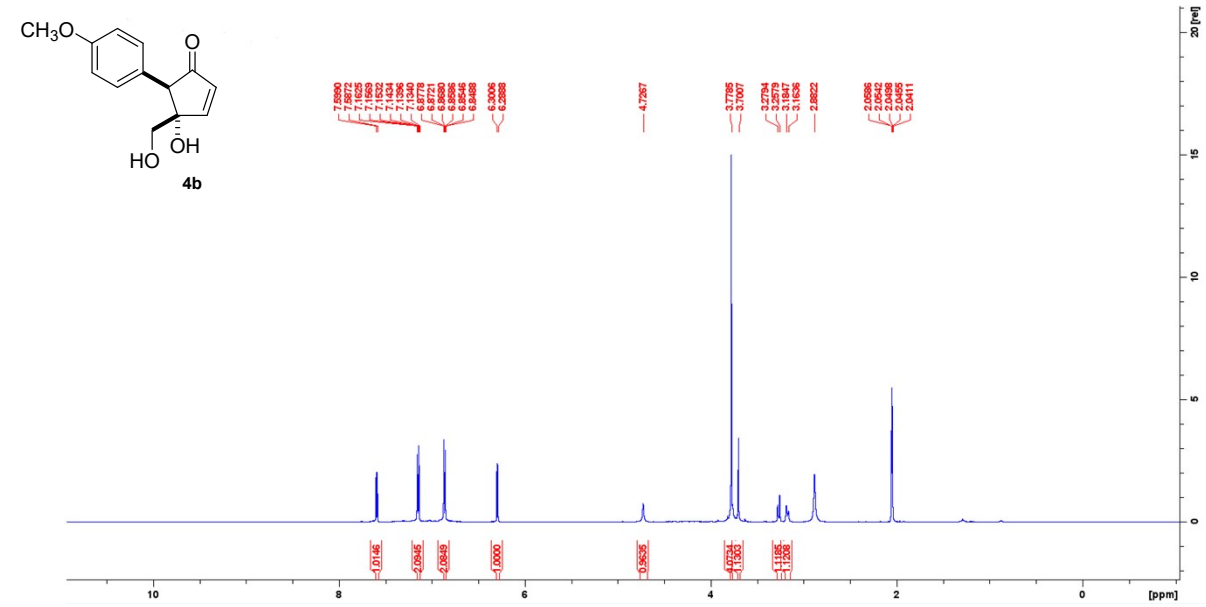
^{1}H NMR (500.1 MHz, acetone-d_6) of 4-(Hydroxy(5-(hydroxymethyl)furan-2-yl)methyl)phenol, 3f



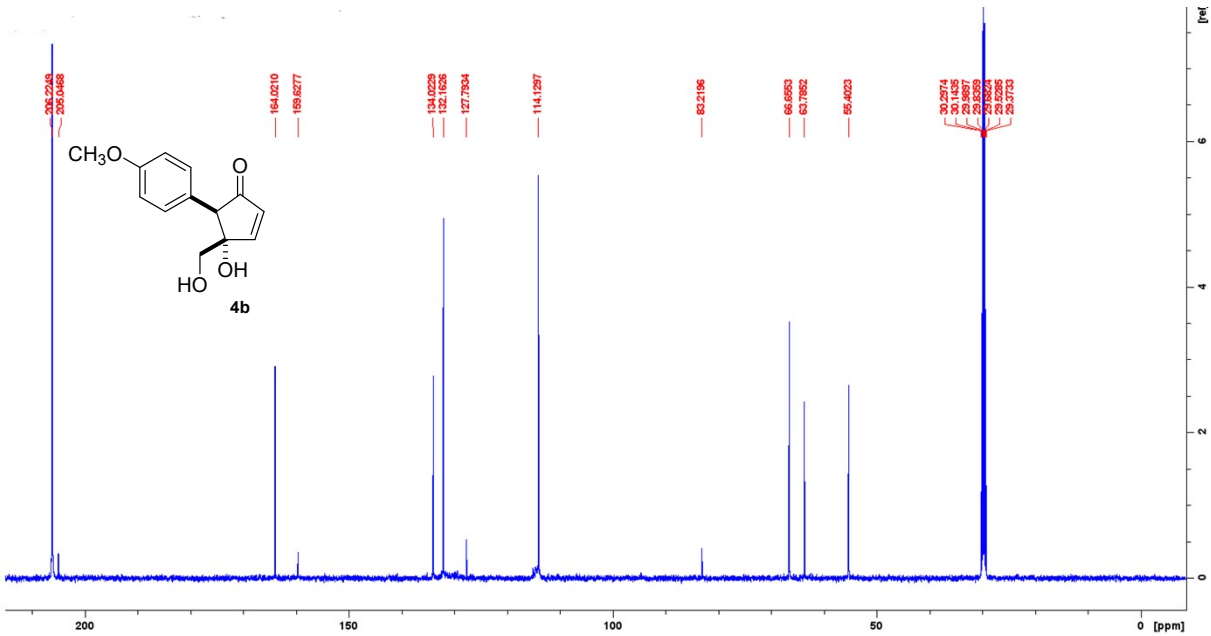
^{13}C NMR (125.8 MHz, acetone-d_6) of 4-(Hydroxy(5-(hydroxymethyl)furan-2-yl)methyl)phenol, 3f



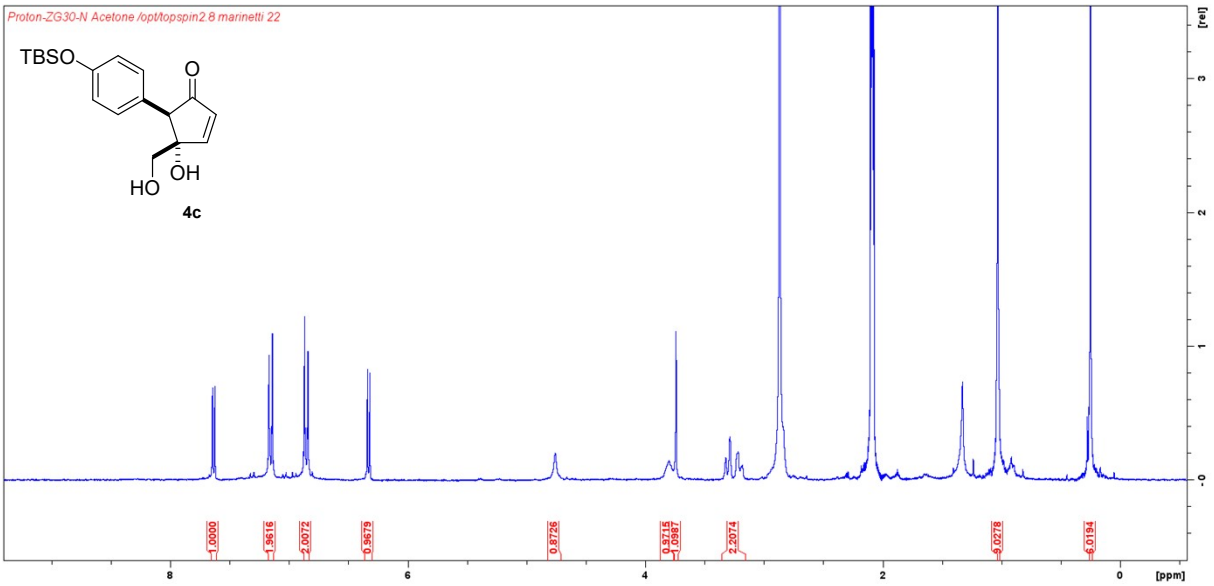
^{1}H NMR (500.1 MHz, acetone-d_6) of 4-Hydroxy-4-(hydroxymethyl)-5-(4-methoxyphenyl)cyclopent-2-en-1-one, 4b



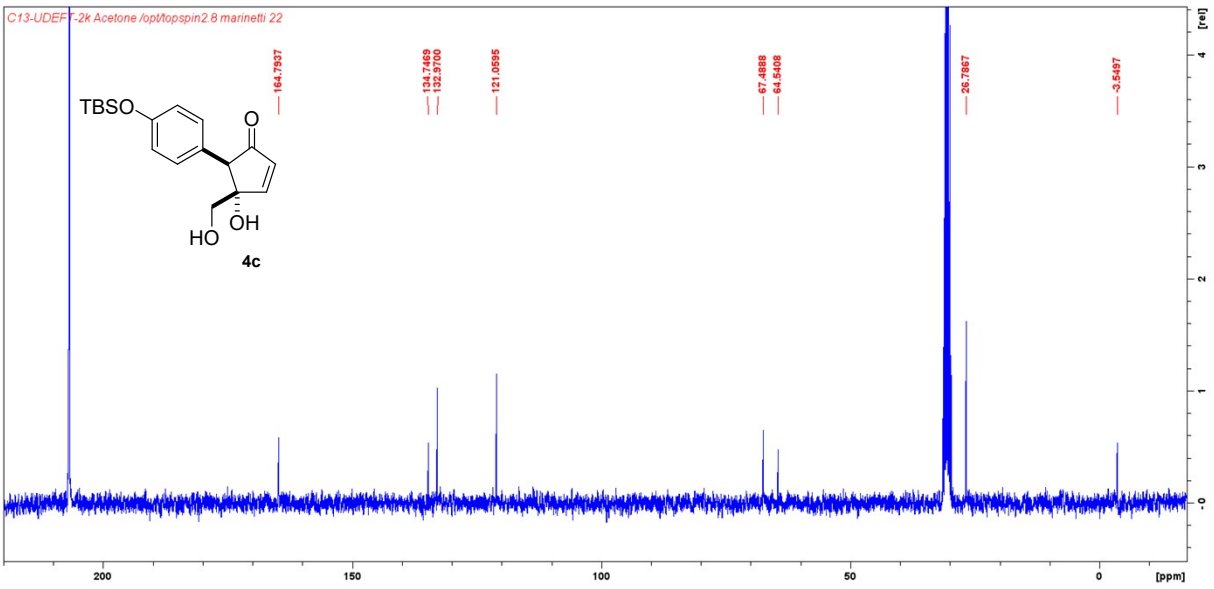
^{13}C NMR (125.8 MHz, acetone-d_6) of 4-Hydroxy-4-(hydroxymethyl)-5-(4-methoxyphenyl)cyclopent-2-en-1-one, 4b



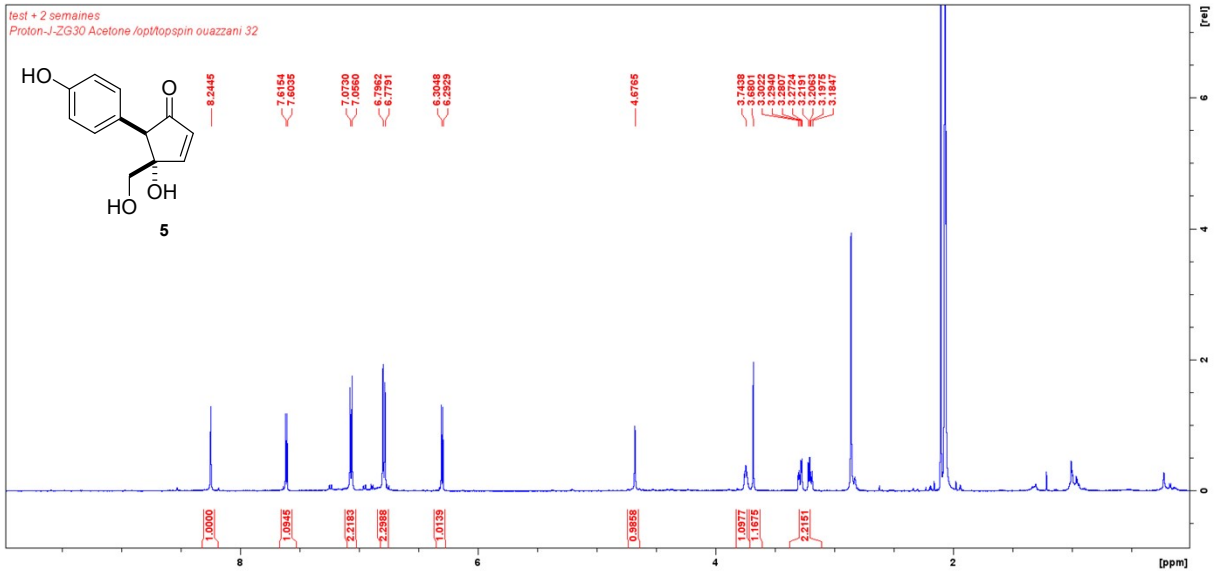
^{1}H NMR (500.1 MHz, acetone-d_6) of (4S,5R)-5-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-4-hydroxy-4-(hydroxymethyl)cyclopent-2-en-1-one, 4c



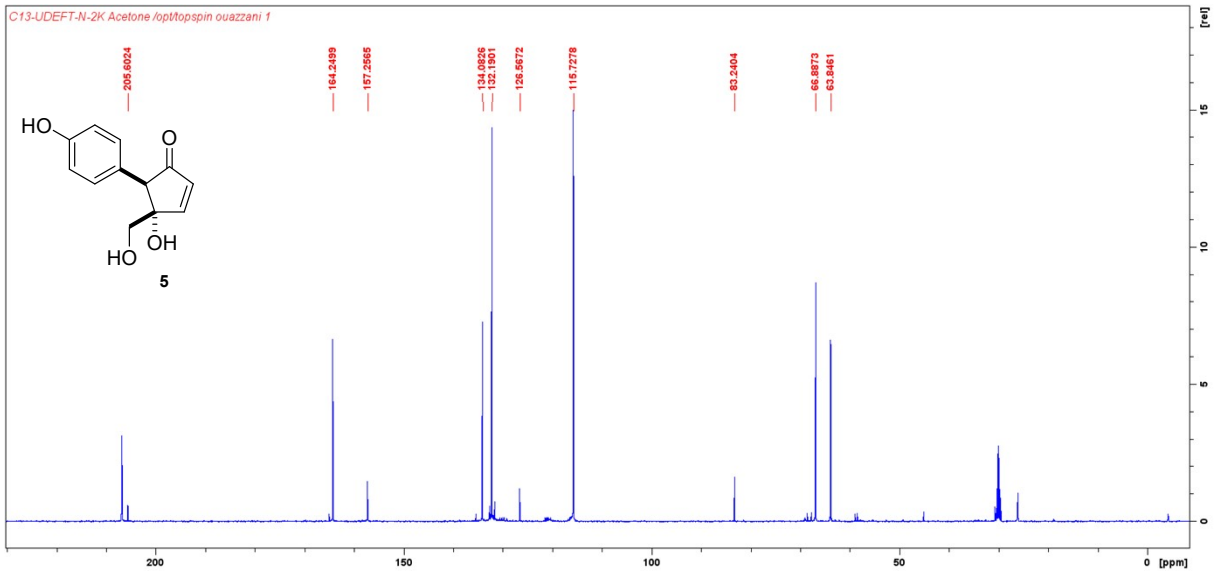
^{13}C NMR (125.8 MHz, acetone-d_6) of (4S,5R)-5-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-4-hydroxy-4-(hydroxymethyl)cyclopent-2-en-1-one, 4c



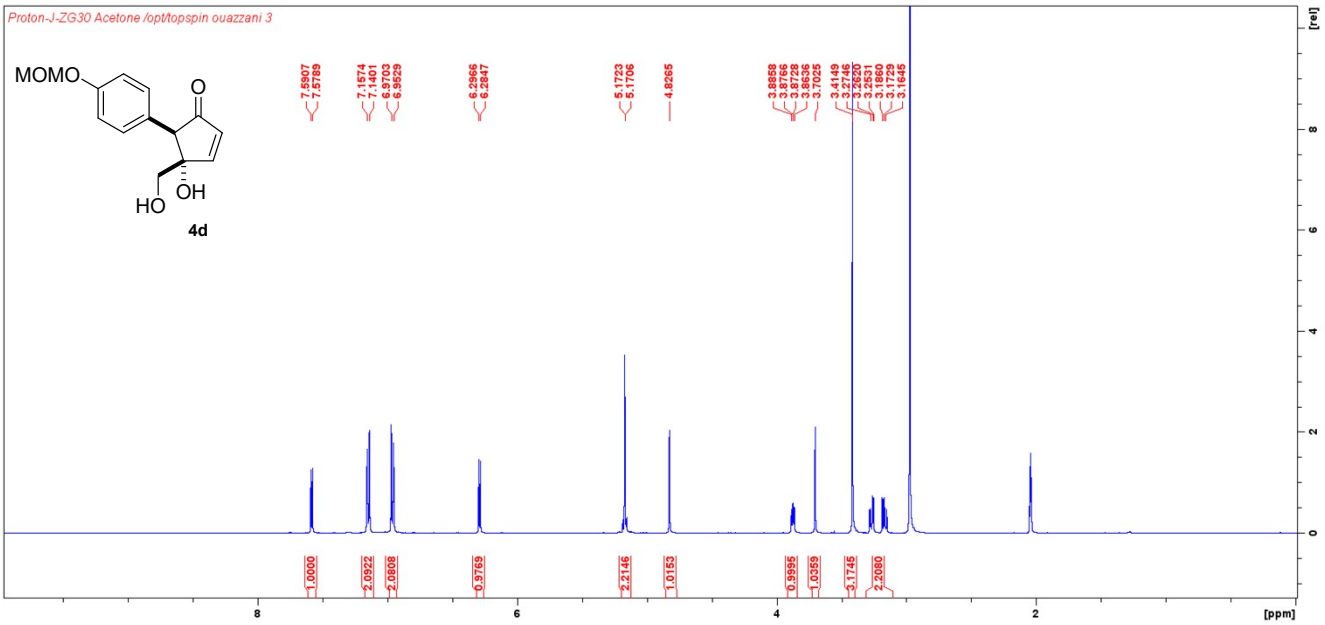
^{1}H NMR (500.1 MHz, acetone-d_6) of (4S,5R)-4-hydroxy-4-(hydroxymethyl)-5-(4-hydroxyphenyl)cyclopent-2-en-1-one, 5



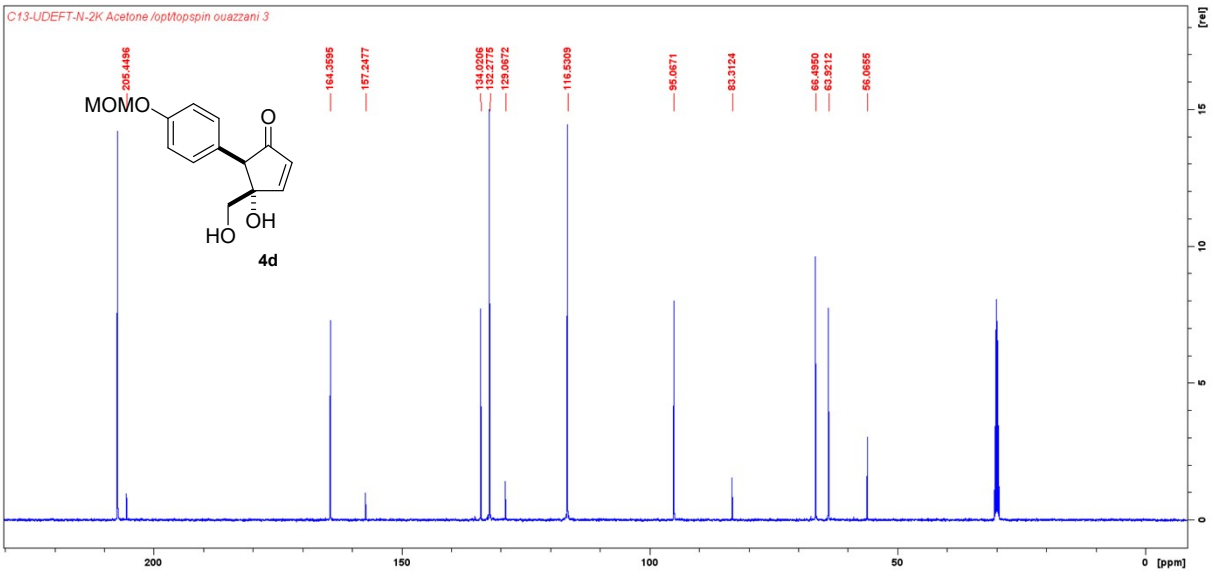
^{13}C NMR (125.8 MHz, acetone-d_6) of (4S,5R)-4-hydroxy-4-(hydroxymethyl)-5-(4-hydroxyphenyl)cyclopent-2-en-1-one, 5



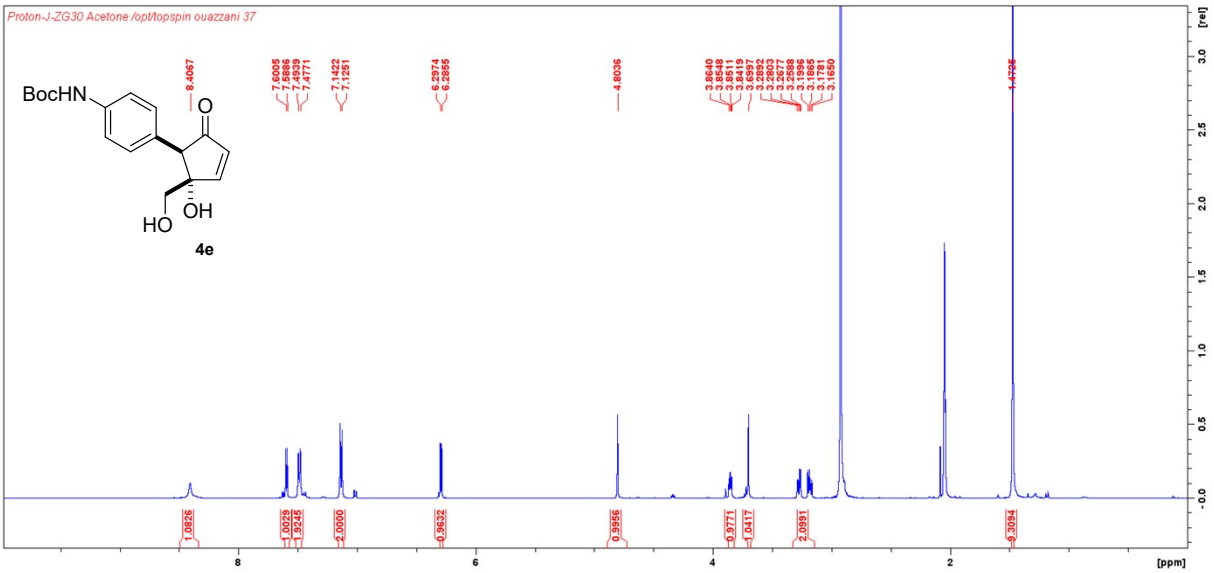
^{1}H NMR (500.1 MHz, acetone-d_6) of (4S,5R)-4-hydroxy-4-(hydroxymethyl)-5-(4-(methoxymethyl)phenyl)cyclopent-2-en-1-one, 4d



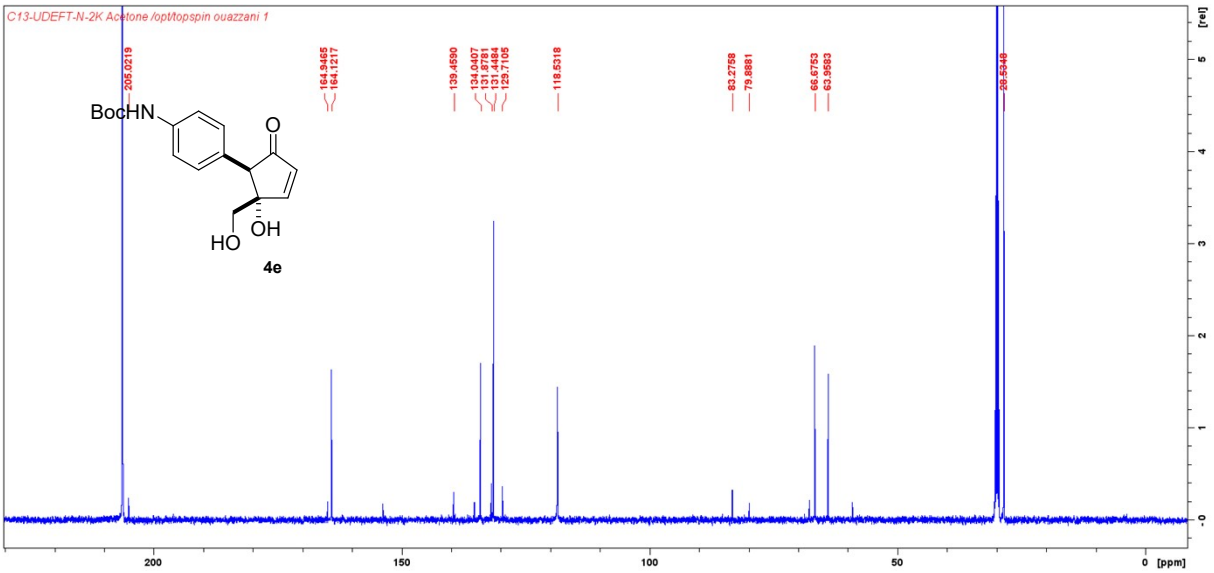
^{13}C NMR (125.8 MHz, acetone-d_6) of (4S,5R)-4-hydroxy-4-(hydroxymethyl)-5-(4-(methoxymethyl)phenyl)cyclopent-2-en-1-one, 4d



^{1}H NMR (500.1 MHz, acetone-d_6) of *tert*-butyl (4-((1R,2S)-2-hydroxy-2-(hydroxymethyl)-5-oxocyclopent-3-en-1-yl)phenyl)carbamate, 4e



^{13}C NMR (125.8 MHz, acetone-d_6) of *tert*-butyl (4-((1R,2S)-2-hydroxy-2-(hydroxymethyl)-5-oxocyclopent-3-en-1-yl)phenyl)carbamate, 4e



V. Single Crystal X-ray Crystallography (SC-XRD) of $[Rh_2(OAc)_4](IPr)$

Experimental

Crystals of compound **$[Rh_2(OAc)_4](IPr)$** were obtained by slow evaporation from a mixture of EtOAc/*n*-heptane solution. Single crystals suitable to X-ray diffraction structural analyses were transferred upon a microscope slide and one of them selected under a binocular, mounted on a nylon loop and fixed with Paratone® oil. Then, X-ray diffraction and crystallographic data were collected at room temperature using redundant ω scans on a Rigaku XtaLabPro single-crystal diffractometer using microfocus Mo Kα radiation and a HPAD PILATUS3 R 200K detector. CrysAlisPro 1.171.39.46 [1] was employed for the data processing, with SCALE3 ABSPACK scaling algorithm implemented for the empirical absorption correction using spherical harmonics.

Using Olex2 [2], the structure was readily solved by intrinsic phasing methods (SHELXT [3]), and refined using SHELXL [4] in the monoclinic space group P21/n. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms have been added geometrically and treated as riding on their parent atoms, precisely aromatic and methyl hydrogen atoms were treated as riding in geometrically idealized positions, with *U*iso (H) = k*U*eq (C), where k = 1.5 for the methyl groups - allowed to rotate around their C-C bond but not to tip-, and 1.2 for the aromatic ones.

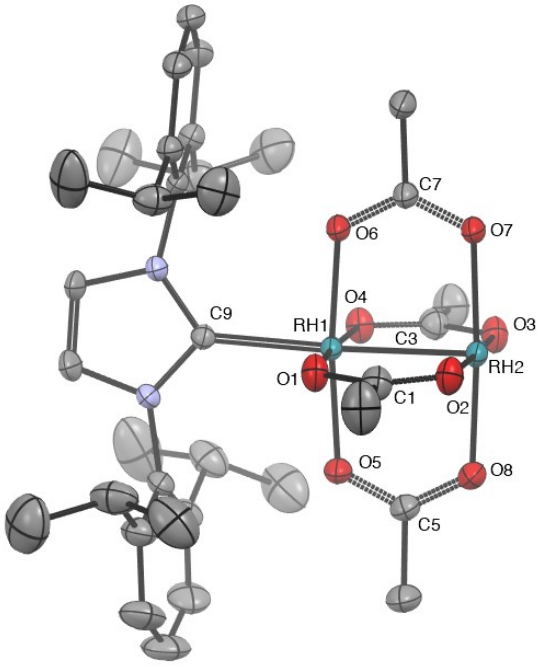
The molecular graphics presented in the article were computed with Mercury 2024.1.0 [5].

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre database (the deposition number is 2383332). Copies of the data can be obtained free of charge from the CCDC at www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for compound $[Rh_2(OAc)_4](IPr)$.

$C_{35}H_{48}N_2O_8Rh_2$, M_r =830.57, monoclinic, $P2_1/n$ (No. 14), a = 10.6750(4) Å, b = 16.8487(5) Å, c = 21.2526(7) Å, β = 95.754(3)°, V = 3803.2(2) Å^3, Z = 4, T = 293(2) K, μ/mm^{-1} = 0.916, 55660 reflections measured, 7771 unique (R_{int} = 0.0388) which were used in all calculations. The final wR_2 was 0.0624 (all data) and R_1 was 0.0252 (I > 2σ(I)) . The goodness-of-fit on F^2 was 1.072.

Figure S1. ORTEP view of compound **$[Rh_2(OAc)_4](IPr)$**.



ORTEP drawing with thermal ellipsoids drawn at the 30% probability level. Hydrogens were omitted for clarity. Selected bond distances and angles are presented: Rh1−Rh2 = 2.427(2) Å, Rh1−C9 = 2.143(10) Å; All of the coordination angles are around 90°.

Table S1: Crystal data and structure refinement

Identification code		**$[Rh_2(OAc)_4](IPr)$**
Empirical Formula		$C_{35}H_{48}N_2O_8Rh_2$
Formula Weight		830.57
Crystal Color, Habit		[purple, rect.prism]
Crystal Dimensions (mm^3)		0.46 × 0.19 × 0.1
Crystal System		monoclinic
Space Group		$P2_1/n$
Unit cell dimensions	*a* (Å)	10.6750(4)
	b (Å)	16.8487(5)
	c (Å)	21.2526(7)
	α (°)	90
	β (°)	95.754(3)
	γ (°)	90
Volume (Å3)		3803.2(2)
Z value		4
Calculated density $D_{calc.}$ ($g.cm^{-3}$)		1.451
Absorption coefficient μ (mm^{-1})		0.916
F (000)		1704.0
Diffractometer		Rigaku XtaLAB PRO
Radiation type		Mo K_α
Wavelength (Å)		0.71073
Voltage, Current (kV, mA)		(50, 0.6)
***T* (K)**		293(2)
2θ range for data collection (°)		4.534 to 52.744
Limiting indices		-12 ≤ h ≤ 13, -21 ≤ k ≤ 21, -26 ≤ l ≤ 26
Reflections collected/unique		55660/7771
Completeness to θ full (%)		99.9
R_{int}		0.0388
Absorption correction		Semi-empirical from equivalents
Refinement method		Full-matrix least-squares on F^2
Data/restraints/parameters		7771/0/440
Goodness-of-fit on F^2		1.072
Final R indices [*I*>2σ(*I*)]	R_1 wR_2	0.0252 0.0588
R indices (all data)	R_1 wR_2	0.0314 0.0624
Largest Δ peak and hole ($e.Å^{-3}$)		0.55/-0.59
CCDC Deposit Number		2383332

Table S2. Selected Bond Distances (Å) for $[Rh_2(OAc)_4](IPr)$

Atom	Atom	Length/Å
Rh1	Rh2	2.4266(2)
Rh1	O1	2.0418(17)
Rh1	O4	2.0442(17)
Rh1	O5	2.0443(15)
Rh1	O6	2.0180(15)
Rh2	C9	2.1430(19)
Rh2	O2	2.0354(18)
Rh2	O3	2.0337(18)
Rh2	O7	2.0565(15)
Rh2	O8	2.0298(16)

Table S3. Selected Bond Angles (°) for $[Rh_2(OAc)_4](IPr)$

Atom	Atom	Atom	Angle/°
O1	Rh1	Rh2	87.18(4)
O2	Rh2	Rh1	87.84(5)
O3	Rh2	Rh1	87.91(5)
O4	Rh1	Rh2	87.21(4)
O5	Rh1	Rh2	86.56(4)
O6	Rh1	Rh2	86.98(4)
O7	Rh2	Rh1	87.83(4)
O8	Rh2	Rh1	88.38(5)

Citations

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VI. Antibacterial assays

Antibacterial activity was measured by the disk inhibition zone method against *Bacillus subtilis* ATCC.6633, *Micrococcus luteus* ATCC.10240 and *Echerichia coli* ATCC.25922. Inhibition was compared to 10 µg gentamycin and 30 µg chloramphenicol. Microbial growth inhibition was determined for 100 µg of pure compound, solubilized in DMSO, after 48 h of incubation at 30 °C for *Bacillus subtilis* ATCC.6633 and *Micrococcus luteus* ATCC.10240, and 24 h of incubation à 37 °C for *Echerichia coli* ATCC.25922.

Compound	Microbial cell growth inhibition percentage of control		
	M. luteus	*B. subtilis*	*E. coli*
3b	31/C	41/P	39/C
3c	28/C	31/P	39/C
3d	20/C	38/P	39/C
3e	22/C	34/P	0/C
4b	0/C	0/P	55/C
4c	0/C	0/P	0/C
4d	16/C	34/P	33/C
4e	0/C	0/P	0/C
5	32/C	30/P	33/C

Microbial growth inhibition was determined for 100 µg of pure compound by the disk inhibition zone technique. Antimicrobial activity is expressed as the percentage of the inhibition obtained for various antibiotics (C for chloramphenicol, 30 µg and P for penicillin, 10 µg).