Supporting Information

Synthesis of functionalized lactones: catalytic cross-coupling of 1,2-diols and allylic alcohols

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General Experimental: All catalytic reactions were performed under inert atmosphere using standard Schlenk techniques. All stoichiometric reactions were performed in nitrogen atmosphere MBRAUN glove box. Ru-MACHO [Carbonylchlorohydrido{bis[2-(diphenylphosphinomethyl) ethyl]amino}ethyl]amino}ruthenium(II)] (**1**) was purchased from Sigma-Aldrich and stored inside glove box. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar, and TCI Chemicals and used without further purification. Dry solvents were prepared according to standard procedures. Infrared (IR) spectra were recorded in Perkin-Elmer FT-IR and Thermo-Nicolet FT-IR spectrophotometers. High-resolution mass spectra (HRMS) were obtained on Bruker micrOTOF-Q II Spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, $[M]^+$. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded at Bruker AV- 400 (^{1}H at 400 MHz, ^{13}C at 100.6 MHz). ^{1}H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethyl silane (TMS, δ 0.00 ppm), and ^{13}C {^{1}H} NMR chemical shifts are referenced in parts per million (ppm) with respect to $CDCl_3$ (δ 77.160 ppm). Coupling constants are reported in Hertz (Hz). *δ-Hydroxybutyrolactones products have three stereocenters and hence eight stereoisomers possible. Some isomers are present in minor amounts, which appearing in both ^{1}H and ^{13}C NMR spectra distinctly in minor intencity. However, due to complex nature of these signals their ratio was not determined.* ^{1}H NMR spectroscopy abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets; qd, quartets of doublets; ddd, doublets of doublets of doublets; m, multiplet; br, broad. EPR spectra at X-band frequency were recorded at 106 K using liquid N_2 with a Bruker EMX (ER 073) spectrometer. The Spectrometer was running under a software WinEPR. A 4 mm OD standard EPR tube was used for all the experiments. Crystal data were collected with Rigaku Oxford diffractometer and with INCOATEC micro source (Cu-Kα radiation, λ = 0.701 Å, multilayer optics) at 298 K.

Experimental procedure for the synthesis of starting materials:

a) General procedure for the synthesis of 1,2-diol derivatives:

To a round-bottom flask (50 mL) charged with a magnetic stir bar, SeO_2 (5 mmol, 1 equiv) in 1,4-dioxane:H_2O (9:1) at 55 °C under N_2 atmosphere was added. After dissolution of SeO_2, acetophenone derivative (5 mmol, 1 equiv) was added slowly, and the reaction mixture was kept under reflux condition for 3 h. The completion of reaction was monitored by TLC. Further, the reaction mixture was filtered, and the solvents were removed under reduced pressure using rotavapor to obtain the reaction mixture residue. The residue was dissolved in MeOH (10 mL) and $NaBH_4$ (2 mmol, 2 equiv) was added in portions at 0 °C. Then the reaction mixture was allowed to stir at room temperature for 2-4 h, and the solvent was removed under reduced pressure. The resulted residue was dissolved in water (10 mL) and extracted using ethyl acetate (10 mL × 3). The collected organic layer was washed with brine, and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure using a rotavapor. The residue obtained was purified by silica-gel column chromatography using ethyl acetate/hexane (50:50) as an eluent, which provided the corresponding 1,2-diol derivatives.[1]

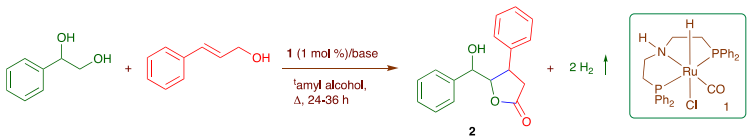
b) General procedure for the synthesis of cinnamyl alcohols derivatives:

To a round-bottom flask (50 mL) charged with a magnetic stir bar, cinnamic acid derivative (5 mmol, 1 equiv) was dissolved in THF (10 mL), and then triethyl amine (1 mmol, 1 equiv) was added under nitrogen atmosphere. The reaction mixture cooled to -7 °C, and $ClCO_2Et$ (1 mmol, 1 equiv) was slowly added. The resulted reaction mixture was stirred for 1 hour at -7 °C and brought to room temperature. Further, the reaction mixture was filtered, and the filtrate was transferred to another oven-dried round bottom flask. $NaBH_4$ (3 mmol, 3 equiv) in MeOH (10 mL) was added drop by drop at 0 °C. The reaction mixture was further stirred at room temperature for 8-12 h, and the solvent was removed under reduced pressure. The resulted residue was dissolved in water (10 mL), and extracted using ethyl acetate (10 mL × 3). The collected organic layer was washed with brine and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure using a rotavapor. The residue obtained was purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) as an eluent, which provided the corresponding cinnamyl alcohol derivatives.[2]

Optimization of reaction condition

The investigation on cross-coupling of allylic alcohols with 1,2-diols was experimented by employing cinnamyl alcohol, and 1-phenylethan-1,2-diol as the benchmark substrates and Ru-macho pincer catalyst **1**. The reaction of cinnamyl alcohol (0.5 mmol, 1 equiv), and 1-phenylethan-1,2-diol (0.5 mmol, 1 equiv) using a catalyst **1** (1 mol %) and base (NaOH, 30 mol %) in tamyl alcohol at 100 °C was performed under nitrogen atmosphere for 24 h, which delivered the anticipated hydroxy functionalized lactone in 41% yield (Table S1, entry 1). Performing a reaction using higher amount of base (50 mol %) at elevated temperature (135 °C) provided the product in 51% yield (Table S1, entry 2). Gratifyingly, upon carrying out a reaction using 50 mol % of base at 100 °C, the hydroxy lactone product was obtained in 67% of yield (Table S1, entry 3). Use of THF as a solvent, turned out to be detrimental to the reaction (Table S1, entry 4). Employing other bases such as LiO^{t}Bu, KO^{t}Bu, LiOH, and KOH provided the product in diminished yields (Table S1, entries 5-8). Reactions performed using increased catalyst load (2 mol %), and base (75 mol %) provided the product in 34% and 42% yields, respectively (Table S1, entries 9 and 10). Hence, a reaction was performed for 36 h following the conditions used for entry 3 of Table 1 in which hydroxy lactone was isolated in 75% yield (Table S1, entry 11). Moreover, the reactions repeated in closed conditions using dioxane solvent and increased temperature of 135 °C, resulted in lower yields of lactone (Table S1, entries 12 and 13). Control experiment carried out in the absence of catalyst **1** under the optimized condition provided no product formation (Table S1, entry 14). Other weaker carbonate bases were also tested under the optimized condition, which provided the desired product in diminished yields (Table S1, entries 15-17).

Table S1. Optimization of reaction conditions for catalytic coupling of allylic alcohols and 1,2-diols[a]



entry	base	base (mol%)	temp (°C)	yield (%)[b]
1	NaOH	30	100	41
2	NaOH	50	135	51
3	NaOH	50	100	67
4[c]	NaOH	50	100	-
5	LiO^{t}Bu	50	100	55
6	KO^{t}Bu	50	100	62
7	LiOH	50	100	35
8	KOH	50	100	17
9[d]	NaOH	50	100	34
10	NaOH	75	100	42
11[e]	**NaOH**	**50**	**100**	**75**
12[f,g]	NaOH	50	135	31
13[g]	NaOH	50	135	45
14[h]	NaOH	50	100	-
15[e]	K_2CO_3	50	100	35
16[e]	Na_2CO_3	50	100	32
17[e]	Cs_2CO_3	50	100	47

[a]1-Phenylethan-1,2-diol (0.5 mmol, 1 equiv), cinnamyl alcohol (0.5 mmol, 1 equiv), ^{t}amyl alcohol (2 mL), catalyst **1** (1 mol %), and base were heated in a 25 mL Schlenk tube at an indicated temperature under nitrogen flow. [b]Yields are reported after isolation. [c]THF was used as a solvent. [d]2 mol % of catalyst 1 was used. [e]The reaction was carried out for 36 h. [f]1,4-Dioxane was used as the solvent. [g]The reaction was carried out in a closed condition in a 25 mL sealed tube. [h]The reaction was carried out in the absence of catalyst **1**.

General optimization procedure for the catalytic synthesis of functionalized lactones: A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005-0.01 mmol), base (0.15-0.38 mmol), 1-phenylethan-1,2-diol (0.5 mmol), cinnamyl alcohol (0.5 mmol) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the reaction mixture was heated at 100 - 135 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 24-36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane (15:85) mixture as an eluent. Yields were calculated for isolated pure products.

General procedure for the catalytic synthesis of functionalized lactones: A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol, 3 mg), NaOH (0.25 mmol, 10 mg), 1,2-diol (0.5 mmol, 69 mg), allylic alcohol (0.5 mmol, 67 µL) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in

an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. Yields were calculated for isolated pure products.

Spectral data for the functionalized lactones:

5-(Hydroxy(phenyl)methyl)-4-phenyldihydrofuran-2(3H)-one (2): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White solid. Yield: 100 mg, 75%. IR (ATR): 3092, 2841, 1819, 1134, 1091, 389 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.18 (m, 5H), 7.17-7.05 (m, 3H), 6.84-6.76 (m, 2H), 5.06 (d, J = 3.1 Hz, 1H), 4.67 (dd, J_1 = 4.6, J_2 = 3.1 Hz, 1H), 3.55 (dt, J_1 = 0.1, J_2 = 5.1 Hz, 1H), 2.99 (dd, J_1 = 18.2, J_2 =10.0 Hz, 1H), 2.52 (dd, J_1 = 18.2, J_2 = 5.6 Hz, 1H), 1.19 (s, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 176.70, 142.07, 137.95, 128.95, 128.62, 128.24, 127.12, 126.55, 126.18, 89.66, 73.84, 39.71, 37.20. HRMS (ESI) m/z calcd for $C_{17}H_{17}O_3$ $(M+H)^+$: 269.1178, found: 269.0916.

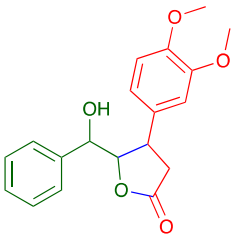
5-(Hydroxy(phenyl)methyl)-4-(p-tolyl)dihydrofuran-2(3H)-one (3): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. Pale yellow solid. Yield: 92 mg, 65%. IR (ATR): 3093, 2863, 1817, 1259, 1159, 296 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.17 (m, 5H), 7.11-6.96 (m, 2H), 6.91 (d, J = 8.1 Hz, 2H), 4.67 (d, J = 3.9 Hz, 1H), 4.58 (dd, J_1 = 6.4, J_2 =3.8 Hz, 1H), 4.37 (d, J = 4.3 Hz, 1H), 3.67-3.52 (m, 1H), 2.90-2.69 (m, 1H), 2.62-2.48 (m, 1H), 224 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 176.12, 139.20, 137.67, 137.35, 133.80, 129.84, 129.71, 129.58, 128.71, 128.58, 128.14, 128.06, 127.32, 126.96, 89.45, 86.20, 85.58, 74.27, 73.25, 72.09, 43.59, 42.99, 42.28, 37.22, 36.97, 35.39, 21.20, 21.10. HRMS (ESI) m/z calcd for $C_{18}H_{19}O_3$ $(M+H)^+$: 282.1256, found: 282.1244.

5-(Hydroxy(phenyl)methyl)-4-(4-isobutylphenyl)dihydrofuran-2(3H)-one (4): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. Yellow sticky liquid. Yield: 91 mg, 56%. IR (ATR): 3088, 2914, 1803, 1243, 1158, 306 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.18 (m, 5H), 7.00 (d, J = 17.7 Hz, 2H), 6.59 (d, J = 7.9 Hz, 1H), 6.35-6.25 (m, 1H), 5.10 (d, J = 3.1 Hz, 1H), 4.71-4.62 (m, 1H), 3.52 (ddd, J_1 = 10.0, J_2 = 5.5, J_3 = 4.5 Hz, 1H), 3.02 (dd, J_1 = 18.2, J_2 = 10.0 Hz, 1H), 2.50 (dd, J_1 = 18.2, J_2 = 5.5 Hz, 1H), 1.89-1.73 (m, 1H), 1.66 (s, 1H), 0.94-0.78 (m, 6H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 176.89, 148.10, 146.62, 138.12, 136.04, 129.83, 128.68, 128.27, 127.03, 126.78, 126.24, 119.77, 108.55, 106.94, 101.17, 89.99, 73.73, 44.99, 42.47, 39.52, 37.37, 30.25, 22.39. HRMS (ESI) m/z calcd for $C_{21}H_{25}O_3$ $(M+H)^+$: 325.1127, found: 325.1112.

5-(Hydroxy(phenyl)methyl)-4-(2-methoxyphenyl)dihydrofuran-2(3H)-one (5): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. Yellow oil. Yield: 100 mg, 67%. IR (ATR): 3533, 2936, 1815, 1262, 1083, 314 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): ^1H NMR

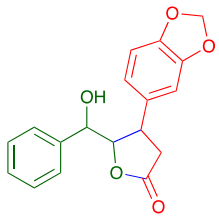
(400 MHz, $CDCl_3$) δ 8.43-6.44 (m, 9H), 5.06-3.89 (m, 2H), 3.83 - 3.55 (m, 3H), 3.29-2.48 (m, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 177.27, 157.51, 157.17, 157.06, 140.06, 139.21, 138.39, 133.78, 130.36, 130.06, 129.18, 129.13, 128.92, 128.70, 128.67, 128.63, 128.61, 128.57, 128.55, 128.30, 128.13, 127.27, 127.13, 126.42, 125.53, 120.96, 120.92, 120.74, 111.10, 110.95, 110.52, 88.60, 88.03, 85.03, 75.62, 74.00, 73.58, 55.38, 55.25, 39.43, 39.35, 36.86, 35.81, 35.22, 33.40. HRMS (ESI) m/z calcd for $C_{18}H_{19}O_4$ $(M+H)^+$: 299.7652, found: 299.7642.

4-(3,4-Dimethoxyphenyl)-5-(hydroxy(phenyl)methyl)dihydrofuran-2(3H)-one (6):



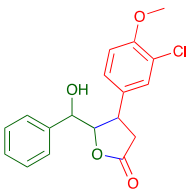
Purified by silica-gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Yellow oil. Yield: 113 mg, 69%. IR (ATR): 3095, 2894, 1143, 1282, 1048, 421 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52-7.22 (m, 4H), 6.91-6.57 (m, 4H), 4.78-4.32 (m, 1H), 4.16-3.97 (m, 1H), 3.87-3.80 (m, 6H), 2.90 (t, J = 7.7 Hz, 1H), 2.65 (t, J = 7.7 Hz, 1H), 2.53 (s, 1zH). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 173.20, 153.77, 147.77, 132.97, 130.24, 128.63, 128.24, 126.94, 126.26, 124.63, 120.20, 112.41, 111.78, 111.46, 111.31, 110.42, 56.01, 55.91, 35.90, 30.39, 29.77. HRMS (ESI) m/z calcd for $C_{19}H_{20}O_5Na$ $(M+Na)^+$: 351.1442, found: 351.1416.

4-(Benzo[d][1,3]dioxol-5-yl)-5-(hydroxy(phenyl)methyl)dihydrofuran-2(3H)-one (7):



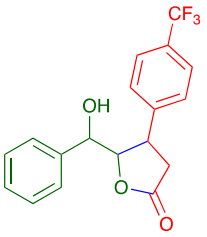
Purified by silica-gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. Pale yellow oil. Yield: 89 mg, 51%. IR (ATR): 3529, 2891, 1825, 1474, 1093, 368 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60-7.06 (m, 5H), 6.75-6.43 (m, 2H), 6.28-6.19 (m, 2H), 5.81 (s, 1H), 5.04 (d, J = 3.0 Hz, 1H), 4.65-4.51 (m, 1H), 3.70-3.34 (m, 1H), 3.04-2.40 (m, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.04, 148.00, 146.52, 138.06, 136.00, 130.15, 128.64, 128.59, 128.47, 128.16, 126.91, 126.16, 121.14, 119.69, 108.90, 108.47, 106.87, 101.10, 100.78, 90.05, 73.56, 62.16, 39.39, 37.32, 31.79. HRMS (ESI) m/z calcd for $C_{18}H_{17}O_5$ $(M+H)^+$: 313.3735, found: 313.3731.

4-(3-Chloro-4-methoxyphenyl)-5-(hydroxy(phenyl)methyl)dihydrofuran-2(3H)-one (8):



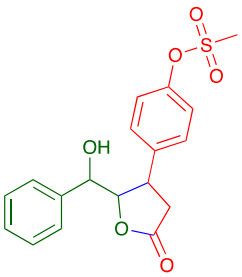
Purified by silica-gel column chromatography using ethyl acetate/hexane (25:75) mixture as an eluent. Pale yellow liquid. Yield: 111 mg, 67%. IR (ATR): 3086, 2853, 1835, 1462, 1073, 384 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (tt, J_1 = 11.6, J_2 = 5.9 Hz, 5H), 7.09-6.92 (m, 1H), 6.89-6.79 (m, 1H), 6.78-6.67 (m, 1H), 5.10-4.62 (m, 1H), 4.59-4.26 (m, 1H), 3.91-3.71 (m, 3H), 2.83-2.40 (m, 2H), 1.18 (s, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 175.71, 154.56, 154.26, 139.02, 138.78, 133.29, 130.25, 130.12, 129.75, 128.97, 128.63, 128.56, 128.52, 128.45, 127.96, 127.25, 126.95, 126.86, 126.15, 126.11, 126.05, 122.81, 112.50, 112.33, 112.20, 89.31, 85.90, 74.45, 73.26, 56.25, 42.98, 41.65, 37.11, 35.32, 31.60, 29.07, 22.67, 14.15, 11.46. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClO_4Na$ $(M+Na)^+$: 335.0713, found: 335.0708.

5-(Hydroxy(phenyl)methyl)-4-(4-(trifluoromethyl)phenyl)dihydrofuran-2(3H)-one (9):



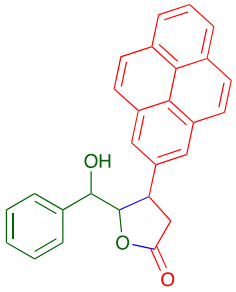
Purified by silica-gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. White solid. Yield: 121 mg, 72%. IR (ATR): 3561, 1883, 1292, 1173, 1046, 714 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.42 (m, 2H), 7.29-7.18 (m, 5H), 7.11 (d, J = 8.0 Hz, 2H), 4.72 (dd, J_1 = 4.7, J_2 = 1.7 Hz, 1H), 4.62 (ddd, J_1 = 5.3, J_2 = 4.6, J_3 = 0.8 Hz, 1H), 3.72-3.58 (m, 1H), 2.86 (ddd, J_1 = 18.1, J_2 = 9.6, J_3 = 1.8 Hz, 1H), 2.56 (ddd, J_1 = 18.0, J_2 = 7.7, J_3 = 1.4 Hz, 1H), 1.69 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 176.67, 176.32, 175.45, 146.24, 146.00, 144.48, 144.46, 138.95, 138.47, 137.87, 128.76, 128.70, 128.64, 128.63, 128.61, 127.41, 127.12, 126.97, 126.03, 125.99, 125.91, 125.37, 125.33, 125.29, 125.25, 123.01, 122.60, 122.53, 119.83, 89.66, 88.99, 85.48, 74.77, 74.67, 73.22, 73.19, 72.35, 68.07, 61.91, 44.63, 43.83, 43.19, 42.45, 39.15, 36.97, 36.33, 35.76, 34.79, 33.81, 31.87, 29.71. $^{19}F\{^{1}H\}$ NMR (376.5 MHz, $CDCl_3$) δ -62.30, -62.36, -62.45, -62.59, -62.63, -62.66, -62.67, -62.68. HRMS (ESI) m/z calcd for $C_{18}H_{15}F_3O_3Na$ $(M+Na)^+$: 359.0871, found: 359.0869.

4-(2-(Hydroxy(phenyl)methyl)-5-oxotetrahydrofuran-3-yl)phenylmethanesulfonate (10):

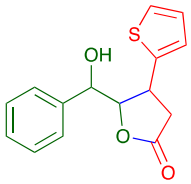


Purified by silica-gel column chromatography using ethyl acetate/hexane (20:85) mixture as an eluent. Pale yellow solid. Yield: 114 mg, 63%. IR (ATR): 3504, 1837, 1482, 1132, 1081, 727 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-7.28 (m, 4H), 7.27-6.96 (m, 3H), 6.88-6.14 (m, 2H), 5.06-4.65 (m, 1H), 4.46-4.11 (m, 1H), 3.97-3.51 (m, 2H), 3.39-2.80 (m, 3H), 1.18 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 166.81, 150.32, 145.61, 143.82, 140.42, 139.79, 139.74, 133.52, 130.14, 129.79, 128.69, 128.66, 128.57, 128.47, 128.39, 128.30, 128.21, 128.05, 127.36, 126.63, 126.23, 126.10, 122.61, 118.72, 116.01, 114.44, 74.72, 72.70, 72.55, 69.53, 69.33, 68.07, 37.72. HRMS (ESI) m/z calcd for $C_{18}H_{18}O_6SNa$ $(M+Na)^+$: 385.0722, found: 385.0718.

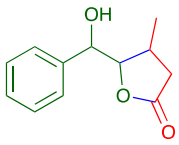
5-(Hydroxy(phenyl)methyl)-4-(pyren-2-yl)dihydrofuran-2(3H)-one (11): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. Brown-yellow solid. Yield: 110 mg, 56%. IR (ATR): cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.12 (m, 4H), 8.10-7.92 (m, 7H), 7.89-7.73 (m, 2H), 5.25 (t, J = 2.9 Hz, 1H), 4.95-4.66 (m, 1H), 3.77 (td, J_1 = 6.3, J_2 = 1.2 Hz, 1H), 3.49-3.35 (m, 1H), 1.59 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 128.92, 127.96, 127.59, 127.37, 126.98, 126.75, 126.19, 125.93, 125.47, 125.12, 124.99, 124.83, 123.42, 121.73, 62.51, 34.63, 29.73. HRMS (ESI) m/z calcd for $C_{27}H_{21}O_3$ $(M+H)^+$: 393.4489, found: 393.4465.



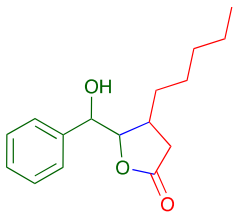
5-(Hydroxy(phenyl)methyl)-4-(thiophen-2-yl)dihydrofuran-2(3H)-one (12): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. Dark yellow solid. Yield: 71 mg, 52%. IR (ATR): 3129, 1866, 1474, 1173, 1029, 304 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.17 (m, 5H), 7.01 (dd, J_1 = 5.1, J_2 = 1.2 Hz, 1H), 6.73 (dd, J_1 = 5.2, J_2 = 3.5 Hz, 1H), 6.46 (dt, J_1 = 3.6, J_2 = 1.0 Hz, 1H), 5.09 (d, J = 3.0 Hz, 1H), 4.71 (dd, J_1 = 5.0, J_2 = 3.0 Hz, 1H), 3.91-3.81 (m, 1H), 3.02 (dd, J_1 = 18.0, J_2 = 9.8 Hz, 1H), 2.61 (dd, J =, 6.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 175.74, 144.73, 137.76, 128.70, 128.34, 127.09, 126.23, 124.17, 124.11, 89.64, 73.54, 37.78, 35.23. HRMS (ESI) m/z calcd for $C_{15}H_{14}O_3SNa$ $(M+H)^+$: 297.0561, found: 297.0541.



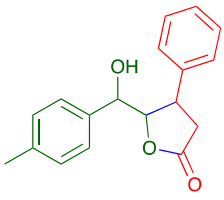
5-(Hydroxy(phenyl)methyl)-4-methyldihydrofuran-2(3H)-one (13): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White solid. Yield: 55 mg, 53%. IR (ATR): 3543, 3027, 1817, 1352, 1164, 324 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.28-7.22 (m, 5H), 4.89-4.43 (m, 1H), 4.35-3.77 (m, 1H), 2.90-1.95 (m, 3H), 1.37-0.60 (m, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 176.31, 138.71, 133.70, 130.25, 128.86, 128.83, 128.75, 128.56, 127.29, 127.13, 126.95, 89.90, 85.52, 75.72, 73.46, 37.32, 36.89, 31.71, 18.58, 14.24. HRMS (ESI) m/z calcd for $C_{12}H_{14}O_3Na$ $(M+Na)^+$: 229.0874, found: 229.0856.



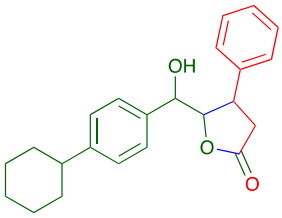
5-(Hydroxy(phenyl)methyl)-4-pentyldihydrofuran-2(3H)-one (14): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White Sticky Liquid. Yield: 46 mg, 27%. IR (ATR): 3528, 2937, 1846, 1194, 1074, 302 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.20 (m, 5H), 5.35-4.51 (m, 1H), 4.31-4.18 (m, 1H), 2.90 (s, 1H), 2.60 (ddd, J_1 = 47.4, J_2 = 17.8, J_3 = 9.3 Hz, 1H), 2.31-1.94 (m, 1H), 1.36-0.63 (m, 12H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 177.77, 138.80, 138.46, 128.72, 128.58, 128.05, 127.01, 126.95, 126.02, 88.44, 75.67, 73.70, 36.43, 35.33, 34.86, 34.56, 33.82, 33.61, 33.37, 31.78, 31.65, 31.33, 31.17, 29.04, 28.92, 26.61, 26.32, 24.74, 22.61, 22.51, 22.34, 14.08, 13.93, 13.88. HRMS (ESI) m/z calcd for $C_{16}H_{23}O_3$ $(M+H)^+$: 263.1730, found: 263.1705.



5-(Hydroxy(p-tolyl)methyl)-4-phenyldihydrofuran-2(3H)-one (15): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White solid. Yield: 95 mg, 67%. IR (ATR): 3146, 2293, 1632, 1248, 1128, 243 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-6.72 (m, 9H), 4.78-4.44 (m, 2H), 3.66-3.45 (m, 1H), 2.88 (ddd, J_1 = 53.9, J_2 = 18.1, J_3 = 9.7 Hz, 1H), 2.59-2.43 (m, 1H), 2.24 (d, J = 8.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 177.25, 176.25, 142.32, 140.60, 138.39, 137.95, 136.10, 135.22, 129.35, 129.25, 129.14, 129.02, 128.88, 128.25, 127.52, 127.27, 127.17, 127.09, 126.93, 126.68, 126.30, 90.03, 89.53, 74.26, 73.77, 73.09, 42.63, 39.90, 37.26, 37.20, 21.23. HRMS (ESI) m/z calcd for $C_{18}H_{19}O_3$ $(M+H)^+$: 282.1256, found: 282.1248.

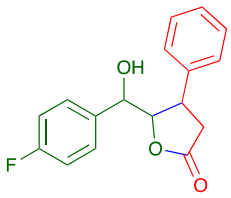


5-((4-Cyclohexylphenyl)(hydroxy)methyl)-4-phenyldihydrofuran-2(3H)-one (16):



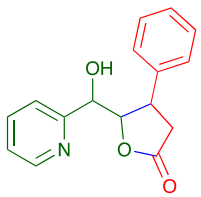
Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White solid. Yield: 137 mg, 78%. IR (ATR): 3517, 2985, 1814, 1179, 1047, 753 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 - 7.18 (m, 2H), 7.17-6.94 (m, 6H), 6.78 (dd, J_1 = 7.8, J_2 = 1.7 Hz, 1H), 5.00 (d, J = 3.0 Hz, 1H), 4.63 (dd, J_1 = 4.8, J_2 = 3.0 Hz, 1H), 3.63-3.49 (m, 1H), 2.95 (dd, J_1 = 18.2, J_2 = 10.0 Hz, 1H), 2.65-2.46 (m, 1H), 2.19 (s, 1H), 1.89-1.62 (m, 6H), 1.45-1.08 (m, 5H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$ δ 177.11, 148.3, 142.18, 135.47, 129.11, 128.96, 128.54, 128.51, 127.12, 127.09, 127.03, 126.72, 126.27, 125.97, 90.01, 73.60, 62.39, 44.37, 39.82, 37.37, 37.31, 34.56, 34.50, 34.28, 32.15, 26.95, 26.21. HRMS (ESI) m/z calcd for $C_{23}H_{26}O_3$ $(M+H)^+$: 351.1846, found: 351.1823.

5-((4-Fluorophenyl)(hydroxy)methyl)-4-phenyldihydrofuran-2(3H)-one (17): Purified by silica-gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. White solid. Yield: 99 mg, 69%. IR (ATR): 3534, 3004, 1839, 1245, 1030, 807 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.08 (m, 5H), 7.06-6.97 (m, 2H), 6.90 (t, J = 8.6 Hz, 2H), 4.68 (d, J = 4.3 Hz, 1H), 4.59 (dd, J_1 = 6.6, J_2 = 4.3 Hz, 1H), 3.56 (td, J_1 = 9.0, J_2 = 6.8 Hz, 1H), 2.88 (dd, J_1 = 18.1, J_2 = 9.5 Hz, 1H), 2.60 (dd, J_1 = 18.1, J_2 = 8.2 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 175.55, 163.99, 161.53, 140.04, 134.69, 134.66, 129.30, 129.14, 128.83, 128.75, 128.06, 127.60, 127.45, 126.97, 115.64, 115.61, 115.43, 89.14, 74.02, 42.78, 37.24. $^{19}F\{^{1}H\}$ NMR (376.5 MHz, $CDCl_3$): δ -112.28, -113.18, -113.21, -113.81, -113.86, -113.92, -113.92, -113.97. HRMS (ESI) m/z calcd for $C_{17}H_{15}FO_3Na$ $(M+Na)^+$: 309.0951, found: 309.09149.



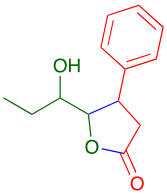
5-(Hydroxy(naphthalen-2-yl)methyl)-4-phenyldihydrofuran-2(3H)-one (18): Purified by silica-gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. White solid. Yield: 101 mg, 64%. IR (ATR): 3516, 2943, 1823, 1334, 1165, 1091 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.68 (m, 6H), 7.51-7.39 (m, 3H), 7.17-7.05 (m, 2H), 5.42-4.88 (m, 1H), 4.85-4.59 (m, 1H), 3.79-3.60 (m, 1H), 3.17-3.00 (m, 1H), 2.72-2.56 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 179.79, 140.28, 133.15, 129.14, 128.95, 128.11, 127.76, 127.08, 126.62, 126.45, 126.21, 125.50, 124.49, 89.28, 74.59, 42.86, 37.23. HRMS (ESI) m/z calcd for $C_{21}H_{19}O_3$ $(M+H)^+$: 319.1346, found: 319.1300.

5-(hydroxy(pyridin-2-yl)methyl)-4-phenyldihydrofuran-2(3*H*)-one (19): Purified by silica-gel column chromatography using ethyl acetate/hexane (20:80) mixture as an eluent. White liquid. Yield: 60 mg, 45%. IR (ATR): 3347, 2893, 1814, 1654, 1140, 1072 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.23 (m, 5H), 7.22-6.73

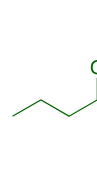


(m, 4H), 5.22-4.85 (m, 1H), 4.85-4.48 (m, 1H), 3.84-3.28 (m, 1H), 3.24-2.56 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.83, 142.06, 140.26, 129.25, 129.03, 128.96, 128.70, 128.31, 128.17, 128.02, 127.71, 127.12, 126.95, 126.71, 126.21, 126.07, 125.69, 88.81, 85.62, 85.39, 70.31, 69.03, 43.91, 43.25, 42.70, 37.12, 36.81, 35.16, 32.01, 22.78, 14.22. HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_3$ $(M+H)^+$: 297.1068, found: 297.1071.

5-(1-Hydroxypropyl)-4-phenyldihydrofuran-2(3H)-one (20): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White liquid. Yield: 26 mg, 75%. IR (ATR): 3517, 3012, 1815, 1423, 1182, 1068 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.19 (m, 3H), 6.45 (d, J = 16.0 Hz, 2H), 4.52 (dd, J_1 = 6.0, J_2 = 3.1 Hz, 1H), 4.10 - 3.49 (m, 1H), 3.41-2.85 (m, 1H), 2.77-2.48 (m, 2H), 1.86-1.12 (m, 2H), 1.08-0.69 (m, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 171.94, 146.99, 134.19, 130.79, 129.33, 129.05, 128.64, 128.44, 128.37, 127.15, 126.44, 117.50, 88.85, 45.69, 35.68, 30.75, 29.79. HRMS (ESI) m/z calcd for $C_{13}H_{17}O_3$ $(M+H)^+$: 221.1263, found: 221.1261.

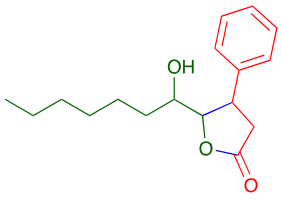


5-(1-Hydroxybutyl)-4-phenyldihydrofuran-2(3H)-one (21): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. White liquid. Yield: 66 mg, 56%. IR (ATR): 3452, 1813, 1284, 1027, 761 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR δ 7.44-7.14 (m, 5H), 4.84 (t, J = 8.0 Hz, 1H), 3.63-3.24 (m, 1H), 2.84-2.66 (m, 1H), 2.44-2.24 (m, 1H), 1.85-1.72 (m, 4H), 1.56 (s, 1H), 1.15-1.02 (m, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 179.24, 139.98, 135.39, 129.44, 128.76, 128.66, 128.58, 128.05, 127.70, 127.39, 126.76, 84.32, 83.82, 64.85, 56.43, 51.80, 46.68, 37.15, 32.85, 26.24, 9.21. HRMS (ESI) m/z calcd for $C_{14}H_{19}O_3$ $(M+H)^+$: 235.1420, found: 235.1415.



5-(1-Hydroxypentyl)-4-phenyldihydrofuran-2(3H)-one (22): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an eluent. Pale yellow liquid. Yield: 29 mg, 23%. IR (ATR): 3528, 2827, 1818, 1583, 1138, 1047 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-6.94 (m, 5H), 4.72-3.84 (m, 1H), 3.77-3.29 (m, 1H), 3.27-2.87 (m, 1H), 2.78-2.26 (m, 1H), 1.96-1.02 (m, 7H), 0.97-0.74 (m, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 177.88, 142.37, 140.36, 129.33, 128.89, 128.65, 128.51, 128.38, 128.05, 127.92, 127.84, 127.39, 127.03, 126.44, 125.88, 88.90, 79.15, 78.79, 74.64, 74.46, 71.28, 50.24, 42.92, 42.17, 37.57, 35.91, 35.60, 34.36, 33.98, 33.77, 33.27, 32.19, 30.73, 29.80, 29.43, 27.81, 27.52, 26.85, 22.80, 22.58, 19.82, 14.55, 14.14, 14.01. HRMS (ESI) m/z calcd for $C_{15}H_{21}O_3$ $(M+H)^+$: 249.1501, found: 249.1498.

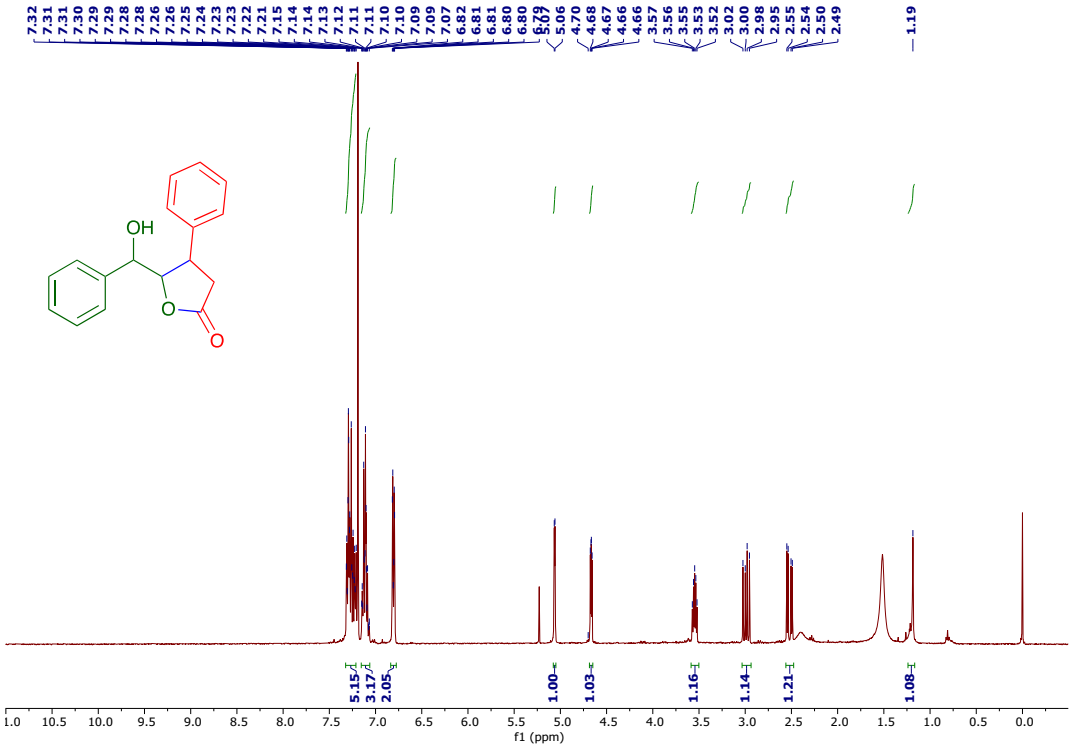
5-(1-Hydroxyheptyl)-4-phenyldihydrofuran-2(3H)-one (23): Purified by silica-gel column chromatography using ethyl acetate/hexane (15:85) mixture as an



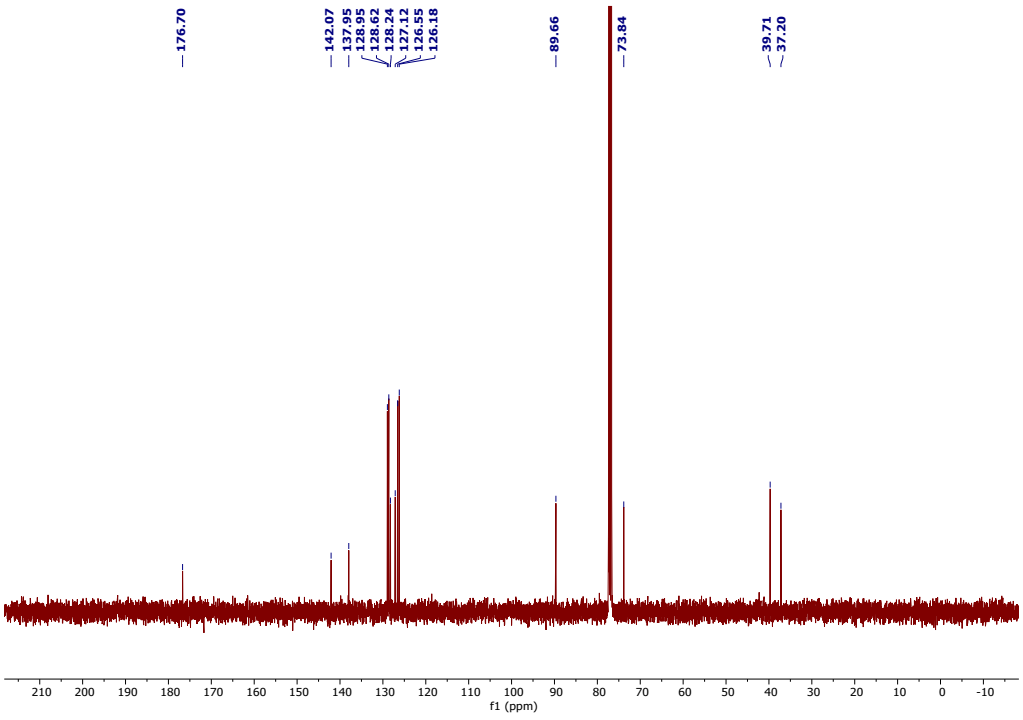
eluent. White solid. Yield: 43 mg, 31%. IR (ATR): 3518, 1825, 1483, 1193, 1037, 734 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.02 (m, 5H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.58 (t, *J* = 6.5 Hz, 1H), 2.92-2.18 (m, 2H), 1.96 (s, 1H), 1.63-1.09 (m, 10H), 0.95-0.71 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 178.34, 171.36, 142.89, 141.83, 139.93, 129.22, 128.89, 128.79, 128.75, 128.53, 128.44, 128.40, 128.28, 127.98, 127.93, 127.83, 127.81, 127.71, 127.29, 127.06, 126.88, 126.56, 126.30, 125.86, 88.86, 79.03, 78.72, 74.42, 71.66, 71.19, 62.19, 60.49, 50.17, 47.29, 45.34, 42.82, 42.32, 40.75, 38.37, 37.74, 37.47, 35.51, 34.14, 33.97, 32.54, 32.24, 32.15, 32.06, 31.97, 31.66, 31.61, 31.45, 30.71, 29.72, 29.42, 29.39, 29.08, 28.77, 27.86, 26.83, 26.27, 25.93, 25.57, 24.73, 23.78, 22.72, 22.67, 22.54, 22.48, 21.06, 14.19, 14.14, 14.12, 14.03. HRMS (ESI) m/z calcd for $C_{17}H_{25}O_3$ $(M+H)^+$: 277.1776, found: 277.17746

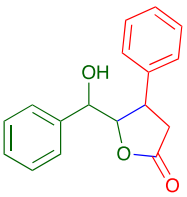
NMR spectra of hydroxy functionalized lactones

^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-phenyldihydrofuran-2(3H)-one (**2**, 400 MHz, $CDCl_3$)

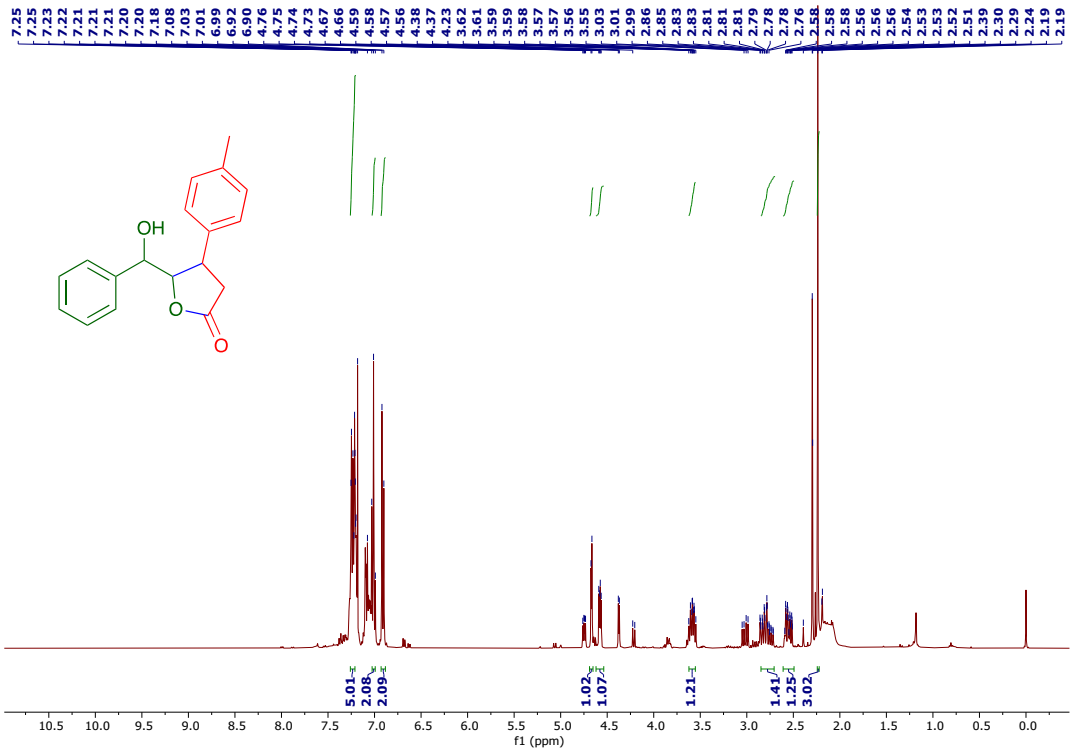


^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-phenyldihydrofuran-2(3H)-one (**2**, 100.6 MHz, $CDCl_3$)



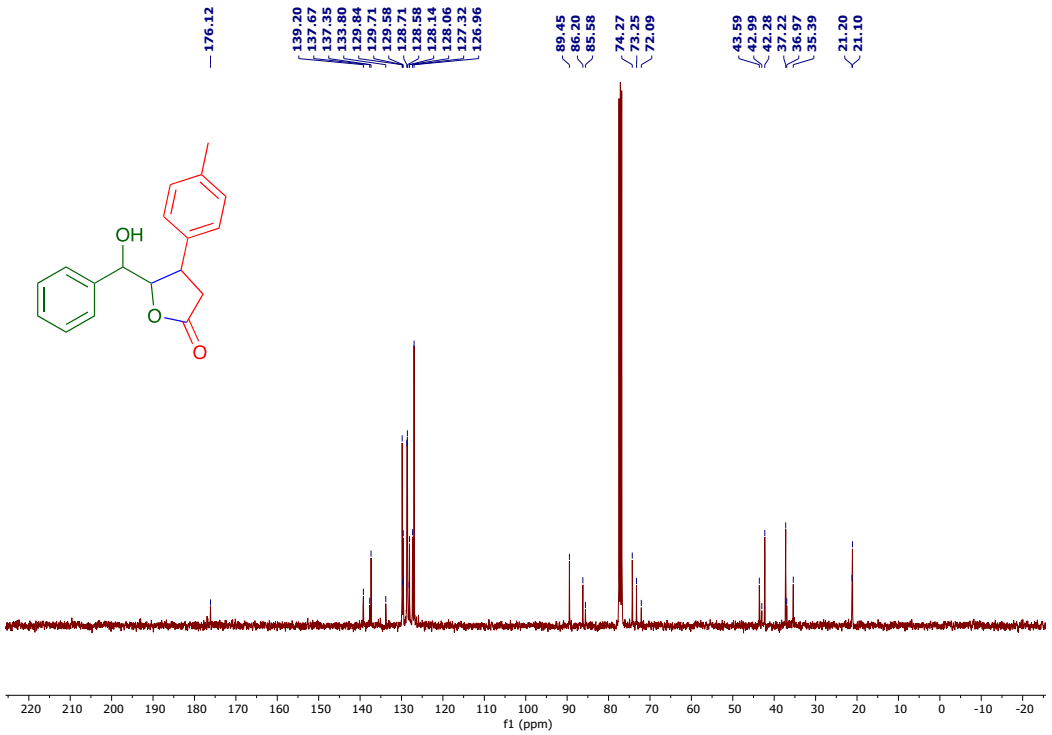


^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(p-tolyl)dihydrofuran-2(3H)-one (**3**, 400

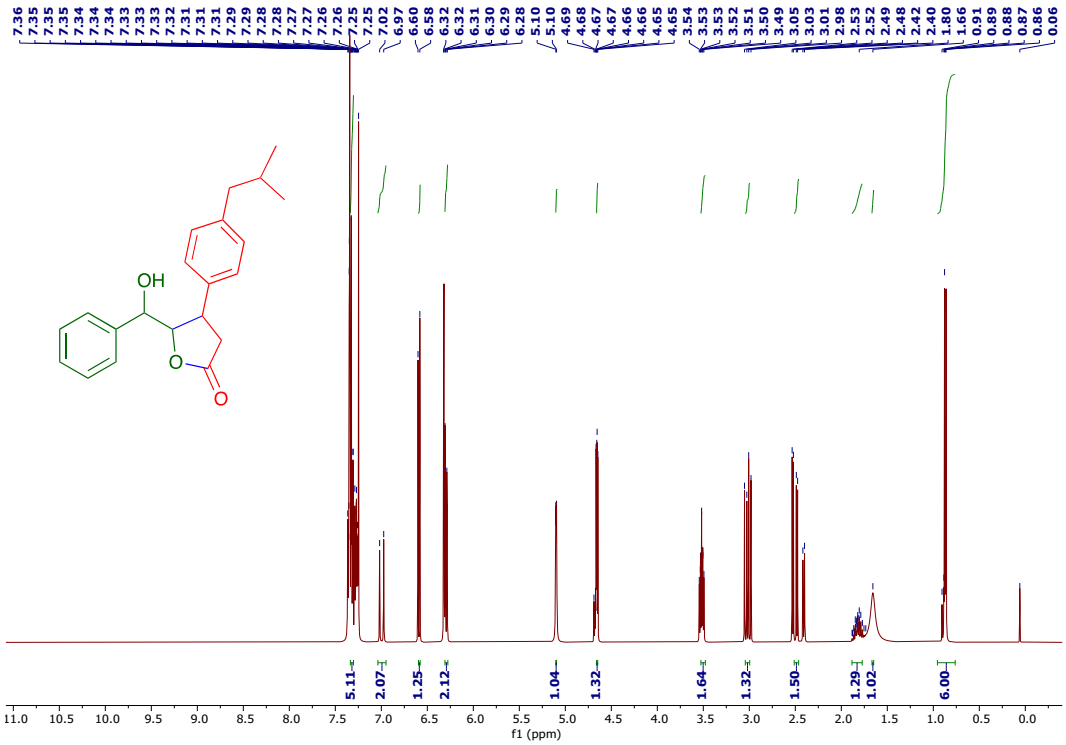


MHz, $CDCl_3$)

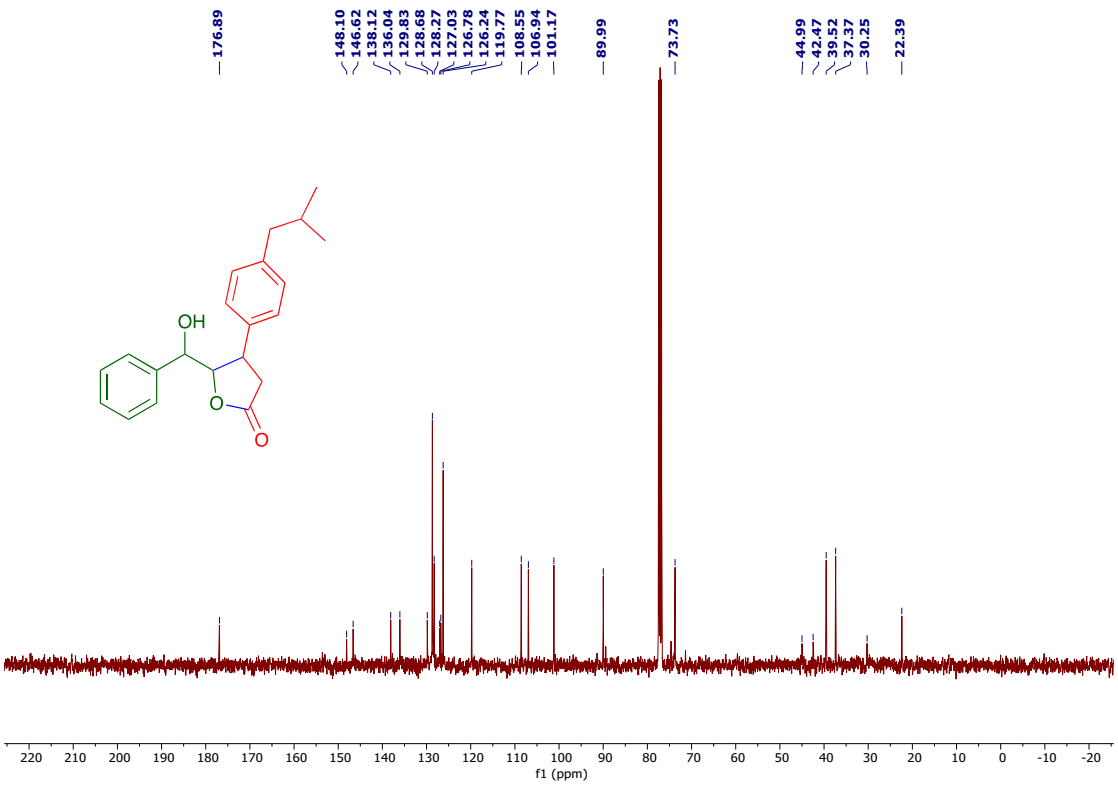
^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(p-tolyl)dihydrofuran-2(3H)-one (**3**, 100.6 MHz, $CDCl_3$)



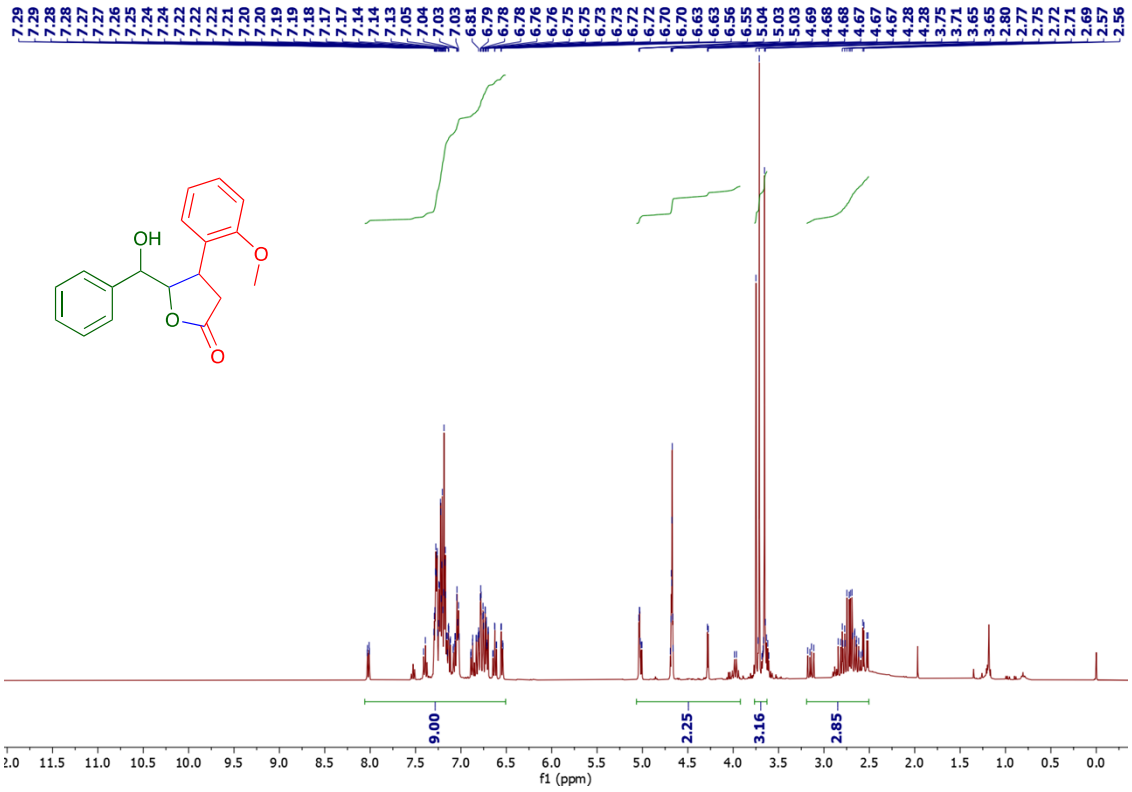
^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(4-isobutylphenyl)dihydrofuran-2(3H)-one (**4**, 400 MHz, $CDCl_3$)



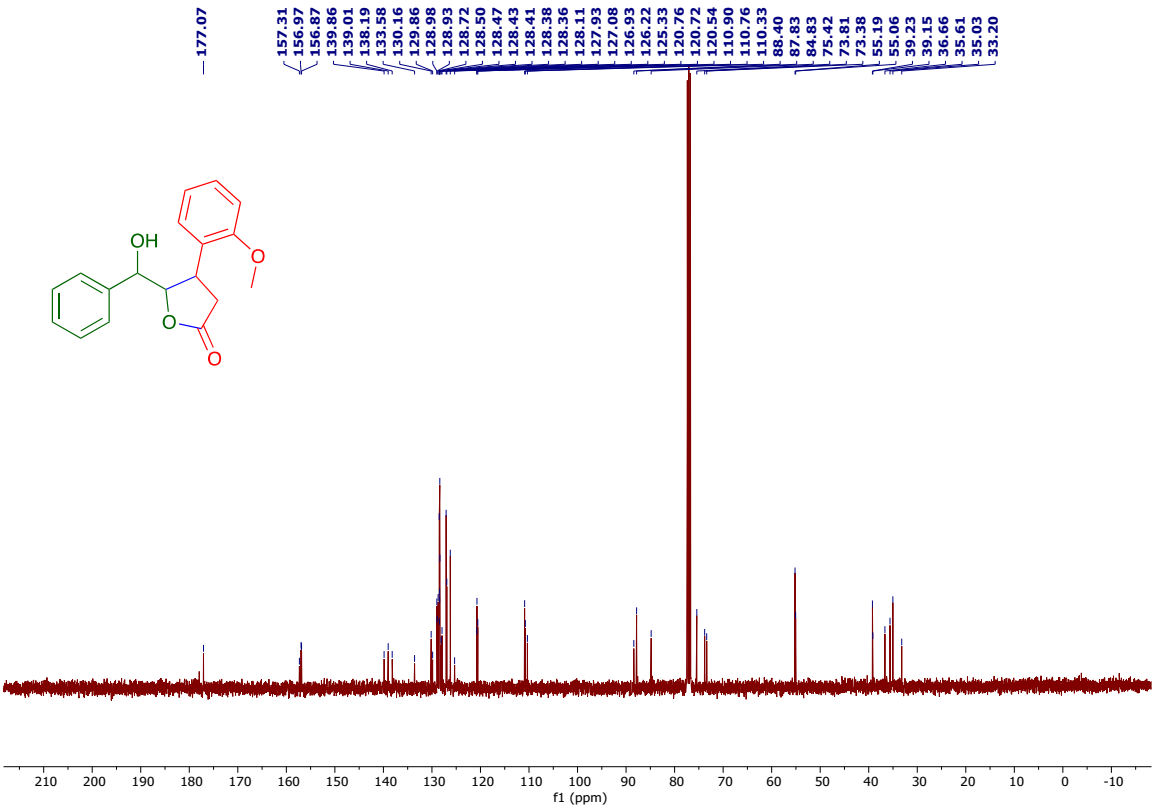
^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(4-isobutylphenyl)dihydrofuran-2(3H)-one (**4**, 100.6 MHz, $CDCl_3$)



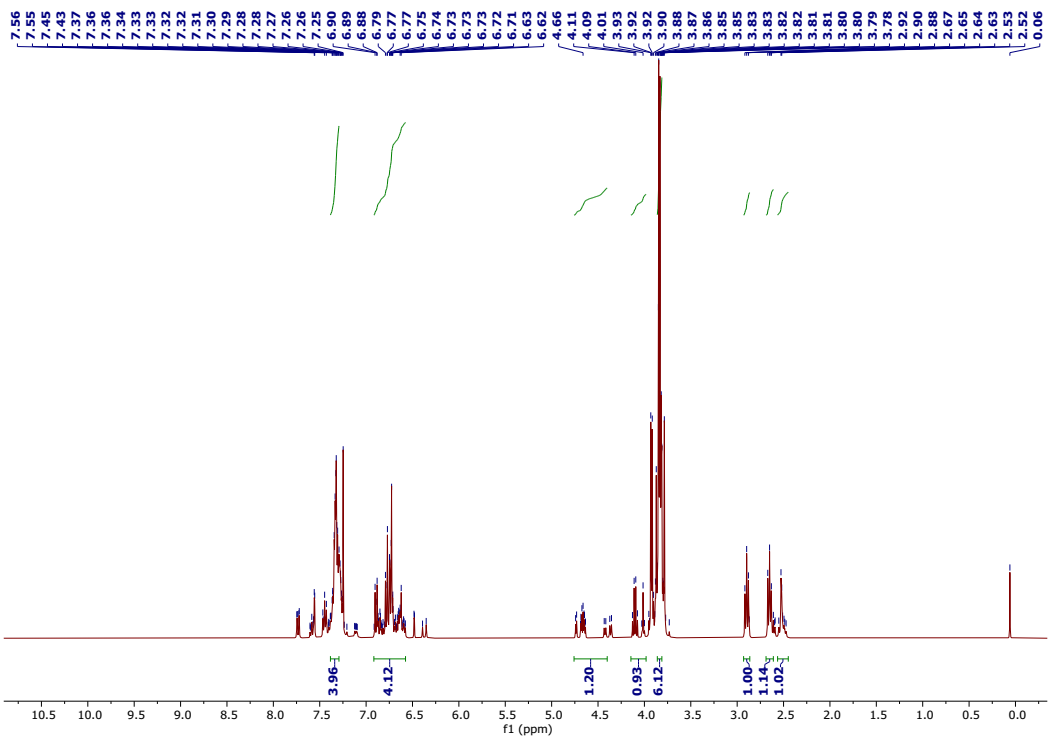
^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(2-methoxyphenyl)dihydrofuran-2(3H)-one (**5**, 400 MHz, $CDCl_3$)

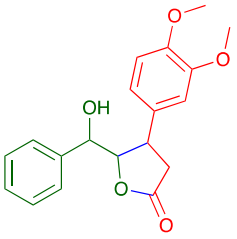


^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(2-methoxyphenyl)dihydrofuran-2(3H)-one (**5**, 100.6 MHz, $CDCl_3$)

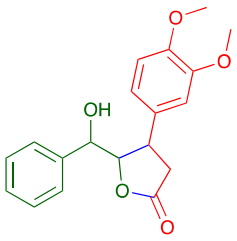


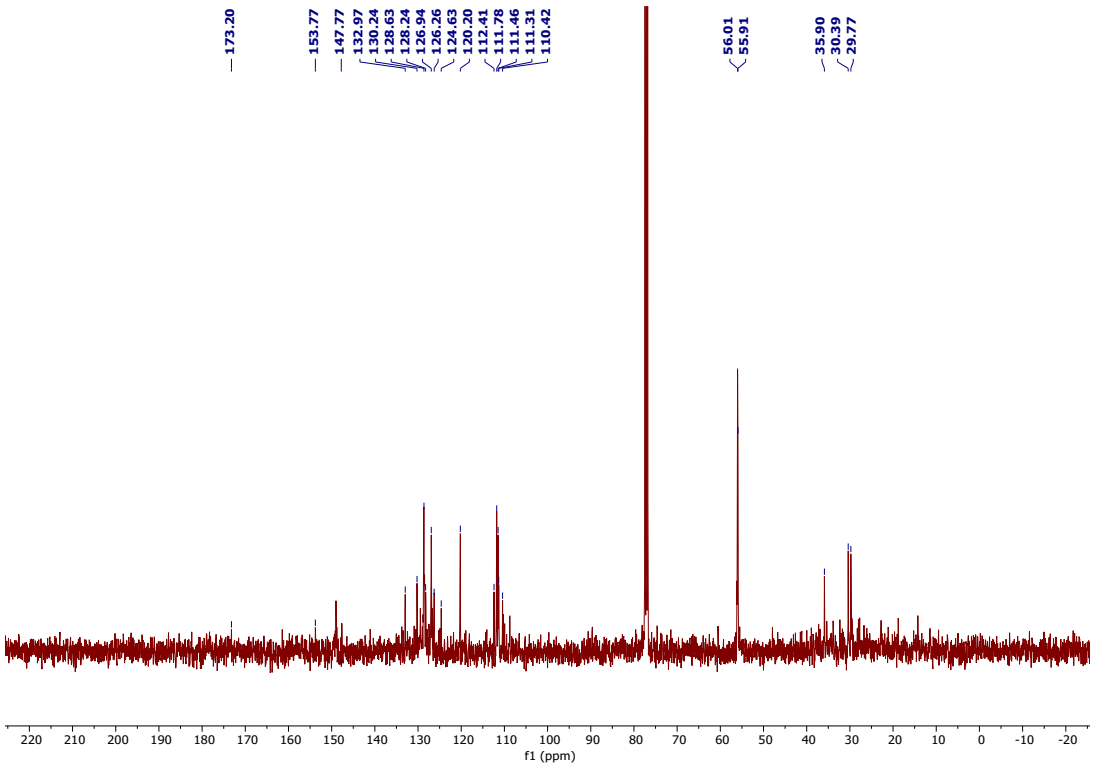
^{1}H NMR spectrum of 4-(3,4-dimethoxyphenyl)-5-(hydroxy(phenyl)methyl)dihydrofuran-2(3H)-one (**6**, 400 MHz, $CDCl_3$)



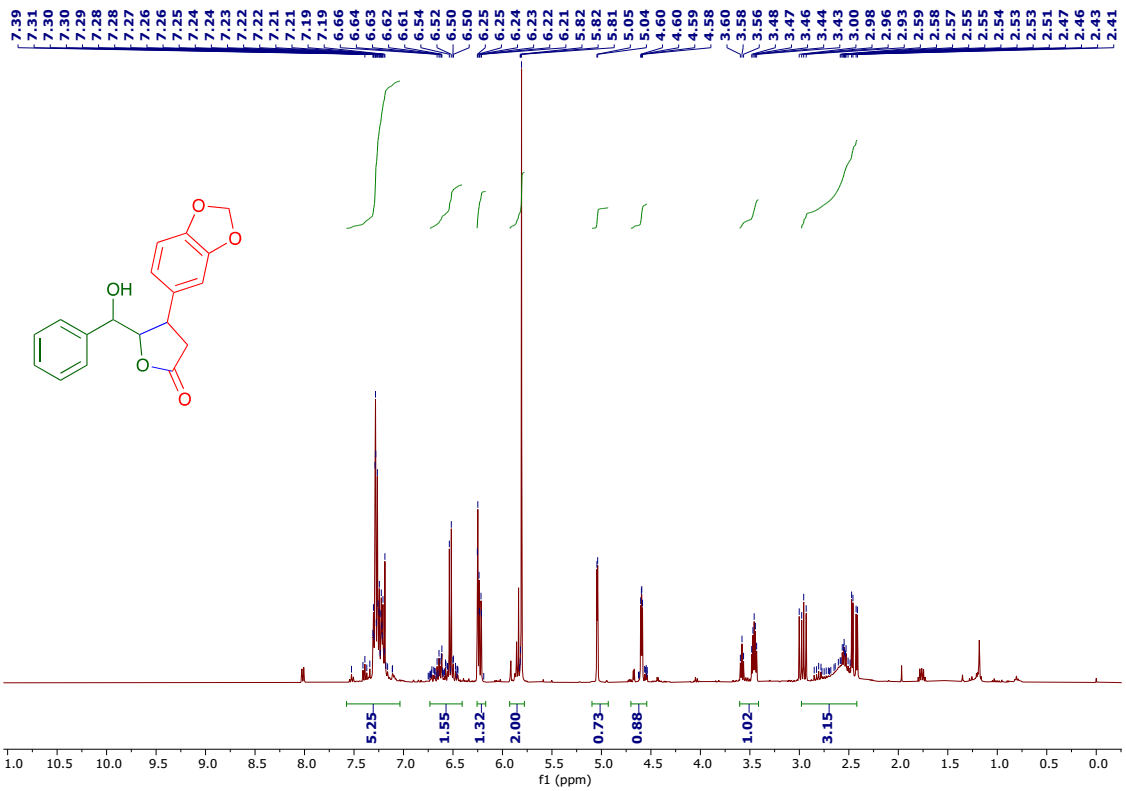


$^{13}C\{^{1}H\}$ NMR spectrum of 4-(3,4-dimethoxyphenyl)-5-(hydroxy(phenyl)methyl)dihydrofura--n-2(3H)-one (**6**, 100.6 MHz, $CDCl_3$)



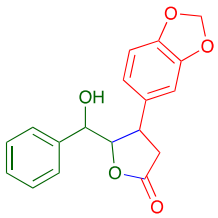


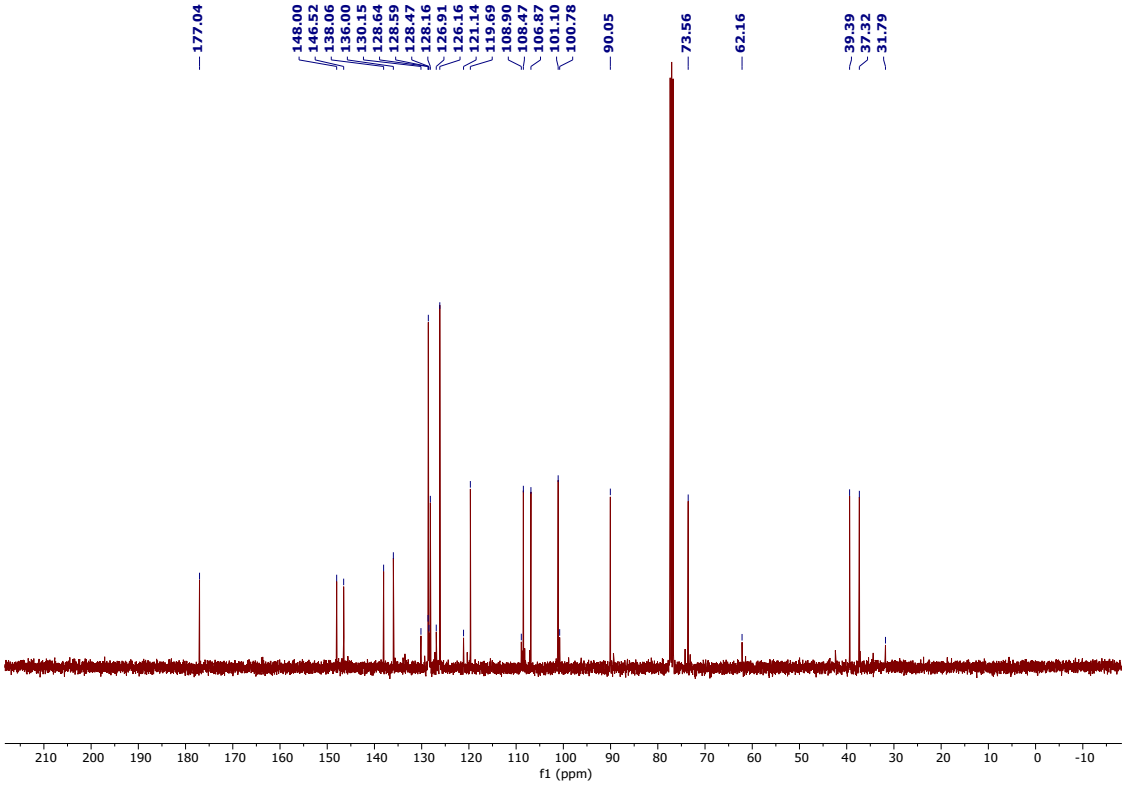
^{1}H NMR spectrum of 4-(benzo[d][1,3]dioxol-5-yl)-5-(hydroxy(phenyl)methyl)dihydrofuran-



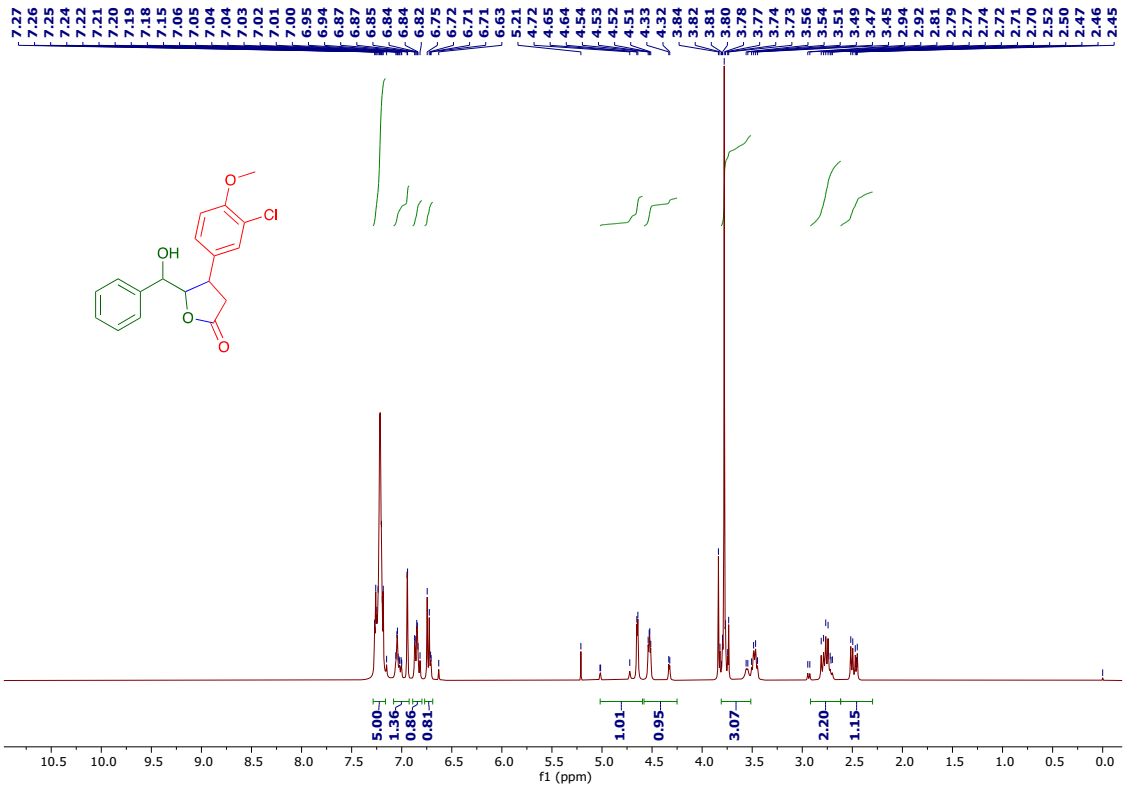
2(3H)-one (**7**, 400 MHz, $CDCl_3$)

^{13}C{^{1}H} NMR spectrum of 4-(benzo[d][1,3]dioxol-5-yl)-5-(hydroxy(phenyl)methyl)dihydro--furan-2(3H)-one (**7**, 100.6 MHz, $CDCl_3$)



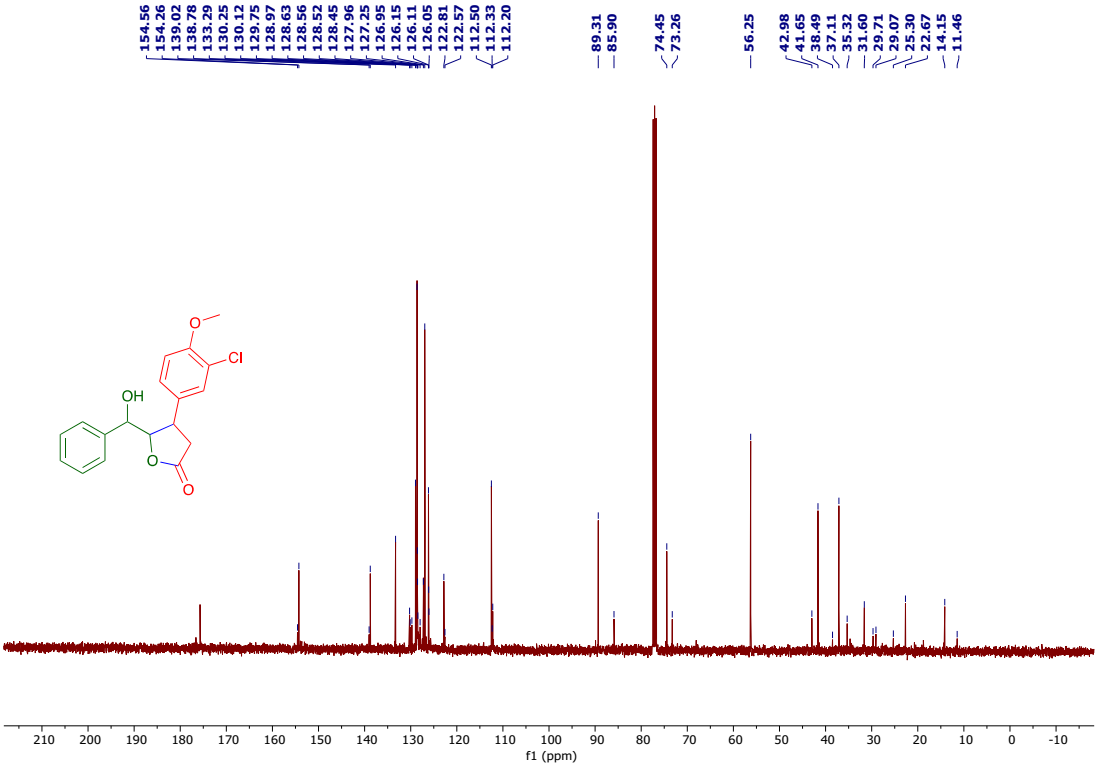

177.04
148.00
146.52
138.06
136.00
130.15
128.64
128.59
128.47
128.16
126.91
126.16
121.14
119.69
108.90
108.47
106.87
101.10
100.78
90.05
73.56
62.16
39.39
37.32
31.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR spectrum of 4-(3-chloro-4-methoxyphenyl)-5-(hydroxy(phenyl)methyl)dihydrofura-



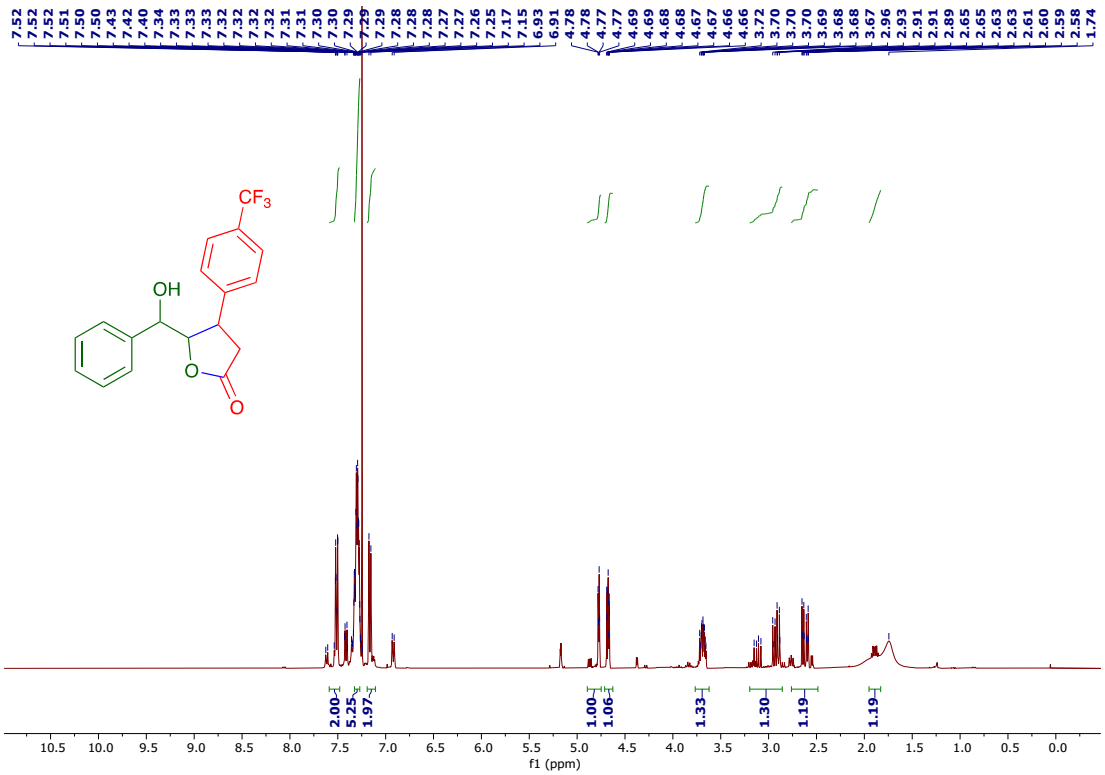
-n-2(3H)-one (**8**, 400 MHz, $CDCl_3$)

^{13}C{^{1}H} NMR spectrum of 4-(3-chloro-4-methoxyphenyl)-5-(hydroxy(phenyl)methyl)dihyd-



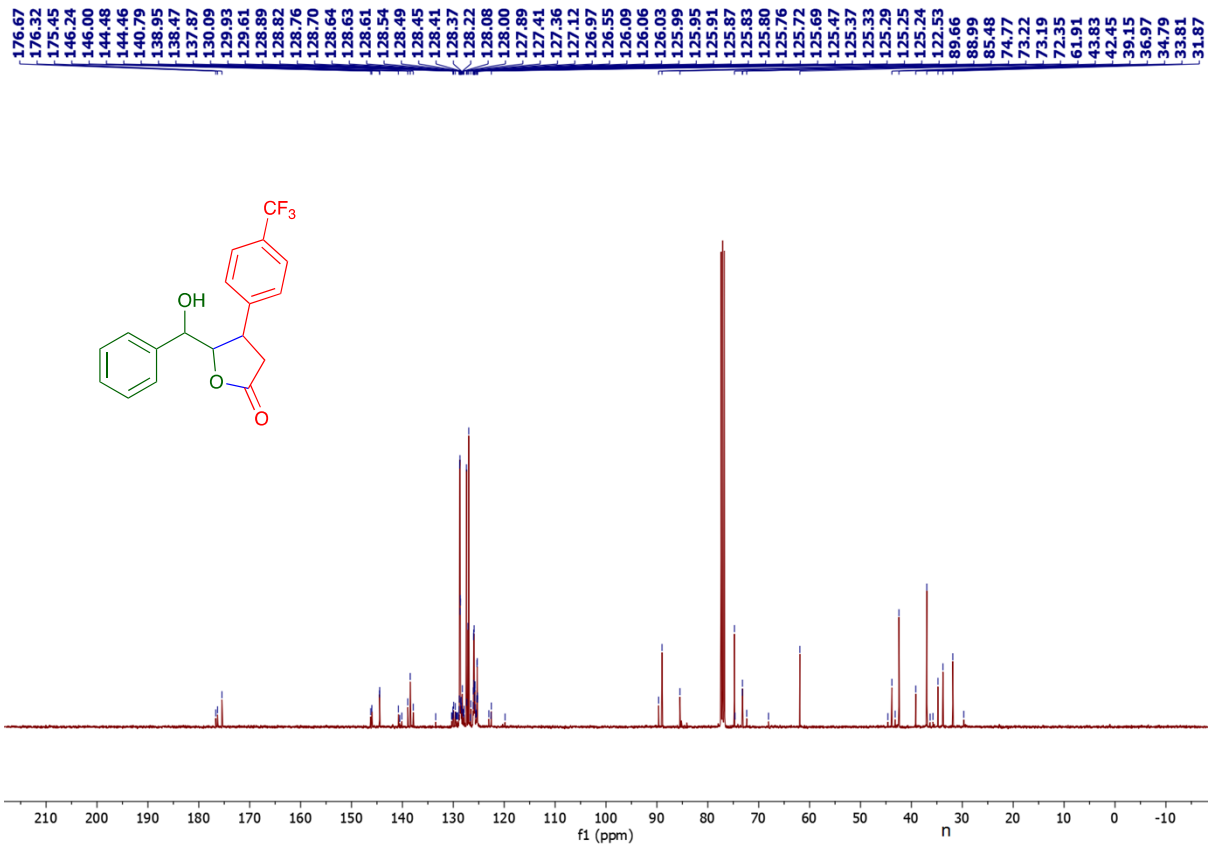
-rofuran-2(3H)-one (**8**, 100.6 MHz, $CDCl_3$)

^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(4-(trifluoromethyl)phenyl)dihydrofuran-

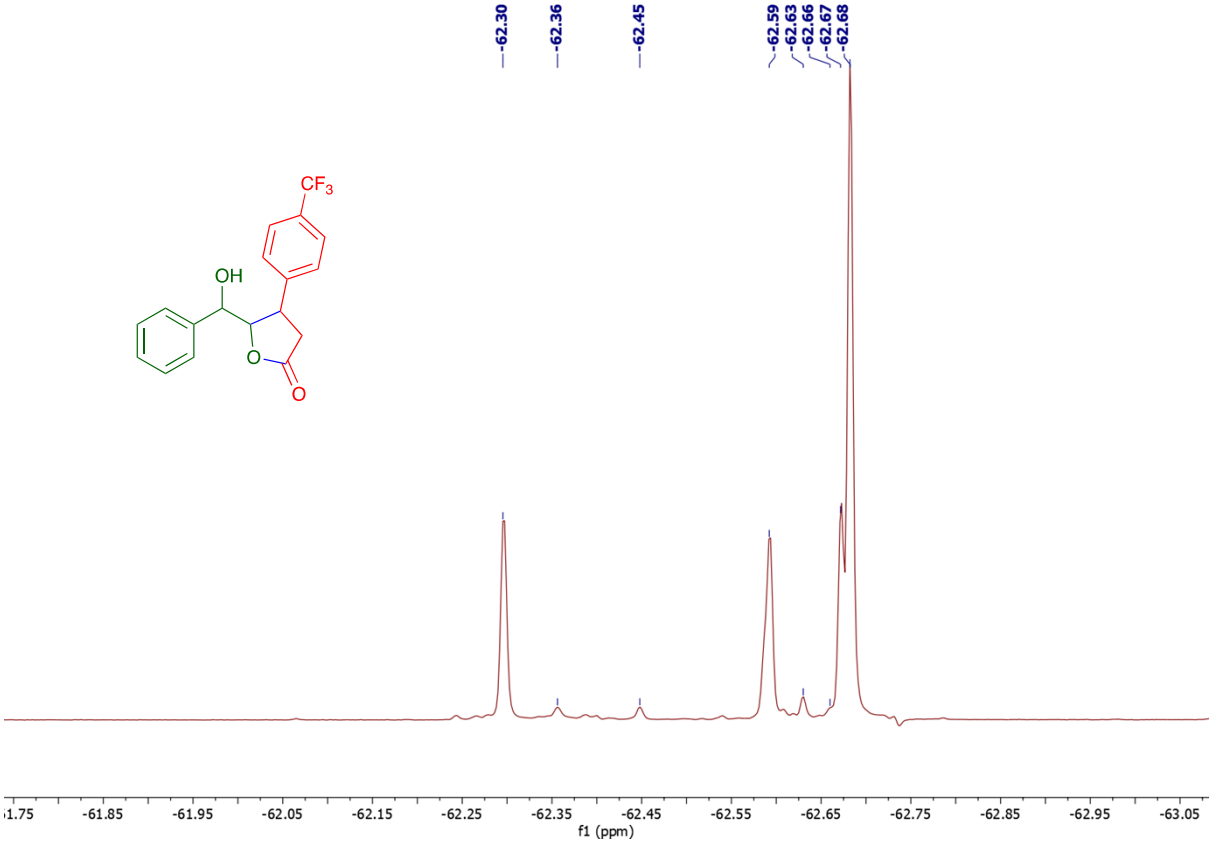


2(3H)-one (**9**, 400 MHz, $CDCl_3$)

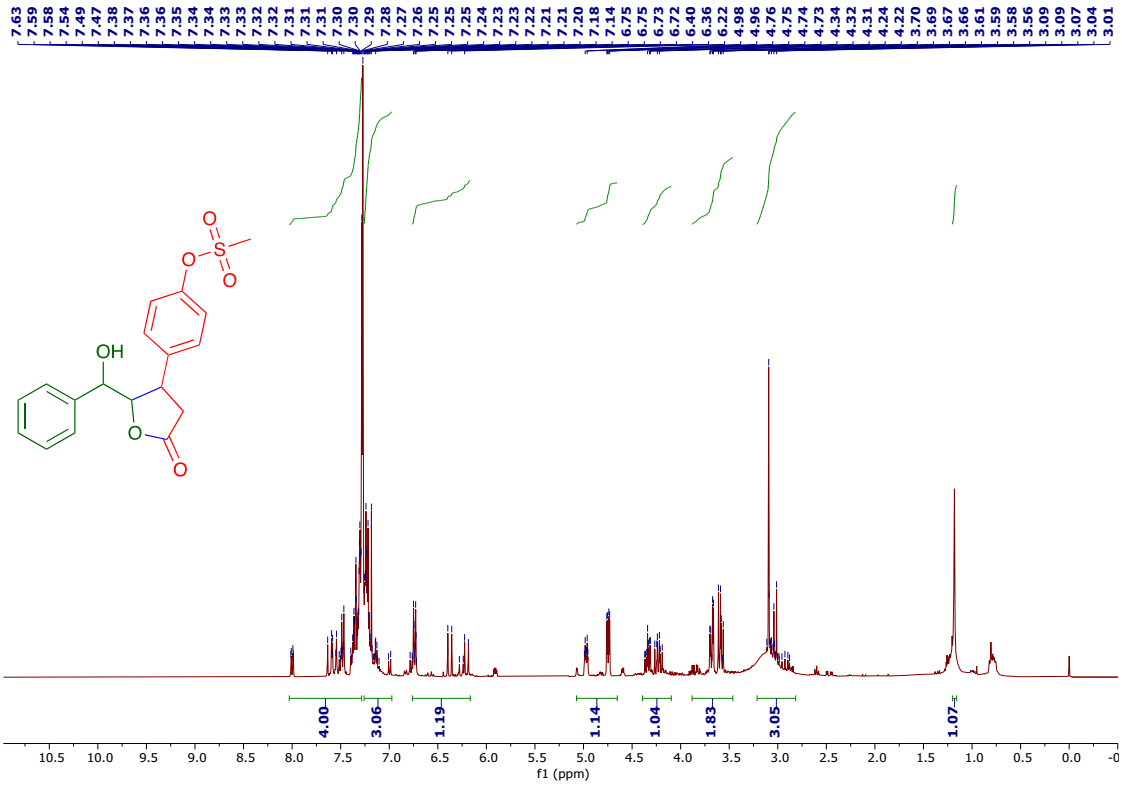
^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(4-(trifluoromethyl)phenyl)dihydr--ofuran-2(3H)-one (**9**, 100.6 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(4-(trifluoromethyl)phenyl)dihydr--ofuran-2(3H)-one (**9**, 376.5 MHz, $CDCl_3$)

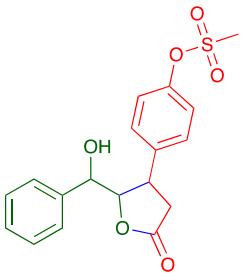

-62.30
-62.36
-62.45
-62.59
-62.63
-62.66
-62.67
-62.68
CF3
OH
O
O
-61.85
-61.95
-62.05
-62.15
-62.25
-62.35
-62.45
-62.55
-62.65
-62.75
-62.85
-62.95
-63.05
f1 (ppm)

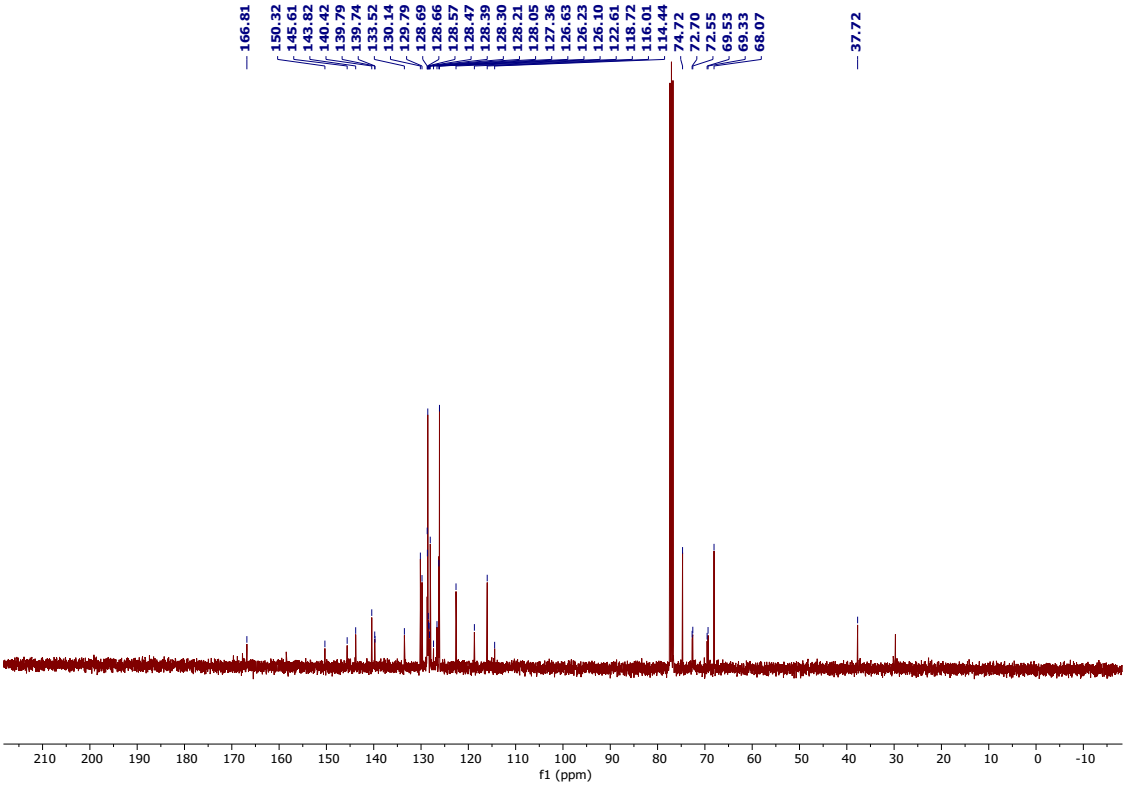
^{1}H NMR spectrum of 4-(2-(hydroxy(phenyl)methyl)-5-oxotetrahydrofuran-3-yl)phenyl



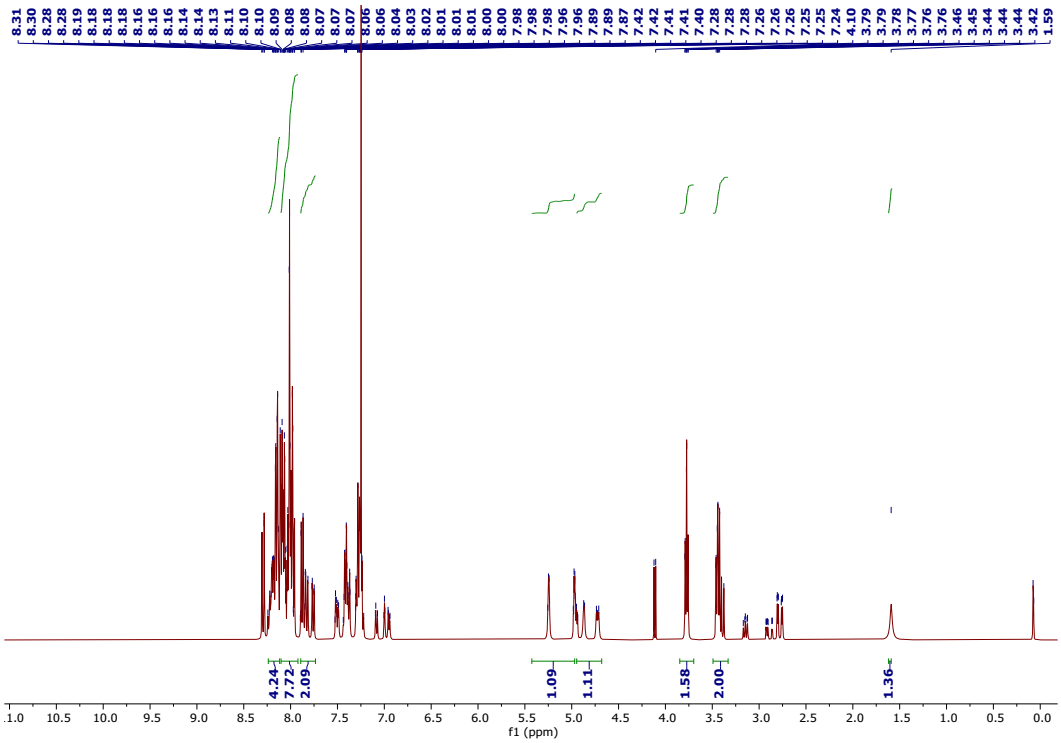
methanesulfonate (**10**, 400 MHz, $CDCl_3$)

$^{13}C\{^{1}H\}$ NMR spectrum of 4-(2-(hydroxy(phenyl)methyl)-5-oxotetrahydrofuran-3-yl)phenyl methanesulfonate (**10**, 100.6 MHz, $CDCl_3$)

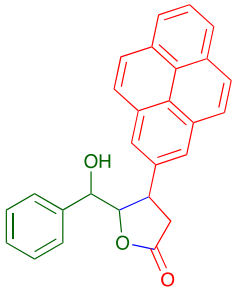




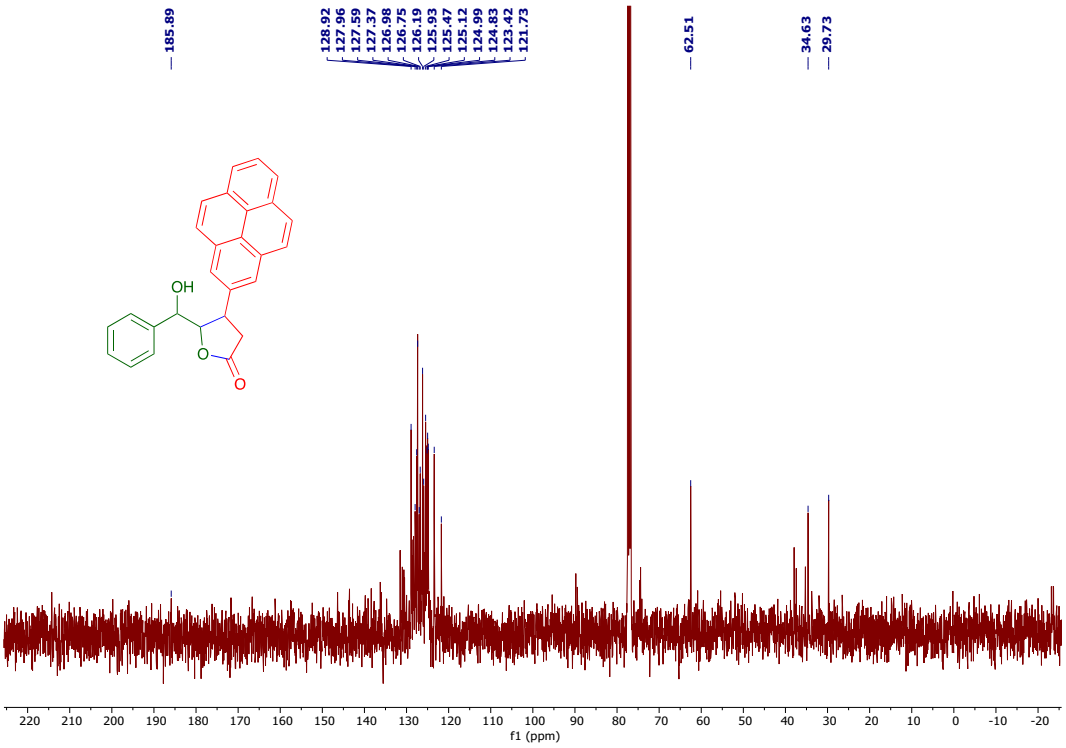
^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(pyren-2-yl)dihydrofuran-2(3H)-one (**11**, 400



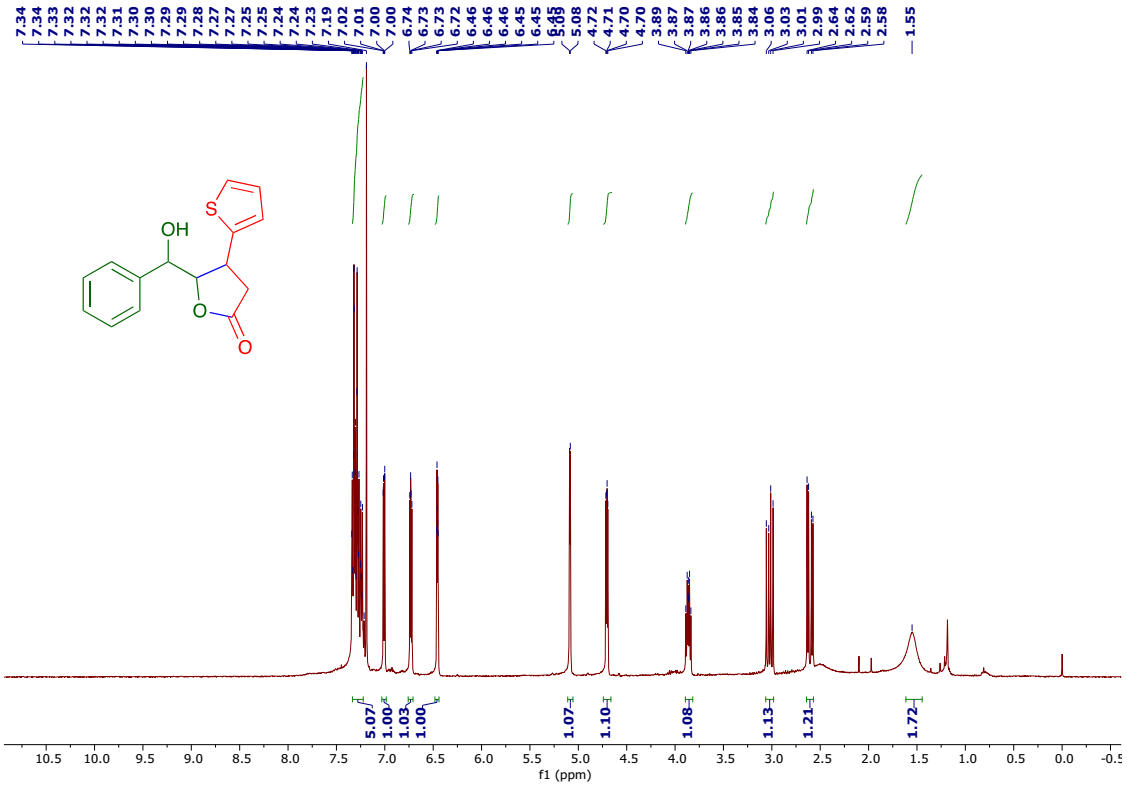
MHz, $CDCl_3$)



^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(pyren-2-yl)dihydrofuran-2(3H)-one (**11**, 100.6 MHz, $CDCl_3$)

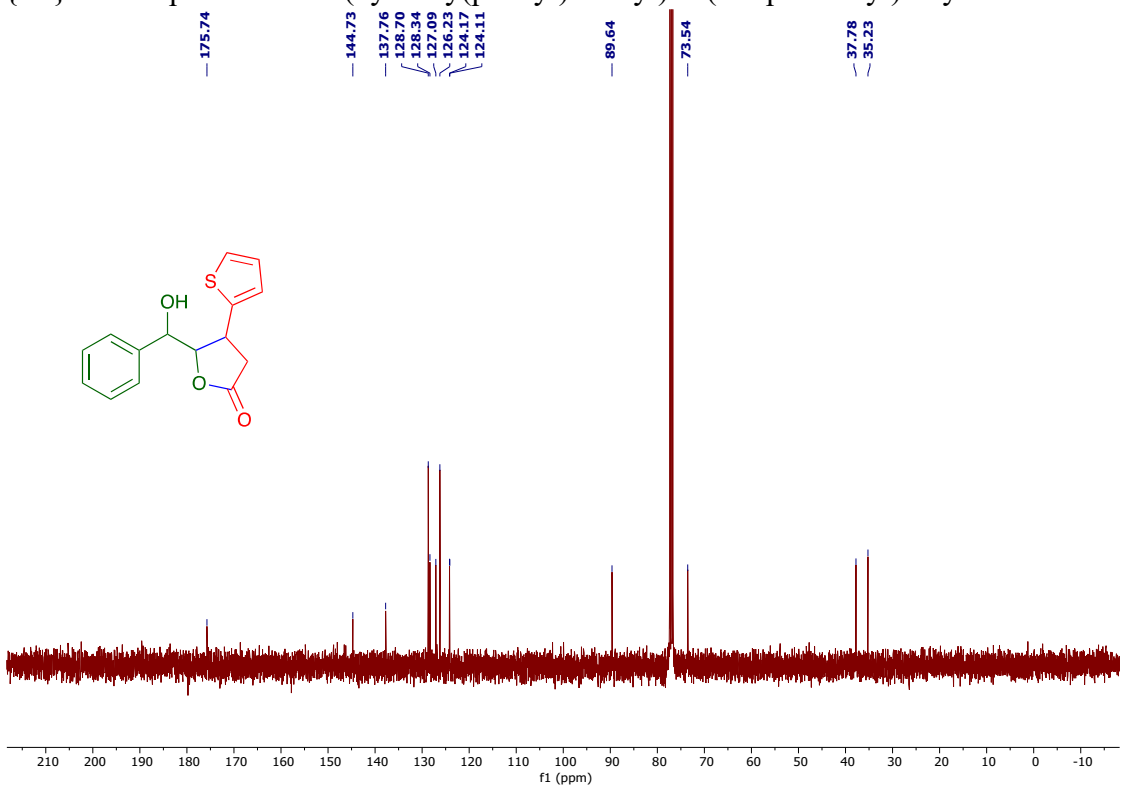

185.89
128.92
127.96
127.59
127.37
126.98
126.75
126.19
125.93
125.47
125.12
124.99
124.83
123.42
121.73
62.51
34.63
29.73
OH
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(thiophen-2-yl)dihydrofuran-2(3H)-one



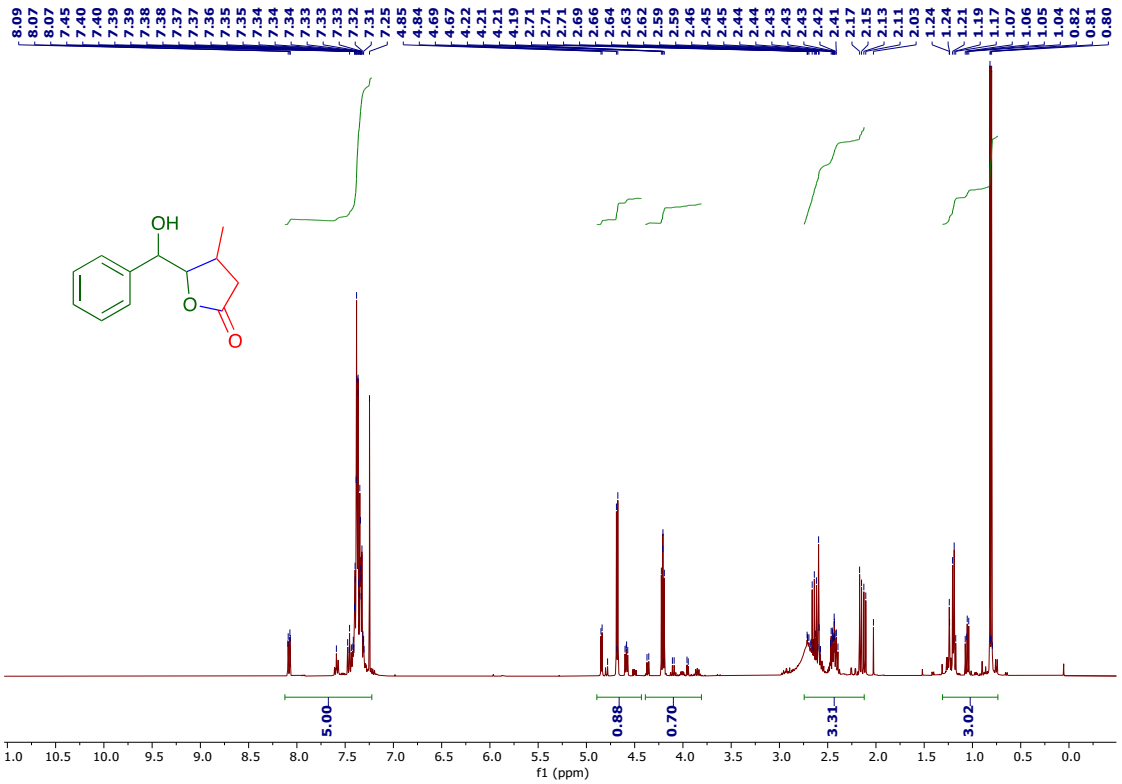
(**12**, 400 MHz, $CDCl_3$)

^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-(thiophen-2-yl)dihydrofuran-



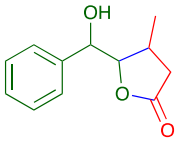
2(3H)-one (**12**): (100.6 MHz, $CDCl_3$)

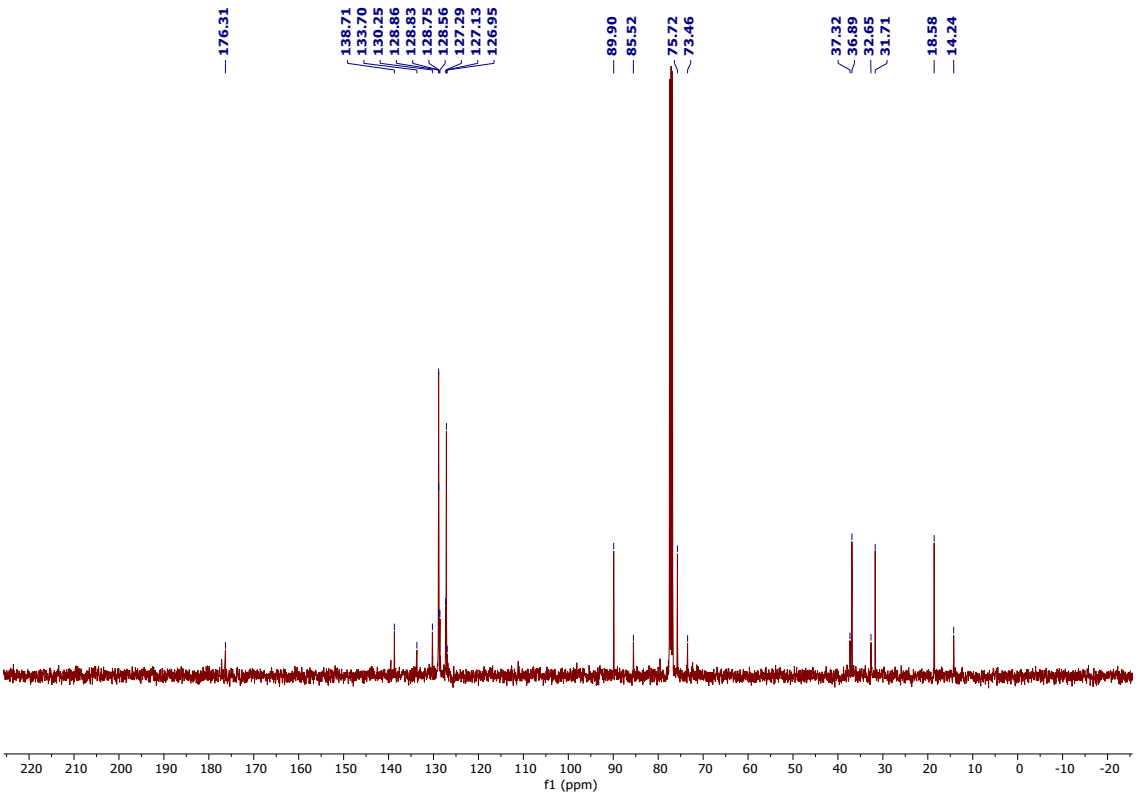
^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-methyldihydrofuran-2(3H)-one (**13**, 400



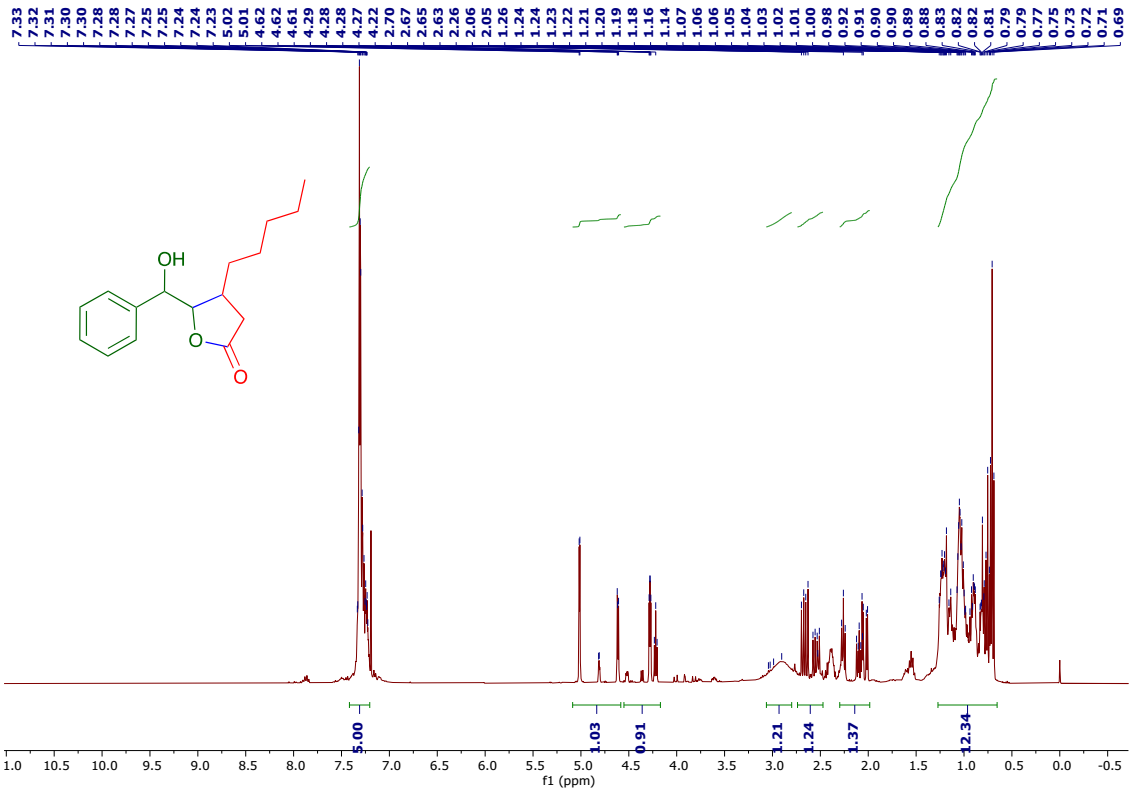
MHz, $CDCl_3$)

$^{13}C\{^{1}H\}$ NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-methyldihydrofuran-2(3H)-one (**13**, 100.6 MHz, $CDCl_3$)



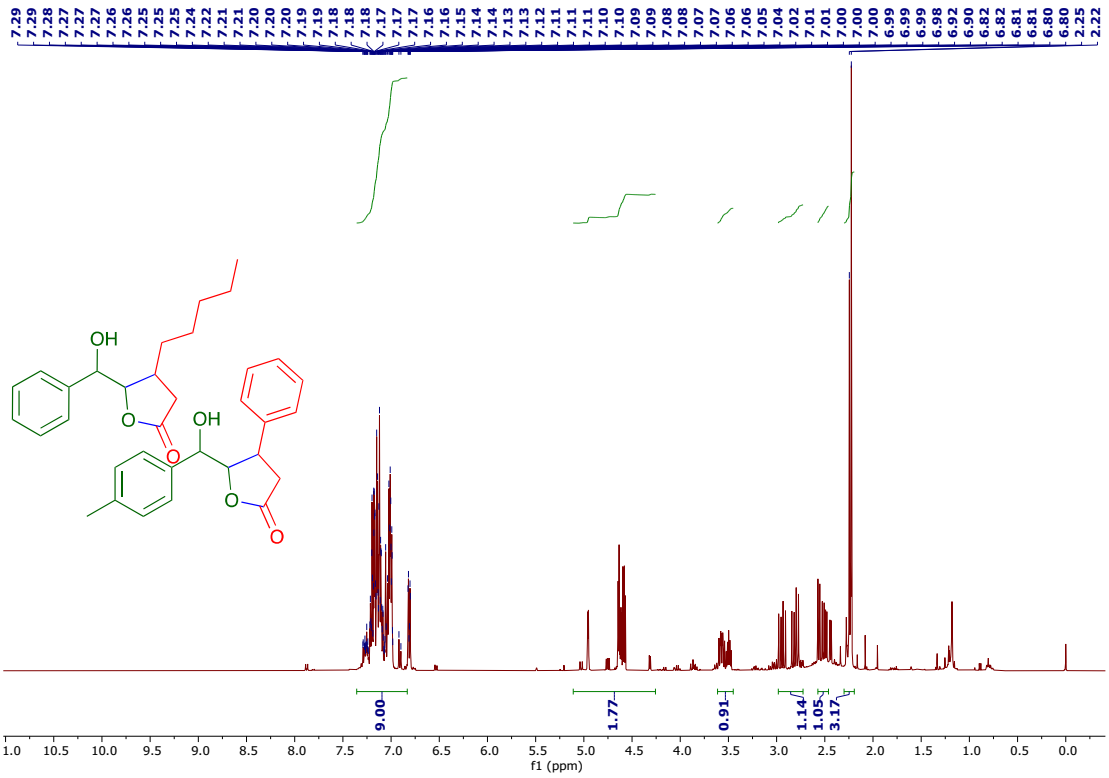


^{1}H NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-pentyldihydrofuran-2(3H)-one (**14**, 400



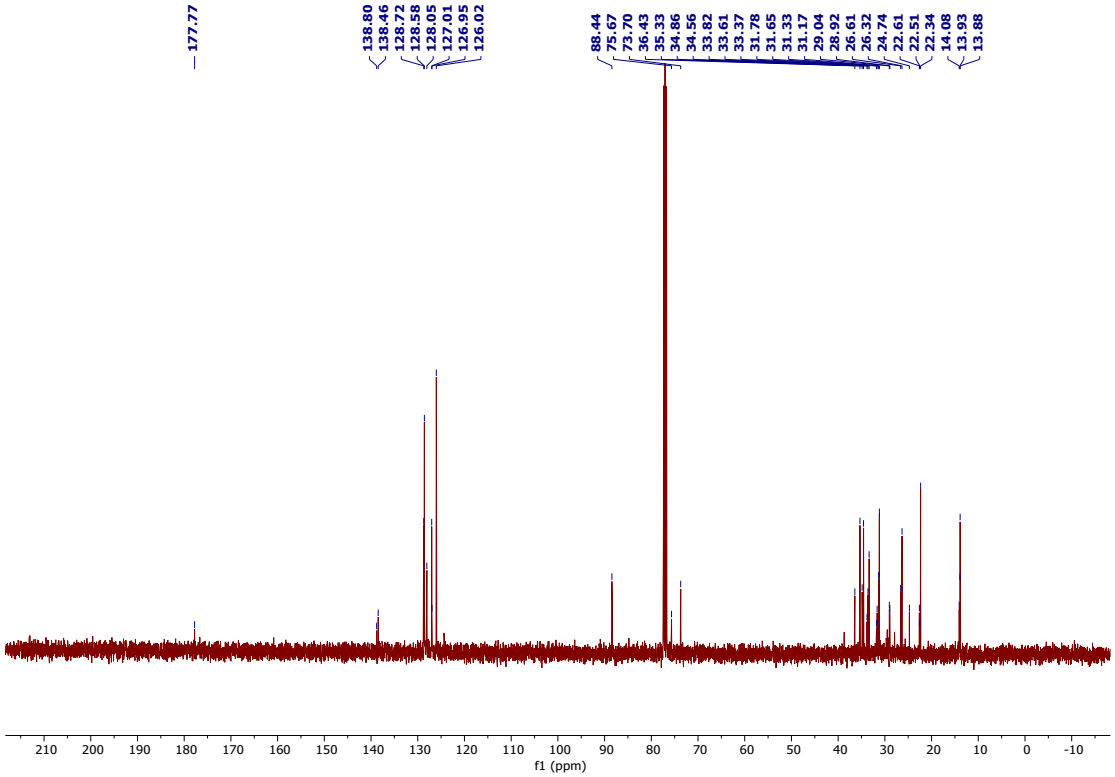
MHz, $CDCl_3$)

$^{13}C\{^{1}H\}$ NMR spectrum of 5-(hydroxy(phenyl)methyl)-4-pentyldihydrofuran-2(3H)-one (**14**,



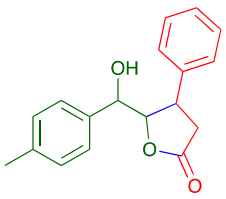
100.6 MHz, $CDCl_3$)

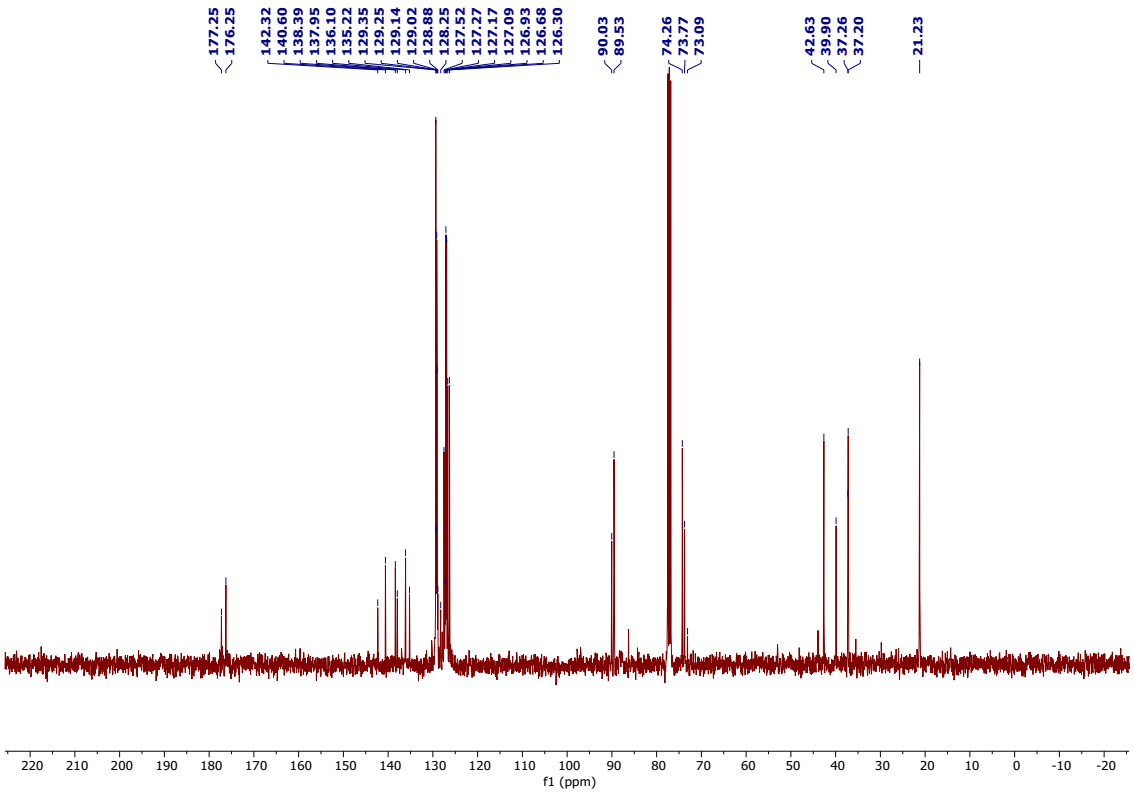
^{1}H NMR spectrum of 5-(hydroxy(p-tolyl)methyl)-4-phenyldihydrofuran-2(3H)-one (**15**, 400



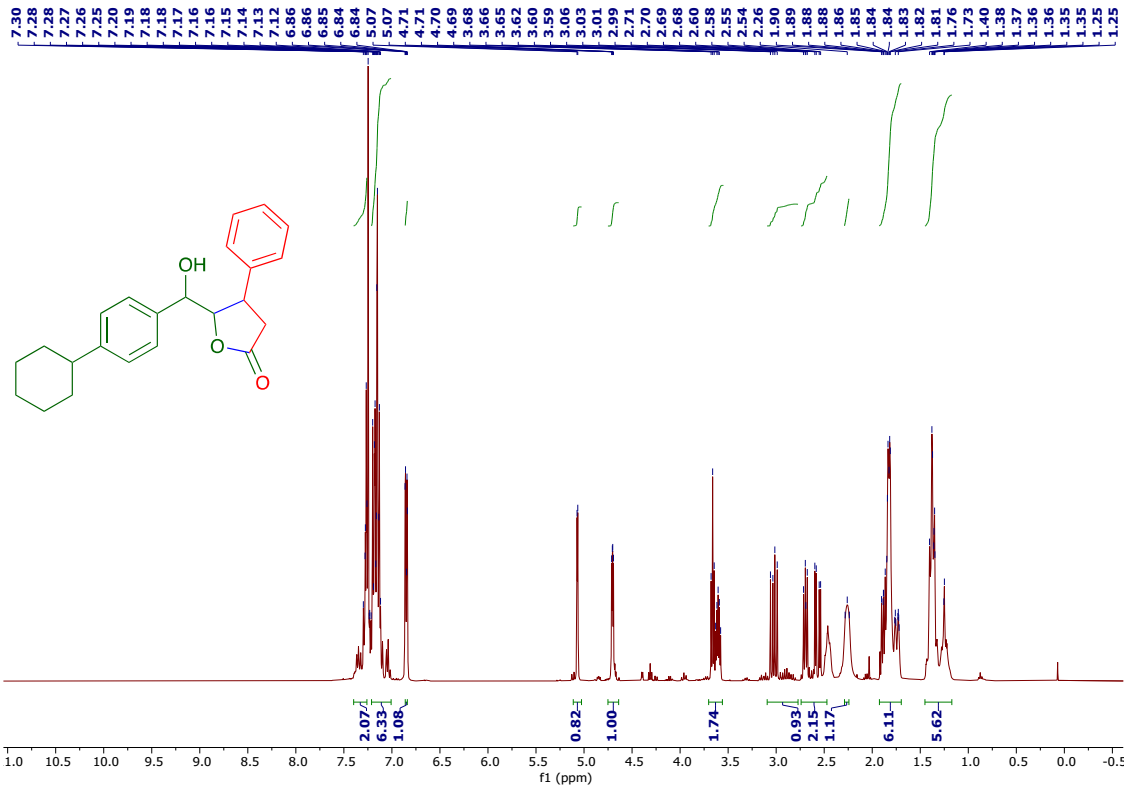
MHz, $CDCl_3$)

$^{13}C\{^{1}H\}$ NMR spectrum of 5-(hydroxy(p-tolyl)methyl)-4-phenyldihydrofuran-2(3H)-one (**15**, 100.6 MHz, $CDCl_3$)



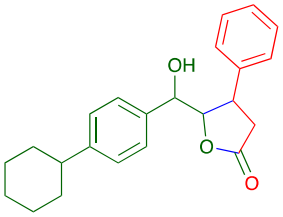


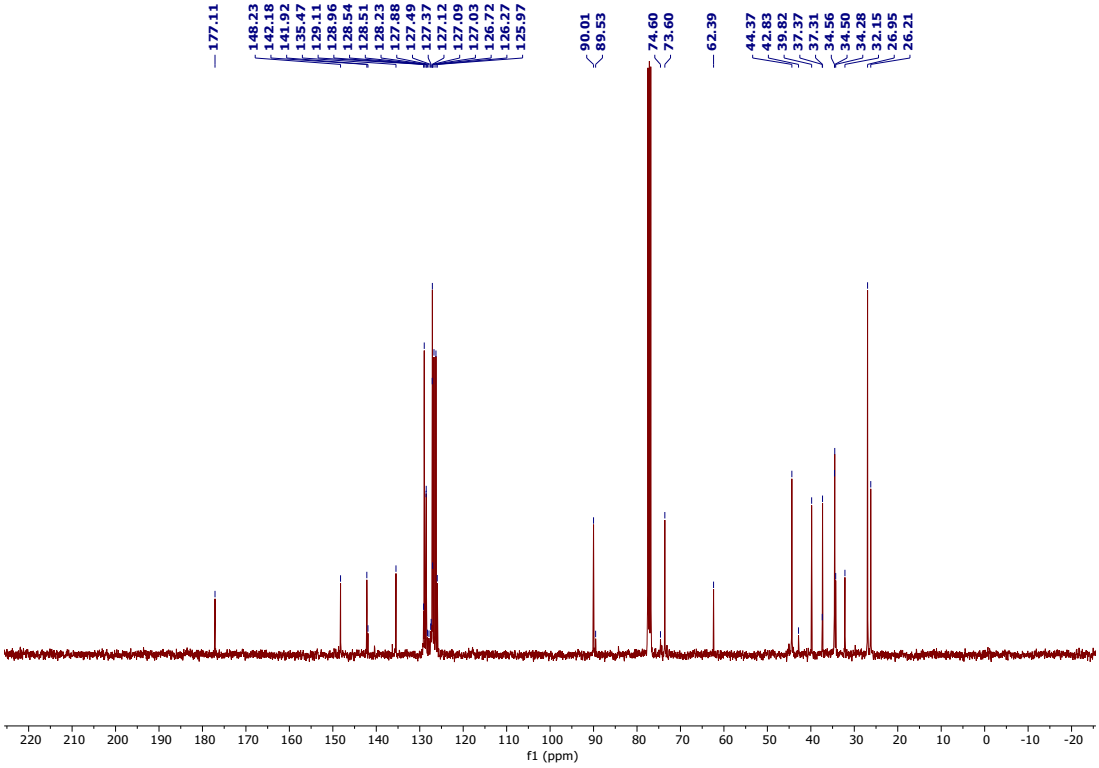
^{1}H NMR spectrum of 5-((4-cyclohexylphenyl)(hydroxy)methyl)-4-phenyldihydrofuran-



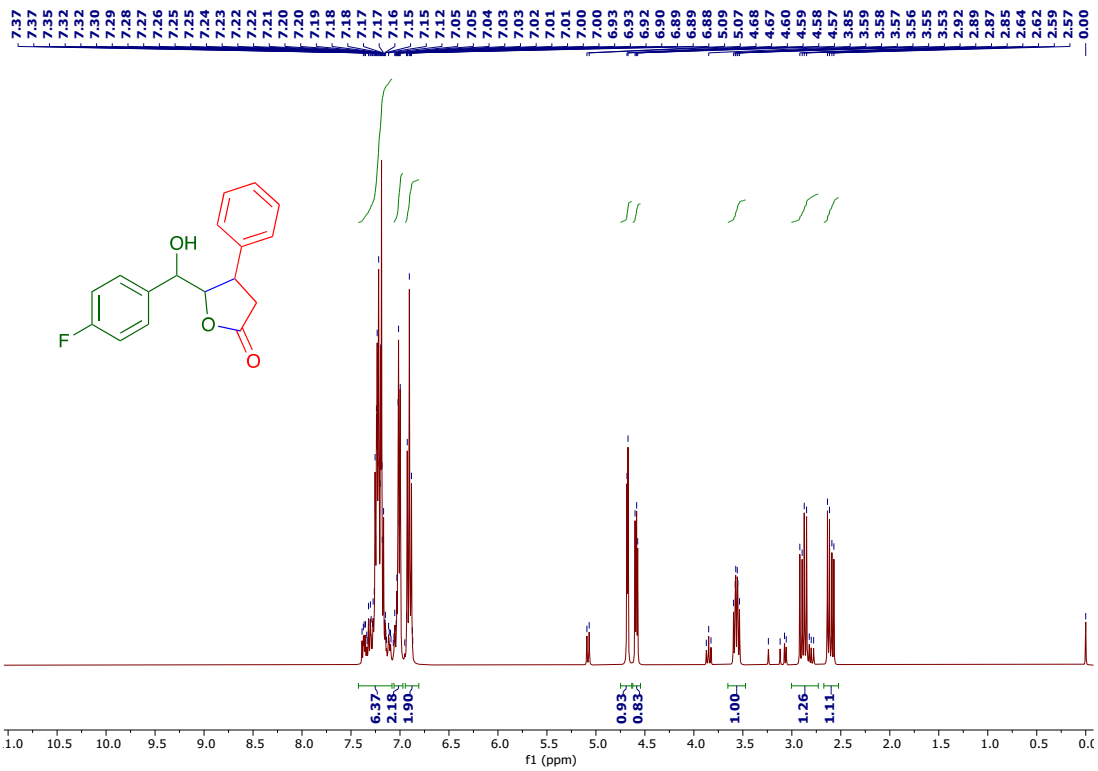
2(3H)-one (**16**, 400 MHz, $CDCl_3$)

$^{13}C\{^{1}H\}$ NMR spectrum of 5-((4-cyclohexylphenyl)(hydroxy)methyl)-4-phenyldihydrofuran-2(3H)-one (**16**, 100.6 MHz, $CDCl_3$)



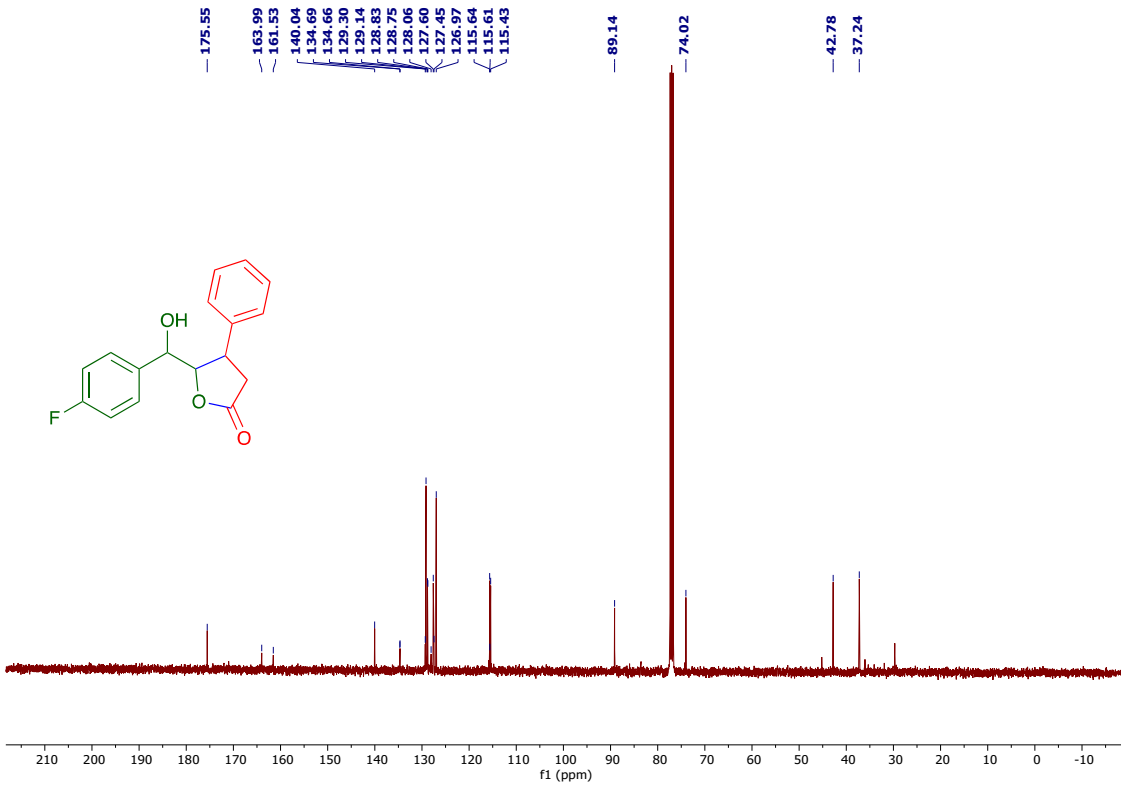


^{1}H NMR spectrum of 5-((4-fluorophenyl)(hydroxy)methyl)-4-phenyldihydrofuran-2(3H)-one



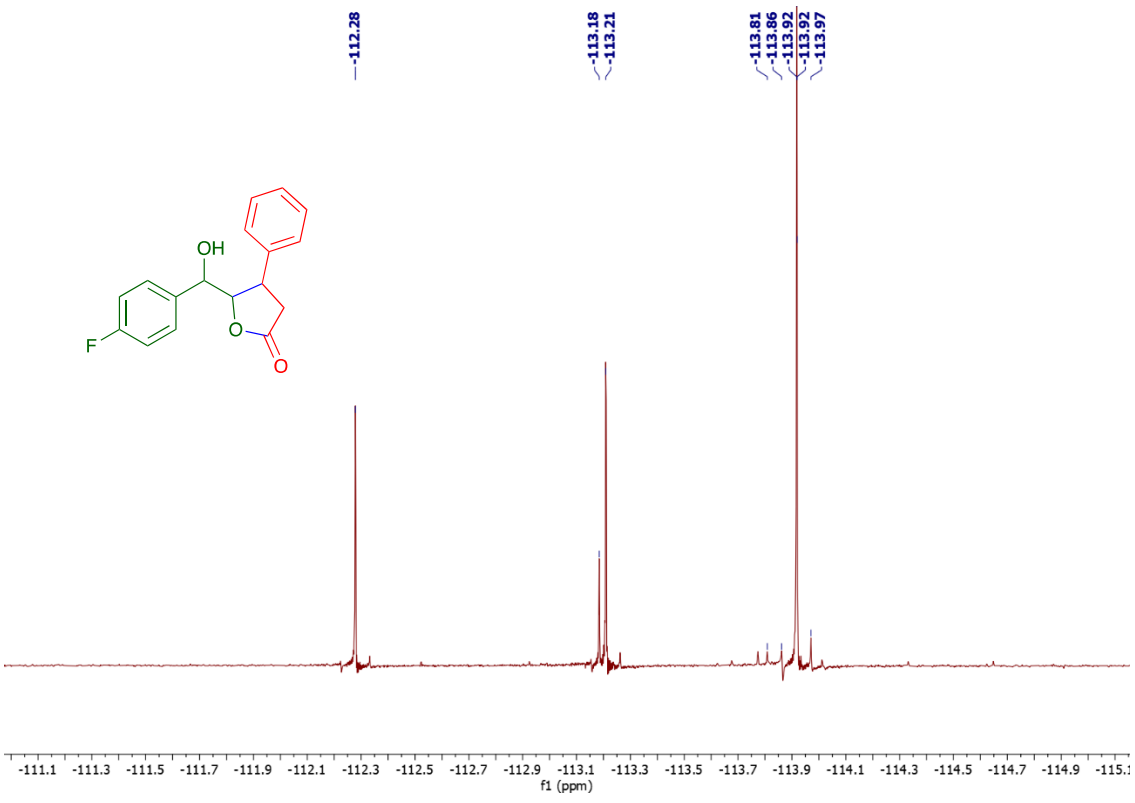
(**17**, 400 MHz, $CDCl_3$)

$^{13}C\{^{1}H\}$ NMR spectrum of 5-((4-fluorophenyl)(hydroxy)methyl)-4-phenyldihydrofuran-

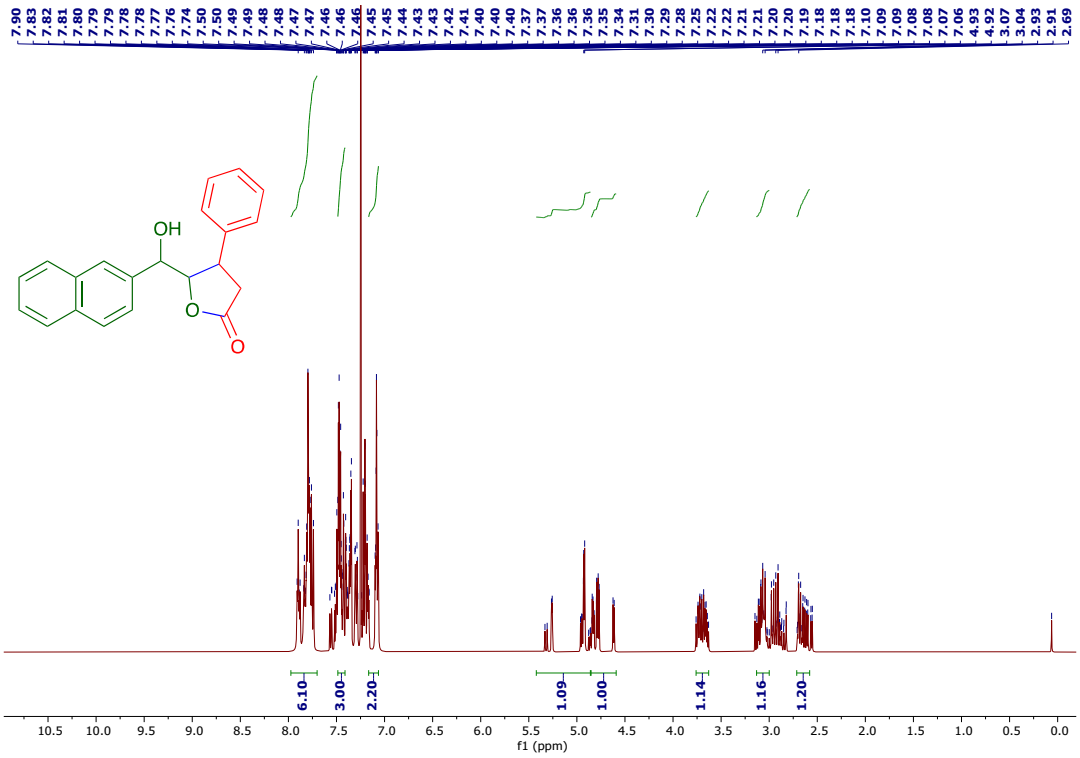


2(3H)-one (**17**, 100.6 MHz, $CDCl_3$)

$^{19}F\{^{1}H\}$ NMR spectrum of 5-((4-fluorophenyl)(hydroxy)methyl)-4-phenyldihydrofuran-2(3H)-one (**17**, 376.5 MHz, $CDCl_3$)

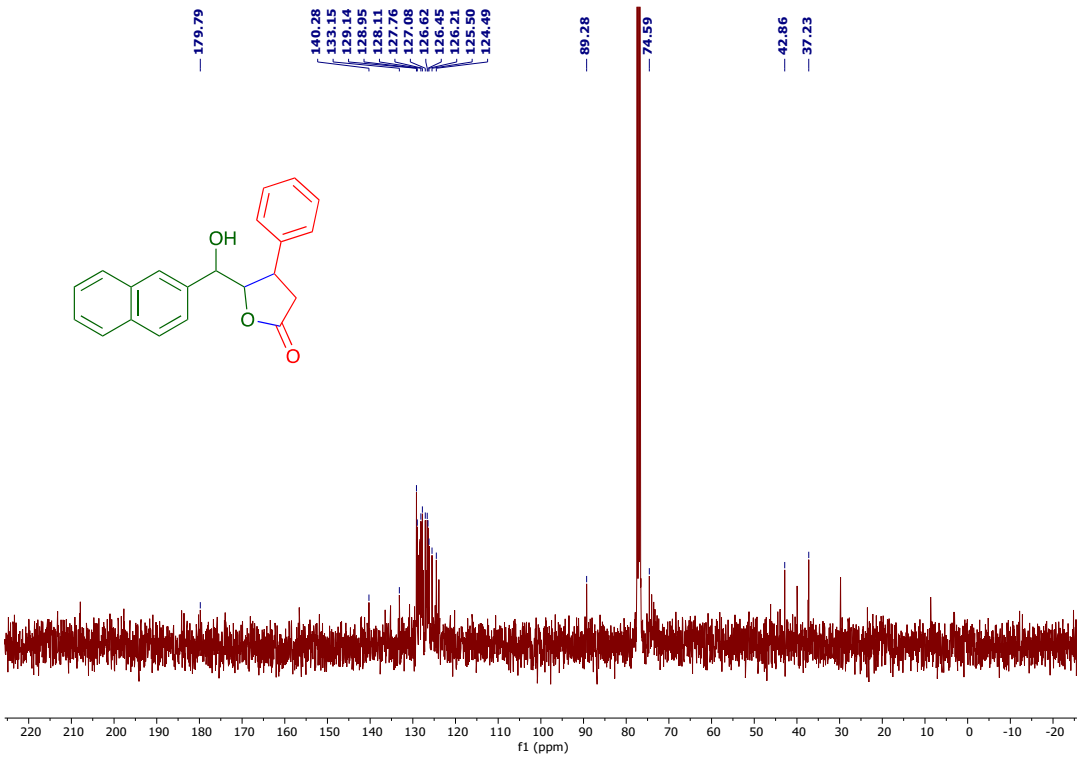


^{1}H NMR spectrum of 5-(hydroxy(naphthalen-2-yl)methyl)-4-phenyldihydrofuran-2(3H)-one

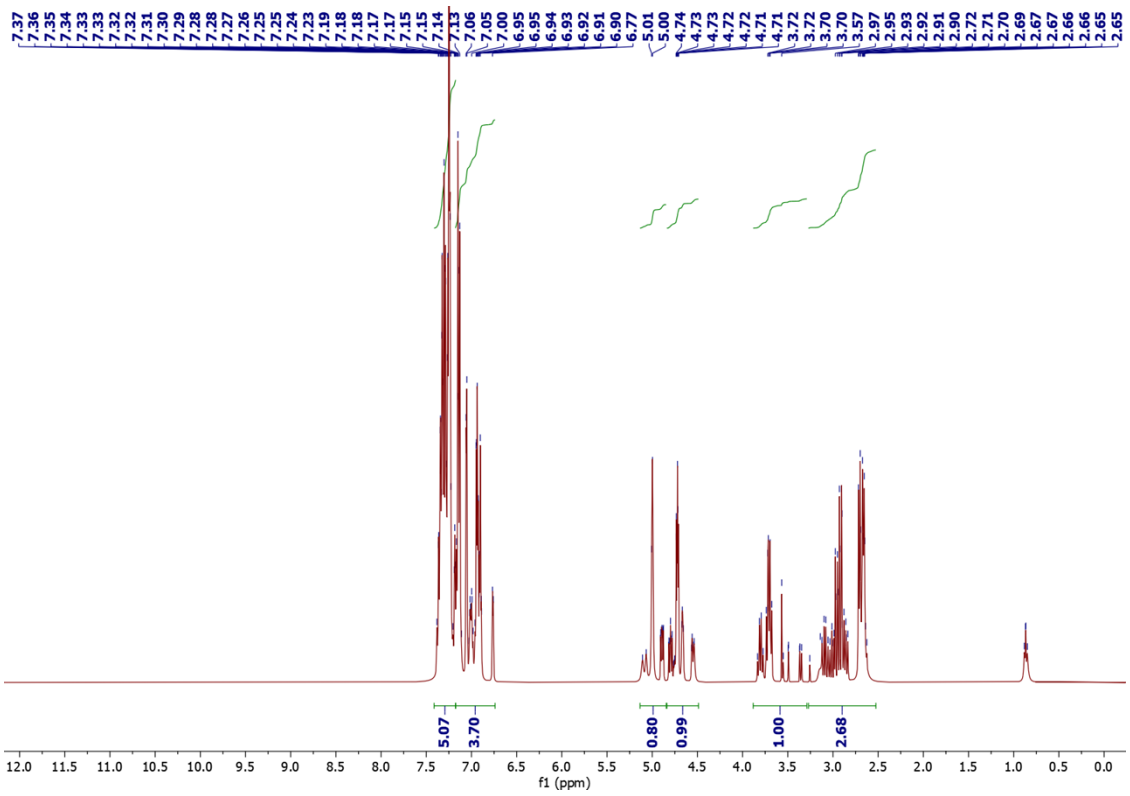


(**18**, 400 MHz, $CDCl_3$)

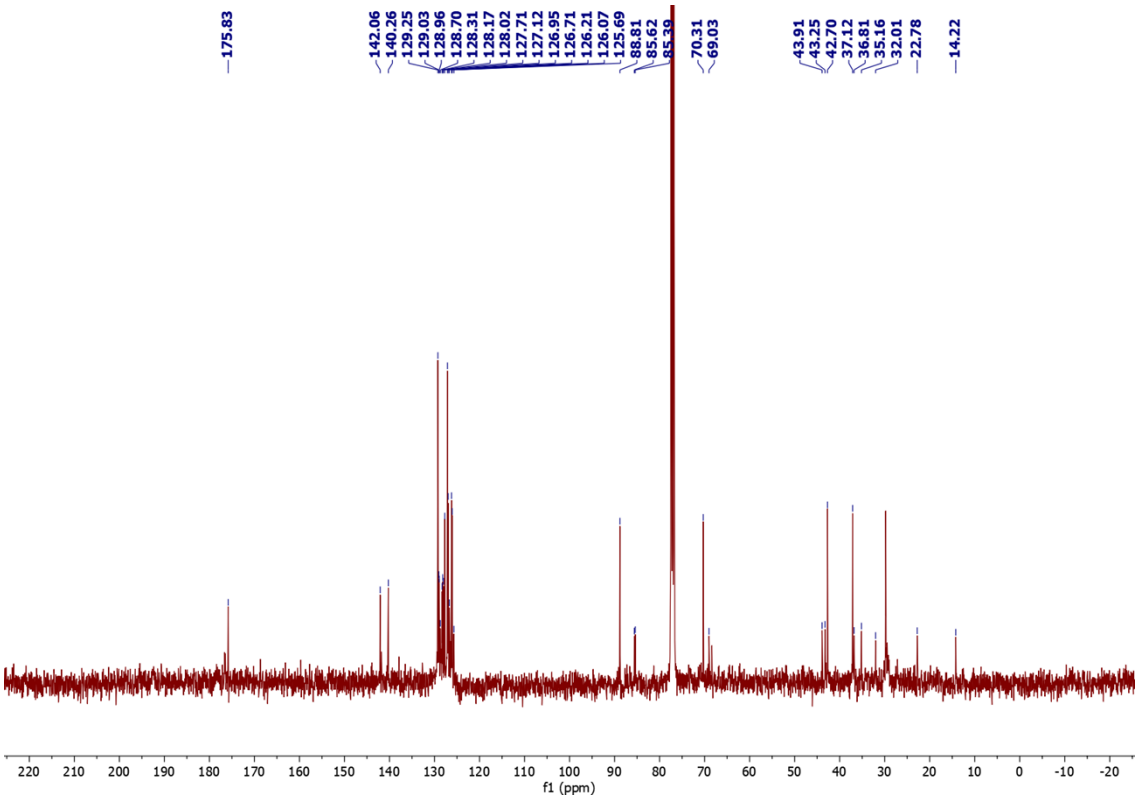
^{13}C{^{1}H} NMR spectrum of 5-(hydroxy(naphthalen-2-yl)methyl)-4-phenyldihydrofuran-2(3H)-one (**18**, 100.6 MHz, $CDCl_3$)



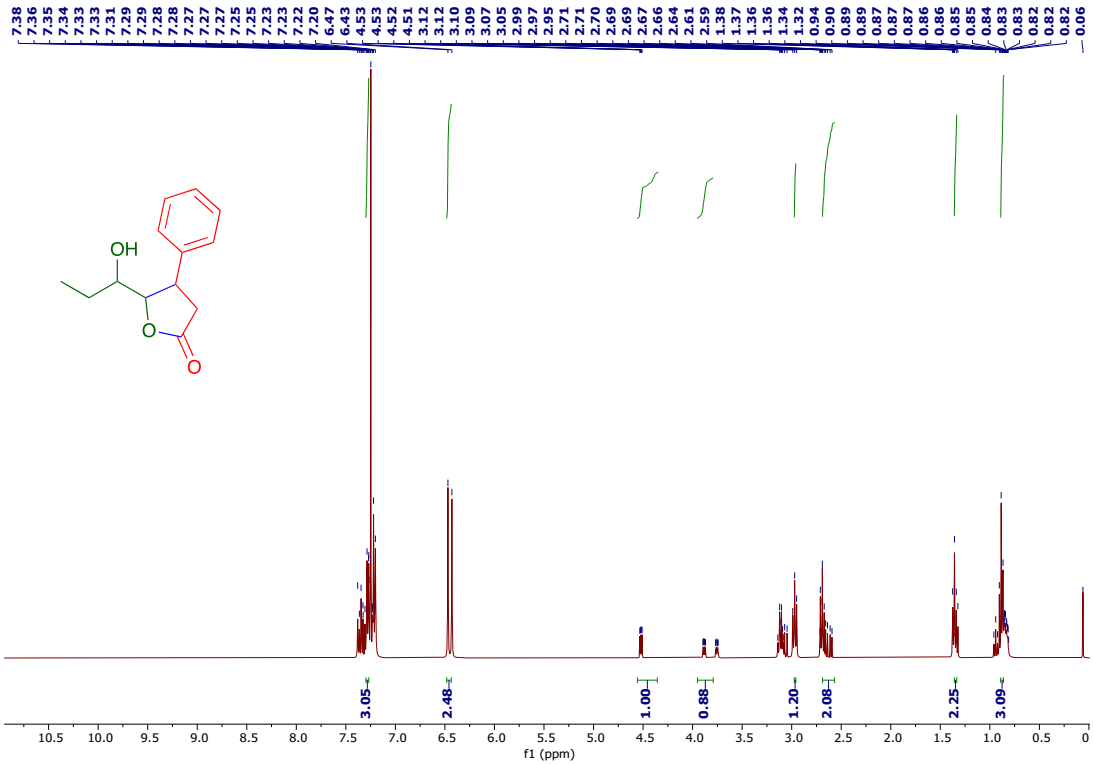
^{1}H NMR spectrum of 5-(hydroxy(pyridin-2-yl)methyl)-4-phenyldihydrofuran-2(3*H*)-one (**19**, 400 MHz, $CDCl_3$)



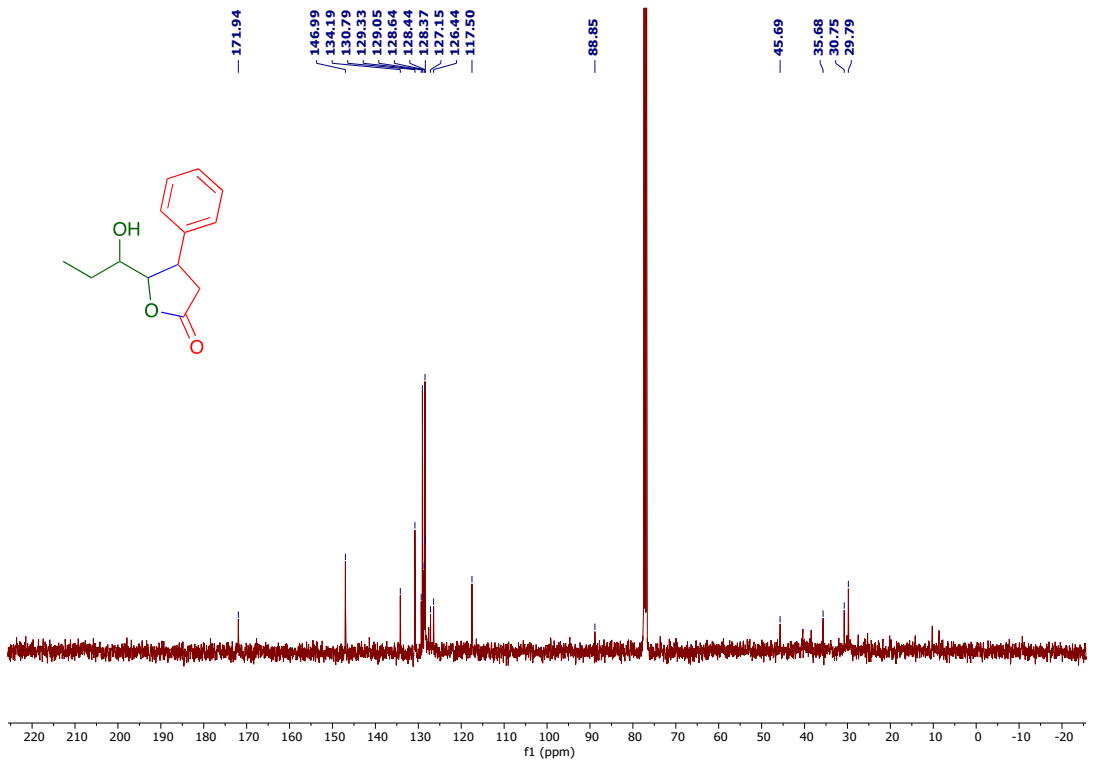
^{13}C {^{1}H} NMR spectrum of 5-(hydroxy(pyridin-2-yl)methyl)-4-phenyldihydrofuran-2(3*H*)-one (**19**, 100.6 MHz, $CDCl_3$)



^{1}H NMR spectrum of 5-(1-hydroxypropyl)-4-phenyldihydrofuran-2(3H)-one (**20**, 400 MHz, $CDCl_3$)

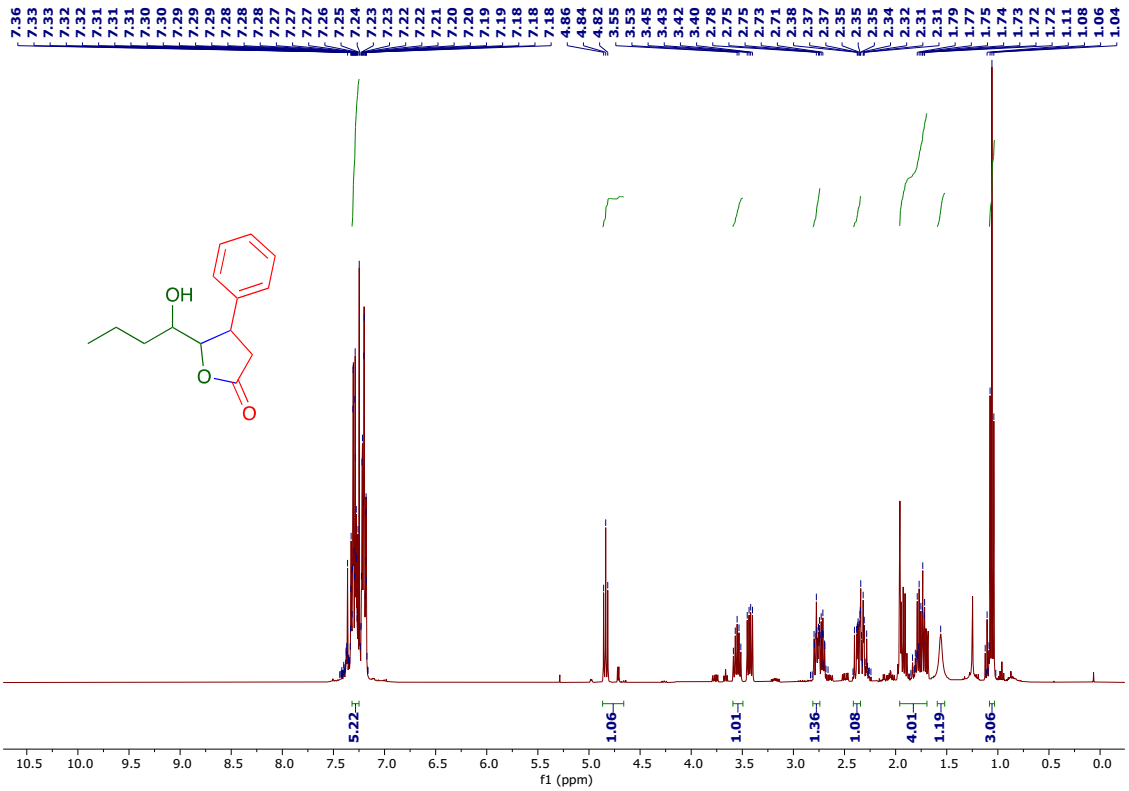


^{13}C{^{1}H} NMR spectrum of 5-(1-hydroxypropyl)-4-phenyldihydrofuran-2(3H)-one (**20**, 100.6



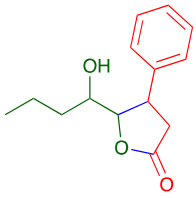
MHz, $CDCl_3$)

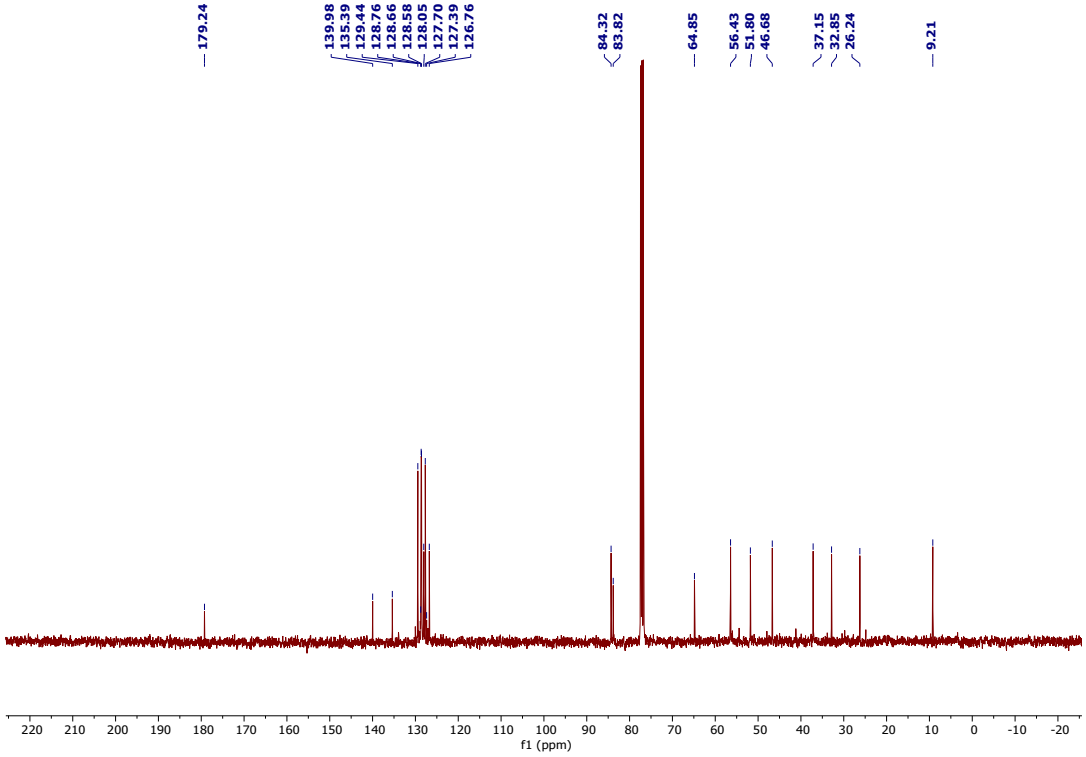
^{1}H NMR spectrum of 5-(1-hydroxybutyl)-4-phenyldihydrofuran-2(3H)-one (**21**, 400 MHz,



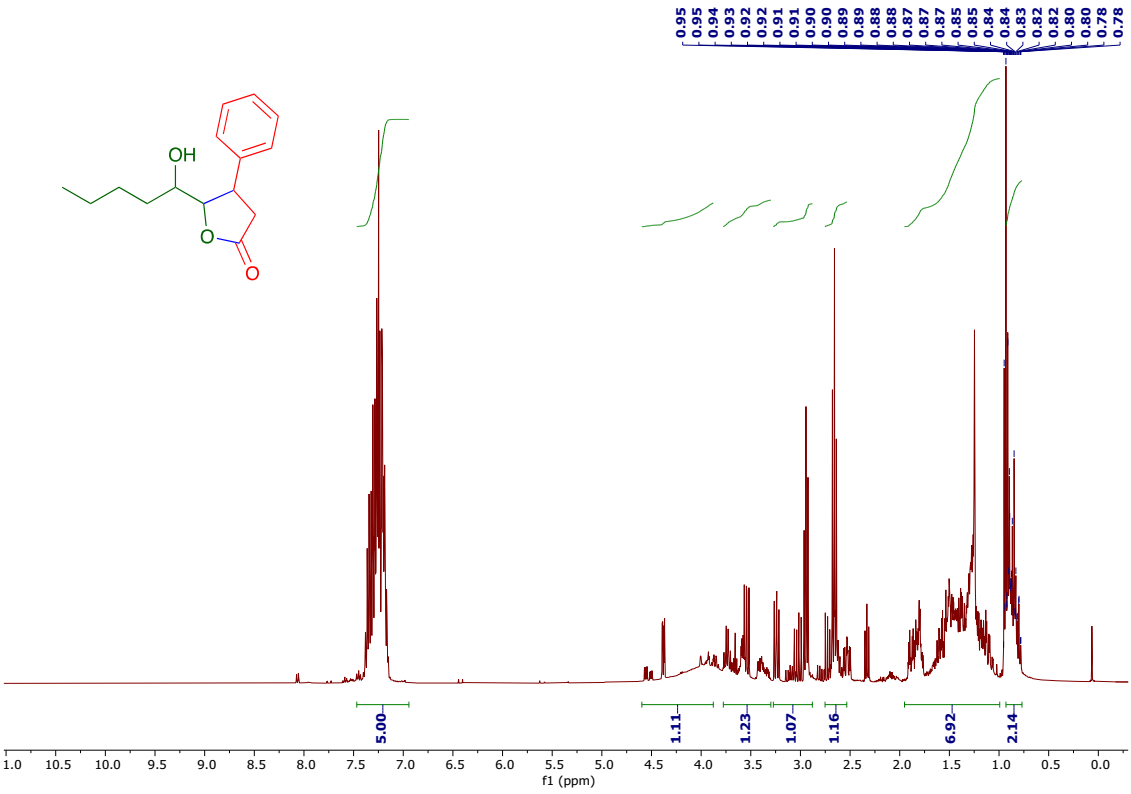
$CDCl_3$)

$s^3C\{^1H\}$ NMR spectrum of 5-(1-hydroxybutyl)-4-phenyldihydrofuran-2(3H)-one (**21**, 100.6 MHz, $CDCl_3$)

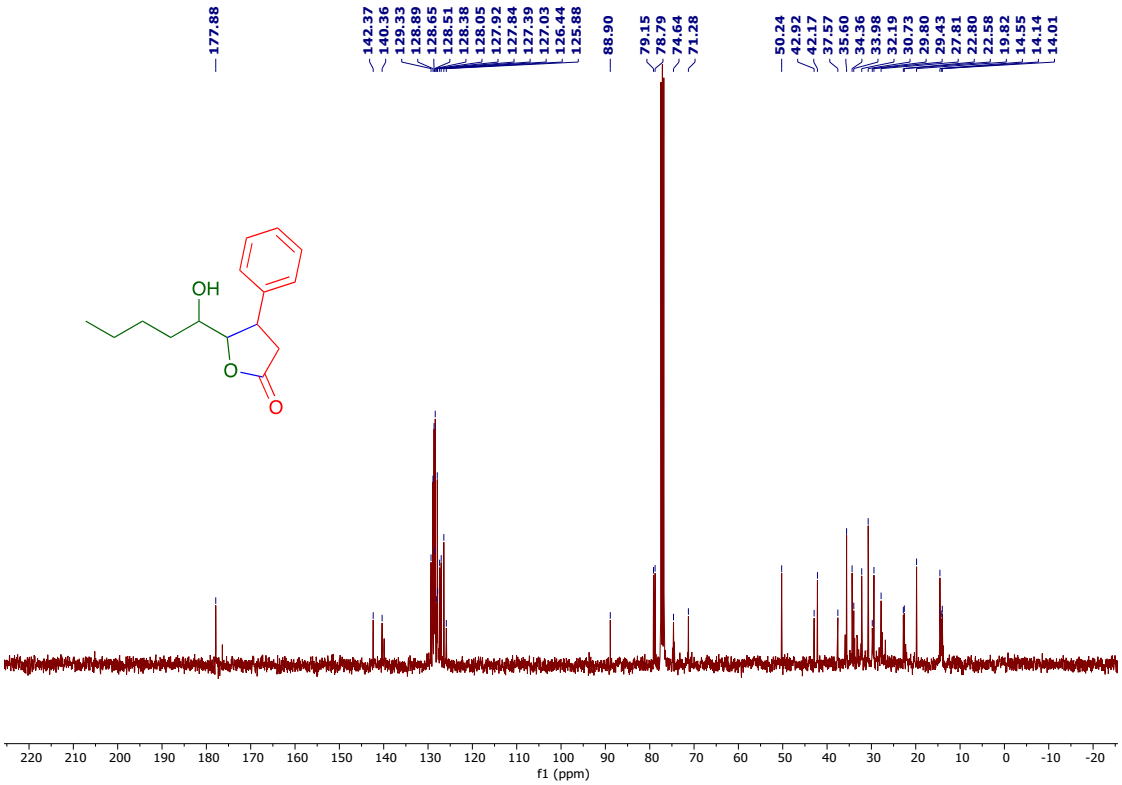




^{1}H NMR spectrum of 5-(1-hydroxypentyl)-4-phenyldihydrofuran-2(3H)-one (**22**, 400 MHz, $CDCl_3$)

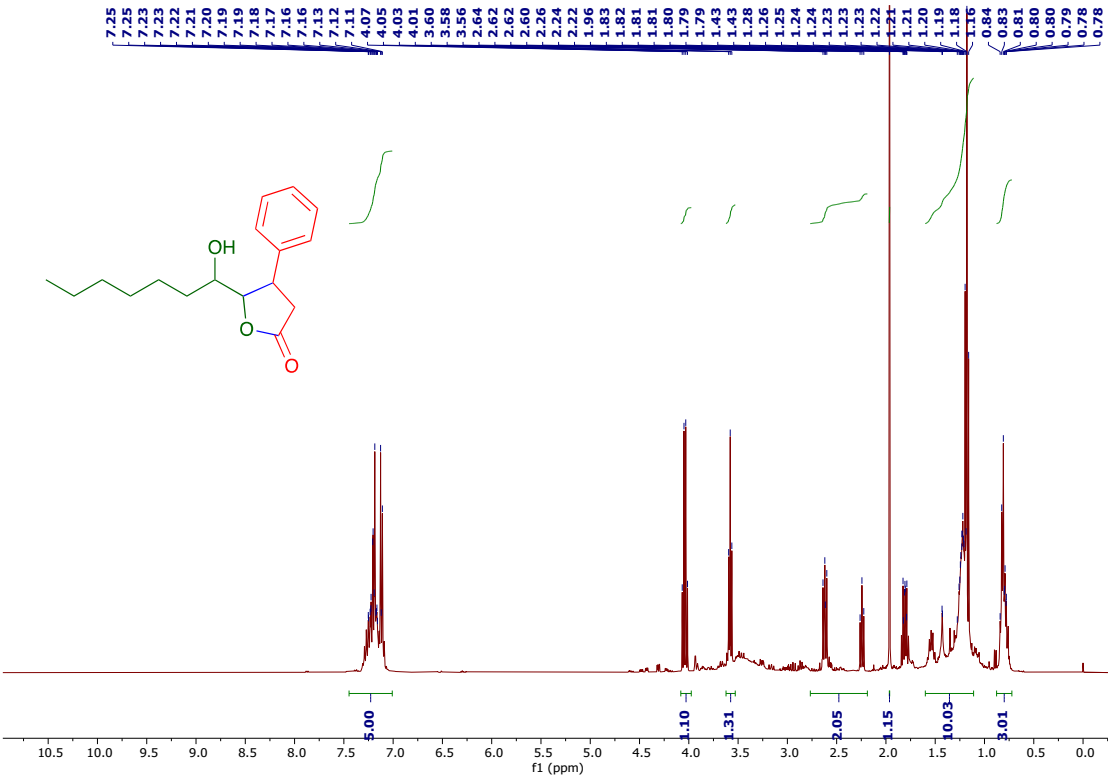


$^{13}C\{^{1}H\}$ NMR spectrum of 5-(1-hydroxypentyl)-4-phenyldihydrofuran-2(3H)-one (**22**, 100.6



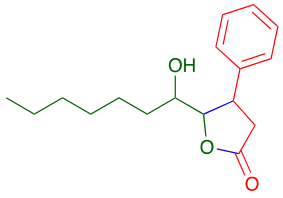
MHz, $CDCl_3$)

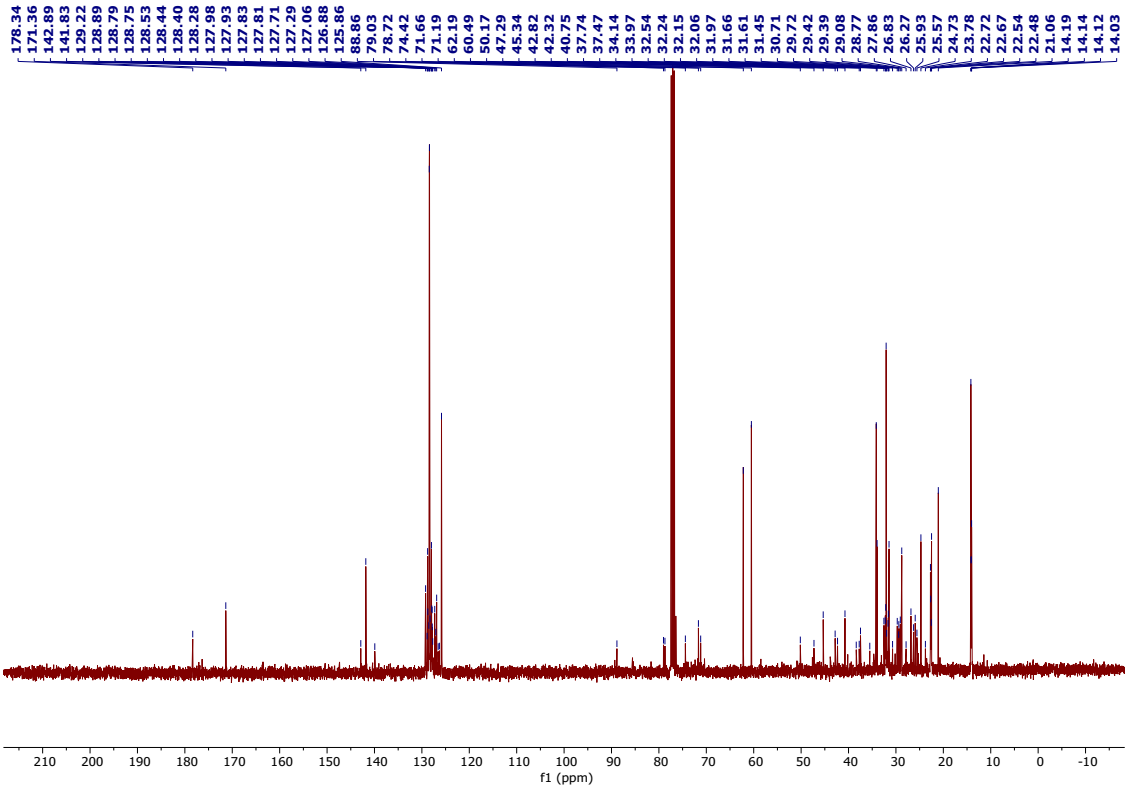
^{1}H NMR spectrum of 5-(1-hydroxyheptyl)-4-phenyldihydrofuran-2(3H)-one (**23**, 400 MHz,



$CDCl_3$)

$^{13}C\{^{1}H\}$ NMR spectrum of 5-(1-hydroxyheptyl)-4-phenyldihydrofuran-2(3H)-one (**23**, 100.6 MHz, $CDCl_3$)





XRD Data

Crystals of products **2** and **11** were obtained after slow evaporation of DCM, layered by hexane at room temperature. Crystals suited for single-crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEXCCD detector and with an Incoatecmicrosource (Cu-Kα radiation, λ = 1.54184 Å, multilayer optics). The temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+ and corrected for absorption with SADABS. The structures were solved by direct methods and refined on F2 with SHELXL-97 using Olex-2 software. Crystal data of product **2** was found already published[3] and hence, data not provided here.

Crystal data of 5-(hydroxy(phenyl)methyl)-4-(pyren-2-yl)dihydrofuran-2(3H)-one (11):

$C_{27}H_{20}O_3$, yellow, crystal dimension : 0.22 x 0.22 x 0.2 mm^{-1}, M = 392.43, triclinic, P-1, a = 8.4872(4) Å, b = 10.3122(5) Å, c = 11.7926(5) Å, α = 96.838(4)°, β = 107.111(4)° , γ = 99.692(4)°, V = 956.66(8) $Å^3$, Z = 2 F(000) = 412.0, μ-(CuKα) = 0.701 mm^{-1} , 2θmax = 86.175, ρcalcd= 1.362 g/cm^3 , T =295.1(4) K, min/max transmission factors = 0.776/1.000, 12861 Reflections collected 3929 unique (*R1*, 0.0482(3143)), *WR2* = 0.1510(3929) (all data). Residual electron density max/min = 0.15/- 0.18e.$Å^{-3}$. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number CCDC **2348651.**

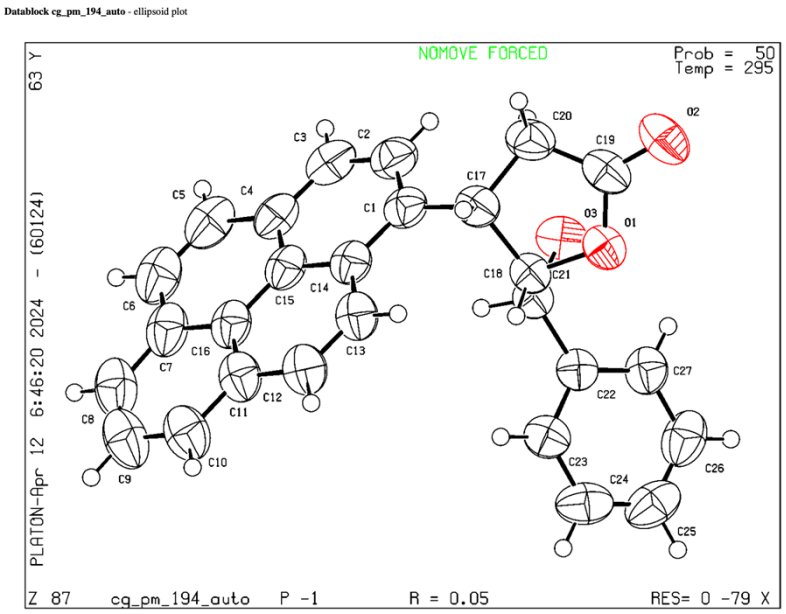


Figure 1. Thermal ellipsoid diagram of 11 drawn with 50% probability.

Procedures for mechanistic studies (Scheme 3) and EPR studies (Figure 1)

Reaction of 1-phenyl-1,2-ethandiol with cinnamyl aldehyde in presence of catalyst (Scheme 3a, with catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1-phenyl-1,2-ethandiol (0.5 mmol), cinnamyl aldehyde (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The expected product **2** was obtained in 52%, 70mg) isolated yield.

Reaction of 1-phenyl-1,2-ethandiol with cinnamyl aldehyde in absence of catalyst (Scheme 3a, without catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, NaOH (0.25 mmol), 1-phenyl-1,2-ethandiol (0.5 mmol), cinnamyl aldehyde (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of the expected product **2** was not observed.

Reaction of α-hydroxyacetophenone with cinnamyl alcohol in presence of catalyst (Scheme 3b, with catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), α-hydroxyacetophenone (0.5 mmol), cinnamyl alcohol (0.5 mmol) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of expected product **2** was not observed.

Reaction of α-hydroxyacetophenone with cinnamyl alcohol in absence of catalyst (Scheme 3b, without catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, NaOH (0.25 mmol), α-hydroxyacetophenone (0.5 mmol), cinnamyl alcohol (0.5 mmol) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of the expected product **2** was not observed.

Reaction of 2-hydroxy-2-phenylethyl cinnamate in presence of catalyst (Scheme 3c, with catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 2-hydroxy-2-phenylethyl cinnamate (0.5 mmol), prepared using reported procedure,[4] and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out

of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of expected product **2** was not observed.

Reaction of 2-hydroxy-2-phenylethyl cinnamate in absence of catalyst (Scheme 3c, without catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, NaOH (0.25 mmol), 2-hydroxy-2-phenylethyl cinnamate (0.5 mmol), prepared using reported procedure,[4] and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of expected product **2** was not observed.

Reaction of phenylglyoxal hydrate with cinnamyl alcohol in presence of catalyst (Scheme 3d, with catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), phenylglyoxal hydrate (0.5 mmol), cinnamyl alcohol (0.5 mmol) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate.

The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of expected product **2** was not observed.

Reaction of phenylglyoxal hydrate with cinnamyl alcohol in absence of catalyst (Scheme 3d, without catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, NaOH (0.25 mmol), phenylglyoxal hydrate (0.5 mmol), cinnamyl alcohol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of the expected product **2** was not observed.

Reaction of phenylglyoxal hydrate with cinnamyl aldehyde in presence of catalyst (Scheme 3d, with catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), phenylglyoxal hydrate (0.5 mmol), cinnamyl aldehyde (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of expected product **2** was not observed.

Reaction of phenylglyoxal hydrate with cinnamyl aldehyde in absence of catalyst (Scheme 3d, without catalyst 1):

A Schlenk flask (25 mL) was equipped with a stir bar, NaOH (0.25 mmol), phenylglyoxal hydrate (0.5 mmol), cinnamyl aldehyde (0.5 mmol) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The formation of the expected product **2** was not observed.

Reaction of 1-phenyl-1,2-ethandiol with but-3-en-1-ol in presence of catalyst 1 (Scheme 3e):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1-phenyl-1,2-ethandiol (0.5 mmol), but-3-en-1-ol (0.5 mmol) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The expected product **13** was obtained in 41% (55 mg) yield.

Catalyst poisoning experiment using mercury (Scheme 3f, Hg):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1-phenyl-1,2-ethandiol (0.5 mmol), cinnamyl alcohol (0.5 mmol) and ^{t}amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, to this Hg (300 equiv w.r.t. catalyst, 1.5 mmol) was added and equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a

flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was decanted and evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The expected product **2** was obtained in 56% (75 mg) yield.

Poisoning experiment with 1,10-phenanthroline (Scheme 3f, 1,10-phenanthroline):

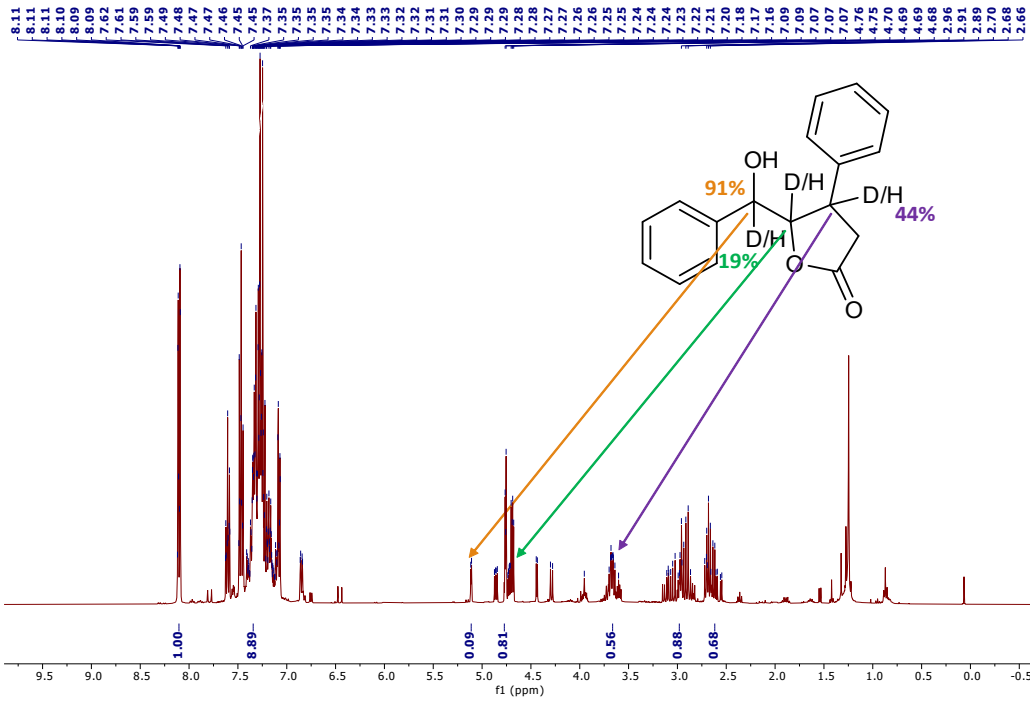
A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1-phenyl-1,2-ethandiol (0.5 mmol), cinnamyl alcohol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, to this 1,10-phenanthroline (10 equiv w.r.t. catalyst, 0.05 mmol) was added and equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (10 mL) and extracted using dichloromethane (15 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl acetate/hexane mixture (15:85) as an eluent. The expected product **2** was obtained in 69% isolated yield.

Deuterium labelling experiment (Scheme 3g):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1-phenyl-1,2-ethandiol-d5 (0.5 mmol), cinnamyl alcohol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 ºC (oil bath temperature) with stirring in an open system under a flow of nitrogen for 36 h. The completion of the reaction was monitored using TLC. After cooling to room temperature, the solvent was evaporated. The resulted residue was dissolved in water (D_2O, 1 mL) and extracted using dichloromethane (5 mL × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure using a rotavapor and the residue was purified by column chromatography over silica-gel (100-200 mesh) using ethyl

acetate/hexane mixture (15:85) as an eluent. The expected product **2-d4** was obtained in 71% isolated yield.

^{1}H NMR of the product **2-d4**: (400 MHz, $CDCl_3$)



Radical trapping experiment in the reaction of catalysts 1, base, cinnamyl alcohol, 1-phenylethan-1,2-diol and tempo (Scheme 3h):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1-phenyl-1,2-ethandiol-d5 (0.5 mmol), cinnamyl alcohol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. The reaction mixture was flitered through celite pad and subjected to mass spectrometric analysis.

EPR study of the reaction of catalysts 1, base, and 1,2-diol (Figure 1a):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1,2-diol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was

heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. EPR of the reaction mixture was recorded at 106 K.

EPR study of the reaction of catalysts 1, base, 1,2-diol and allylic alcohol (figure 1b):

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1,2-diol (0.5 mmol), allylic alcohol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. EPR of the reaction mixture was recorded at 106 K.

Stoichiometric reactions, epr studies, and mass spectrometric analysis

^{31}P NMR studies of stoichiometric reactions:

Stoichiometric experiment of catalyst 1, base and cinnamyl alcohol:

In an oven-dried vial (6 mL), equipped with a magnetic stir bar, catalyst **1** (0.025 mmol), NaOH (0.03 mmol), and toluene-d8 (500 µL) were taken and cooled down to -20 °C in a globe box. To this, cinnamyl alcohol (0.025 mmol) was added and the reaction was allowed to continue at -20 °C for 2 h. The resulting solution was subjected to ^{31}P NMR analysis.

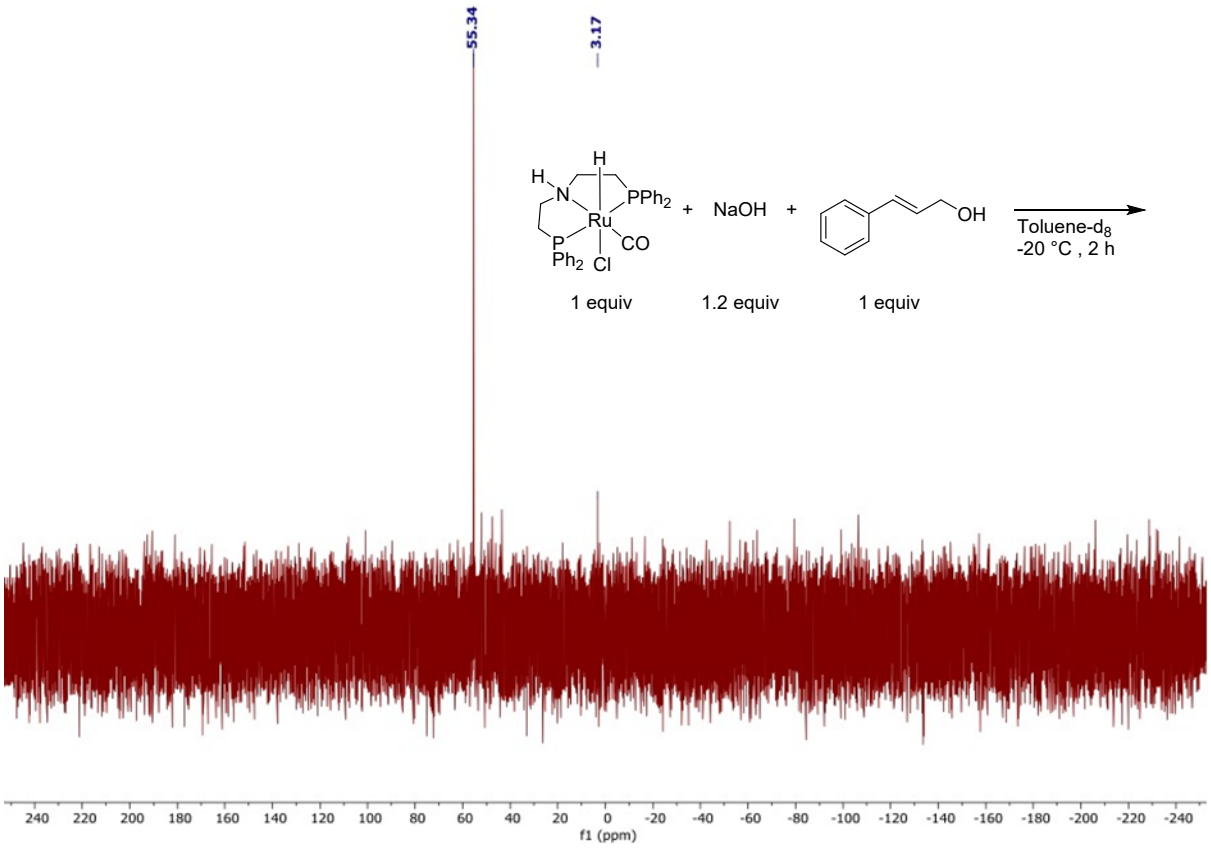


Figure S2. ^{31}P NMR spectrum of catalyst 1, base and cinnamyl alcohol.

Stoichiometric experiment of catalyst 1, base and 1,2-diol:

In an oven-dried vial (6 mL), equipped with a magnetic stir bar, catalyst **1** (0.025 mmol), NaOH (0.03 mmol), and toluene-d8 (500 µL) were added and cooled down to -20 °C in a globe box. To this, 1,2-diol (0.025 mmol) was added, and the reaction was allowed to continue at -20 °C for 2 h. The resulting solution was subjected to ^{31}P NMR analysis.

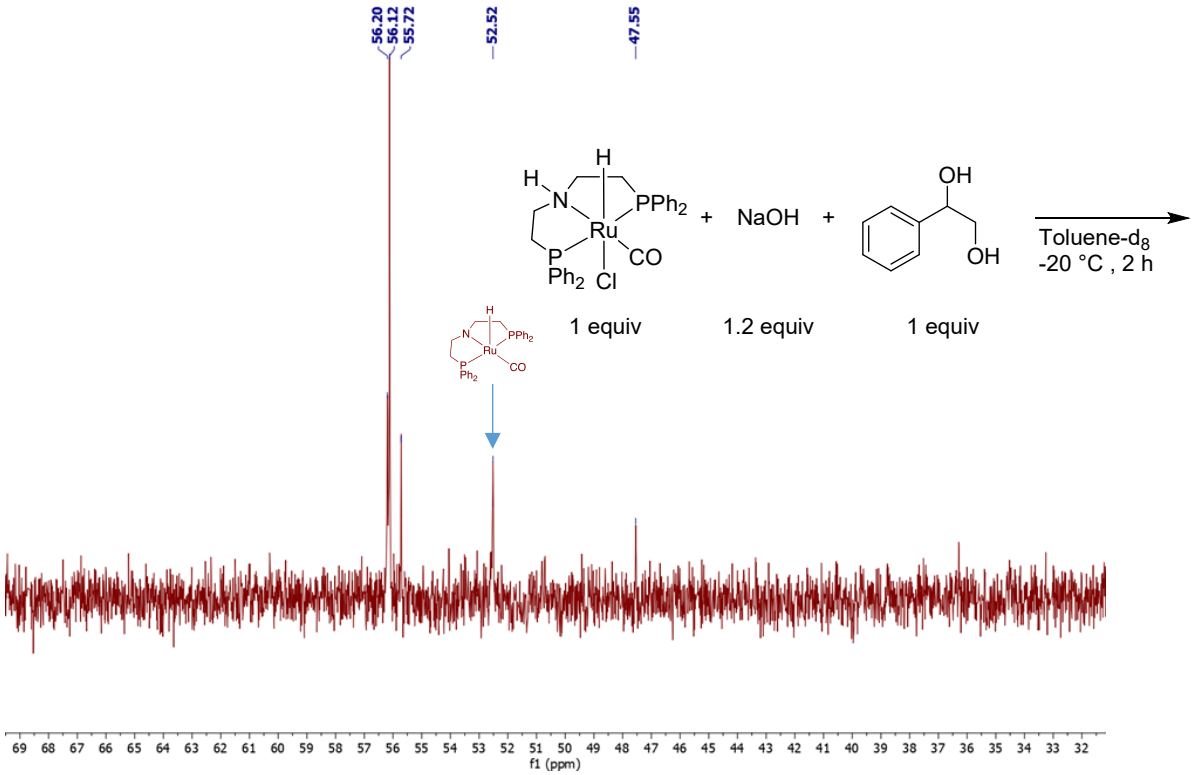


Figure S3. ^{31}P NMR spectrum of catalyst 1, base and 1,2-diol.

Stoichiometric experiment of catalyst 1, base and 1-phenylethanol:

In an oven-dried vial (6 mL), equipped with a magnetic stir bar, catalyst **1** (0.025 mmol), NaOH (0.03 mmol) and toluene-d8 (500 µL) were added and cooled down to -20 °C in a globe box. To this, 1-phenylethanol (0.025 mmol) was added and the reaction was allowed to continue at -20 °C for 2 h. The resulting solution was subjected to ^{31}P NMR analysis.

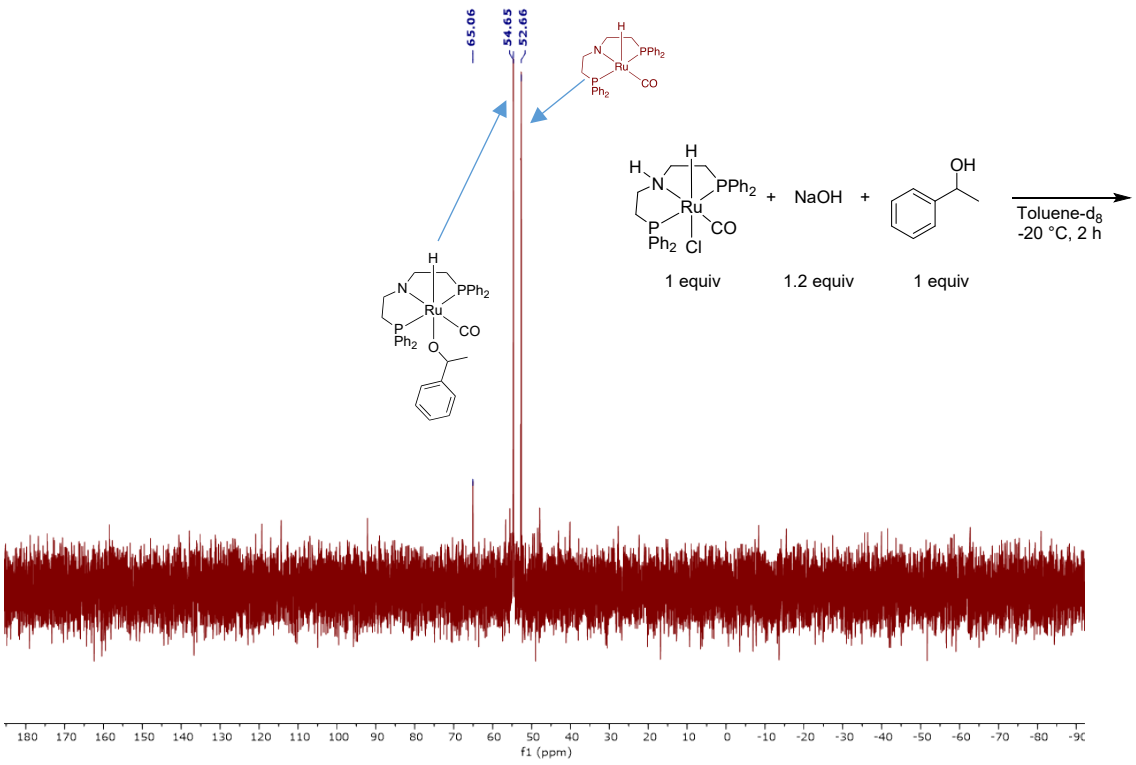


Figure S4. ^{31}P NMR spectrum of catalyst 1, base and 1-phenylethanol.

Stoichiometric experiment of catalyst 1, base, 1,2-diol and cinnamyl alcohol:

In an oven-dried vial (6 mL), equipped with a magnetic stir bar, catalyst **1** (0.025 mmol), NaOH (0.03 mmol), and toluene-d8 (500 µL) were taken and cooled down to -20 °C in a globe box. To this, 1,2-diol (0.025 mmol) followed by cinnamyl alcohol (0.025 mmol) were added, and the reaction was allowed to continue at -20 °C for 2 h. The resulting solution was subjected to ^{31}P NMR analysis.

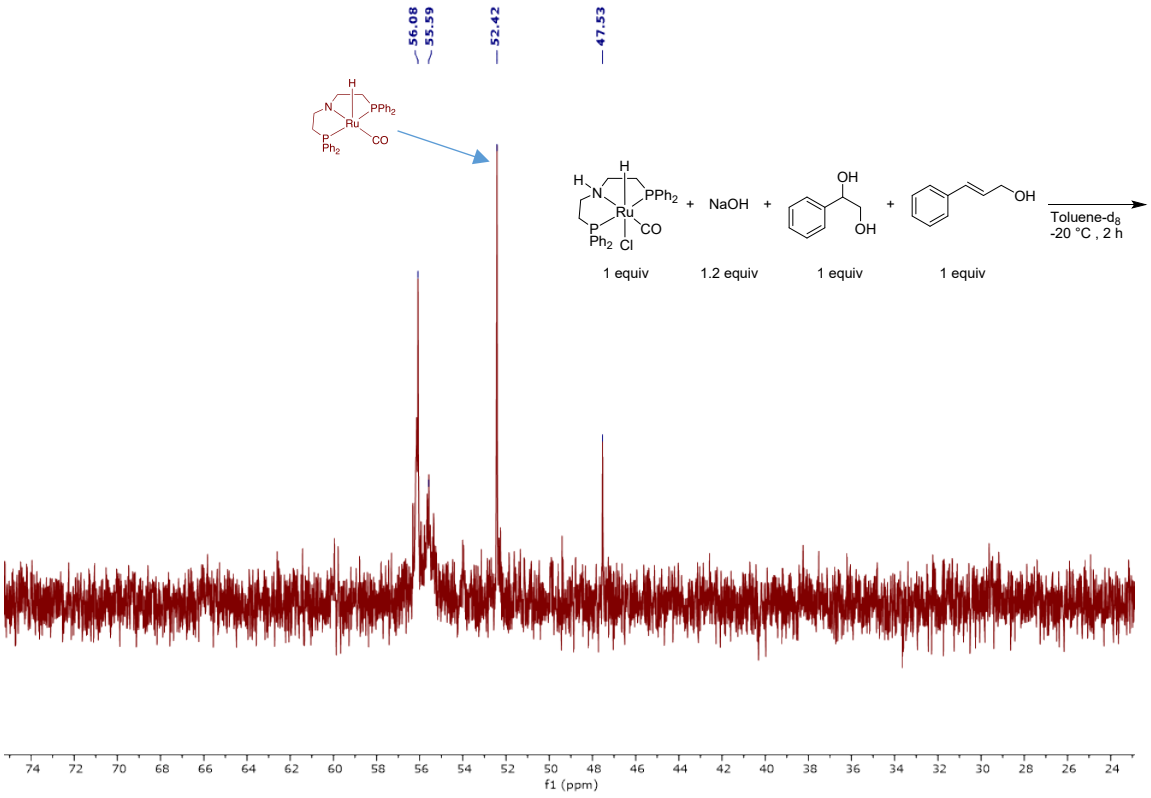


Figure S5. ^{31}P NMR spectrum of catalyst 1, base, 1,2-diol and cinnamyl alcohol.

EPR studies:

EPR study of the reaction of catalysts 1, base, and cinnamyl alcohol:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), cinnamyl alcohol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. EPR of the reaction mixture was recorded at 106 K.

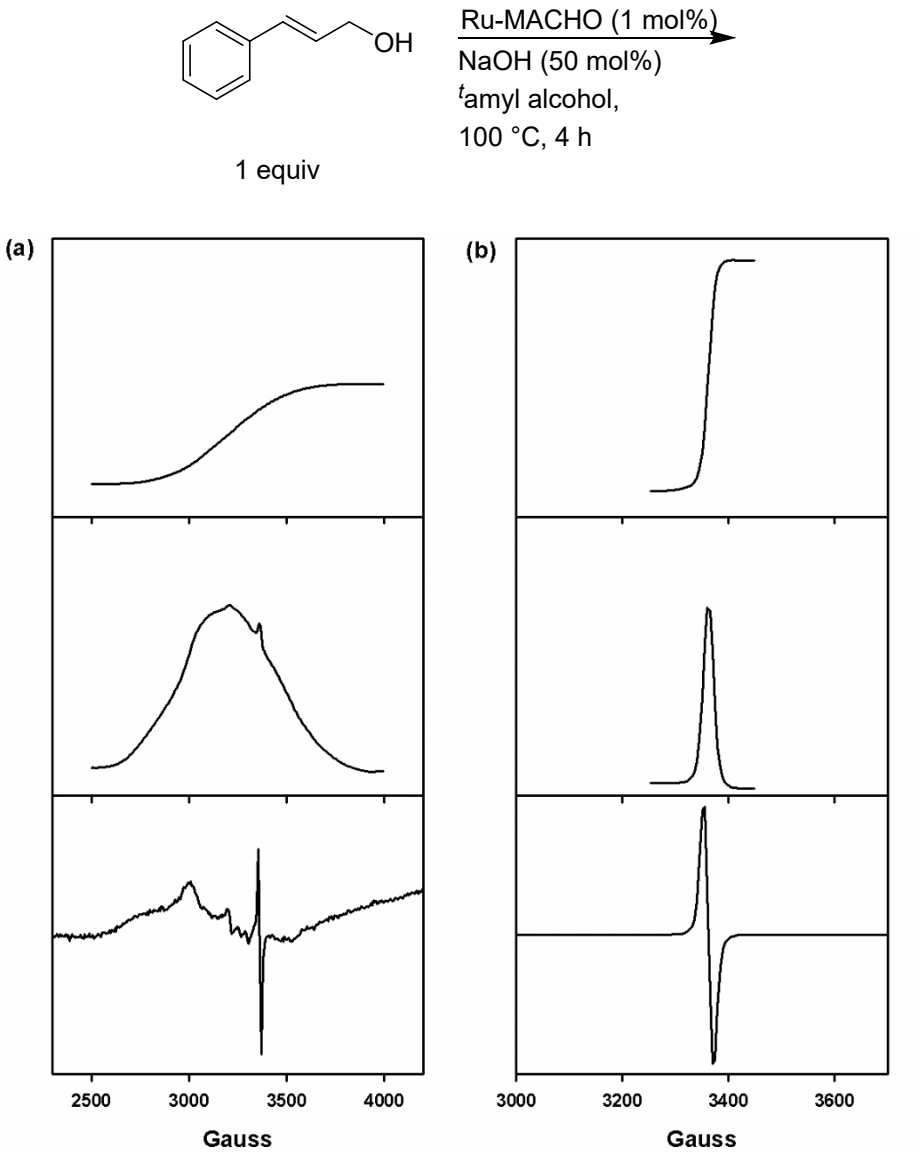


Figure S6. First derivative (bottom lines), integrated (middle lines) and doubly integrated (top lines) EPR spectra of (a) catalyst **1**, base and cinnamyl alcohol (scale = 0.5 mmol), and (b) galvinoxyl radical (0.5 mmol) used as a reference. The spin amount of the low-spin Ru(III) along with radical is determined to be 40(3)%. Spectra were recorded at 106 K.

EPR study of the reaction of catalysts 1, base, and 1,2-diol:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.005 mmol), NaOH (0.25 mmol), 1,2-diol (0.5 mmol) and *t*amyl alcohol (2 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. EPR of the reaction mixture was recorded at 106 K.

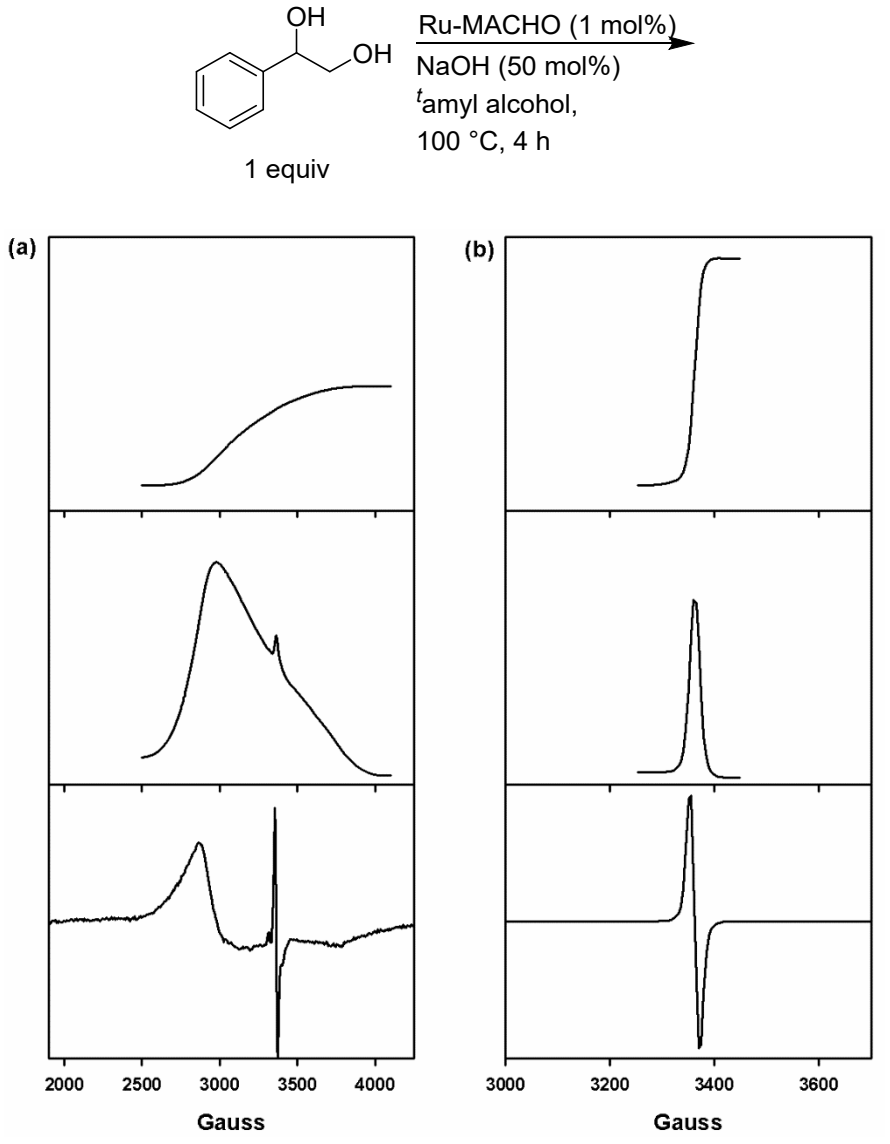
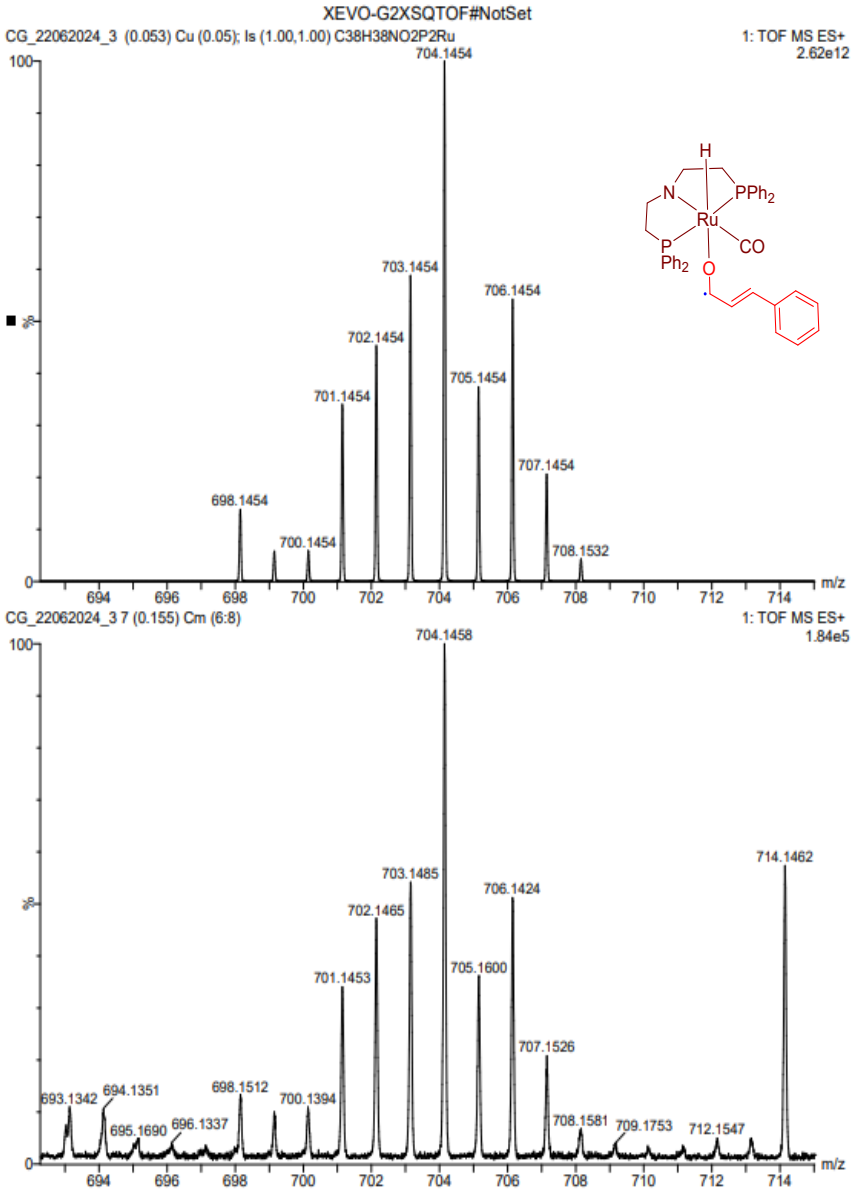


Figure S7. First derivative (bottom lines), integrated (middle lines) and doubly integrated (top lines) EPR spectra of (a) catalyst **1**, base and 1,2-diol (scale = 0.5 mmol), and (b) galvinoxyl radical (0.5 mmol) used as a reference. The spin amount of the low-spin Ru(III) along with radical is determined to be 45(5)%. Spectra were recorded at 106 K.

Mass spectrometric analysis:

Mass spectrometric analysis of the reaction of catalysts 1, base, and cinnamyl alcohol:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.0025 mmol), NaOH (0.125 mmol), cinnamyl alcohol (0.25 mmol) and ᵗamyl alcohol (1 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. The reaction mixture was flitered through celite pad and subjected to mass spectrometric analysis. HRMS (ESI) m/z calcd for $C_{38}H_{38}NO_2P_2Ru$ $(M+H)^+$: 704.1454,



found: 704.1458.

Figure S8. HRMS of intermediate iv in reaction with catalyst 1, base, and cinnamyl alcohol.

ESI m/z found for C_9H_9O : 133.8952.

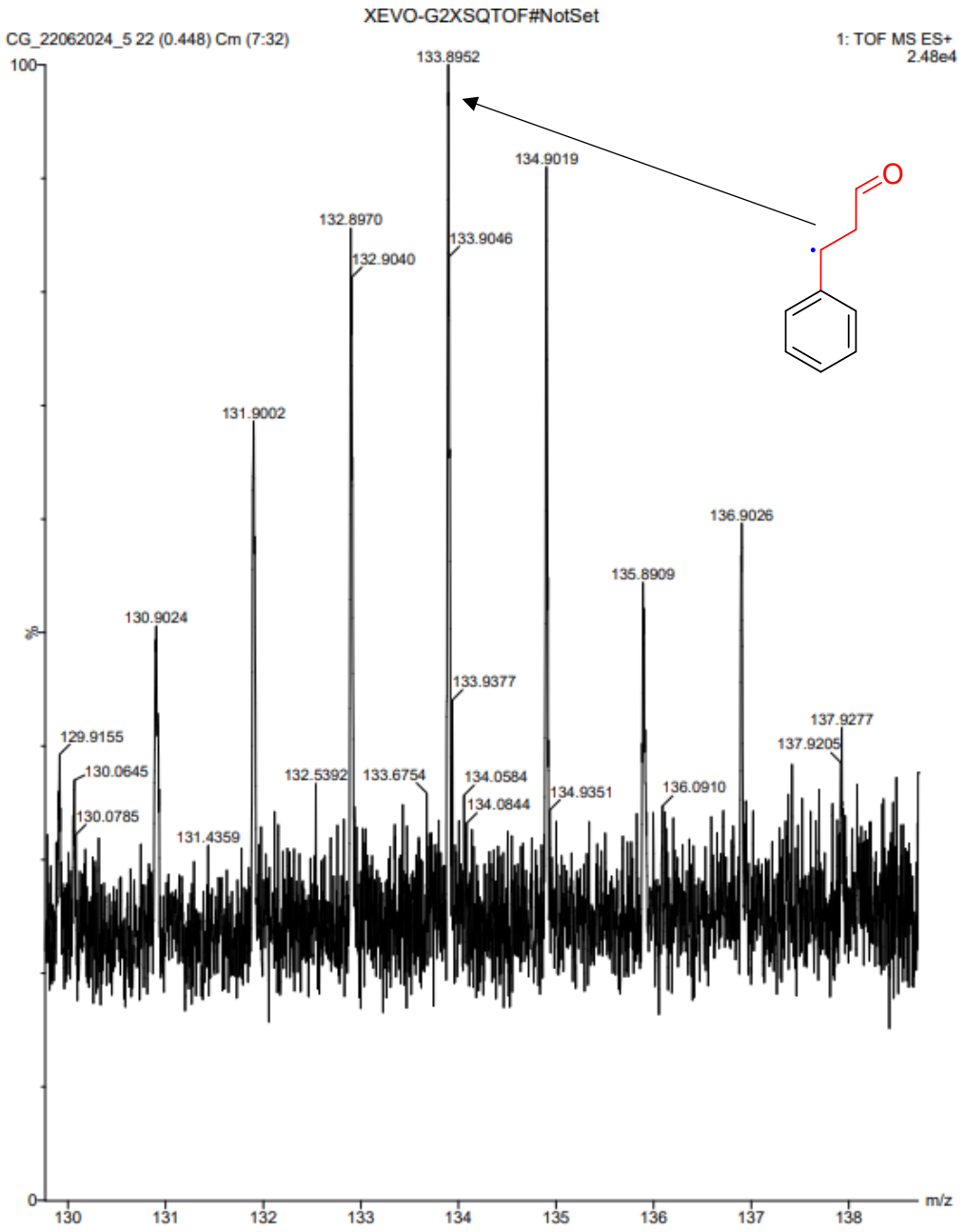


Figure S9. ESI of intermediate v in reaction with catalyst 1, base, and cinnamyl alcohol.

Mass spectrometric analysis of the reaction of catalysts 1, base, and 1-phenylethan-1,2-diol:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.0025 mmol), NaOH (0.125 mmol), 1-phenylethan-1,2-diol alcohol (0.25 mmol) and ^{t}amyl alcohol (1 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. The reaction mixture was flitered through celite pad and subjected to mass spectrometric analysis. ESI m/z found for $C_{37}H_{37}NO_3P_2Ru$: 707.1146.

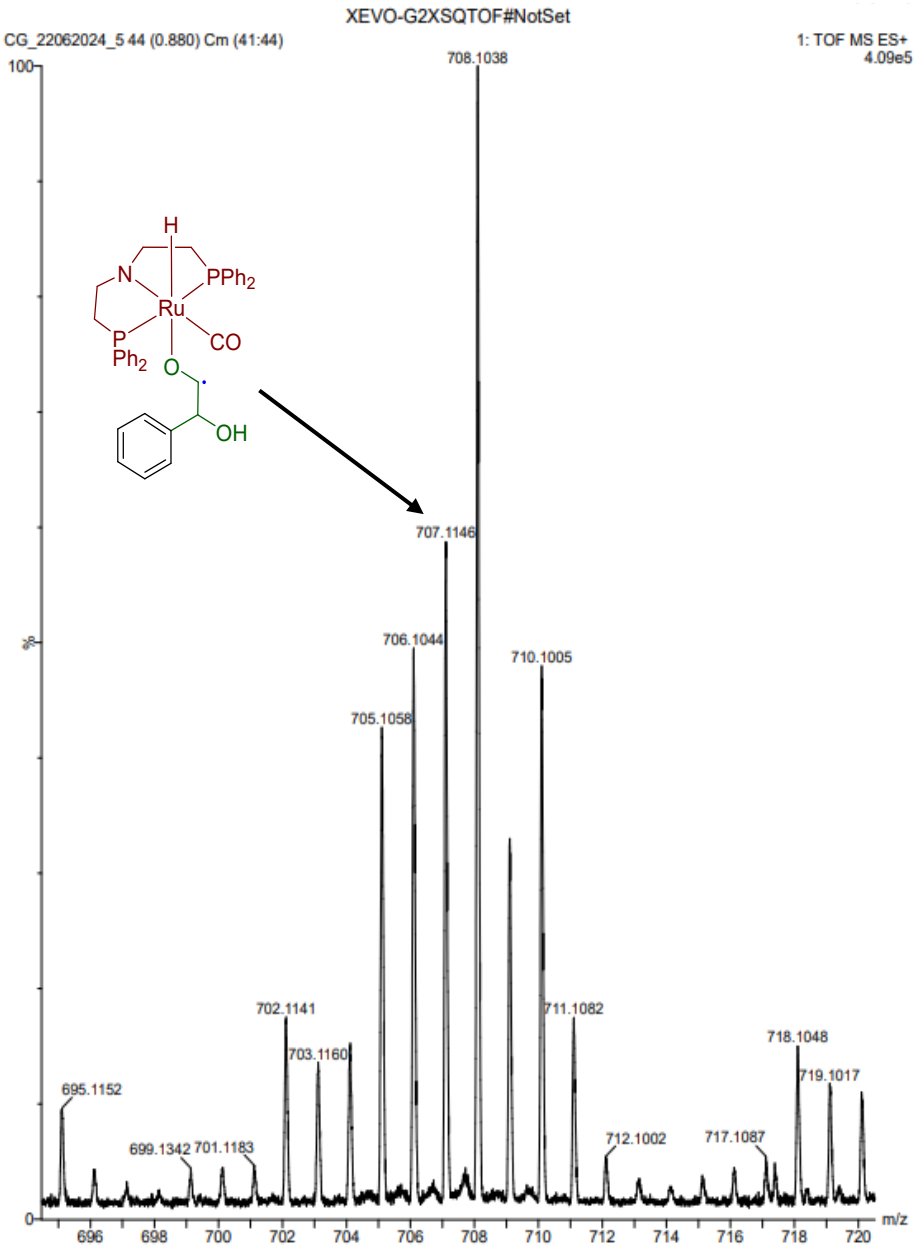
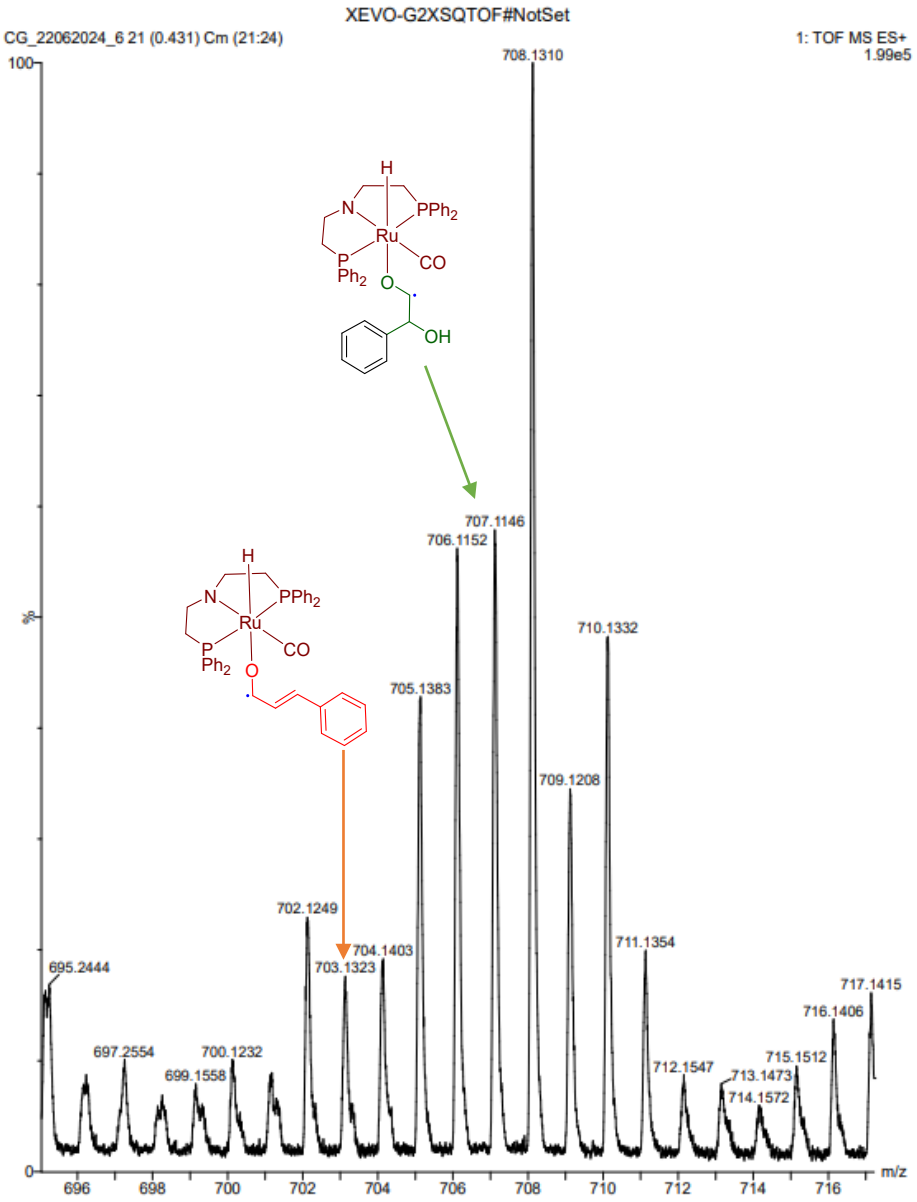


Figure S10. ESI of intermediate vi in reaction with catalyst 1, base, and 1-phenyl-ethan-1,2,diol

Mass spectrometric analysis of the reaction of catalysts 1, base, cinnamyl alcohol, 1-phenylethan-1,2-diol and tempo:

A Schlenk flask (25 mL) was equipped with a stir bar, catalyst **1** (0.0025 mmol), NaOH (0.125 mmol), cinnamyl alcohol (0.25 mmol), 1-phenylethan-1,2-diol alcohol (0.25 mmol), TEMPO (0.75 mmol) and ᵗamyl alcohol (1 mL) under nitrogen atmosphere in a glove box. The flask was taken out of the glove box, equipped with a condenser and the solution was heated at 100 °C (oil bath temperature) with stirring in an open system under a flow of nitrogen for 4 h. The reaction mixture was flitered through celite pad and subjected to mass spectrometric analysis.



ESI m/z found for $C_{37}H_{37}NO_3P_2Ru$: 707.1146. ESI m/z found for $C_{38}H_{37}NO_2P_2Ru$: 703.1323.

Figure S11. ESI of intermediate iv and vi in reaction of cinnamyl alcohol, 1-phenylethan-1,2-diol, catalyst 1 and base with TEMPO.

ESI m/z found for $C_{29}H_{30}NOP_2Ru$ $(M+H)^+$: 572.0879, found: 572.0906.

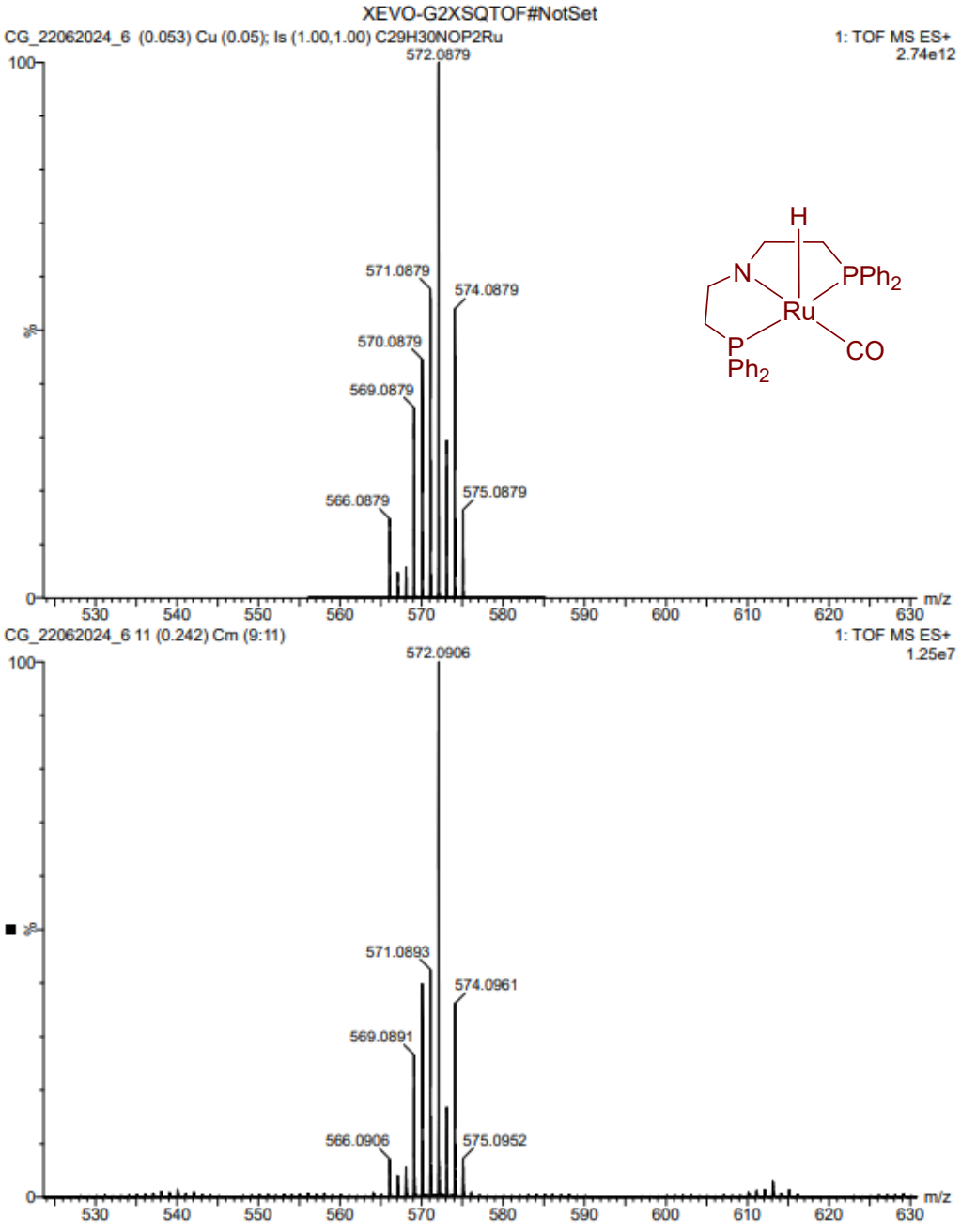


Figure S12. ESI of intermediate in reaction of cinnamyl alcohol, 1-phenylethan-1,2-diol, catalyst 1 and base with TEMPO.

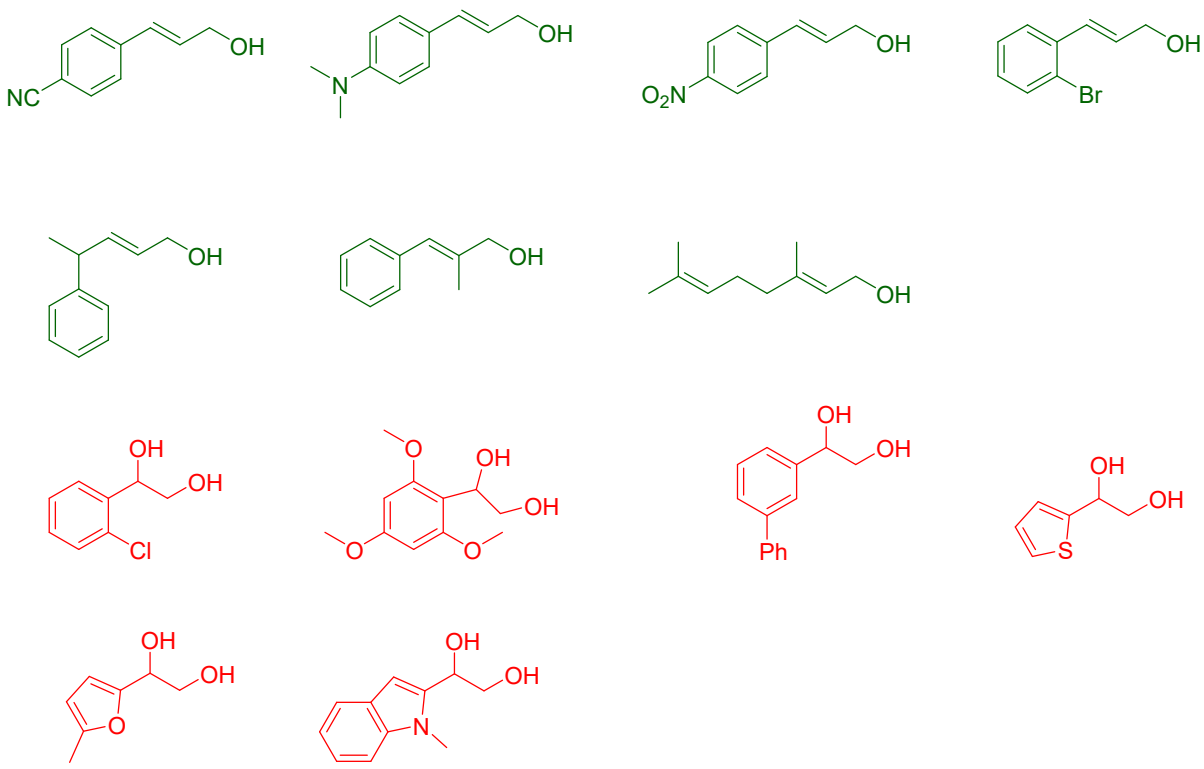


Figure S13. Unsuccessful substrates.

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