SUPPLEMENTARY INFORMATION

Cytotoxicity and preliminary mode of action studies of novel 2-aryl-4-thiopyrone-based organometallics

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Syntheses of the ligands

2-Bromo-3-hydroxy-6-methyl-4H-pyran-4-one (2).

Allomaltol (1.00 g, 7.90 mmol) and ammonium acetate (0.07 g, 0.87 mmol) were dissolved in acetonitrile (50 mL), NBS (1.55 g, 8.70 mmol) was added and the reaction mixture was stirred for 4 hours at room temperature. The solvent was evaporated and the residue extracted with a mixture of water/dichloromethane. The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The obtained solid was dried *in vacuo* and used without further purification for the next step. Yield 1.15 g, 5.61 mmol, 71%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.27 (s, 3 H, -CH_3), 6.30 (s, 1 H, H5), 9.79 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): 172.25(C4), 166.2 (C6), 143.8 (C3), 128.9 (C2) 111.6 (C5), 19.0 (C7). Elemental anal. calc for $C_6H_5BrO_3$: C, 35.15; H, 2.45; Found: C, 34.79; H, 2.27 %. ESI-MS$^-$ m/z: 204.8 [M-H]$^-$.

3-(Benzyloxy)-2-bromo-6-methyl-4H-pyran-4-one (3). Bromoallomaltol **2** (1.25 g, 6.10 mmol) was dissolved in dichloromethane (20 mL). Benzylbromide (0.94 mL, 7.91 mmol) and 18-crown-6 ether (0.11 mg, 0.42 mmol), dissolved in dichloromethane (10 mL) were added. KOH solution (15%, 10 mL) was added and the mixture was vigorously stirred overnight. The phases were separated, the water phase was extracted with dichloromethane, the organic layers were combined, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification by column chromatography (*n*-hexane/ethyl acetate = 1/1) yielded the product as yellow oil. Yield: 1.21 g, 4.09 mmol, 62%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.27 (s, 3 H, -CH_3), 5.10 (s, 2 H, -OCH_2-), 6.35 (s, 1 H, H5), 7.32 – 7.44 (m, 5 H,-C_6H_5) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): 173.4 (C4), 166.4 (C6), 144.0 (C3), 139.6 (C_{Ar}), 136.3 (C2), 128.5 (C_{Ar}), 128.27 (C_{Ar}), 114.2 (C5), 73.1 (-OCH_2-), 18.7 (C7) ppm. HR-ESI-MS$^+$ m/z calc.: 295.1286; found: 294.9963 [M-H]$^+$.

General procedure for Suzuki-Miyaura coupling reactions.

Benzylated bromoallomaltol **3** (1.50 g, 5.08 mmol, 1 eq), phenylboronic acid (6.10 mmol, 1.20 eq.) and potassium phosphate (4.00 g, 15.20 mmol, 3 eq.) were dissolved in acetonitrile/water (2:1, 40 mL). Tetrakis(triphenylphosphine)palladium(0) (10 mol%) was added and the mixture was stirred overnight at 75 °C under an argon atmosphere. After cooling to room temperature, the phases were separated, the water phase was extracted with acetonitrile, the combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification by column chromatography (*n*-hexane/ethyl acetate = 1/1) yielded the respective product.

3-(Benzyloxy)-6-methyl-2-phenyl-4H-pyran-4-one (4a).

The synthesis was performed according to the general procedure using phenylboronic acid (0.85 g). Yield: 1.28 g, 4.38 mmol, 86%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.34 (s, 3 H, -CH_3), 5.08 (s, 2 H, -OCH_2-), 6.34 (s, 1 H, H5), 7.27 (br s, 5 H, -C_6H_5), 7.29 – 7.34 (m, 2 H, H_{Ar}), 7.85 – 7.90 (m, 2 H, H_{Ar}) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 175.4 (C4), 165.0 (C6), 155.0 (C2), 142.2 (C3),136.7 (C_{Ar}), 130.3 (C4'), 130.1 (C1'), 128.4 (C2', C6'), 128.3 (C_{Ar}), 128.1 (C_{Ar}), 128.0 (C_{Ar}), 127.9 (C3', C5'), 113.9 (C5), 72.6 (-OCH_2-), 19.1 (C7) ppm. ESI-MS$^+$ m/z: 315.31 [M+Na]$^+$.

3-(Benzyloxy)-2-(4-fluorophenyl)-6-methyl-4H-pyran-4-one (4b).

The synthesis was performed according to the general procedure using 4-fluorophenylboronic acid (0.74 g). Yield: 1.32 g, 4.57 mmol, 84%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.33 (s, 3 H, -CH_3), 5.08 (s, 2 H, -OCH_2-), 6.34 (s, 1 H, H5), 7.28 (br s, 5 H, -C_6H_5), 7.28 – 7.34 (m, 2 H, H_{Ar}), 7.85 – 7.89 (m, 2 H, H_{Ar}) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 175.3 (C4), 165.0 (C6), 162.9 (d, $^1J_{C,F}$ = 249 Hz, C4'), 154.1 (C2), 141.9 (C3),136.5 (C_{Ar}), 130.5 (d, $^3J_{C,F}$ = 8 Hz, C2', C6'), 128.4 (C_{Ar}), 128.1 (C_{Ar}), 128.0 (C_{Ar}), 126.6 5 (d, $^4J_{C,F}$ = 3 Hz, C1'), 115.4 (d, $^2J_{C,F}$ = 22 Hz, C3', C5'), 113.9 (C5), 72.6 (-OCH_2-), 19.0 (C7) ppm. ESI-MS$^+$ m/z: 333.29 [M+Na]$^+$.

3-(Benzyloxy)-6-methyl-2-(*p*-tolyl)-4H-pyran-4-one (4c).

The synthesis was performed according to the general procedure using 4-methylphenylboronic acid (0.83 g). Yield: 1.23 g, 4.03 mmol, 79%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.33 (s, 3 H, -CH_3), 2.36 (s, 3 H, -CH_3) 5.06 (s, 2 H, -OCH_2-), 6.32 (s, 1 H, H5), 7.26 – 7.31 (m, 7 H,-C_6H_5, H_{Ar}), 7.73 – 7.76 (m, 2 H, H_{Ar}) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 175.4 (C4), 164.9 (C6), 155.0 (C2), 142.0 (C3), 140.3 (C4'), 136.7 (C_{Ar}), 129.0 (C3', C5'), 128.3 (C_{Ar}), 128.2 (C_{Ar}), 128.0 (C_{Ar}), 127.8 (C2', C6'), 127.3 (C1'), 113.8 (C5), 72.5 (-OCH_2-), 21.0 (-CH_3), 19.1 (C7) ppm. ESI-MS$^+$ m/z: 307.29 $[M+H]^+$, 329.27 $[M+Na]^+$

3-(Benzyloxy)-6-methyl-2-(4-methoxyphenyl)-4H-pyran-4-one (4d).

The synthesis was performed according to the general procedure using 4-methoxyphenylboronic acid (0.93 g). Yield: 1.40 g, 4.33 mmol, 85%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.33 (s, 3 H, -CH_3), 3.82 (s, 3 H, -OCH_3) 5.06 (s, 2 H, -OCH_2-), 6.30 (s, 1 H, H5), 7.03 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 7.30 (br s, 5 H,-C_6H_5), 7.83 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 175.3 (C4), 164.6 (C6), 160.7 (C4'), 154.9 (C2), 141.4 (C3), 136.7 (C_{Ar}), 128.2 (C_{Ar}), 128.1 (C_{Ar}), 128.0 (C_{Ar}), 129.5 (C2', C6'), 122.3 (C1'), 113.8 (C5), 113.7 (C3', C5'), 72.4 (-OCH_2-), 55.3 (-OCH_3), 19.0 (C7) ppm. ESI-MS$^+$ m/z: 323.36 $[M+H]^+$, 345.31 $[M+Na]^+$.

General procedure for cleavage of the benzyl group.

The respective protected pyrone **4a–d** (4.00 mmol) was suspended in acetic acid (10 mL), HCl conc. (15 mL) was slowly added and the mixture was refluxed for 3 hours. If not other stated, the solvent was removed after cooling to room temperature, the residue suspended in acetone, filtered, washed with acetone and dried *in vacuo*.

3-Hydroxy-6-methyl-2-phenyl-4H-pyran-4-one (5a).

The synthesis was performed according to the general procedure using 3-(benzyloxy)-6-methyl-2-phenyl-4H-pyran-4-one **4a** (1.17 g, 4.00 mmol). The solvent was removed and the residue was taken up in 20 mL dichloromethane and washed with water (3x 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. Yield: 0.86 g, 3.92 mmol, 98%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.37 (s, 3 H, -CH_3), 6.33 (s, 1 H, H5), 7.42 – 7.46 (m, 1 H, H_{Ar}), 7.49 – 7.53 (m, 2 H, H_{Ar}), 8.00 – 8.03 (m, 2 H, H_{Ar}) 9.41 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 174.1 (C4), 164.9 (C6), 144.3 (C2), 141.9 (C3), 131.0 (C1'), 129.2 (C4'), 128.4 (C2', C6'), 126.72 (C3', C5'), 110.4 (C5), 19.3 (C7) ppm. HR-ESI-MS$^+$ m/z calc. 202.0630; found: 203.0702 $[M+H]^+$, 225.0521 $[M+Na]^+$.

3-Hydroxy-2-(4-fluorophenyl)-6-methyl-4H-pyran-4-one (5b).

The synthesis was performed according to the general procedure using 3-(benzyloxy)-2-(4-fluorophenyl)-6-methyl-4H-pyran-4-one **4b** (1.14 g, 4.00 mmol). Yield: 0.81 g, 3.69 mmol, 92%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.37 (s, 3 H, -CH_3), 6.32 (s, 1 H, H5), 7.33 – 7.38 (m, 2 H, H_{Ar}), 8.04 – 8.09 (m, 2 H, H_{Ar}) 9.50 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 174.0 (C4), 164.8 (C6), 162.2 (d, $^{1}J_{C,F}$ = 248 Hz, C4'), 143.6 (C2), 141.7 (C3), 129.1 (d, $^{3}J_{C,F}$ = 8 Hz, C2', C6'), 127.5 (d, $^{4}J_{C,F}$ = 3 Hz, C1'), 115.5 (d, $^{2}J_{C,F}$ = 22 Hz, C3', C5'), 110.4 (C5), 19.3 (C7) ppm. HR-ESI-MS$^+$ m/z calc.: 220.0536; found: 221.0607 $[M+H]^+$, 243.0427 $[M+Na]^+$.

3-Hydroxy-6-methyl-2-(*p*-tolyl)-4H-pyran-4-one (5c).

The synthesis was performed according to the general procedure utilizing 3-(benzyloxy)-6-methyl-2-(*p*-tolyl)-4H-pyran-4-one **4c** (1.23 g, 4.00 mmol). The solvent was removed and the product was taken up in 20 mL dichloromethane and washed with water (3x 20 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. Yield: 0.85 g, 3.92 mmol, 98%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.36 (s, 3 H, -CH_3), 2.36 (s, 3 H, -CH_3), 6.30 (s, 1 H, H5), 7.31 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 7.91 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 9.33 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 174.0 (C4), 164.7 (C6), 144.6 (C2), 141.5 (C3), 139.0 (C4'), 129.1 (C3', C5'), 128.2 (C1'), 126.7 (C2', C6'), 110.4 (C5), 20.9 (-CH_3), 19.3 (C7) ppm. HR-ESI-MS$^+$ m/z calc.: 216.0786; found: 217.0857 $[M+H]^+$, 239.0676 $[M+Na]^+$.

3-Hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-pyran-4-one (5d).

The synthesis was performed according to the general procedure utilizing 3-(benzyloxy)-6-methyl-2-(4-methoxyphenyl)-4H-pyran-4-one **4d** (1.29 g, 4.00 mmol). Yield: 0.90 g, 3.88 mmol, 97%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.35 (s, 3 H, -CH_3), 3.82 (s, 3 H, -OCH_3), 6.28 (s, 1 H, H5), 7.07 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 7.97 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 9.21 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 173.9 (C4), 164.4 (C6), 159.9 (C4'), 144.8 (C2), 141.0 (C3), 128.4 (C2', C6'), 123.4 (C1'), 114.0 (C3', C5'), 110.3 (C5), 55.3 (-OCH_3), 19.3 (C7) ppm. HR-ESI-MS$^+$ m/z calc.: 232.0736; found: 233.0808 $[M+H]^+$.

General synthesis for the thiopyrones

Pyrone **5a–d** (5.00 mmol, 1 eq) and Lawesson's reagent (1.01 g, 2.49 mmol, 1 eq) were suspended in dry THF (30 mL, dried over molecular sieves 3 Å) and were refluxed under inert conditions for 6 hours. The solvent was removed and the pure product was obtained by recrystallization from ethanol.

3-Hydroxy-6-methyl-2-phenyl-4H-pyran-4-thione (6a).

The synthesis was performed according to the general procedure utilizing 3-hydroxy-6-methyl-2-phenyl-4H-pyran-4-one **5a** (1.01 g, 5.00 mmol). Yield: 0.57 g, 2.61 mmol, 52%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.45 (s, 3 H, -CH_3), 7.41 (s, 1 H, H5), 7.51 – 7.59 (m, 3 H, H_{Ar}), 8.10 – 8.13 (m, 2 H, H_{Ar}) 8.83 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 187.2 (C4), 159.5 (C6), 147.3 (C3), 141.6 (C2), 130.4 (C4'), 130.1 (C1'), 128.8 (C3', C5'), 127.6 (C2', C6'), 122.4 (C5), 18.7 (C7) ppm. Elemental anal. calc for $C_{12}H_{10}O_2S$·: C, 66.03; H, 4.62; S, 14.69; Found: C, 65.74; H, 4.67; S, 14.66 %. ESI-MS$^+$ m/z: 218.96 $[M+H]^+$.

3-Hydroxy-2-(4-fluorophenyl)-6-methyl-4H-pyran-4-thione (6b).

The synthesis was performed according to the general procedure utilizing 3-hydroxy-2-(4-fluorophenyl)-6-methyl-4H-pyran-4-one **5b** (1.10 g, 5.00 mmol). Yield: 0.78 g, 3.30 mmol, 66%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.44 (s, 3 H, -CH_3), 7.39 – 7.45 (m, 3 H, H_{Ar}, H5), 8.15 – 8.20 (m, 2 H, H_{Ar}) 8.86 (s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 187.6 (C4), 162.9 (d, $^{1}J_{C,F}$ = 250 Hz, C4'), 159.4 (C6), 147.1 (C3), 141.0 (C2), 130.2 (d, $^{3}J_{C,F}$ = 9 Hz, C2', C6), 126.6 (d, $^{4}J_{C,F}$ = 3 Hz, C1'), 122.4 (C5), 115.9 (d, $^{2}J_{C,F}$ = 22 Hz, C3', C5'), 18.7 (C7) ppm. Elemental anal. calc for $C_{12}H_9FO_2S$: C, 61.00; H, 3.84; S, 13.57 Found: C, 61.09; H, 3.76; S, 13.50 %. ESI-MS$^+$ m/z: 236.93 $[M+H]^+$.

3-Hydroxy-6-methyl-2-(*p*-tolyl)-4H-pyran-4-thione (6c).

The synthesis was performed according to the general procedure utilizing 3-hydroxy-6-methyl-2-(*p*-tolyl)-4H-pyran-4-one **5c** (1.08 g, 5.00 mmol). Yield: 0.91 g, 3.90 mmol, 78%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.38 (s, 3 H, -CH_3), 2.44 (s, 3 H, -CH_3), 7.36 – 7.40 (m, 3 H, H5, H_{Ar}) 8.02 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 8.79 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 186.7 (C4), 159.2 (C6), 147.1 (C3), 142.0 (C2), 140.5 (C4'), 129.4 (C3', C5'), 127.5 (C2', C6'), 127.2 (C1'), 122.1. (C5), 21.1 (-CH_3), 18.7 (C7) ppm. Elemental anal. calc for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21; S, 13.80 Found: C, 67.10; H, 5.31; S, 13.74 %. HR-ESI-MS$^+$ m/z calc.: 232.0558; found: 233.0625 $[M+H]^+$, 255.0445 $[M+Na]^+$.

3-Hydroxy-2-(4-methoxyphenyl)-6-methyl-4H-pyran-4-thione (6d).

The synthesis was performed according to the general procedure utilizing 3-hydroxy-6-methyl-2-(4-methoxyphenyl)-4H-pyran-4-one **5d** (1.16 g, 5.00 mmol). Yield: 1.07 g, 4.30 mmol, 86%. ^{1}H NMR (DMSO-d_6, 500.10 MHz, 25 °C): δ = 2.43 (s, 3 H, -CH_3), 3.84 (s, 3 H, -OCH_3), 7.12 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 7.35 (s, 1 H, H5), 8.08 (d, 2 H, $^{3}J_{H,H}$ = 8 Hz, H_{Ar}), 8.75 (br s, 1 H, -OH) ppm. ^{13}C NMR (DMSO-d_6, 125.75 MHz, 25 °C): δ = 186.0 (C4), 160.9 (C6), 158.9 (C4'), 146.6 (C3), 142.2 (C2), 129.4 (C2', C6'), 122.2 (C1'), 121.8 (C5), 114.3 (C3', C5'), 55.4 (-OCH_3), 18.7 (C7) ppm. Elemental anal. calc for $C_{13}H_{12}O_3S$·0.1H_2O: C, 62.43; H, 4.92; S, 12.82 Found: C, 62.46; H, 4.90; S, 12.84 %. ESI-MS$^+$ m/z: 248.97 $[M+H]^+$.

Solubility determination

The solubility of all ligands and complexes was determined in 1% v/v DMSO/H_2O. A stock solution in DMSO was prepared and diluted with water to an overall concentration of 1% v/v DMSO. The solubility refers to the highest concentration of compound without observation of precipitation for at least 18 h. Same solubilities were observed for the system 1% v/v DMSO/PBS

Overview of synthesized complexes

Table S1: Overview of synthesized complexes with corresponding yields.

	metal	-R	yield
7a	Ru	-H	66%
7b	Ru	-F	62%
7c	Ru	-CH3	64%
7d	Ru	-OCH3	67%
8a	Rh	-H	71%
8b	Rh	-F	66%
8c	Rh	-CH3	66%
8d	Rh	-OCH3	68%

Crystallographic parameters

Table S2. Crystallographic parameters for structures **6c** and **8b**.

	6c	**8b**
Empirical formula	$C_{13}H_{12}O_2S$	$C_{22}H_{23}ClFO_2RhS$
Formula weight [g/mol]	232.06	508.82
Temperature/K	100(2)	90(2)
Wavelength/Å	0.71073	0.71073
Crystal size/mm	0.016x0.136x0.255	0.009x0.039x0.223
Crystal system	monoclinic	orthorhombic
Space group	*P2₁/c*	$P2_12_12_1$
a [Å]	11.1036(4)	8.0870(5)
b [Å]	6.9087(2	8.4811(4)
c [Å]	14.7366(5)	30.4205(17)
α [deg]	90	90
β [deg]	101.072(13)	90
γ [deg]	90	90
Volume [Å^3]	1109.42(6)	2086.4(2)
Z	4	4
Calculated density/mg/m^3	1.391	1.62
Absorption coefficient/mm^{-1}	0.272	1.071
F(000)	488	1032
Θ range for data collection[°]	1.78–30.09	1.34-25.45
Index ranges	-15<=h<=15	-9<=h<=9
	-9<=k<=9	-10<=k<=10
	-20<=l<=20	-36<=l<=36
Reflections collected/unique	52010/3261	67109/3862
Data/restraints/parameters	3261/0/151	3862/6/332
R(Int)	0.0443	0.0616
Final R indices [I > 2σ(I)]	2854	3473
R_1[a]	0.0331	0.0254
wR_2[b]	0.0965	0.0553
GOF[c]	1.038	1.093

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$.
[b] $wR_2 = \{\Sigma[w(Fo2 - Fc2)2]/\Sigma[w(Fo2)2]\}1/2$.
[c] GOF = {Σ[w(Fo2 − Fc2)2]/(n − p)}1/2, where n is the number of reflections and p is the total number of parameters refined.

Table S3. Selected bond lengths for structures **7c**, **7d**, **8b** and **8b**.

bond	**7c**	**7d**	**8b**	**8d**
M1-S1	2.3560(8)	2.3537(6)	2.3517(13)	2.3619(5)
M1-O2	2.082(2)	2.0904(15)	2.085(3)	2.0765(12)
M1-Cl1	2.4140(7)	2.6164(6)	2.359(16)	2.4288(4)
M1-Ar	2.183(3)	2.179(2)	2.143(11)	2.1486(18)
S1-M1-O2	82.17(6)	82.15(5)	82.71(9)	82.72(4)
S1-M1-Cl1	88.02(3)	86.82(2)	84.1(9)	88.531(16)
O2-M1-Cl1	86.31(6)	85.14(5)	79.2(11)	86.18(4)

Crystal structures

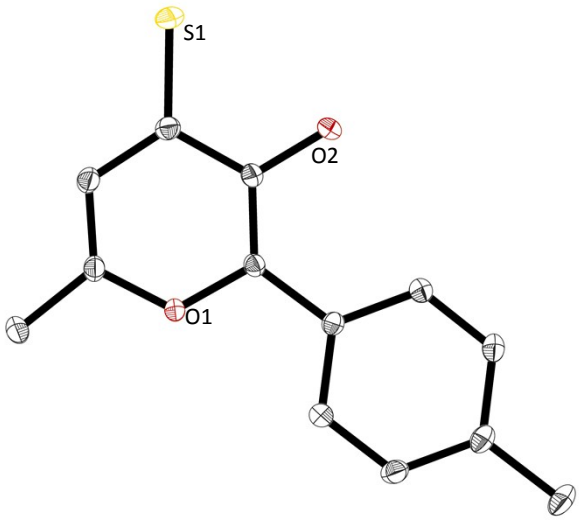

Figure S1: Molecular structure of **6c** drawn at 50% probability level.

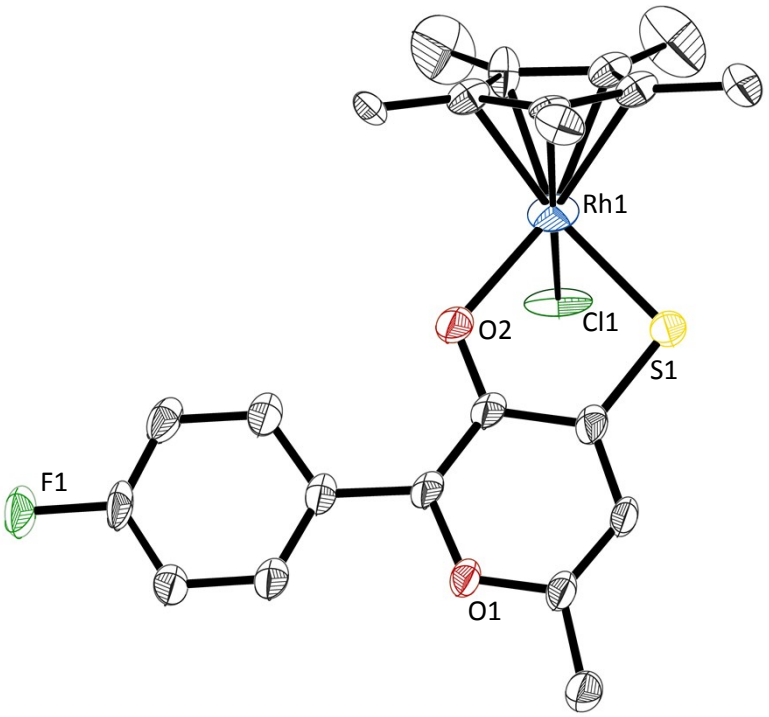

Figure S2: Molecular structure of **8b** drawn at 50% probability level.

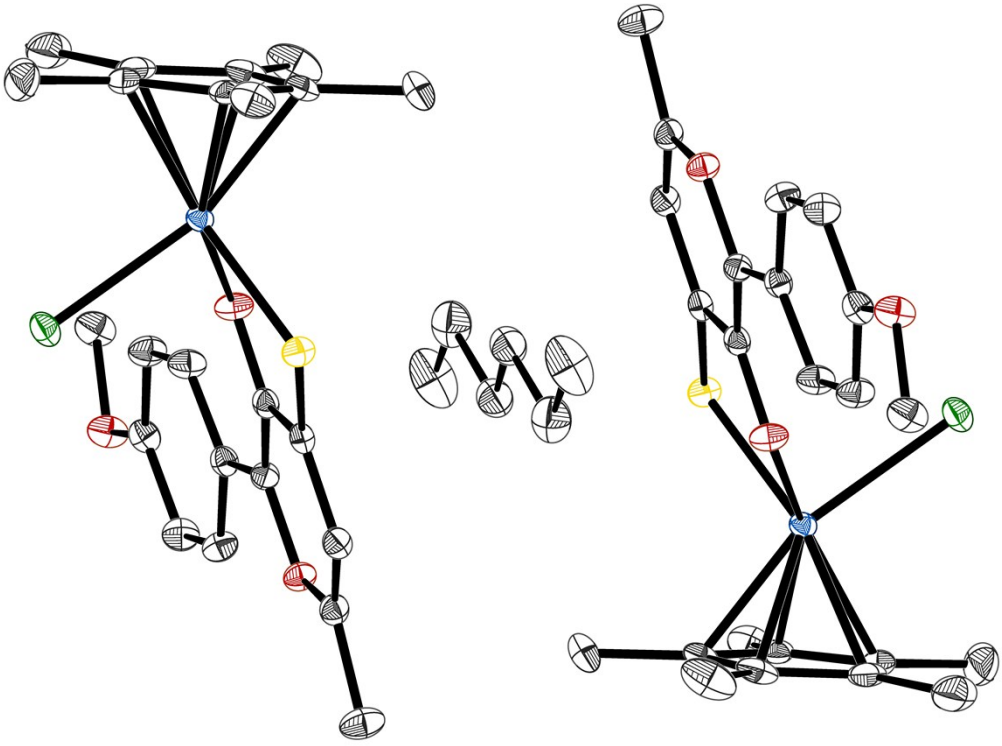

Figure S3: Molecular structure of **8d** drawn at 50% probability level.

Stability ^{1}H NMR measurements of 7c

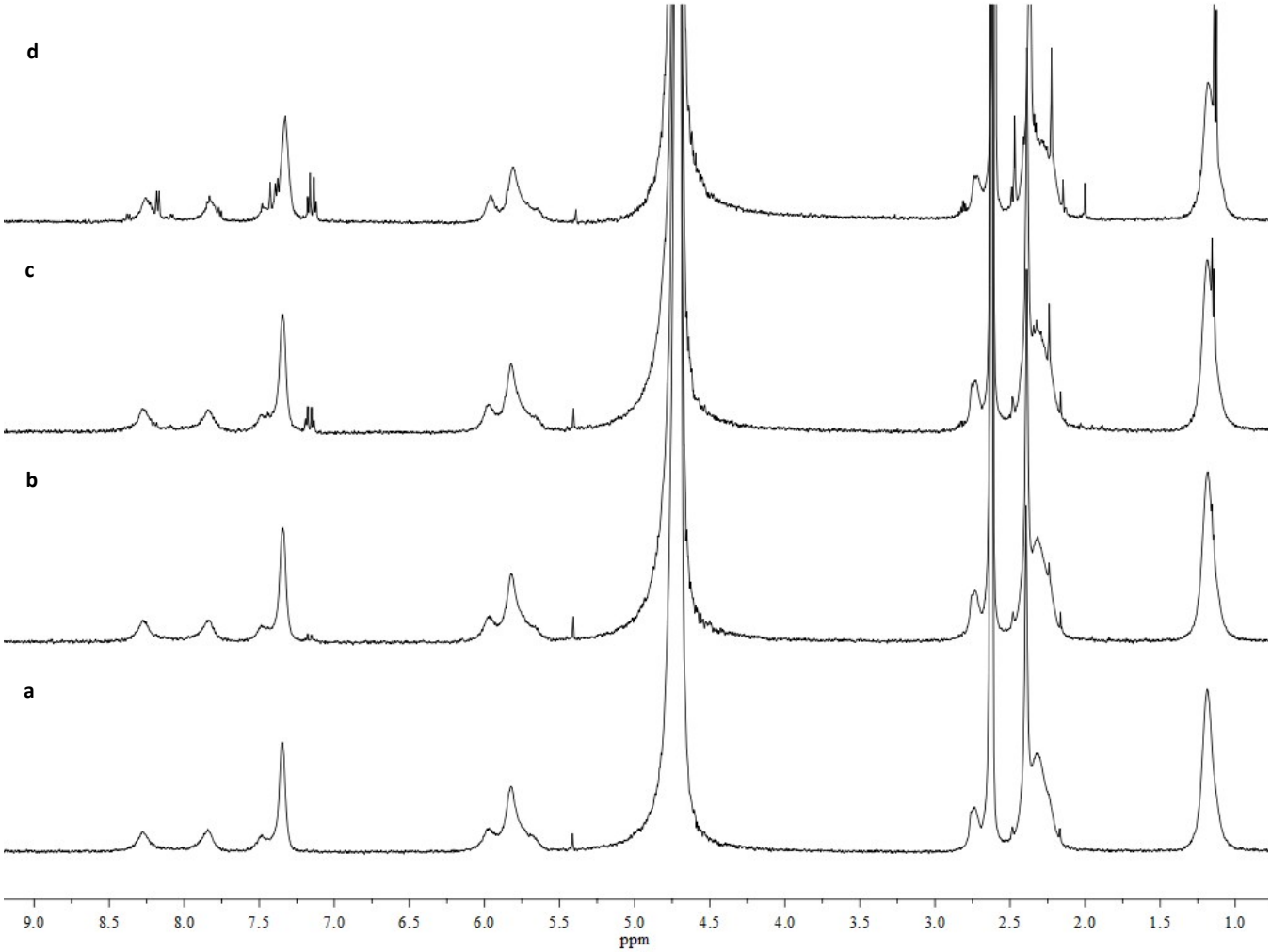

Figure S3. Full ^{1}H NMR spectra of **7c** in D_2O after **a)** 5 minutes, **b)** 5 hours, **c)** 24 hours and **d)** 7 days. ^{1}H NMR (D_2O, 500.10 MHz, 25 °C): δ = 1.23 (br s, 6 H, -$CH_{3cym\text{-}f}$), 2.38 (br s, 6 H, -CH_3), 2.45 (s, 3 H, -CH_3), 2.78 (br s, 1 H, $CH_{cym\text{-}e}$), 5.69 – 6.10 (m, 4 H, H_{cym}), 7.31 – 7.60 (m, 3 H, H5, H_{Ar}), 7.90 (br s, 1 H, H_{Ar}), 8.32 (br s, 1 H, H_{Ar}) ppm, signals at 1.20, 2.30, 7.21, 7.23, 7.50 and 8.25 ppm were assigned to decomposition products.

Stability ^{1}H NMR measurements of 8c

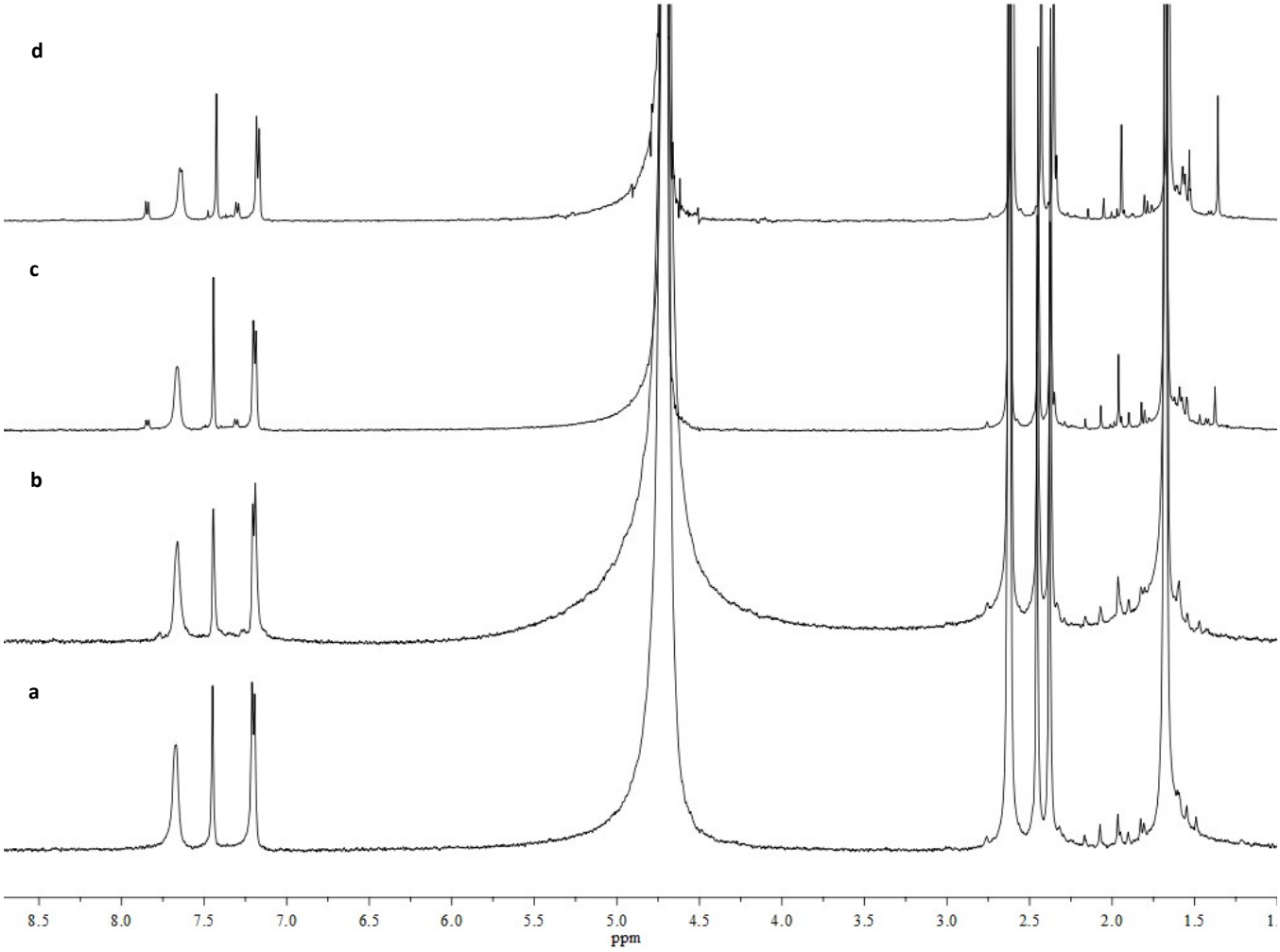

Figure S4. Full ^{1}H NMR spectra of **8c** in D_2O after **a)** 5 minutes, **b)** 5 hours, **c)** 24 hours and **d)** 7 days. ^{1}H NMR (D_2O, 500.10 MHz, 25 °C): δ = 1.75 (s, 15 H, Cp*), 2.45 (s, 3 H, -CH_3), 2.53 (s, 3 H, -CH_3), 7.27 (d, ^{3}JH,H = 8 Hz, 2 H, H_{Ar}), 7.52 (s, 1 H, H5), 7.75 (s, 2 H, H_{Ar}), ppm; signals at 1.43, 2.02, 7.37 and 7.92 ppm were assigned to decomposition products.

Stability ^{1}H NMR measurements of 7c under exclusion of light

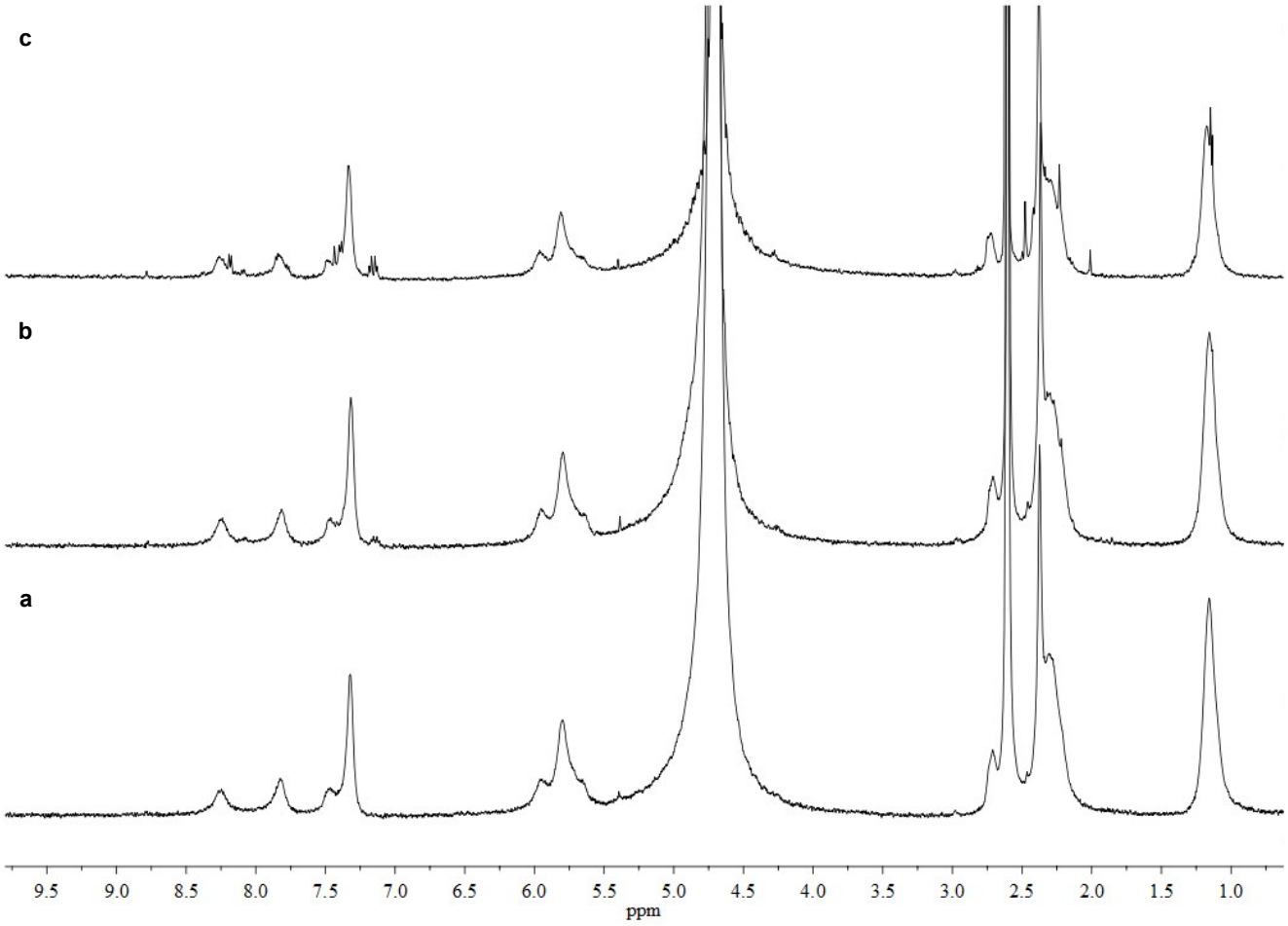

Figure S5. Full ^{1}H NMR spectra of **7c** in D_2O after after **a)** 5 minutes, **b)** 24 hours and **c)** 7 days. ^{1}H NMR (D_2O, 500.10 MHz, 25 °C): δ = 1.23 (br s, 6 H, -$CH_{3cym\text{-}f}$), 2.38 (br s, 6 H, -CH_3), 2.45 (s, 3 H, -CH_3), 2.78 (br s, 1 H, $CH_{cym\text{-}e}$), 5.69 – 6.10 (m, 4 H, H_{cym}), 7.31 – 7.60 (m, 3 H, H5, H_{Ar}), 7.90 (br s, 1 H, H_{Ar}), 8.32 (br s, 1 H, H_{Ar}) ppm, signals at ca. 1.22, 2.31, 7.22, 7.24, 7.50 and 8.25 ppm were assigned to decomposition products.