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DIPLOMARBEIT

„Organometallische Rhodiumkomplexe mit Flavon-ähnlichen Liganden als potentielle Therapeutika für die Krebstherapie: Synthese und Charakterisierung“

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DIPLOMARBEIT

"The First Organometallic Rhodium Compounds with Flavone-derived Ligand Systems as Potential Anticancer Agents: Synthesis and Characterization"

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Abstract

Cancer is still one of the most common diseases leading to death in economically developed countries. This fact is caused by an unhealthy lifestyle and poor nutrition as well as several other factors. Therefore, further development of chemotherapeutics is still required. Based on todays knowledge about mechanisms of action of established chemotherapeutic agents, scientists are searching for more selective and better tolerated substances to increase the quality of life of patients and their chances of curing.

Several platinum complexes are used for cancer treatment in up to 50% of chemotherapy schemes being the dominating compounds on the market. Unfortunately, the efficacy of these drugs is not covering all kinds of cancer diseases making the research on development of new compounds essential. Additionally the occurrence of resistance of tumors against platinum compounds requires treatment with other types of chemotherapeutics.

An increasing field of research is the development of ruthenium-based complexes which show promising results in biological studies. Two of these compounds, namly NAMI-A and KP1019, passed clinical phase I trials and demonstrate that the research on further metal based complexes with different metal ions and ligands is reasonable.

Since rhodium shows chemical properties similar to ruthenium many rhodium complexes have been synthesized and tested for cytotoxic properties in the last years yielding in some cases promising results. Unfortunately until now none of these compounds reached clinical trial stage. Based on recent successes of cytotoxic rhodium compounds this diploma thesis deals with the synthesis and characterization of rhodium(III) complexes with 3-hydroxyflavone ligands. As studies in 3-hydroxyflavones show cytotoxic properties on cancer cells, the use of these substances as chelating ligands might exhibit advantages for cancer treatment.

Zusammenfassung

Krebs gehört zu den häufigsten Erkrankungen mit Todesfolge in den wirtschaftlich entwickelten Ländern. Eine ungesunde Lebensweise und Ernährung sowie eine Reihe anderer Faktoren tragen zu diesem Effekt bei, sodass eine Weiterentwicklung der bereits zugelassenen Chemotherapeutika sowie die Entwicklung neuer Substanzen im Fokus der Wissenschaft steht. Basierend auf dem derzeitigen Wissen über Wirkmechanismen der heute am häufigsten verwendeten Substanzen in der Chemotherapie, versucht man selektivere und für den Patienten verträglichere Substanzen zu finden, um die Heilungschancen sowie die Lebensqualität von Krebspatienten zu verbessern.

Platinkomplexe werden in bis zu 50% der Krebsbehandlungen eingesetzt und sind eine der dominieren Verbindungsklassen auf dem Markt. Die Wirksamkeit dieser Präparate erstreckt sich jedoch leider nur über einen Teil der heute bekannten Krebserkrankungen des Menschen, weshalb die Entwicklung und Erforschung neuer Substanzen unerlässlich ist. Ebenso macht das Auftreten von Tumoren mit Resistenzen ein Ausweichen auf andere Substanzen notwendig. Ein großer Forschungssektor im Bereich Krebstherapie ist die Entwicklung von Rutheniumkomplexen, welche sich bereits in Studien vielversprechend und wirksam zeigen. Ruthenium-Chemotherapeutika wie NAMI-A und KP1019 zeigten gute Aktivität in der ersten Phase von klinischen Studien und demonstrieren, dass die Erforschung weiterer Nicht-Platinkomplexe und anderen Ligandensystemen sinnvoll ist.

Da Rhodium aufgrund seiner Stellung im Periodensystem und seiner chemischen Eigenschaften viele Ähnlichkeiten zu Ruthenium aufweist, wurden in den letzten Jahren zahlreiche Rhodiumkomplexe synthetisiert und deren Eignung als Substanzen für die Krebstherapie getestet. Hierbei konnten vielversprechende Ergebnisse erzielt werden, jedoch schaffte es bisher kein Komplex bis zu klinischen Tests. Basierend auf den bisherigen Erfolgen bei der Synthese zytotoxischer Rhodiumkomplexe beschäftigt sich diese Diplomarbeit mit der Synthese und Charakterisierung von Rhodium(III) Komplexen mit 3-Hydroxyflavonliganden. Da Studien an 3-Hydroxyflavonen einen zytotoxischen Effekt auf Tumorzellen zeigten, ist ihre Verwendung als Chelatliganden potentiell mit Vorteilen für die Krebstherapie verbunden.

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ABBREVIATIONS

1D/2D	one- or two-dimensional NMR spectroscopy
NMR	nuclear magnetic resonance
δ	chemical shift (NMR spectroscopy)
J	coupling constant (NMR spectroscopy)
s	singlet (NMR spectroscopy)
d	doublet (NMR spectroscopy)
t	triplet (NMR spectroscopy)
m	multiplet (NMR spectroscopy)
ppm	parts per million
Hz	Hertz
CD_3OD	deuterated methanol
$CDCl_3$	deuterated chloroform
d_6-DMSO	deuterated dimethyl sulfoxide
MeOH	methanol
EtOH	ethanol
M	molar
mM	millimolar
µM	micromolar
nM	nanomolar
AcOH	acetic acid
NaOMe	sodium methoxide
PVC	polyvinyl chloride
DNA	2'-deoxyribonucleic acid
CT DNA	calf thymus DNA
RNA	ribonucleic acid
e.g.	for example (exempli gratia)
et al.	et alii (and others)
etc.	et cetera (and other things)
FDA	US Food and Drug Administration
g	gram
h	hour
eq	equivalent

mg	milligram
min	minute
°C	degree Celsius
mmol	millimol
mL	milliliter
pH	pondus Hydrogenii (power of hydrogen)
pK_a	log K_a (acid dissociation constant)
UV	ultraviolet
WHO	World Health Organization
ASR(W)	age-standardized rate (world)
AIDS	acquired immunodeficiency syndrome
DCO	Death Certificate Only
IC_{50}	drug concentration that causes 50% inhibition (of cell growth)

1. INTRODUCTION

1.1 Cancer

1.1.1 Definition and statistical data

Cancer is the term for a malignant tumor in which cells show uncontrolled growth and intrude into neighbouring tissues destroying them. They often spread to other sections of the body using the bloodstream or the lymphatic system.[1]

In addition to physical, chemical and biological carcinogens, ageing is a major factor for developing cancer because cellular repair mechanisms loose efficiency with increasing age.[2] Due to increasing life expectancy as well as the growth of the world population and the development of cancer-causing behavior, cancer has become a global problem.[3]

In 2008 worldwide 7.6 million people died as a consequence of cancer disease with the most frequent types being lung, stomach, liver, colorectal and breast cancer. The WHO projects more than 11 million deaths from cancer worldwide until 2030.[2] Fig 1 gives an overview over the most frequent cancers in men and women worldwide.

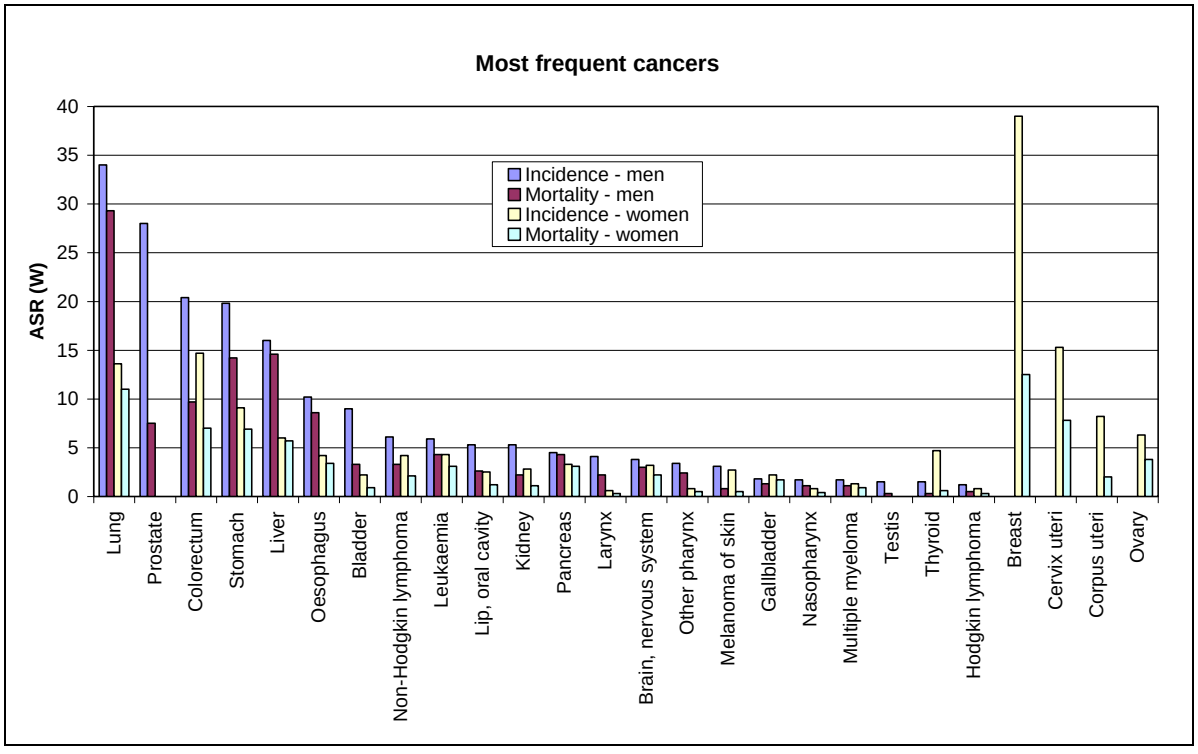

Fig 1: Incidence and mortality of the most frequent cancer types in the world [3]

[1] P. Anand, A.B. Kunnumakkara, et al, *Pharm Res*, 25(9): 2097-116, **2008**.

[2] WHO, Fact sheet N°297, **2011**.

[3] A. Jemal, F. Bray, M.M. Center, J. Ferlay, E. Ward, D. Forman, *CA Cancer J Clin*, 61:69-90, **2011**.

	Cancer	Men		Women	
		Incidence ASR (W)	Mortality ASR (W)	Incidence ASR (W)	Mortality ASR (W)
	All cancers excl. non-melanoma skin cancer	203.8	128.6	165.1	87.6
1	Lung	34.0	29.3	13.6	11.0
2	Prostate	28.0	7.5		
3	Colorectum	20.4	9.7	14.7	7.0
4	Stomach	19.8	14.2	9.1	6.9
5	Liver	16.0	14.6	6.0	5.7
6	Oesophagus	10.2	8.6	4.2	3.4
7	Bladder	9.0	3.3	2.2	0.9
8	Non-Hodgkin lymphoma	6.1	3.3	4.2	2.1
9	Leukaemia	5.9	4.3	4.3	3.1
10	Lip, oral cavity	5.3	2.6	2.5	1.2
11	Kidney	5.3	2.2	2.8	1.1
12	Pancreas	4.5	4.3	3.3	3.1
13	Larynx	4.1	2.2	0.6	0.3
14	Brain, nervous system	3.8	3.0	3.2	2.2
15	Other pharynx	3.4	2.4	0.8	0.5
16	Melanoma of skin	3.1	0.8	2.7	0.5
17	Gallbladder	1.8	1.3	2.2	1.7
18	Nasopharynx	1.7	1.1	0.8	0.4
19	Multiple myeloma	1.7	1.1	1.3	0.9
20	Testis	1.5	0.3		
21	Thyroid	1.5	0.3	4.7	0.6
22	Hodgkin lymphoma	1.2	0.5	0.8	0.3
23	Breast			39.0	12.5
24	Cervix uteri			15.3	7.8
25	Corpus uteri			8.2	2.0
26	Ovary			6.3	3.8

Table 1: Incidence and mortality of the most frequent cancers in the world[2]

In Austria 36.000 people develop cancer every year.[4] Fig 2 displays incidence and mortality of males and females from 1990 to 2007 in Austria. Cancer incidence describes the number of annual diagnosed cancer cases while mortality is defined as the number of cancer deaths every year. To compare between groups of different ages the ASR (age standardized rate) is used which is calculated by 100.000 people of same age and gender belonging to one group. This also enables comparisons of the risks between the different groups.

[4] Statistik Austria, Österreichisches Krebsregister und Todesursachenstatistik, **2010**.

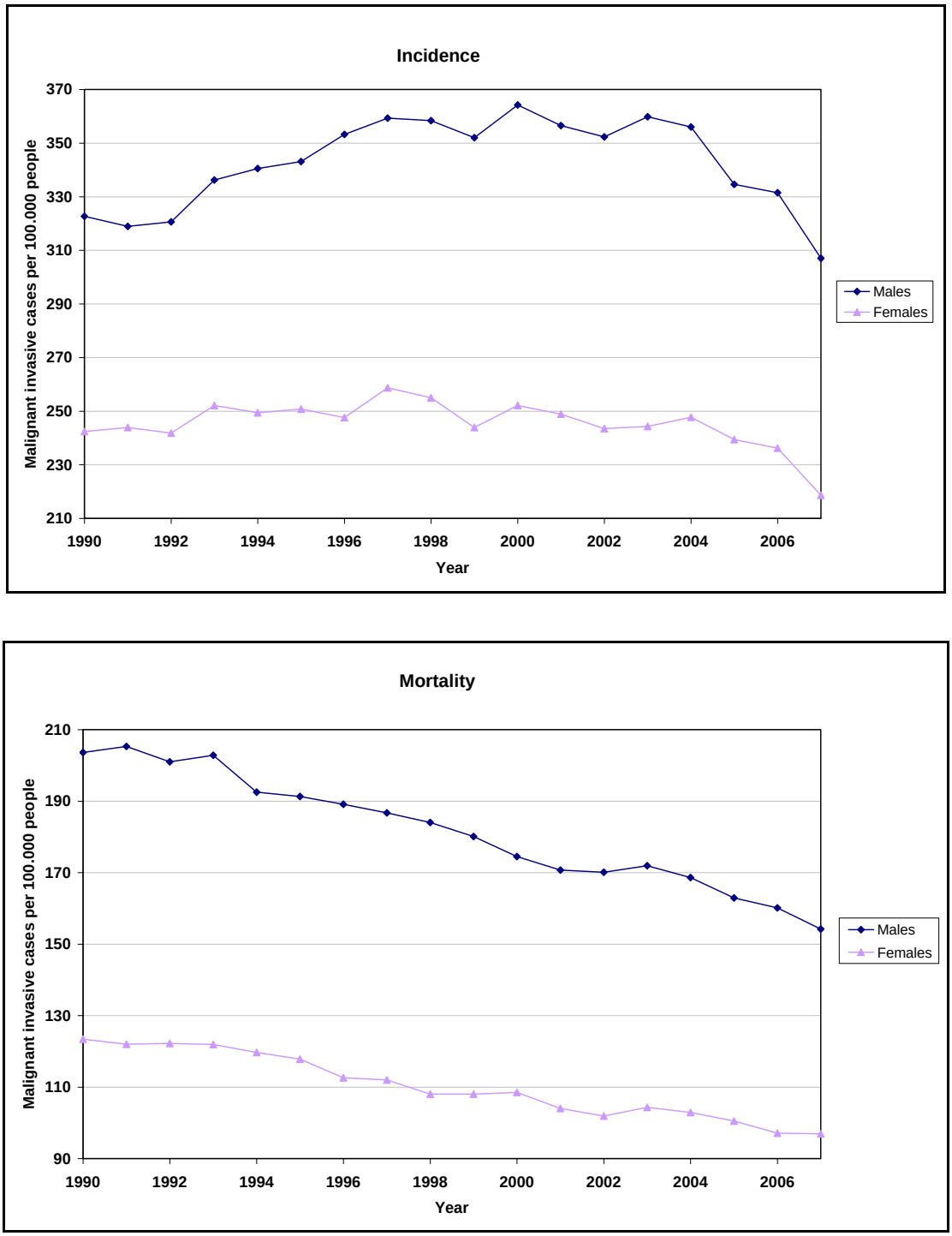

Fig 2: Incidence and mortality of males and females (malignant invasive cases in Austria including DCO cases, ASR per 100.000 people [4]

According to these graphs, the age standardized incidence rates of men and women have decreased by 15% between 1997 and 2007 while the incidences of men were 1.4 times higher than for women. For men prostate cancer is the most common cancer since 1994 in absolute numbers, whereas in the years before, lung cancer was the most often diagnosed cancer disease. The most common cancer between

women is breast cancer. The age standardized rate of newly diagnosed breast cancer cases has decreased by 14% over the last 10 years. As screening tests have been performed more often the last years, the numbers of incidence rates of breast and prostate cancers are increasing.

Among women the cancer which causes most of deaths is breast cancer, while for men it is not prostate cancer but lung cancer followed by colon cancer. The risk of developing cancer related to smoking has always been and is still significantly higher for men than for women.

Regarding all malignant neoplasia an increasing rate correlated to people of higher age can be observed. While in the group with the 35 to 44 years old persons about 265 people developed cancer, about 3000 people in the group of 65-74 years was diagnosed with cancer.[4]

Nowadays, knowledge about risk factors and causes of cancer enables prevention. In addition, better detection by modern screening tests allows treatment at an earlier stage. Avoiding key risk factors like tobacco use, low fruit and vegetable intake, alcohol use, physical inactivity, overweight or obesity can prevent approximately 30% of cancer cases.

While many cancers caused by those risk factors are preventable, 20% of cancer deaths in the low- and middle-income countries are caused by certain infections. In the high-income countries this number is significant lower constituting 9% of cancer deaths.

According to the WHO noncommunicable diseases action plan, standards and tools to guide planning and implementation for prevention, early detection, treatment and care of cancer need to be developed and further research on the causes of human cancer and the mechanisms of carcinogenesis is essential as well as the development of scientific strategies for cancer prevention and control. [2]

1.1.2 Carcinogenesis [5]

Steps of carcinogenesis

Initiation

At this stage the cell is exposed to the cancer-causing substance, which leads to the first genetic change. Therefore the initiation equates to a permanent damage of DNA. These changes in the cell are not observable but irreversible. Initiation on its own does not lead to the development of cancer.

Chemicals which cause initiation are for example alkylating substances, arenes, azo dyes and nitrosamide.

Lag period

During this phase proliferation of the initiated cells occurs. At the end of this period first visible changes can be observed.

Promotion

The transformation to a cancer cell happens when the initiated cell is exposed to another cancer-causing factor which is called promoter. Promotion can occur because of the same carcinogenic which caused initiation or it is caused by another tumorigenic substance.

Like initiation, promotion on its own does not lead to the development of a malign tumor. Genetic changes in cells caused by promoters can be reversible and therefore target DNA only indirectly by changes of the expression of defined genes.

For the effect of a promoter a specific threshold needs to be achieved, whereas below-threshold doses are non-effective.

Progression

Tumor progression is labelled by visual perceptibility of the tumor, invasion to adjacent tissue and metastasis.

[5] A. Margulies, K. Fellinger, T. Kroner, A. Gaisser, *Onkologische Krankenpflege*, **1994.**

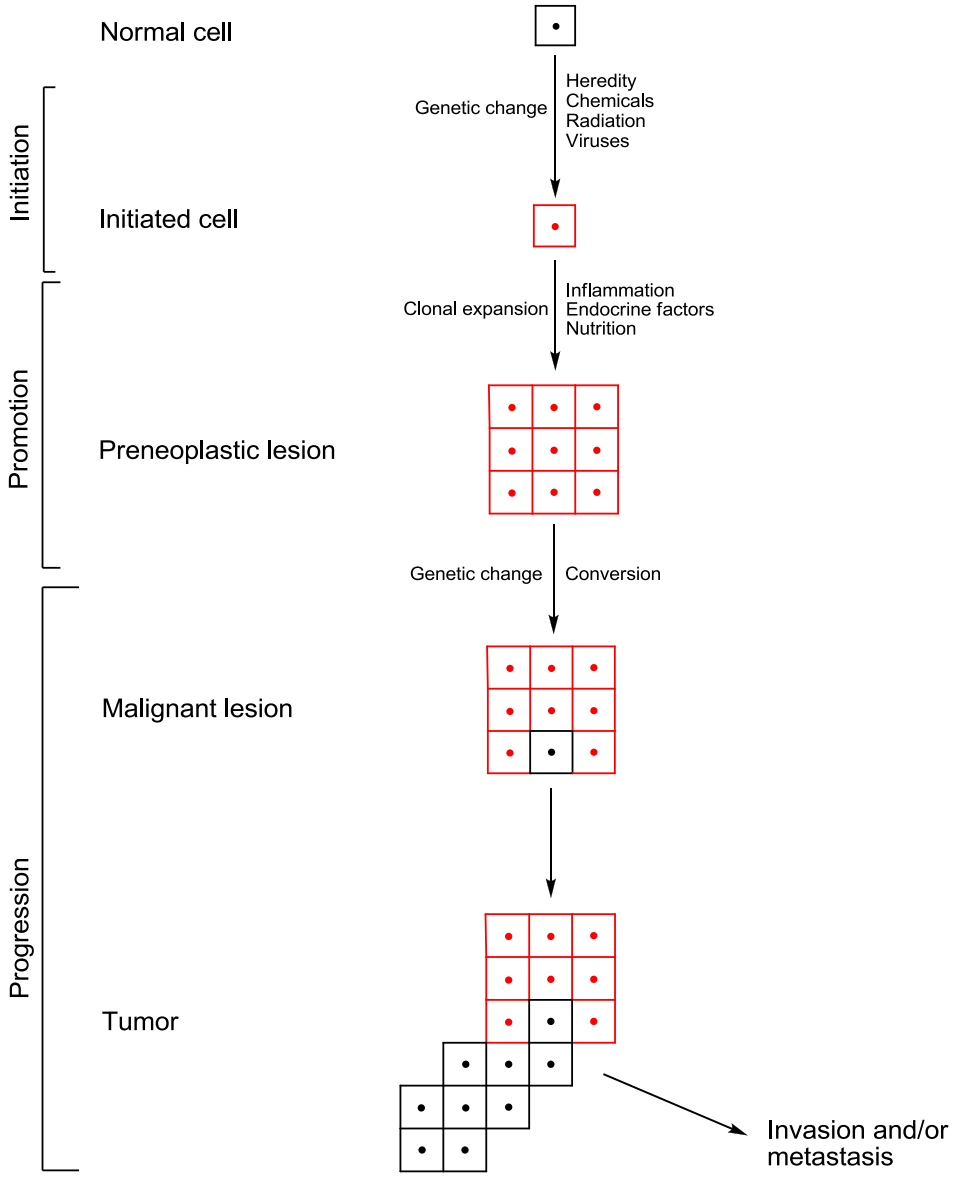

Fig 3: Steps of carcinogenesis[6]

[6] C.M. Haskell, *Cancer Treatment*, Saunders, Philadelphia, **2000**.

1.1.3 Carcinogens

1.1.3.1 Physical carcinogens

Ionizing radiation

Radiation of high energy, which is able to remove electrons from atoms or molecules or to split atoms or molecules into charged fragments, is called ionizing radiation. It is a consequence of the decay of atomic nuclei and occurs when electrons are decelerated (X-radiation).

More than 70% of the ionizing radiation which affects us derives from our native environment (cosmic radiation, earth radiation, radiation of water, etc.). The remaining 30% are caused by diagnostic and therapeutic radiology, uranium mines, nuclear explosions and nuclear accidents.

The cancer causing effect of ionizing radiation is verified and children are - relative to adults - more susceptible to radiation induced tumors. It is assumed that chromosome breakage and other changes in the DNA lead to the carcinogenic effect.

Solar (ultraviolet) radiation

Ultraviolet radiation also causes cancer and is the main cause of skin cancer, especially melanomas. Changes in the way of clothing, a tendency to intensive sunbathing and the decrease of ozone in the stratosphere show a correlation to the increasing number of skin cancer cases. Ultraviolet light probably activates mutations of DNA and blocks DNA repair mechanism.[5]

1.1.3.2 Biological carcinogens

Several types of cancer show relations to viral infections like for example the hepatitis B virus. Over 8% of the population of regions of Asia and Africa suffer from chronic HBV infections and this shows coherence to increased liver cancer rates.[3] In developing countries HBV infection induces approximately 60% of the total number of liver cancer cases, whereas in developed countries this percentage amounts to 23%.[7]

[7] D.M. Parkin, *Int J Cancer*, 118: 3030-3044, **2006**.

70% of cervical cancers are known to be caused by the most common human papilloma virus (HPV) strains, which are the types 16 and 18. Therefore a vaccination for types 16, 18, 6 and 11 was developed but for the remaining 30% no protection is offered.[8,9,10]

Another example of cancer related to viral exposure is the Burkitt's lymphoma which is a subtype of the non-Hodgkin lymphoma (NHL) caused by the Epstein-Barr virus (EBV) among children.
Additionally to the Epstein-Barr virus the human immunodeficiency virus (HIV) is associated to NHL with increasing incidences in Thailand and Uganda according to the occurrence of AIDS epidemics.[11,12,13,14,15]

Kaposi sarcoma, a cancer of cells that affect lymph and blood vessels, is caused by the human herpes virus type 8 (HHV-8) combined with immunosuppressive conditions as observed in HIV infected humans.[16,17]

[8] R. Sankaranarayanan, *Indian J Med Res*, 130: 322-326, **2009**.

[9] L.L. Villa, R.L Costa, C.A. Petta, et al., *Lancet Oncol*, 6: 271-278, **2005**.

[10] D.M. Harper, E.L. Franco, C.M. Wheeler, et al., *Lancet Oncol*, 367: 1247-1255, **2006**.

[11] P. Hartge, S.S. Wang, P.M. Bracci, S.S. Devesa, E.A. Holly, D. Schottenfeld , J.F. Fraumeni Jr, *Cancer epidemiology and prevention,* New York: *Oxford University Press;* 898- 918, **2006**.

[12] H. Sriplung, D.M. Parkin, *Cancer*; 101(11): 2660-2666, **2004**.

[13] S.M. Mbulaiteye, E.T. Katabira, H. Wabinga, et al., *Int J Cancer*, 118: 985-990, **2006**.

[14] M.M. Abdel-Fattah, O.G. Yassine, *Eur J Cancer Prev*, 16: 479-485, **2007**.

[15] V. Bouvard, R. Baan, K. Straif, et al., *Lancet Oncol*, 10: 321-322, **2009**.

[16] J. Iscovich, P. Boffetta, S. Franceschi, E. Azizi, R. Sarid, *Cancer*, 88: 500-517, **2000**.

[17] T.F. Schulz, *J Infect*, 41: 125-129, **2000**.

1.1.3.3 Chemical carcinogens

Several substances are strong carcinogens like the pesticide dichloro-diphenyl-trichloroethane (DDT) which can cause breast cancer when exposure prior to puberty occurs. Another example for a carcinogenic chemical is 1,3-butadiene which can lead to the development of leukemia.
Whereas the contact with such substances is unlikely, an exposure with chemical carcinogens released by air pollution or tobacco smoking causing lung cancer is common in the economically developed countries.[18]

1.1.3.4 Hereditary factors

Some types of cancer occur more frequently in some families, thus, the disposition for this particular cancer is inherited from generation to generation.[7] Actual molecular genetic analyses lead to the assumption of a correlation between the development of pancreatic adenocarcinoma and Werner syndrome (WS), a genetic disorder. This syndrome is characterized by mutations in the Werner syndrome RecQ helicase gene (WRN) which cause a loss of the function and lead to accelerated aging as well as cancer predisposition.[19]

For renal cell cancer (RCC), which is hereditarily caused in 2-4% of cases, several predisposing genes exist like the VHL (Von Hippel–Lindau disease), the FH (hereditary leiomyomatosis) the MET (hereditary papillary renal cell cancer (HPRC), and the BHD (Birt–Hogg–Dubé syndrome).[20,21]

In the case of breast cancer 5-10% of onsets are caused by hereditary factors like mutations in genes like BRCA1 and BRCA2. Breast carcinomas occurring in a family history exhibit a notable risk factor for the development of this type of cancer.[22]

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[18] R.W. Clapp, M.M. Jacobs, E.L. Loechler, *Rev Environ Health*, 23(1): 1-37, **2008**.

[19] S.G. Chun and N. S. Yee, *Cancer biology & therapy*, 10 430-437, **2010**.

[20] H. Allgayer, H. Rehder, S. Fulda, L. Spruijt, N. Hoogerbrugge, *Hereditary Tumors*, Chapter 15. http://onlinelibrary.wiley.com/doi/10.1002/9783527627523.ch15/summary, **2009**.

[21] P.H. Axwijk, I. Kluijt, D. de Jong, H. Gille, J. Teertstra and S. Horenblas, *Eur J Clin Invest*, 40: 433-439, **2010**.

[22] M. Lacroix, G. Leclercq, *Breast Cancer Research and Treatment,* 89: 297-304, **2005**.

1.1.3.2 Lifestyle

Lifestyle is one of the most important cancer risk factors, especially smoking, alimentation, sex behavior, consumption of alcohol as well as behavior at work and in spare time. According to estimations, 25-40% of all cancer-caused deaths can be related to tobacco smoking.

Smoking

Tobacco smoke is a complex mixture of chemical substances and contains potent cancerogenic components as nitrosamines and polycyclic hydrocarbons. It is causally connected to the development of lung, oral and esophagus cancer as well as bladder cancer and possibly also involved in the formation of pancreatic and cervical cancer.

Alimentation

Eating habits play a crucial role in the development of tumors of the gastrointestinal tract and many other types of cancer. For example hormone-dependent tumors, such as breast, cervical cancer and prostate cancer, show correlation to the daily intake of fat. It is assumed that around 30% of cancer-caused mortality is related to our nutrition. Natural toxins and metabolic products of plants can cause cancer in laboratory animals. It is difficult to prove this correlation in humans because of their lower sensibility to these substances. For example, trials on rats have shown that aflatoxins which can get into the nutriment during food-processing steps, lead to hepatic cancer when the intake lasts for several months.[5]

1.1.4 Therapy [5]

For the treatment of malignant tumors 3 main types of therapy exist:

- Surgery
- Radiation therapy
- Systemic treatment (medication)

These three treatment options can be applied separately or in recombination therapy approaches, either used simultaneously or in a staggered way.

1.1.4.1 Surgery

Surgery has been applied for long time and is even nowadays the modality with the best prospects of cure. This applies to breast cancer, cancers of the gastro-intestinal tract, renal cancer, bladder cancer, cancer of the skin as well as a portion of the bronchial carcinomas. On the other handy surgery has been replaced by systemic treatment and partly by radiation therapy in the case of testicular tumors, small cell lung carcinoma and malignant lymphoma.

1.1.4.2 Radiation therapy

In addition to surgery the treatment of cancer patients with high energy ionizing radiation has been established for tumor therapy and has been refined remarkably over the last years. Some malignant lymphomas as well as several types of solid tumors can be cured effectively and solely with radiation therapy. Great importance is also attached to radiation therapy regarding pain relief whereas long-term side effects have to be considered especially for curable patients.

1.1.4.3 Systemic treatment

Systemic treatment comprises tumor therapy with cytostatic drugs (chemotherapy), hormones or with biologically active substances (interferons, interleukins). A remarkable advantage is the effect on the whole organism because these drugs reach all regions of the body using the bloodstream. On the other hand, this is also a major disadvantage with regard to side effects.
Therefore this treatment is suitable for non-localized cancers (like for example leukemia) or for metastasizing tumors which can not be treated by surgery or radiation.

1.1.4.3.1 Hormone therapy

Many tumors like those of breast, uterus and prostate can be affected by hormones. Since the growth of these organs is controlled by hormones, malignant cells are also susceptible to such substances.
As a consequence, one aim of hormone therapy is the deactivation of the hormone production of the sex hormones which can be approached by the intake of drugs.
Another option is the treatment with anti-hormones like tamoxifen which inhibits the effect of estrogen.

1.1.4.3.2 Cytokines

Cytokines are biologically active substances which regulate processes in the body like cell division or the activity of the immune system. Some of them can already be genetically engineered and are therefore available for therapeutic use. One example is the use of interferon for the treatment of certain leukemias.
Furthermore cytokines are used to compensate side effects of cytostatic drugs. Thus, it is possible to increase the dose of cytostatic agents or radiation which has a positive effect on the chances of curing the patient.

1.1.4.3.3 Chemotherapy

Chemotherapy is defined as the treatment with compounds which significantly affect the cell division of the diseased cells. Unfortunately many drugs are not very specific and also affect healthy cells, though to a lesser extent. Therefore, chemotherapy is often accompanied by undesired side effects like impairment in the formation of blood, nausea, vomiting and temporary loss of hair. Nowadays improved drugs, expert knowledge regarding dosage and effective drugs against nausea make the therapy better tolerated by patients.

Different mechanisms are responsible for the effect of cytostatic compounds. Some important examples are:

- Inhibition of DNA mismatch repair (MMR)

Some cytostatic substances called antimetabolites lead to cell cycle arrest and apoptosis by inhibiting DNA mismatch-repair (MMR). Their effect is caused by offering a “wrong component” to the enzyme like e.g. 5-fluorouracil (Fig. 4) which is incorporated into DNA instead of uracil. Therefore, MMR-deficient cells show resistance to these drugs making them useless for some kinds of tumors.[23,24]

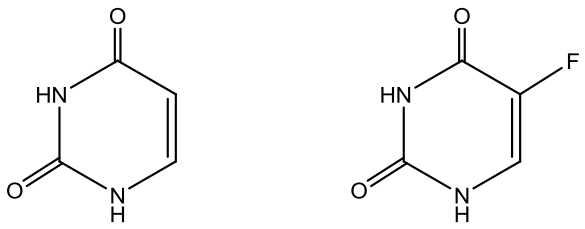

Fig 4: Chemical structures of uracil and 5-fluorouracil

[23] J.M. Carethers, D.P. Chauhan, D. Fink, S. Nebel, R.S. Bresalier, S.B. Howell, C.R. Boland, *Gastroenterology*, 117:123-131, **1999**.

[24] S. Aebi, D. Fink, R. Gordon, H.K. Kim, H. Zheng, J.L. Fink, S.B. Howell, *Clin Cancer Res*, 3:1763-1767, **1997**.

- Inhibition of the spindle apparatus

Some cytostatic substances interrupt the development and the function of the spindle apparatus and as a consequence of this damage cell division is inhibited.

- Modification of the structure of DNA

  - By “cross-linking”

Many cytostatic compounds belong to the group of the alkylating agents representing reactive molecules which easily connect themselves with the DNA at two different positions. It is known that platinum compounds like cisplatin belong to the group of chemotherapeutics which react according to this mode of action.
DNA replication is blocked by crosslinking and as a consequence replication arrest and cell death occur if the crosslink is not repaired. Additionally the synthesis of RNA is interfered because the DNA can not be read any more.

  - By intercalation

Antibiotics are substances which slow down growth or kill bacteria.[25] Therefore, most of them are used to treat bacterial infections but some are used for cancer therapy because they show little effect on bacteria but exhibit cytostatic properties. This effect is caused by modifications of the DNA structure by e.g. intercalation. The antibiotic molecule attaches itself between the bases of DNA and inhibits the replication.

  - By inhibition of topoisomerases

Topoisomerases are ubiquitous proteins (enzymes) which are able to cleave the strands of DNA at specific positions and conjugate them at a later point in time. Therefore they are essential in the processes of DNA replication, transcription and recombination. [5,26]

[25] *Dorlands Medical Dictionary*, **2010**.

[26] A. Sharma, A. Mondragón, *Current Opinion in Structural Biology*, 5:39-47, **1995**.

Topoisomerases can be classified in different types according to their function. For example, type I topoisomerases break one DNA strand at a time, and pass another strand through the resulting space break while type II enzymes break both DNA strands concertedly and pass the double-stranded DNA through the gap.

Topoisomerase poisons are substances which interfere in the function of topoisomerase enzymes by binding selectively to the toposiomerase-DNA-complex stopping the process of replication. Typical type I topoisomerase poisons are topotecan and camptothecin (Fig. 5). For inhibition of type II topoisomerases the substances doxorubicin, epirubicin, and mitoxantrone (Fig. 6) are used.[27]

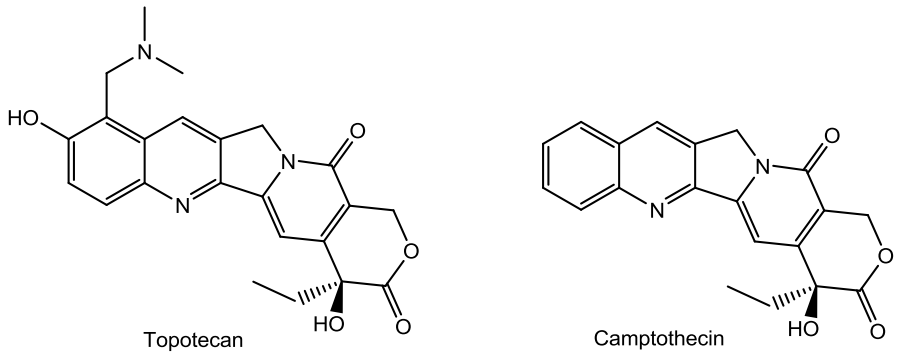

Fig 5: Typical type I topoisomerase poisons[28]

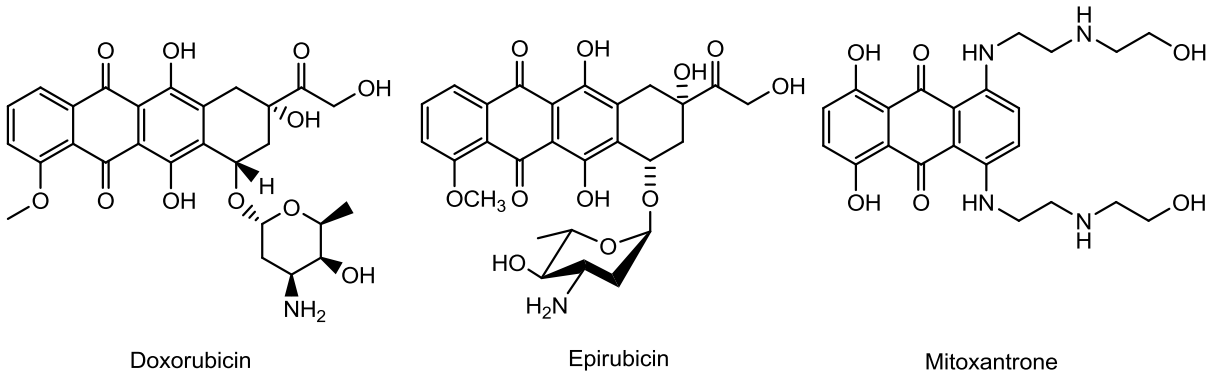

Fig 6: Typical type II topoisomerase poisons[28]

[27] A. Fedier, V.A. Schwarz, H. Walt, R.D. Carpini, U. Haller, D. Fink, *Int J Cancer*, 93, 571-576, **2001**.

[28] U.S. National Library of Medicine, National Institutes of Health, http://pubchem.ncbi.nlm.nih.gov

1.2 Metal-based chemotherapeutics

In 1909 Paul Ehrlich developed the first chemotherapeutic called “salvarsan” (Fig. 7) for the treatment of syphilis, an infectious disease.

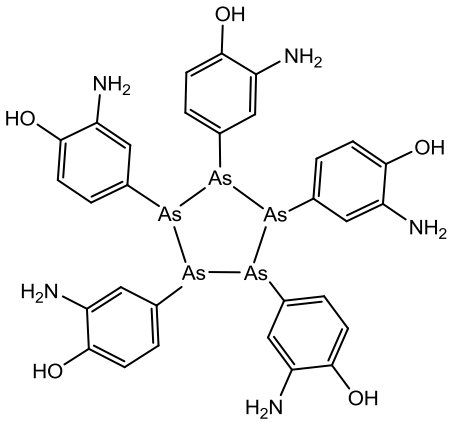

Fig 7: Arsphenamin (“Salvarsan”)[29]

Until the 1960s radiotherapy and surgery were dominating cancer therapy but new data showed the effectiveness of a combination with chemotherapy especially in patients with advanced forms of cancer. Therefore, the treatment of cancers combining surgery, radiation and drugs maximized the anti-tumor effect and as a consequence became standard in clinical practice.[30]

1.2.1 Platinum

In 1978 the first platinum(II) chemotherapeutic named cisplatin (*cis*-diamminedichloridoplatinum(II)) obtained approval for worldwide clinical practice (Fig 8).

Due to its high efficiacy it is used for the treatment of several types of cancer e.g. testicular and ovarian cancer. Additionally it is applied in therapy against cervical carcinoma, gastric cancer, osteosarcoma, head and neck cancer and in case of bronchogenic carcinoma. A significant disadvantage of this drug are adverse effects such as nephrotoxicity, neuropathy, ototoxicity, nausea, vomiting and occasionally myelosuppression accompanying treatment.[31]

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[29] A.F.A. Peacock, P.J. Sadler, *Chem Asian J*, 3, 1890-1899, **2008**.

[30] V.T. DeVita, Jr. and E. Chu, *Cancer Res*, 68 (21): 8643-53, **2008**.

[31] M. Galanski, V.B. Arion, M. A. Jakupec and B.K. Keppler, *Curr Pharm Design*, 9, 2078-2089, **2003**.

Synthesis of cisplatin

Several procedures for the synthesis of cisplatin were developed in the last decades and most of them produced impure products or went at low yield. The methods used today are based on Dharas "A rapid method for the synthesis of *cis*-$[PtCl_2(NH_3)_2]$" published in 1970.[32] In the first step some saturated solution of potassium iodide (KI) is added to potassium tetrachloridoplatinate(II) ($K_2[PtCl_4]$) to prepare tetraiodidoplatinate(II) ($K_2[PtI_4]$). By addition of NH_3, *cis*-$[PtI_2(NH_3)_2]$ is obtained which is converted to the bivalent charged complex $[Pt(OH_2)_2(NH_3)_2]^{2+}$ using an aqueous solution of $AgNO_3$. During this step, solid AgI precipitates which can be separated by filtration. The final step comprises the exchange of the two aqua ligands of $[Pt(OH_2)_2(NH_3)_2]^{2+}$ by two chlorido ligands by addition of KCl in excess leading to the precipitation of yellow cisplatin (*cis*-$[PtCl_2(NH_3)_2]$) which can be collected by filtration (Fig 8).

The difficulty of yielding the cis-configuration compound is caused by the trans effect which was explained by Chernyaev[33] in 1926 based on empirical observations. In octahedral or square planar complexes the rate of substitution of a ligand is mainly depending on the group being present in trans position to it. The decreasing trans effect of ligands has been determined by studies presenting the order $I^- > Cl^- > NH_3$, H_2O for the groups which show relevance in the cisplatin synthesis.

According to these facts the intermediate $[PtI_3(NH_3)]^-$ forms the desired *cis*-$[PtI_2(NH_3)_2]$ when NH_3 is added due to the stronger trans-directing influence of I^- compared to NH_3. Iodido ligands show a stronger trans effect than chlorido ligands so that the conversion in the first step guarantees the formation of the pure cis isomer prohibiting the formation of a contaminant called Magnus' Green salt, $[Pt(NH_3)_4][PtCl_4]$.[34]

[32] S.C. Dhara, *Indian J Chem*, 8: 193–134, **1970**.
[33] I.I. Chernyaev, *Ann Inst Platine USSR*, 4: 261, **1926**.
[34] R.A. Alderden, M.D. Hall, T.W. Hambley, *J Chem Ed*, 83: 728-734, **2006**.

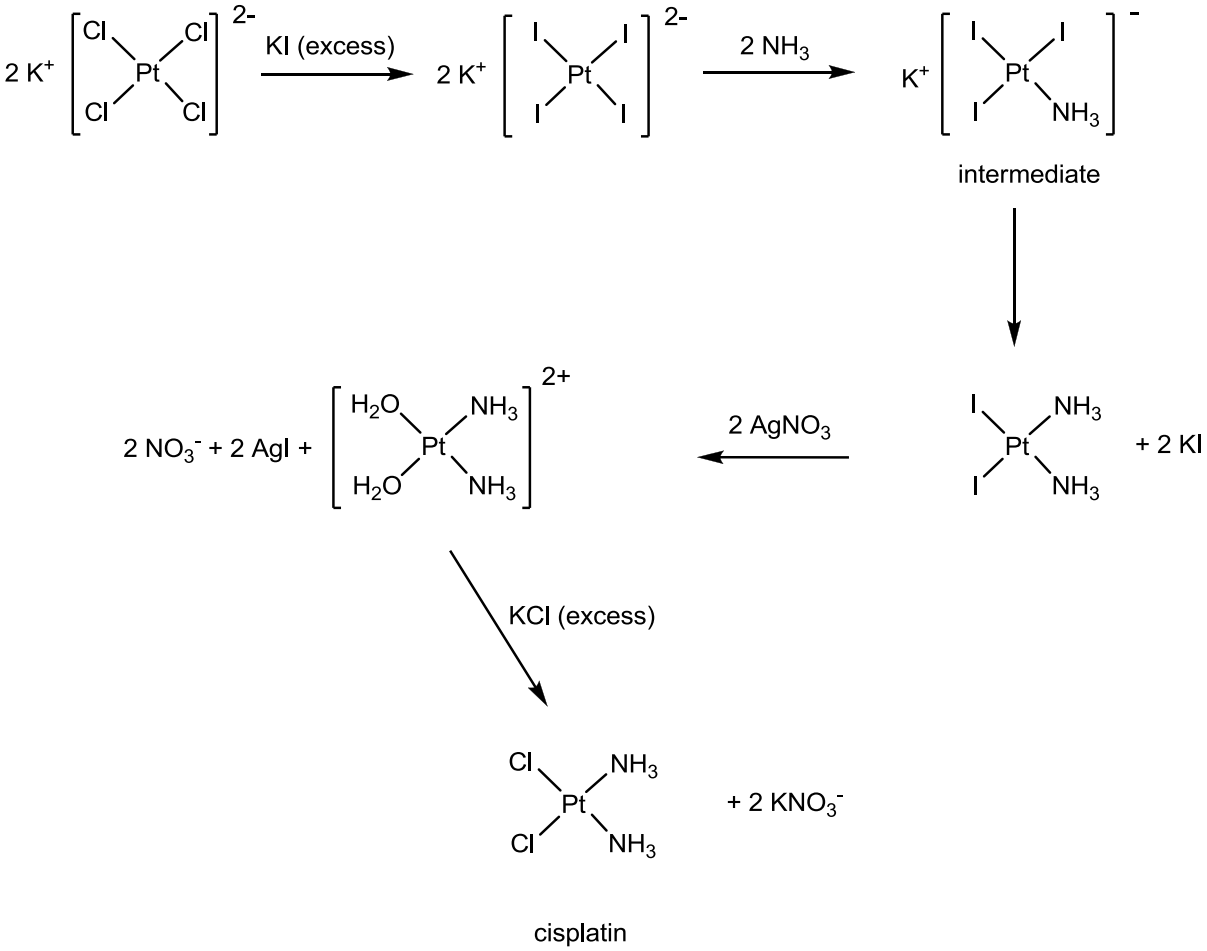

Fig 8: Synthesis of cisplatin[35]

The second and third generation platinum compounds carboplatin (*cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II) and oxaliplatin [(1R,2R)-cyclohexanediamine]oxalatoplatinum(II)) (Fig. 9) were approved in 1989 and 2002, respectively.[31,36,37,38]

In the case of carboplatin, myelosuppression was established to be dose-limiting whereas the other toxic side effects are generally milder and better tolerable in comparison to cisplatin while it is offering an identical spectrum of activity.

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[35] S.C. Dhara, *Indian J Chem*, 8: 193-134, **1970**.

[36] FDA/Center for Drug Evaluation and Research, Office of Communications, Division of Information Services

[37] M.A. Jakupec, M. Galanski, B.K. Keppler, *Rev Physiol Biochem Pharmacol*, 146:1-53, **2003**.

[38] M. Galanski, M.A. Jakupec, B.K. Keppler, *Curr Med Chem*, 12: 2075-2094, **2005**.

Oxaliplatin provides good effects in the treatment of metastatic colorectal cancer. For this drug sensory neuropathy was found to be the dose-limiting factor. [31]

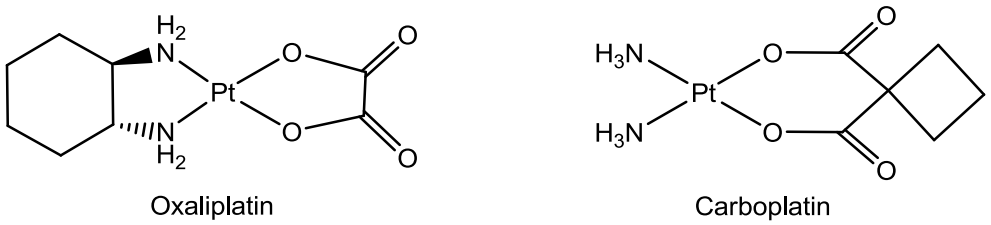

Fig 9: 2nd and 3rd generation platinum(II) complexes for chemotherapy approved for worldwide clinical practice[36]

Although causing side effects platinum complexes are applied in approximately 50-70% of cancer treatments.[39]

During the last years the ligands of these complexes were modified and also other metals were considered to be used to cover a significantly wider range of treatable tumors.[40]

1.2.2 Ruthenium

Ruthenium complexes show similarities to platinum compounds concerning rates of ligand exchange, coordination geometry and accessibility of different oxidation states (+2, +3 and +4) in case of ruthenium. Additionally, ruthenium offers the opportunity to use the transferrin cycle for transport to cancer cells because it exhibits the characteristic of mimicking iron and therefore of binding to human serum transferrin. Ruthenium complexes offer a different spectrum of treatable tumors especially of those which show resistance against platinum compounds making them interesting for the development of new anticancer drugs.[31]

The advantage of ruthenium-based drugs is their lower toxicity compared to platinum compounds while exhibiting activity in a different tumor spectrum than platinum complexes. KP1019 (indazolium *trans*-[tetrachloridobis(1H-indazole)ruthenate(III)]) as well as NAMI-A (imidazolium *trans*-[tetrachlorido-(S-dimethyl sulfoxide)(1H-imidazole)ruthenate(III)]) were successful in clinical phase I trials and therefore

[39] P.J. Dyson, G. Sava, *Dalton Trans*, 1929-1933, **2006**.

[40] M.A. Jakupec, M. Galanski, V.B. Arion, C.G. Hartinger, B.K. Keppler, *Dalton Trans*,183-194, **2008**.

created interest in the development of further ruthenium-based anticancer agents.[41,42,43]

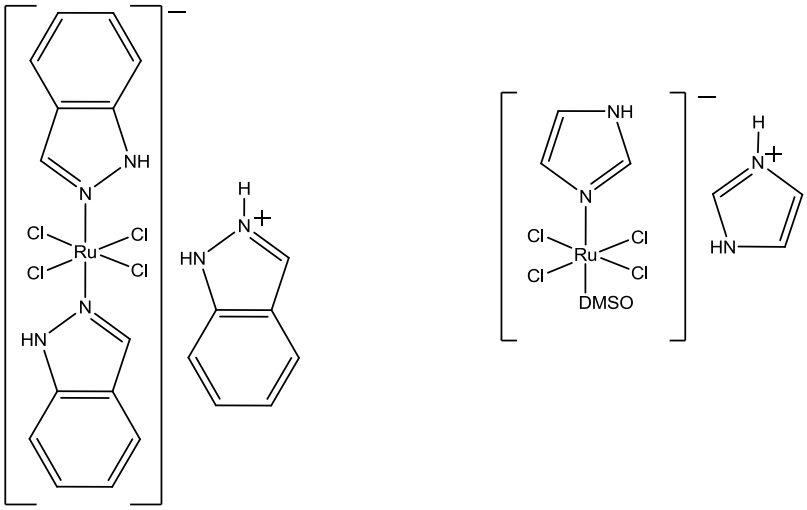

Fig 10: Structures of KP1019 and NAMI-A[41]

While reduction of platinum(IV) complexes to a platinum(II) compound is related to a change in the coordination number and a variation of the bond distances, the octahedral ruthenium complexes shown in Fig 10 exhibit facile electron transfer for Ru(II)/Ru(III) couples leading to the assumption that there must be a significant difference between the modes of action of platinum and ruthenium complexes.[27,44]

Due to the promising results of the studies of KP1019 and NAMI-A further ruthenium based compounds have been developed like the so-called RAPTA complexes (ruthenium(II)–arene–pta complexes) (Fig 11) which are in the focus of interest, since they show water solubility in addition to adequate lipophilicity to cross the membranes of cells. According to their structures they are referred to as piano-stool complexes.[45]

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[41] C.G. Hartinger, S. Zorbas-Seifried, M.A. Jakupec, B. Kynast, H. Zorbas, B. K. Keppler, *J Inorg Biochem*, 100: 891–904, **2006**.

[42] C.G. Hartinger, M. A. Jakupec, S. Zorbas-Seifried, M. Groessl, A. Egger, W. Berger, H. Zorbas, P. J. Dyson and B.K. Keppler, *Chem Biodiversity*, 5: 2140-2155, **2008**.

[43] C.G. Hartinger, P.J. Dyson, *Chem Soc Rev*, 38: 391-401, **2009**.

[44] M.J. Clarke, F. Zhu, D.R. Frasca, *Chem Rev*, 99: 2511–2533, **1999**.

[45] L.D. Dale, J.H. Tocher, T.M. Dyson, D.I. Edwards, D.A. Tocher*, Anti-Cancer Drug Des*, 7: 3-14, **1992**.

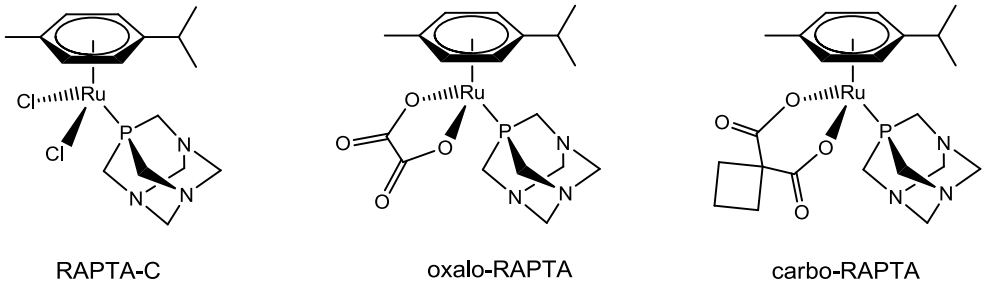

Fig 11: Structures of some RAPTA complexes[46]

They are known because of their metastasis inhibition in vivo while they are not toxic to healthy cells in vitro. This effect enables the treatment of secondary metastatic tumors after surgical elimination of the primary tumor, increasing the chance of survival of patients.

Since RAPTA compounds seem to be promising substances for anticancer therapy several modifications of the ligands have been performed and also other ruthenium–arene complexes e.g. with monodentate ligands have been studied.[47,48,49]

1.2.3 Rhodium

Rhodium is a rare, chemically inert transition metal of the platinum group discovered in 1803 by William Hyde Wollaston.[50] Compared to the other members of group 9, which are cobalt, iridium and meitnerium, rhodium has an atypical configuration in its outermost electron shells. Like platinum, metallic rhodium is not attacked by most acids but can be dissolved slowly by aqua regia and sulfuric acid (conc.). Rhodium compounds exist in the oxidation states 0 ($Rh_4(CO)_{12}$), +1 ($RhCl(PH_3)_2$), +2 ($Rh_2(O_2CCH_3)_4$), +3 ($RhCl_3$, Rh_2O_3), +4 (RhF_4, RhO_2), +5 (RhF_5, Sr_3LiRhO_6), and +6 (RhF_6) whereas +3 is the most common.

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[46] A. Casini, G. Mastrobuoni, W.H. Ang, C. Gabbiani, G. Pieraccini, G. Moneti, P.J. Dyson, L. Messori, *Chem Med Chem*, 2: 631-635, **2007**.

[47] M. Melchart, P.J. Sadler, *Bioorganometallics*, 39-64, **2006**.

[48] W.H. Ang, E. Daldini, C. Scolaro, R. Scopelliti, L. Juillerat-Jeanneret, P.J. Dyson, *Inorg Chem*, 45: 9006-9013, **2006**.

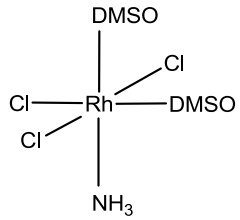
[49] C.A. Vock, A.K. Renfrew, R. Scopelliti, L. Juillerat-Jeanneret, P.J. Dyson, *Eur J Inorg Chem*, 1661-1671, **2008**.

[50] W.H. Wollaston, *Philosophical Transactions of the Royal Society of London*, 94: 419–430, **1804**.

In the oxidation state +3 (d^6) rhodium forms many octahedral and diamagnetic low-spin complexes with t^6_{2g} configuration. [51]

In addition to platinum and ruthenium also rhodium complexes show potential for the development of anticancer agents. Several rhodium compounds have shown remarkable anticancer activity but severe side effects prohibited further application.[52]

Recent data suggest that octahedral chloridorhodium(III) complexes may provide significant potential for use as anticancer therapeutics. For example, *mer,cis*-$[RhCl_3(DMSO)_2(NH_3)]$ exhibits promising cytotoxicity towards human ovarian (A2780) and colon carcinoma (LoVo) cell lines.[53]



mer,cis-$RhCl_3(DMSO)_2(NH_3)$

Fig 12: Structure of *mer,cis*-$[RhCl_3(DMSO)_2(NH_3)]$ [53]

mer-$[RhCl_3(DMSO)(pp)]$ complexes with a coordinated bidentate polypyridyl (pp) ligand like 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen) or dipyrido[3,2-f:2',3'-h]quinoxaline (dpq) reveal a considerable antitumor effect dependent on the ligand size.[54]

Another type of rhodium complexes currently being researched on are the (η^5-Cp*)Rh(III) compounds (Cp* = pentamethylcyclopentadienyl). All complexes shown in Fig. 13 show in vitro cytotoxicity (except $[(\eta^5\text{-}C_5Me_5)RhCl(bpy)](CF_3SO_3)$) in human

[51] A.F. Holleman; E. Wiberg; N. Wiberg, *Lehrbuch der Anorganischen Chemie* (91–100 ed.). 1056–1057, **1985**.

[52] N. Katsaros, A. Anagnostopoulou, *Crit Rev Oncol Hematol*, 42: 297– 308, **2002**.

[53] G. Mestroni, E. Alessio, A. Sessanti o Santi, S. Geremia, A. Bergamo, G. Sava, A. Boccarelli, A. Schettino, M. Coluccia, *Inorg Chim Acta,* 273: 62-71, **1998**.

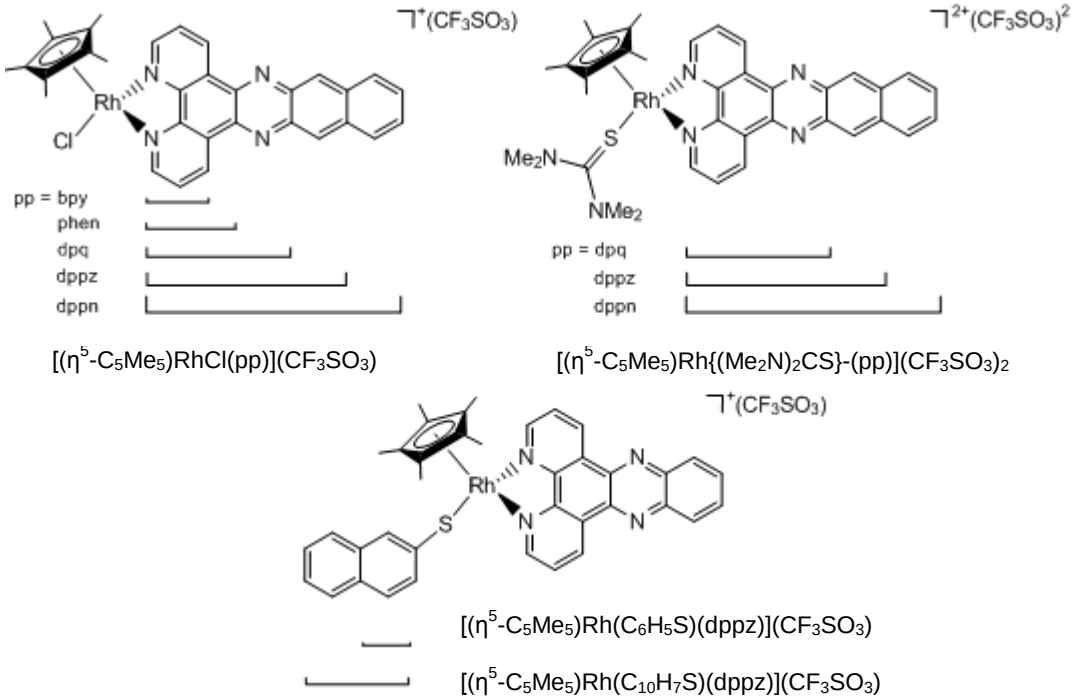
[54] M. Harlos, I. Ott, R. Gust, H. Alborzinia, S. Wçlf, A. Kromm, W.S. Sheldrick, *J Med Chem*, 51: 3924-3933, **2008**.

MCF-7 (breast cancer) and HT-29 (colon cancer) cell lines with IC_{50} values in the range of 0.56-10.7 µM.

Cyclopentadiene donates six electrons to the metal center binding to it through π interactions.[29] Pentamethylcyclopentadienyl ligands are additionally stabilized by the five methyl groups which have an electron-donating effect.[55]

The chlorido complexes coordinated to dpq, dppz (dipyrido-[3,2-a:2',3'-c]phenazine) and dppn (benzo[i]dipyrido[3,2-a:2',3'-c]phenazine)[56] as well as the $(Me_2N)_2CS$ complexes with dppz and dppn ligands show a correlation between their cytotoxicity and the size of the ligand whereas IC_{50} values decrease with increasing ligand size (dpq > dppz > dppn). A rapid exchange of the chloride to a H_2O in the chloro compounds results in the formation of double positively charged cations showing similar cytotoxicities and comparable levels of cellular uptake as those identified for the $(Me_2N)_2CS$ complexes.

In the case of $[(\eta^5\text{-}C_5Me_5)Rh(C_6H_5S)(dppz)](CF_3SO_3)$ and $[(\eta^5\text{-}C_5Me_5)Rh(C_{10}H_7S)(dppz)](CF_3SO_3)$ DNA intercalation is inhibited because of intramolecular interactions between the dppz ligands and the aromatic thiolate.[56]



$[(\eta^5\text{-}C_5Me_5)RhCl(pp)](CF_3SO_3)$

$[(\eta^5\text{-}C_5Me_5)Rh\{(Me_2N)_2CS\}\text{-}(pp)](CF_3SO_3)_2$

$[(\eta^5\text{-}C_5Me_5)Rh(C_6H_5S)(dppz)](CF_3SO_3)$

$[(\eta^5\text{-}C_5Me_5)Rh(C_{10}H_7S)(dppz)](CF_3SO_3)$

Fig 13: Structures of Rh(III) complexes with different polypyridyl ligands

[55] K.P.C. Vollhardt, N.E. Schore, *Organische Chemie*, **2000**.

[56] M.A. Scharwitz, I. Ott, Y. Geldmacher, R. Gust, W.S. Sheldrick, *J Organomet Chem*, 693: 2299-2309, **2008**.

As already mentioned, ligand size seems to be correlated to the IC_{50} values in several Cp*-rhodium(III) compounds. Therefore, it is not surprising that in vitro studies on $[([9]aneS_3)RhCl(pp)]Cl_2$ (($[9]aneS_3$= κ^3S 1,4,9-trithiacyclononane) (Fig 14) and other ($[9]aneS_3$)Rh(III) complexes show that IC_{50} values decrease with increasing size of the pp ligand in HT-29 cells. Accordingly it has to be assumed that complexes with different polypyridyl ligands diversify in their modes of action and varying targets have been proposed dependent on the ligand size.[57]

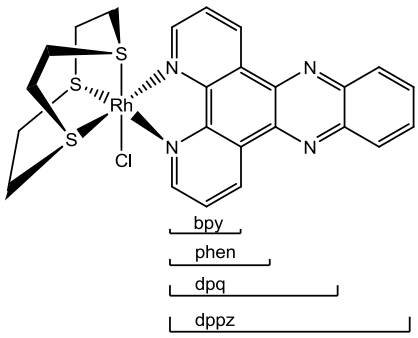


Fig 14: $[([9]aneS_3)RhCl(pp)]Cl_2$ complexes [57]

[57] R. Bieda,M. Dobroschke, A. Triller, I. Ott,M. Spehr, R.Gust, A. Prokop, W.S. Sheldrick, C*hem Med Chem*, 5:1123-1133, **2008**.

1.3 Flavonoids

1.3.1 Chemical structure and biological effect

Flavonoids are a class of secondary metabolites of plants named after the Latin word *flavus* meaning yellow. Generally they are present in fruit, nuts, vegetables, seeds, flowers, stems, tea, wine, propolis and honey. As they are pigments, their natural function in plants is to provide colors but they have many other functions. In leaves they are assumed to protect from UV-B radiation as well as fungal pathogens. Additionally flavonoids are known to play a crucial role in the energy transfer, photosensitization, respiration, photosynthesis and several other processes in plants. The basic structure of flavonoids is built by a 2-phenyl-benzo[α]pyrane (flavane), which consists of two benzene rings (A and B) connected by a heterocyclic pyrane ring (C) (Fig. 15).

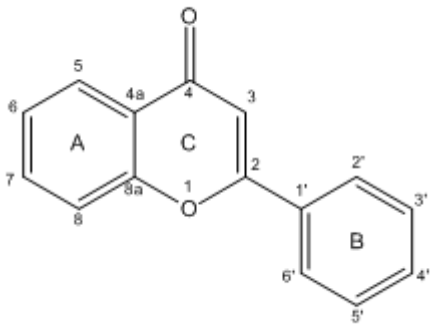


Fig 15: Basic structure of flavonoids.[59]

Flavonoids tested in several in vitro studies are shown to exhibit many useful poperties such as antiinflammatory, antiallergic, antifungal, antiviral, antibacterial, antimicrobial, antidiarrheal, estrogenic, antioxidant, vascular and anticancer activities.[58,59,60,61,62] Therefore flavonoid containing drugs have been used for centuries for the treatment of human diseases.

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[58] Y. Yamamoto, R.B. Gaynor, *J Clin Invest*, 107 (2): 135, **2001**.

[59] T.P.T Cushnie, A.J. Lamb, *Int J Antimicrob Agents*, 26 (5): 343-356, **2005**.

[60] T.P.T Cushnie, A.J. Lamb, *Int J Antimicrob Agents*, 38 (2): 99-107, **2011**.

[61] R.R. Sousa, K.C. Queiroz , A.C. Souza, S.A. Gurgueira, A.C. Augusto, M.A. Miranda, M.P. Peppelenbosch, C.V. Ferreira, H. Aoyama, *J Enzyme Inhib Med Chem*, 22 (4): 439-444, **2007**.

[62] M. Schuier, H. Sies, B. Illek, H. Fischer, *J. Nutr.* 135 (10): 2320-5, **2005**.

For example, Scutellaria baicalensis, a species of flowering plant in the Lamiaceae family, containing the flavone baicalein, has been used for thousands of years in China to treat infected oral wounds or periodontal abscesses.[59]

Flavonols or 3-hydroxyflavones (3-hydroxy-2-phenylchromen-4-one) feature additionally a hydroxyl group at the C3 atom (Fig. 16).

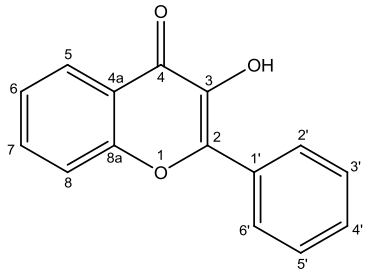


Fig 16: Structure of 3-hydroxyflavones.

Several naturally occurring substances like Quercetin, Myricetin, Kaempferol, Fisetin, Isorhamnetin, Rhamnazin and Pachypodol are representatives of this group (Fig. 17).

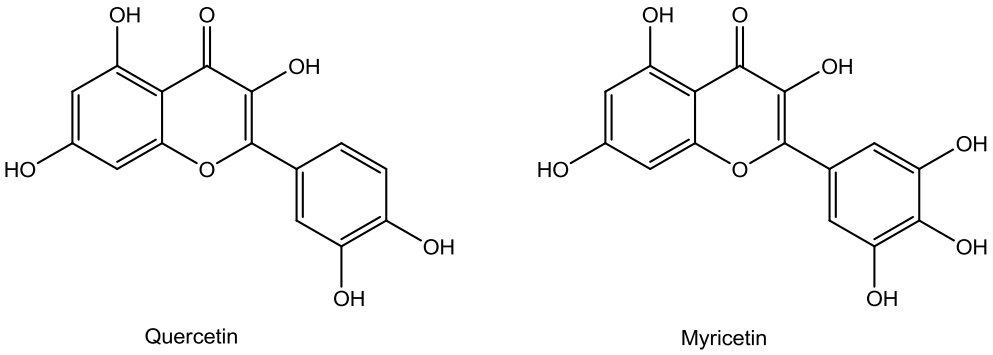


Fig 17: Chemical structures of Quercetin and Myricetin.

Studies on quercetin, and myricetin have shown that they might have an effect on the downregulation of the NF-κB pathway of living organisms. NF-κB terms a class of inducible transcription factors which are known to play a role in the inflammatory and immune response. In case of cytokine treatment or DNA damage NF-κB protects the cells from undergoing apoptosis. As a consequence, inhibition of these transcription factors by flavanoids might lead to enhanced efficacy of chemotherapy.[58]

1.3.2 3-Hydroxyflavones – function as chelating ligands

As some of the representatives of the 3-hydroxyflavone family show properties which are advantageous for cancer treatment, their use as ligands in metal-based chemotherapeutics might be favorable. Due to their keto and hydroxy functional groups, they are suitable chelating ligands (Fig. 18). Several complexes using 3-hydroxyflavones have been synthesized with the oxygens donating electrons from a lone electron pair into an empty metal orbital. Several metals like Fe(III),[63] Al(III),[64,65] Zn(II),[66] Pb(II),[67] Mg(II), Cu(II)[68] and Ba(II) have been used as central ions and studies of their physical and chemical properties have been undertaken.[69]

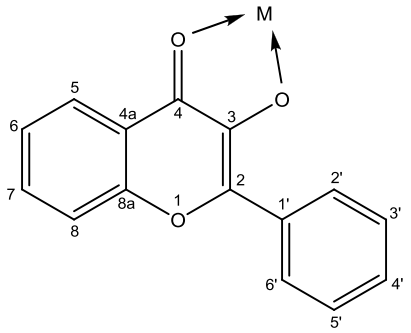


Fig 18: Schematic representation of the coordination of 3-hydroxyflavones to metal centers.

[63] M.D. Engelmann, R. Hutcheson, I.F. Cheng, *J Agric Food Chem*, 53: 2953-2960, **2005**.

[64] S. Sathish, G. Narayan, N. Rao, C. Janardhana, *J Fluoresc*, 17: 1-5, **2007**.

[65] J.P. Santos, M.E.D. Zaniquelli, W.F. De Giovani, S.E. Galembeck, *Colloids Surf, A: Physicochemical and Engineering Aspects*, 198-200, 569-576, **2000**.

[66] C. Lapouge, L. Dangleterre, J. Cornard, *J Phys Chem A*, 110(45): 12494-12500, **2006**.

[67] L. Dangleterre, J. Cornard, *Polyhedron*, 24: 1593-1598, **2005**.

[68] F. Ben-Allal el Amrani, L. Perell, J. Borrgts, L. Tortes, *Metal Based Drugs*, 7(6), **2000**.

[69] A.D. Roshal, A.V. Grigorovich, A.O. Doroshenko, V.G. Pivovarenko, A.P. Demchenko, *J Photoch Photobio A*, 127: 89-100, **1999**.

2. RESULTS AND DISCUSSION

2.1 Synthesis and characterization of the 3-hydroxyflavone ligands

The aim of my diploma thesis was the synthesis of novel rhodium(III) complexes by coordination of the metal center to the oxygens of different substituted 3-hydroxyflavones using them as chelating ligands.
For characterization of the obtained compounds analytical methods like ^{1}H, $^{13}C\{^{1}H\}$ and 2D NMR spectroscopy as well as elemental analysis were performed.
Furthermore, crystal structures of all complexes were determined by X-ray diffraction analysis.

2.1.1 Synthesis of 3-hydroxyflavones

The 3-hydroxyflavones were synthesized according to an established method, in a 2-step synthesis:[70]

First step:
2-Hydroxyacetophenone was mixed with a benzaldehyde in alkaline solution and stirred at room temperature to yield in an aldol condensation 2-hydroxychalcone (Fig. 19). To obtain the solid intermediate 2-hydroxychalcone the solution was acidified with acetic acid whereby the light yellow solid precipitated. The precipitate was filtered and used for the second step without further purification.

[70] C.X. Qin, X. Chen, R.A. Hughes, S.J. Williams, O.L. Woodman, *J Med Chem*, 51:1874-1884, **2008**.

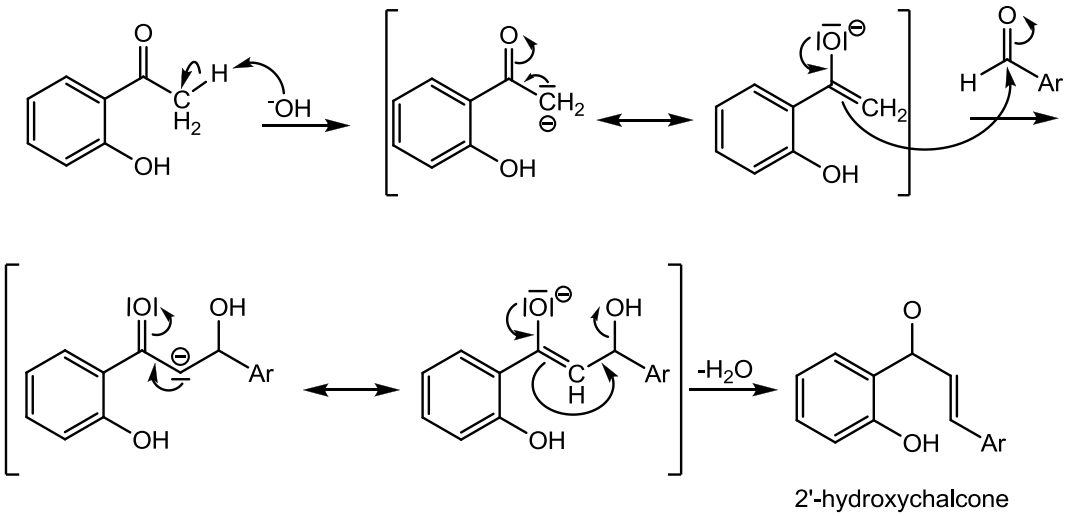


Fig 19: Mechanism of the base-catalyzed aldol condensation

Second step:

In the second step the intermediate was suspended in ethanol and oxidized by hydrogen peroxide under alkaline conditions in an Algar-Flynn-Oyamada (AOF) reaction. The final product was obtained in moderate to good yields (30-75%) by acidification with hydrochloric acid and filtration.

At present several different mechanisms are possible to describe how the AOF–reaction proceeds but still none of them could be unambiguously verified. It has been proposed that the product is formed in a two-stage mechanism. In the first step a dihydroflavonol is generated which is subsequently oxidized to a flavonol.[70]

Others have proposed mechanisms in which an epoxy compound occurs, not supported by data presented by Gormley et al. [71] Therefore, two possible ways of action have been prognosed (Fig. 20):

1) By addition of a base like sodium hydroxide a phenolate is built which attacks the double bond in a nucleophilic way. The double bond directly reacts with the hydrogen peroxide to yield the 3-hydroxyflavone.

2) Nucleophilic attack of the phenolate building an enolate which subsequently reacts with hydrogen peroxide.

[71] T. R. Gormley, et al., *Tetrahedron*, 29: 369, **1973**.

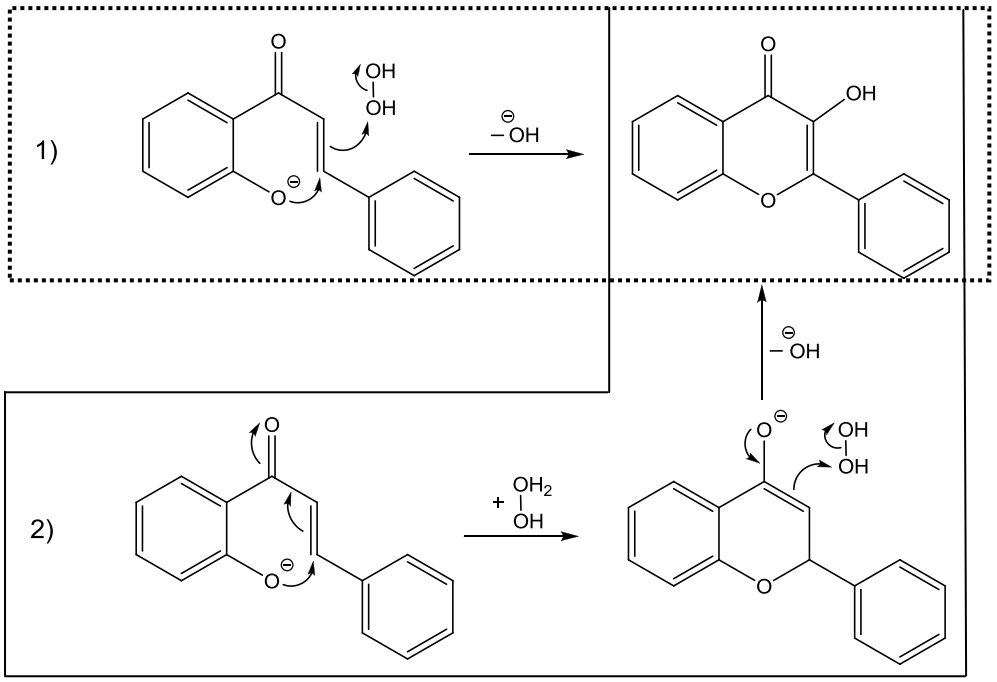


Fig 20: Proposed mechanisms for the Algar-Flynn-Oyamada reaction

These two steps result in an overall reaction according to the scheme in Fig. 21.

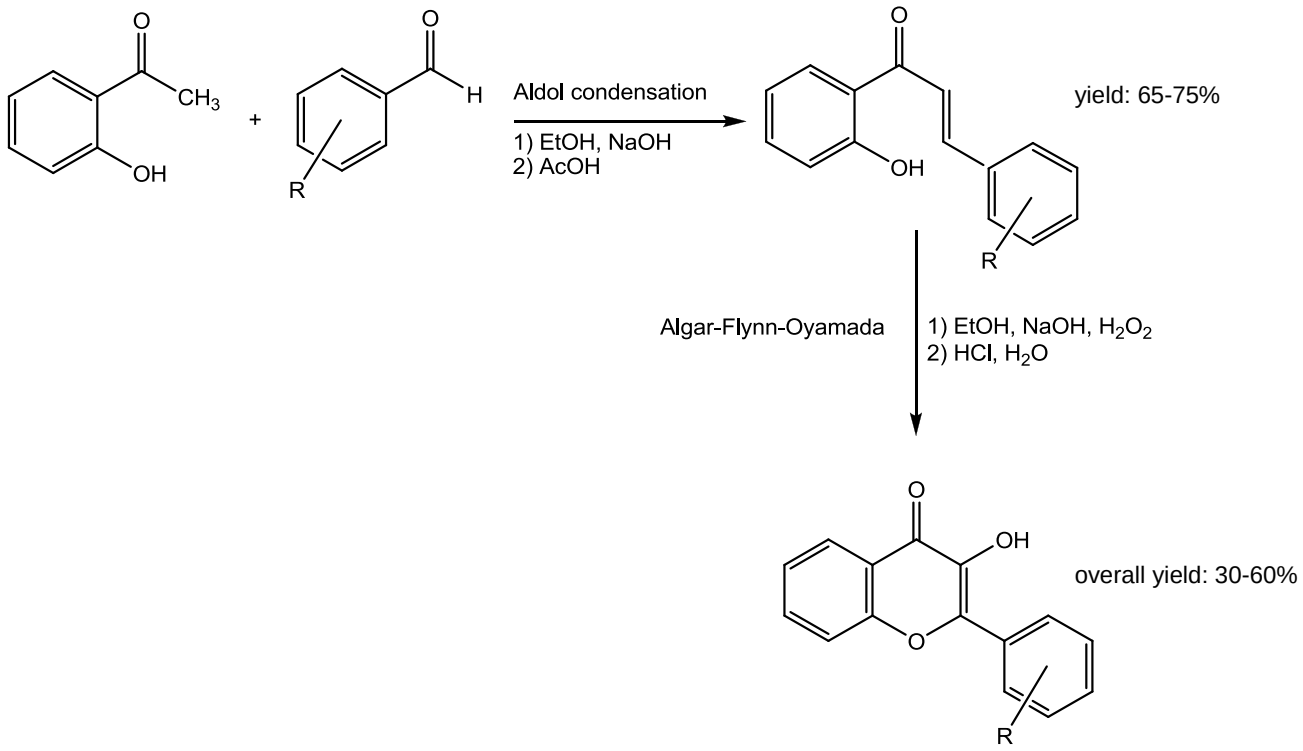


Fig 21: General pathway to the synthesis of 3-hydroxyflavones

According to this procedure five different substituted 3-hydroxyflavones have been synthesized (Fig 22).

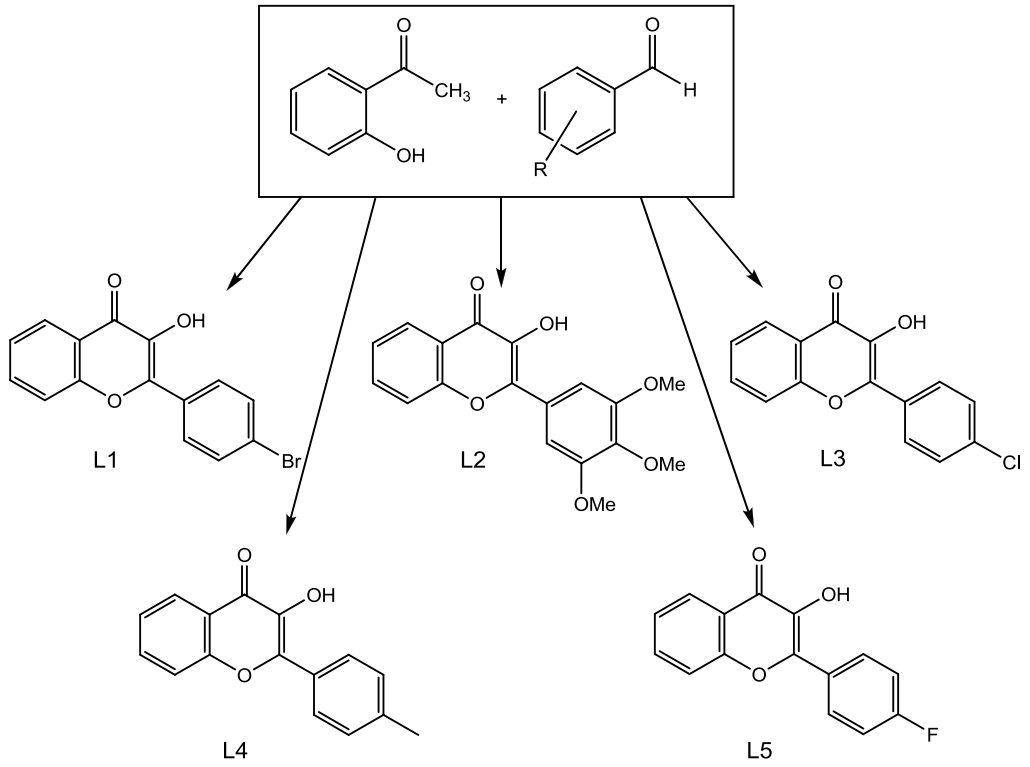


Fig 22: Overview of the synthesized 3-hydroxyflavone ligands

2.1.2 Characterization of the 3-hydroxyflavone ligands

^{1}H-NMR spectroscopy

The peak for the hydroxyl-proton occurs typically in the range 8.25-9.84 ppm. The signals of the protons H5, H6, H7 and H8 were assigned by 2D NMR spectroscopy. In the spectrum of ligand L5 the protons H2'/H6' and H3'/H5' show a quadruplet and a multiplet instead of a doublet because of additional couplings with the fluoro substituent in para position (^{4}J (F,H) = 5.5 Hz, H2'/H6').

^{13}C{^{1}H}-NMR spectroscopy

The signal for the C=O groups is visible at about 173 ppm. The primary methyl group of ligand L4 appears typically at 21.3 ppm. Additional couplings of C4', C2'/C6' and C3'/C5' with the fluoro substituent can be notified in the spectrum of ligand L5 showing doublets instead of singulets (^{1}J(C,F) = 248.8 Hz, C4', ^{4}J(C,F) = 8.5 Hz, C2'/C6', ^{3}(C,F) = 21.7 Hz, C3'/C5').

2.2 Synthesis and characterization of the Rh(III)-(η^5-Cp*) complexes

2.2.1 Synthesis of bis[dichlorido(η^5-pentamethylcyclopentadiene)rhodium(III)]

Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)] was synthesized by suspending the violet crystals of $RhCl_3$ in methanol and refluxing for 24 hours after addition of pentamethylcyclopentadiene. The red solid product was filtered and needed no further purification steps. It was obtained in good yields of 75% and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy for the use as starting compound for the complexations (Fig. 23).

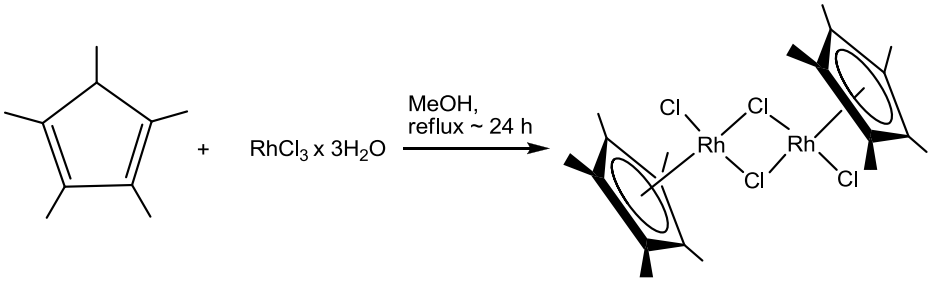


Fig 23: Synthesis of bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)]

2.2.2 Synthesis of the (η^5-Cp*)Rh(III) complexes with 3-hydroxyflavone ligands

Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III) (0.45 eq) was suspended in methanol and the flavone (1 eq) as well as the silver trifluoromethanesulfonate (2.2 eq) were added. In some cases sodium methoxide (1.1 eq) was additionally added for activation of the flavone hydroxyl group. The mixture was refluxed for about 18 hours, filtered, extracted from dichloromethane and recrystallized from methanol/diethyl ether by diffusion at 4°C (Fig. 24).

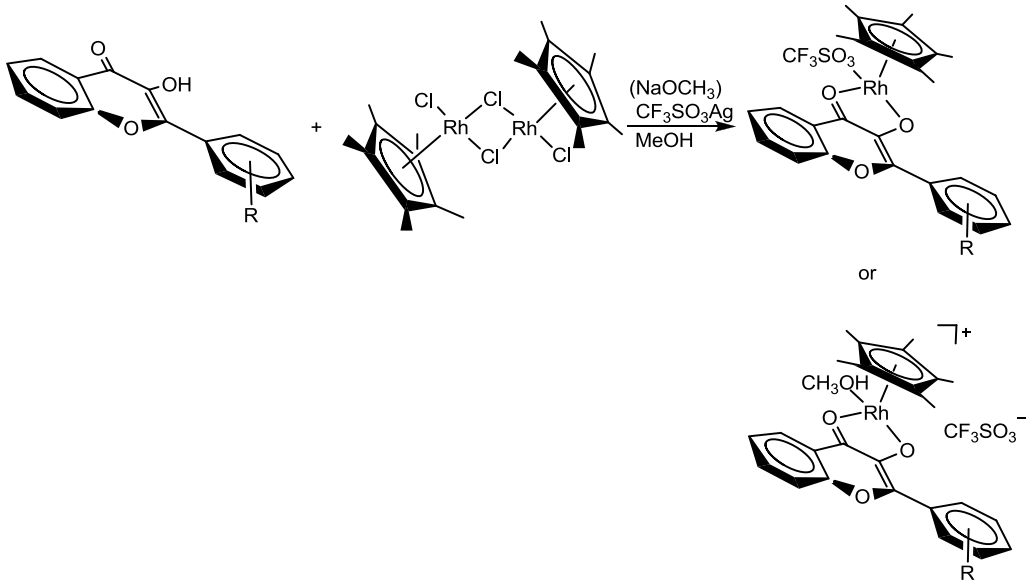


Fig 24: General concept for the synthesis of (η^5-Cp*)Rh(III) complexes with 3-hydroxyflavone ligands

According to this procedure five rhodium complexes have been synthesized (Fig. 25).

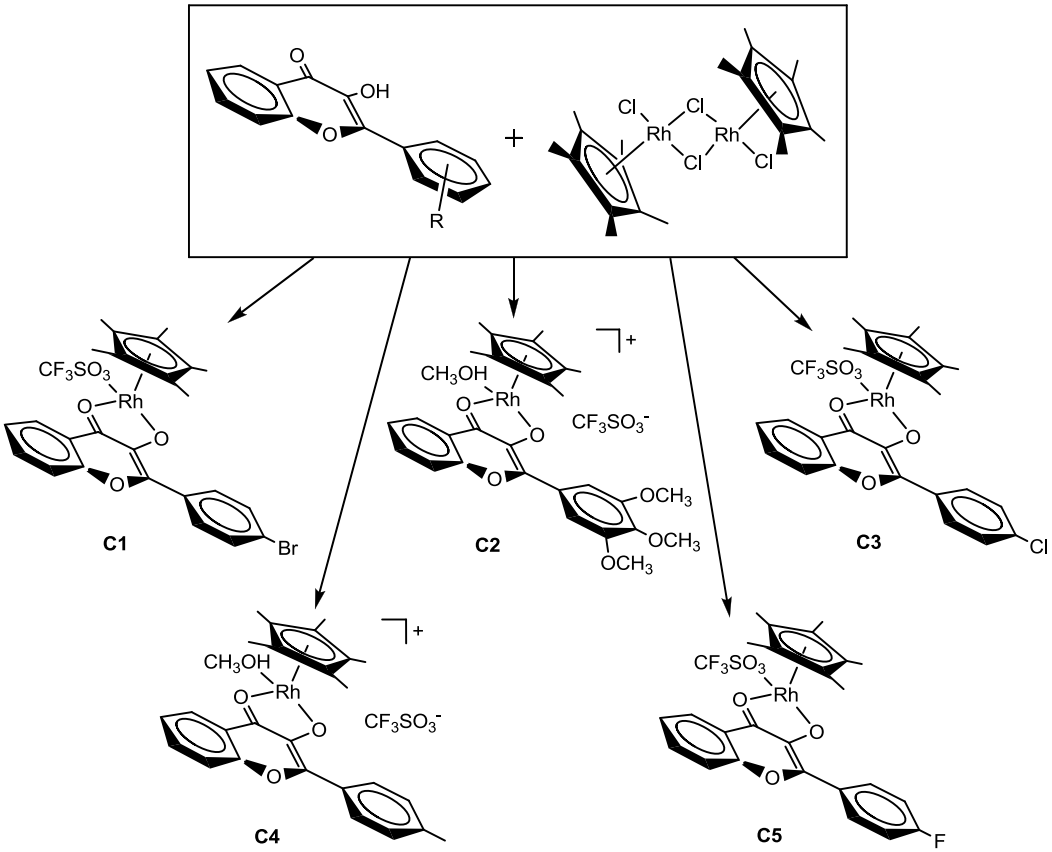


Fig 25: Overview of the synthesized (η^5-Cp*)Rh(III) complexes with 3-hydroxyflavone ligands

Furthermore, complexes coordinated to chloride instead of trifluoromethanesulfonate have been synthesized but unfortunately purification failed.

2.2.3 Characterization of the (η^5-Cp*)Rh(III) complexes with 3-hydroxyflavone ligands by ^{1}H, ^{13}C{^{1}H } and 2D NMR spectroscopy

2D NMR spectroscopy

In order to assign the signals in ^{1}H and ^{13}C{^{1}H } NMR, 2D NMR ^{1}H,^{1}H-COSY, HMBC and HSQC spectra were measured exhibiting couplings between the proton atoms and between protons and carbons. ^{1}H,^{1}H -COSY (Correlation Spectroscopy) spectra offer spin-spin couplings between protons and provide information which protons are neighbored (Fig. 29). The HSQC (Heteronuclear Single Quantum Coherence) spectrum reveals direct C-H couplings over one bond (Fig. 31), whereas the HMBC (Heteronuclear Multiple Bond Coherence) spectrum gives information about couplings between H and C separated by 2-4 bonds (Fig. 30).

For unambiguous assignment of the protons in the ^{1}H-NMR spectra, the spectrum of complex C1 was used (Fig 26). The aromatic area is shown.

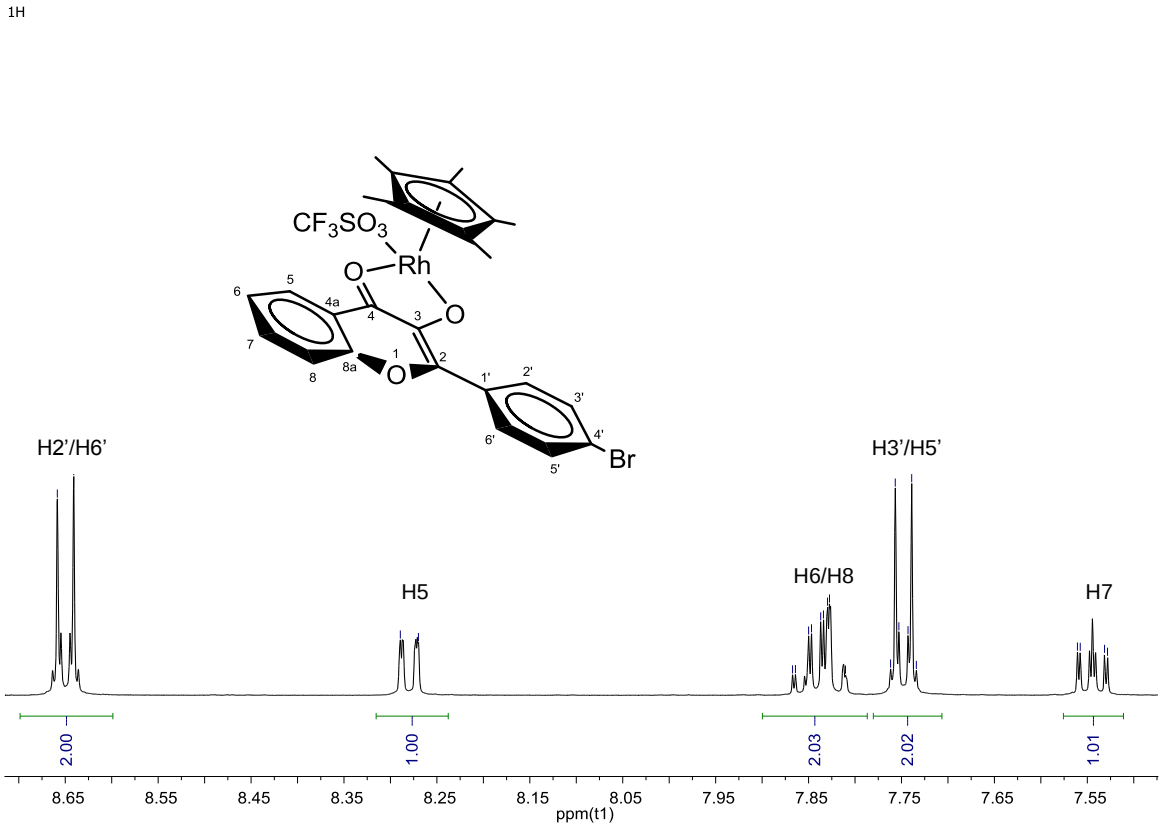


Fig 26: Aromatic area of the ^{1}H-NMR spectrum of C1 in CD_3OD

The $^{13}C\{^{1}H\}$ NMR spectrum shows the typical singlet for the five carbons of the CH_3 groups of the cyclopentadienyl ligand at 8.9 ppm. The five carbon atoms forming the cyclopentadiene ring appear as a doublet around 94 ppm (Fig. 27).

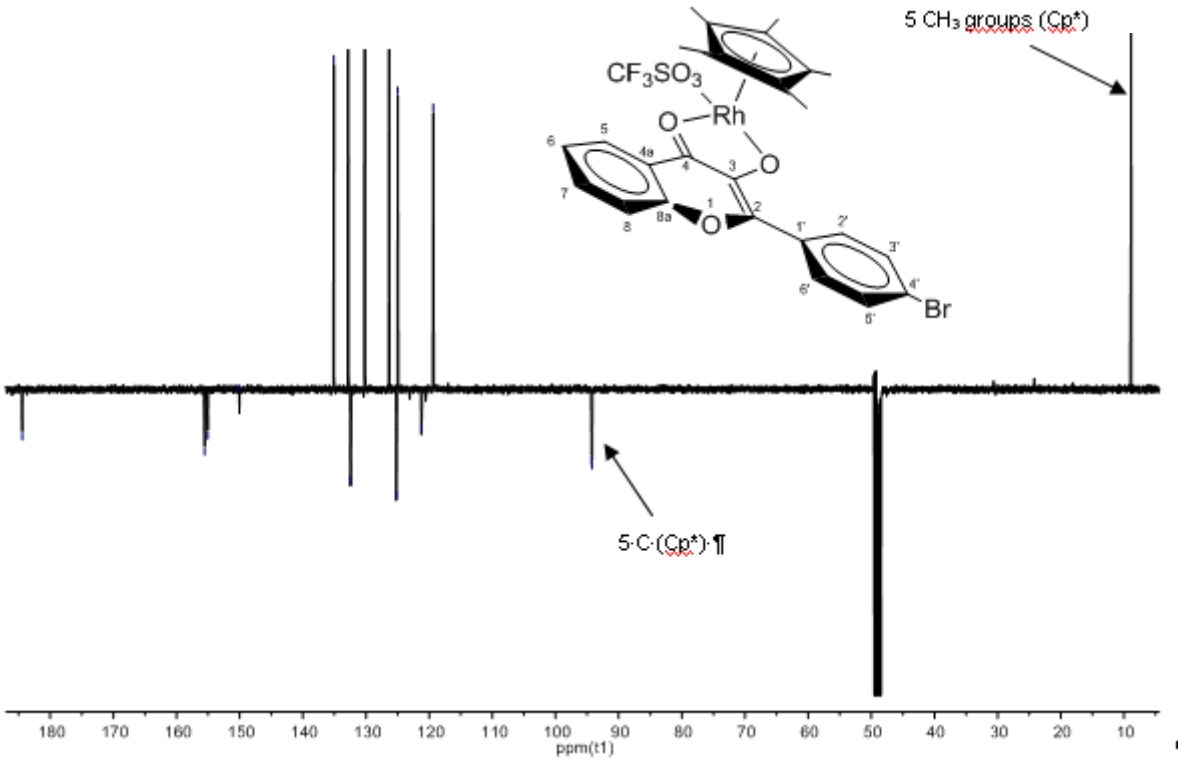


Fig 27: ^{13}C NMR spectrum of C1 in CD_3OD.

Signals of the aromatic area appear in a typical range of 115 to 190 ppm (Fig. 28). Compared to the spectra of the ligands, the signals of the carbons C4, C4a and C3 are shifted 10-15 ppm to a higher range. The five carbons of the cyclopentadienyl ring show a doublet ($^{2}J(C,H)$ = 10 Hz) around 94 ppm. The five CH_3 group carbons of the Cp* ligand can be notified as a singlet at 8.9 ppm.

In the spectrum of complex C5 couplings with the fluorine can be noticed: A doublet at 162 ppm ($^{1}J(C,F)$ = 248.8 Hz, C4'). C2' and C6' show a doublet at 130 ppm ($^{3}J(C,F)$ = 8.5 Hz). The carbons C3' and C5' are visible at 115.6 ppm forming a doublet ($^{2}J(C,F)$ = 21.7 Hz).

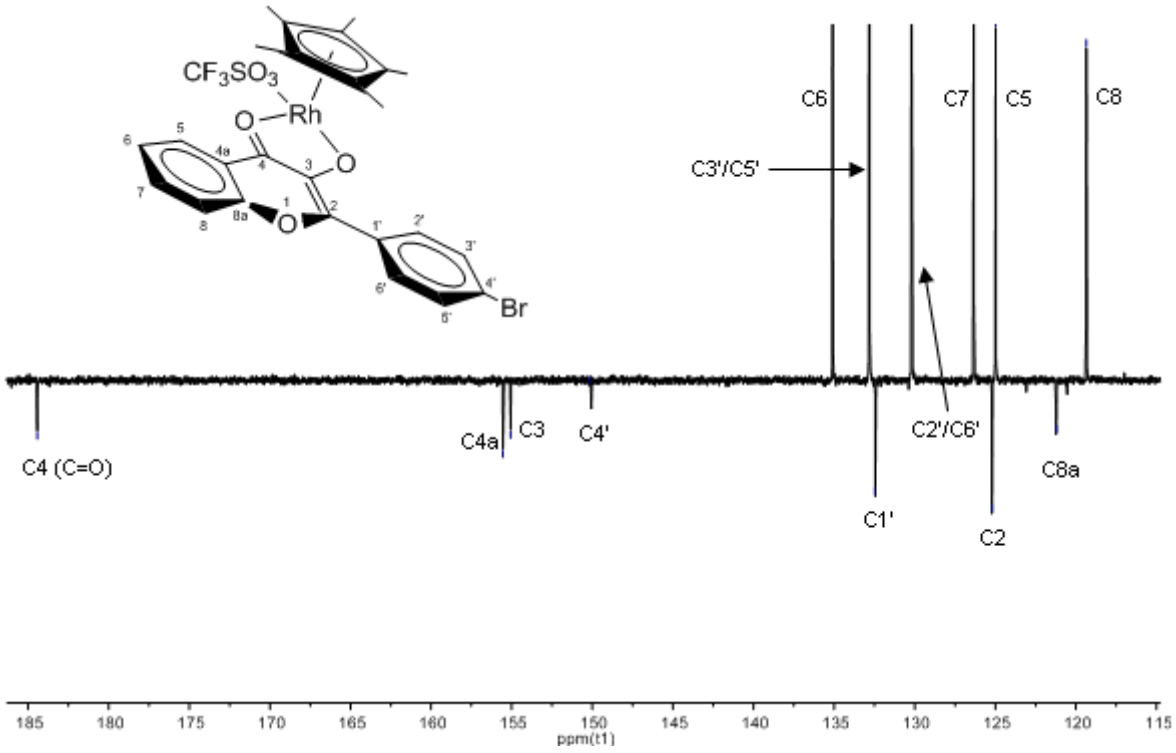


Fig 28: Area 90-180 ppm of $^{13}C\{^{1}H\}$ NMR spectrum of C1 in CD_3OD.

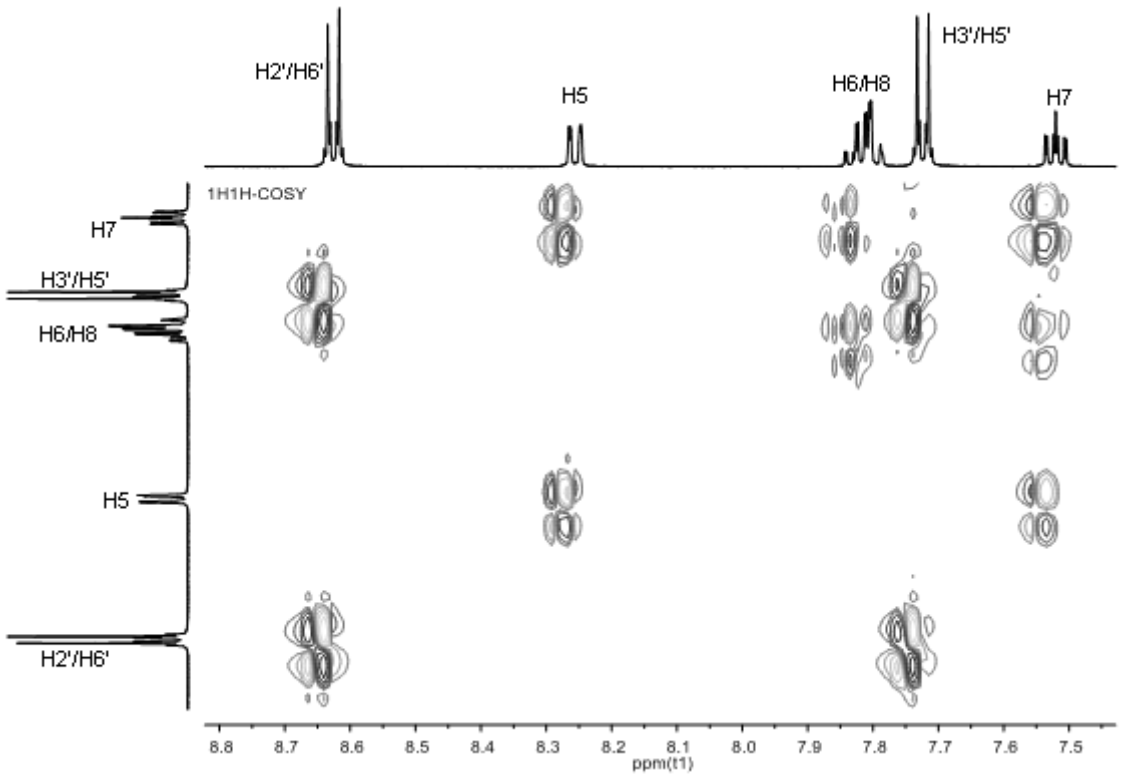


Fig 29: $^{1}H,^{1}H$-COSY NMR spectrum of C1 in CD_3OD (aromatic area).

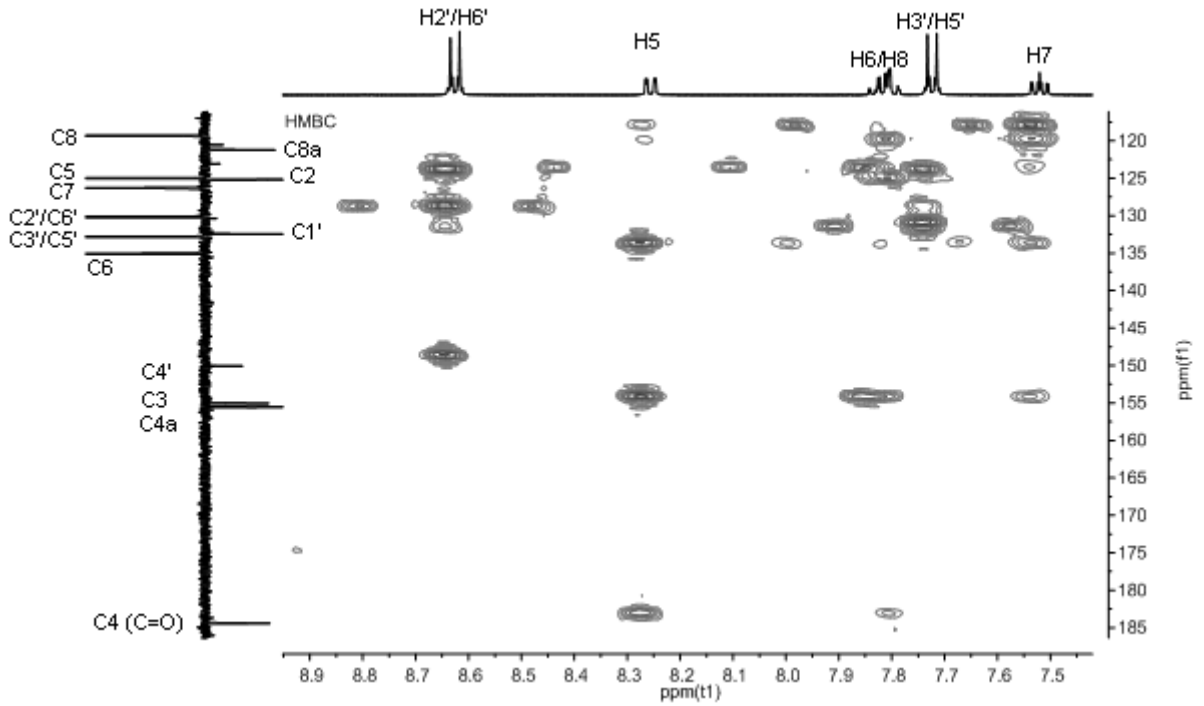


Fig 30: HMBC spectrum of C1 in CD_3OD.

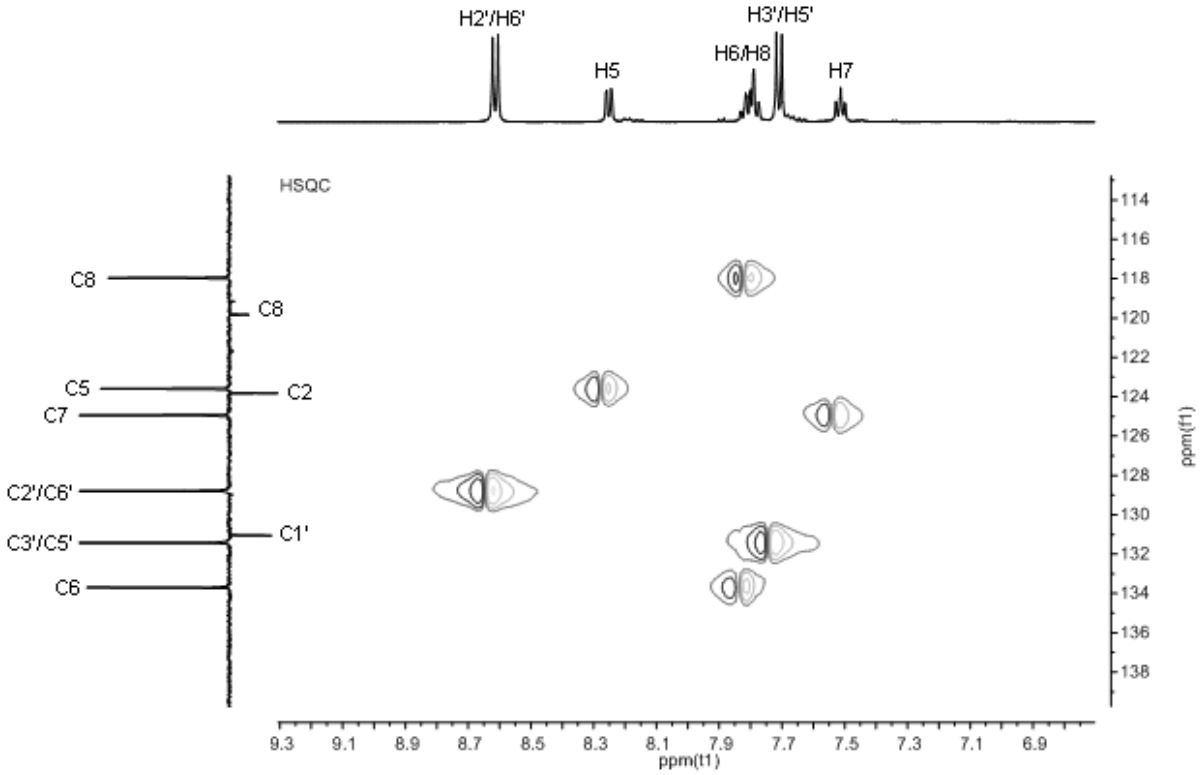


Fig 31: HSQC spectrum of C1 in CD_3OD.

X-ray diffraction analysis

Complexes C1-C5 were characterized by X-ray diffraction analysis. Crystals were grown from methanol and diethyl ether at 4 °C. The binding parameters are very similar in all molecular structures. The torsion angle between the substituted benzene ring and the pyrane ring is around 3-4° for the chloride and fluoride substituted B ring, whereas the other complexes show values of 1-2°. Therefore, the two rings are nearly co-planar. The bond lengths between rhodium and the 3 coordinated oxygens range from 2.0 to 2.2 Å, independent of the substituents of the ligand. The distances between the rhodium center and the carbons of the cyclopentadienyl ring vary in the range of 2.0-2.6 Å.

Solubility

Solubility is an important parameter to translate a component to clinical studies, especially if considering intravenous administration. Drug candidates for cancer treatment need to be soluble in buffers in which they can be used for both in vitro testing in cancer cells and at a later stage for being administered to the patients. Unfortunately the synthesized rhodium compounds showed low solubility in media used for in vitro tests on tumor cells, such as RPMI 1640. Therefore, *in vitro* anticancer activity assays were not accessible.

3. EXPERIMENTAL PART

3.1 Materials and Methods

Melting points were determined with a Büchi *Melting Point* B-540 apparatus. Elemental analyses were done by the Microanalytical Laboratory of the University of Vienna out with a Perkin Elmer 2400 CHN Elemental Analyser.

NMR spectra were recorded on a Bruker FT-NMR spectrometer Avance III^{TM} 500 MHz at 25 °C. ^{1}H-NMR spectra measurements were performed at 500.10 MHz and ^{13}C-NMR spectra at 125.75 MHz in d_6-DMSO (for ligands) and CD_3OD or $CDCl_3$ (for complexes) at 22°C. The 2D NMR spectra were measured applying a gradient-enhanced mode.

For X-ray diffraction analysis single crystals of the respective complex were selected for measurement on a Bruker X8 APEX II CCD diffractometer at 100 K.

3.1.1 Chemicals used for synthesis

2-Hydroxyacetophenone (Fluka, Acros Organics), p-toluolaldehyde (Acros Organics), 4-fluorobenzaldehyde (Fluka), 4-chlorobenzaldehyde (Fluka), 3,4,5-trimethoxybenzaldehyde (Aldrich), 4-bromobenzaldehyde (Fluka), rhodium(III)chloride (Aldrich), 1,2,3,4,5-pentamethylcyclopentadiene (Alrich) and sodium methoxide (Aldrich) were purchased and used without further purification.

3.1.2 General procedure for the synthesis of 3-hydroxyflavone ligands

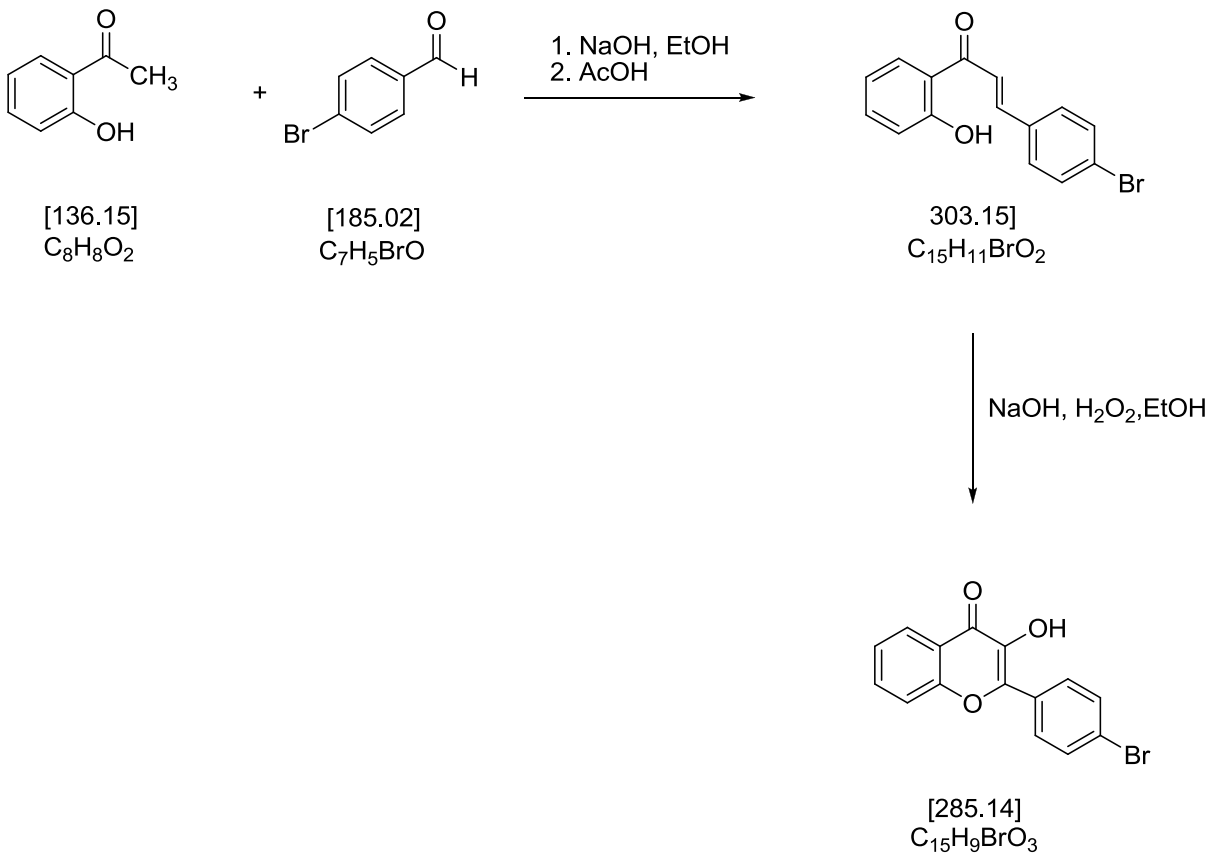
2-Hydroxyacetophenone (2.00 g, 14.7 mmol, 1 eq) and an aldehyde (14.7 mmol, 1 eq) were dissolved in ethanol (90 mL) and NaOH (5 M, 63.2 mmol, 12.6 mL) was added. The yellow solution was stirred for 18 h at room temperature during which it turned into red. The reaction mixture was acidified by addition of AcOH (30%) to precipitate the 2'-hydroxychalcone which was filtrated and used without further purification for the second step of the synthesis (yield 65-75%).

The 2’-hydroxychalcone (10.3 mmol, 1 eq) was suspended in ethanol (50 mL) and the pH was raised by addition of NaOH (5 M, 20.6 mmol, 4.12 mL, 2 eq). The suspension was cooled to 4°C and H_2O_2 (30%, 95.0 mmol, 2.3 mL, 2.2 eq) was added for oxidation.

The mixture was stirred for 18 h at room temperature and acidified with HCl (2 M). For precipitation the solution was poured onto water (400 mL) and the yellow solid was collected by filtration in moderate yields of 30%. To obtain the pure product recrystallization from methanol was performed.

3.2 3-Hydroxyflavone ligands

3.2.1 3-Hydroxy-2-(4-bromophenyl)-4H-chromen-4-one L1



[136.15]
$C_8H_8O_2$

[185.02]
C_7H_5BrO

303.15]
$C_{15}H_{11}BrO_2$

[285.14]
$C_{15}H_9BrO_3$

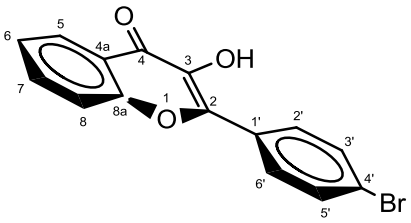
Synthesis

The synthesis was performed according to the general procedure of 3-hydroxyflavone ligands described in section 3.1.2 using 2.72 g 4-bromobenzaldehyde.

Overall yield: 1.68 g (40%), yellow crystals

Melting point: 165-166°C

NMR – spectroscopy of **L1**



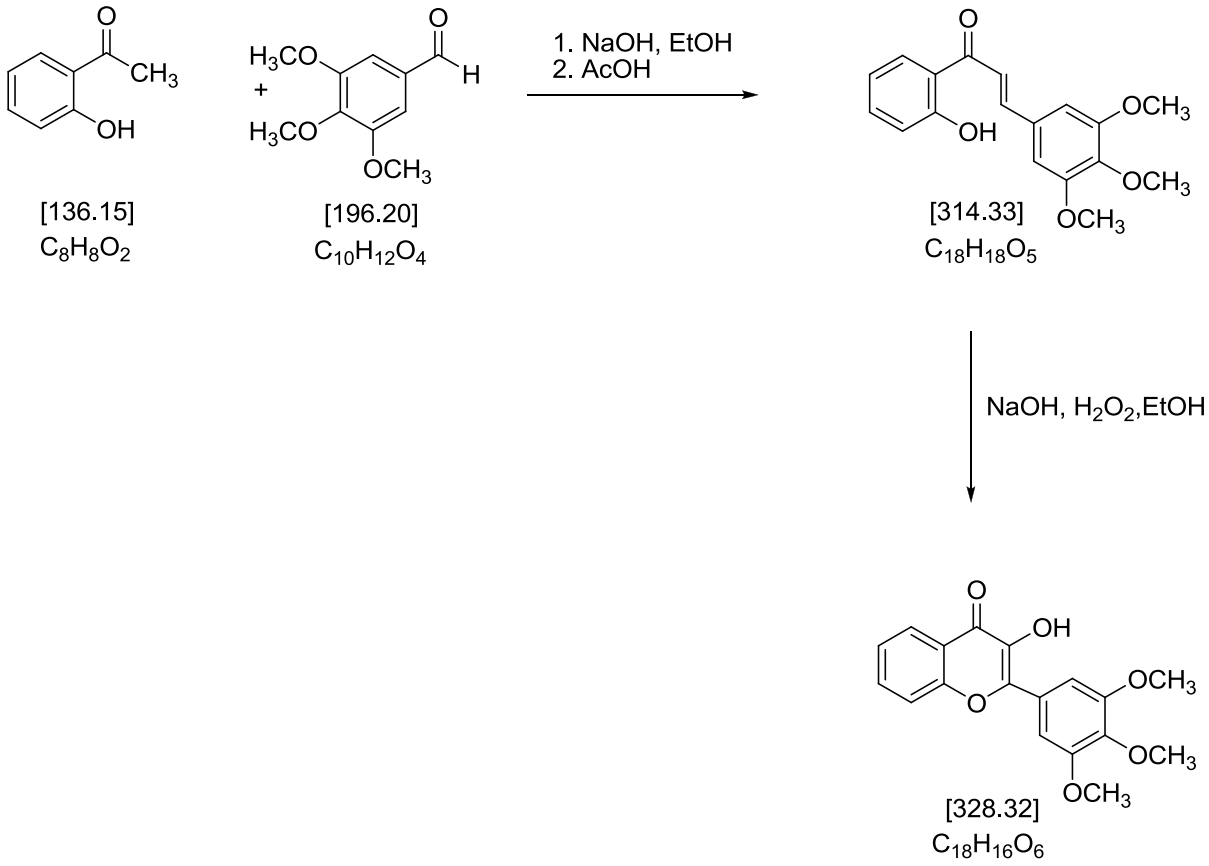
^{1}H-NMR spectrum of **L1**:

NMR (500.10 MHz, d_6-DMSO): δ = 9.84 (s, 1H, 3-OH), 8.18 (d, ^{3}J(H,H) = 8.7 Hz, 2H, H2'/H6'), 8.12 (dd, ^{3}J(H,H) = 8.0, ^{4}J(H,H) = 1.4 Hz, 1H, H5), 7.88-7.75 (m, 4H, H6/H8/H3'/H5'), 7.51-7.45 (m, 1H, H7).

^{13}C{^{1}H }-NMR spectrum of **L1**:

NMR (125.75 MHz, d_6-DMSO): δ = 173.0 (C4, C=O), 154.5 (C4'), 144.0 (C4a), 139.4 (C3), 133.9 (C6), 131.6 (C3'/C5'), 131.3 (C2'/C6'), 130.5 (C1'), 129.5, C7), 124.7 (d, ^{3}J(C,H) = 21.1 Hz, C5), 123.3 (C2), 121.3 (C8a), 118.4 (C8).

3.2.2 3-Hydroxy-2-(3,4,5-trimethoxyphenyl)-4H-chromen-4-one L2



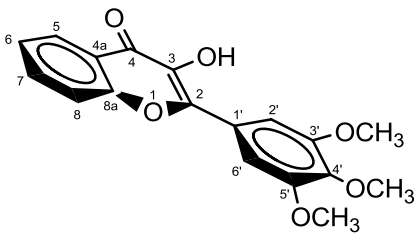
Synthesis

The synthesis was performed according to the general procedure of 3-hydroxyflavone ligands described in section 3.1.2 using 2.88 g 3,4,5-trimethoxybenzaldehyde.

Overall yield: 1.70 g (35 %), beige solid

Melting point: 186-187°C

NMR – spectroscopy of **L2**



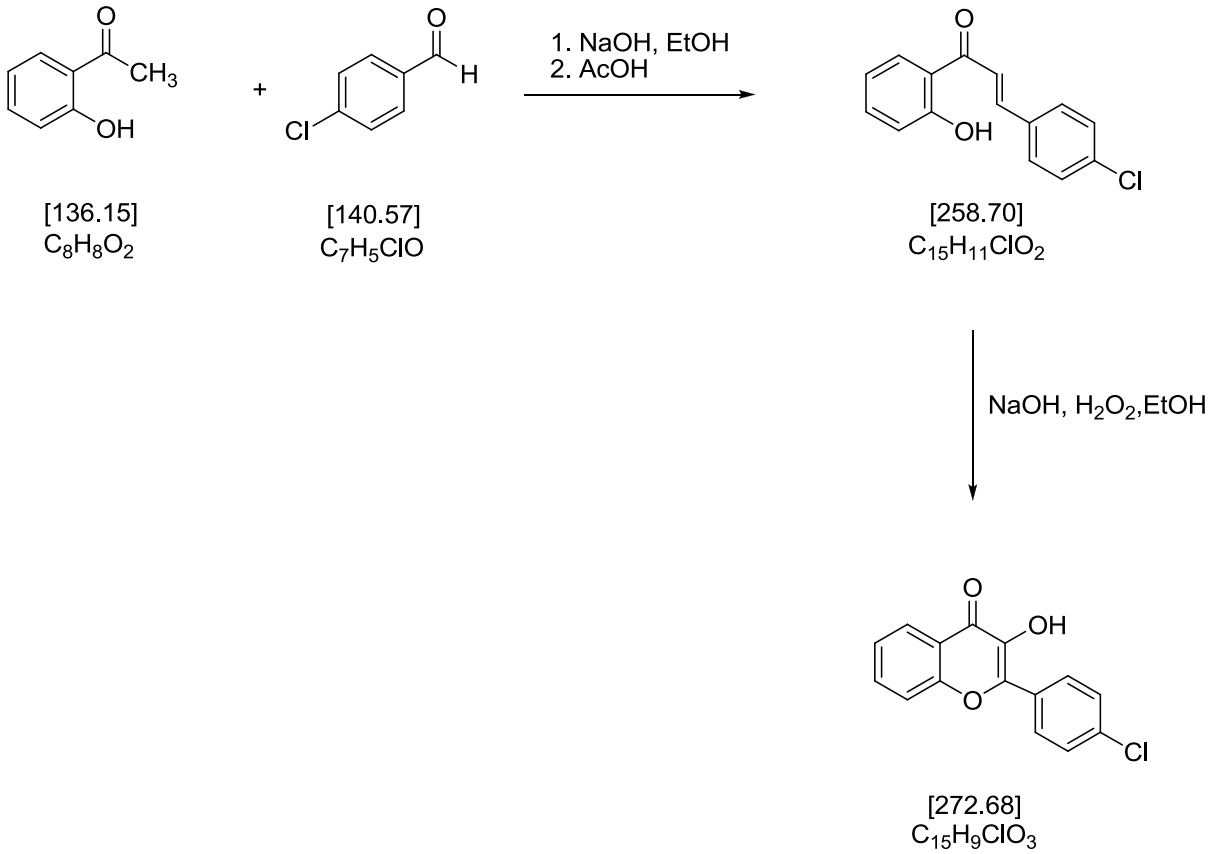
^{1}H-NMR spectrum of **L2:**

NMR (500.10 MHz, in d_6-DMSO): δ = 8.25 (dd, ^{3}J(H,H) = 8.0, ^{4}J(H,H) = 1.5 Hz, 1H, H5), 7.70-7.73 (m,1H, H6), 7.63 – 7.58 (m, 1H, H8), 7.56 (s, 2H, H2'/H6'), 7.42 (t, ^{3}J(H,H) = 7.9 Hz, 1H, H7), 3.97 (s, 6H, 3'/5'-CH_3), 3.94 (s, 3H, 4'-CH_3).

^{13}C{^{1}H }-NMR spectrum of **L2**:

NMR (125.75 MHz, d_6-DMSO): δ = 172.8 (C4, C=O), 154.5 (C4'), 152.8 (C3'/C5'), 145.0 (C4a), 139.2 (C3), 138.8 (C1'), 133.6 (C6), 126.6 (C2), 124.8 (C7), 124.6 (C5), 121.2 (C8a), 118.6 (C8), 105.7 (C2'/C6'), 60.2 (4'-OCH_3), 56.1 (3'/5'-OCH_3).

3.2.3 3-Hydroxy-2-(4-chlorophenyl)-4H-chromen-4-one L3



[136.15]
$C_8H_8O_2$

[140.57]
C_7H_5ClO

[258.70]
$C_{15}H_{11}ClO_2$

[272.68]
$C_{15}H_9ClO_3$

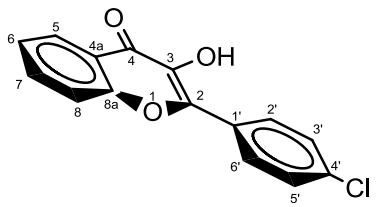
Synthesis

The synthesis was performed according to the general procedure of 3-hydroxyflavone ligands described in section 3.1.2 using 2.88 g 4-chlorobenzaldehyde.

Overall yield: 1.28 g (32 %), yellow powder

Melting point: 202-204°C

NMR – spectroscopy of **L3**



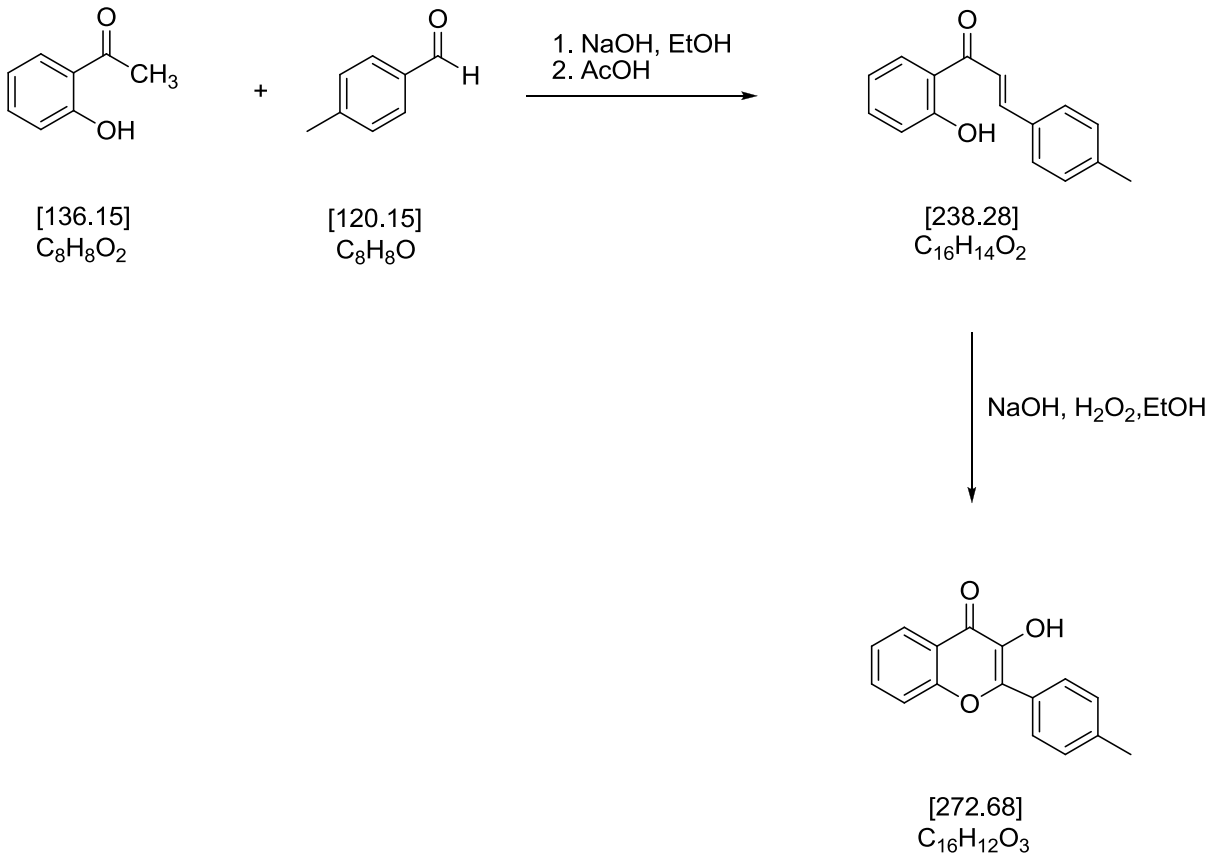
^{1}H-NMR spectrum of ligand **L3**:

NMR (500.10 MHz, d_6-DMSO): δ = 9.84 (s, 1H, 3-OH), 8.26 (d, ^{3}J(H,H) = 8.7 Hz, 2H, H2'/H6'), 8.13 (dd, ^{3}J(H,H) = 8.0, ^{2}J(H,H) = 1.3 Hz, 1H, H5), 7.85-7.75 (m, 2H, H6/H8), 7.66 (d, ^{3}J = 8.7 Hz, 2H, H3'/H5'), 7.48 (t, ^{3}J(H,H) = 7.4 Hz, 1H, H7).

^{13}C{^{1}H }-NMR spectrum of ligand **L3**:

NMR (125.75 MHz, d_6-DMSO): δ = 173.0 (C4), 154.6 (C4'), 144.0 (C4a), 139.3 (C3), 134.4 (C1'), 133.9 (C6), 130.2 (C2), 129.3 (C3'/C5'), 128.7 (C2'/C6'), 124.8 (C7), 124.7 (C5), 121.3 (C8a), 118.4 (C8).

3.2.4 3-Hydroxy-2-(4-methylphenyl)-4H-chromen-4-one L4



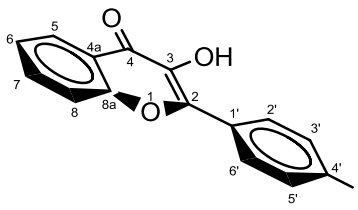
Synthesis

The synthesis was performed according to the general procedure of 3-hydroxyflavone ligands described in section 3.1.2 using 1.77 g p-toluolaldehyde.

Overall yield: 2.41 g (60 %), yellow crystals

Melting point: 192-196 °C

NMR – spectroscopy of **L4**



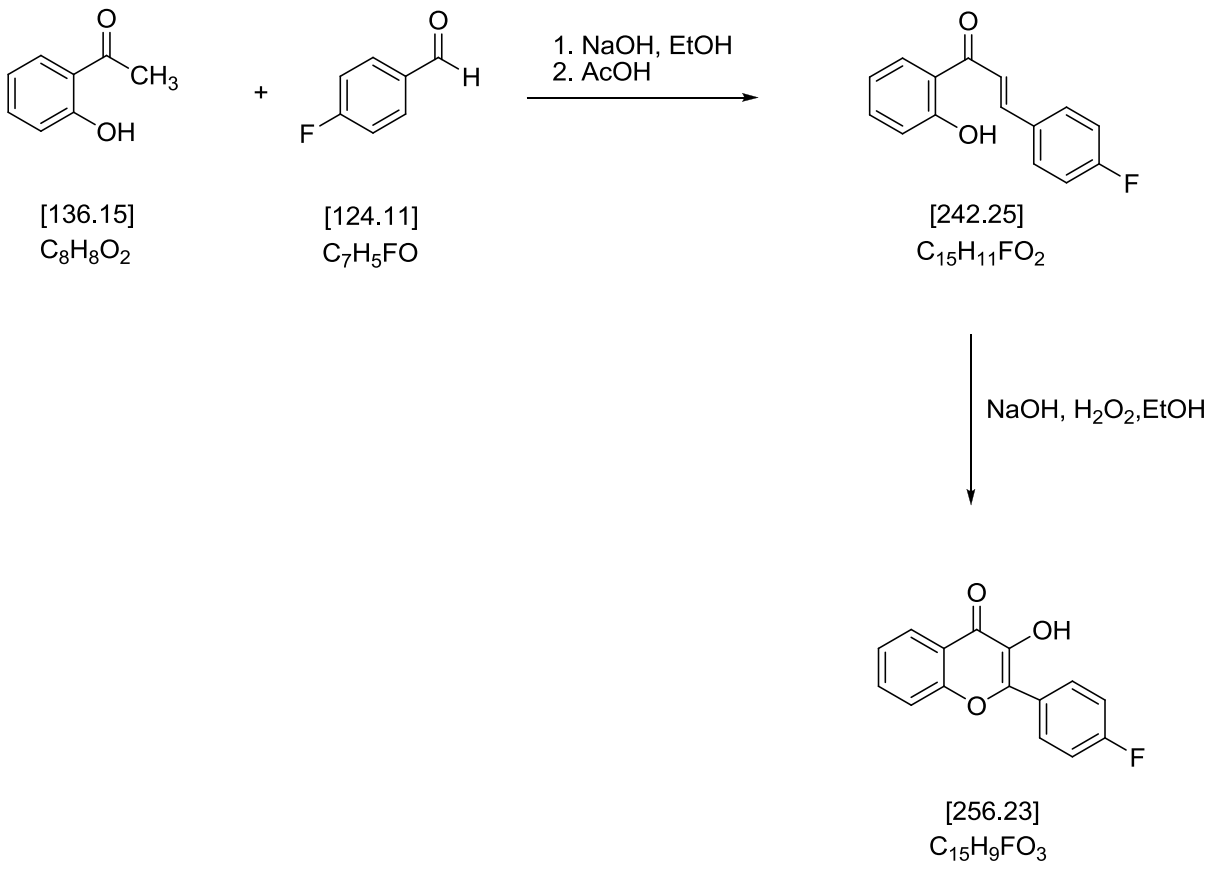
^{1}H-NMR spectrum of ligand **L4**:

NMR (500.10 MHz, d_6-DMSO): δ = 9.54 (s, 1H, 3-OH), 8.17-8.11 (m, 3H, H2'/H6'/H5), 7.84-7.75 (m, 2H, H6/H8), 7.46-4.49 (m, 1H, H7), 7.39 (d, ^{3}J(H,H) = 8.2 Hz, 2H, H3'/H5')), 2.40 (s, 3H, 4'-CH_3).

^{13}C{^{1}H }-NMR spectrum of ligand **L4**:

NMR (125.75 MHz, d_6-DMSO): δ = 172.9 (C4), 154.5 (C4'), 145.4 (C4a), 139.8 (C3), 138.8 (C1'), 133.7 (C6), 129.2 (C3'/C5'), 128.5 (C2), 127.6 (C2'/C6'), 124.77 (C7), 124.53 (C5), 121.31 (C8a), 118.4 (C8), 21.3 (4'-CH_3)

3.2.5 3-Hydroxy-2-(4-fluorophenyl)-4H-chromen-4-one L5



[136.15]
$C_8H_8O_2$

[124.11]
C_7H_5FO

[242.25]
$C_{15}H_{11}FO_2$

[256.23]
$C_{15}H_9FO_3$

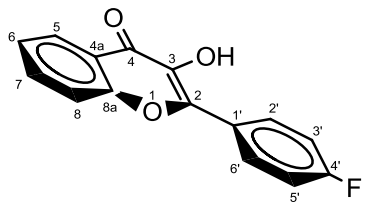
Synthesis

The synthesis was performed according to the general procedure of 3-hydroxyflavone ligands described in section 3.1.2 using 1.82 g 4-fluorobenzaldehyde.

Overall yield: 1.13 g (30%), yellow crystals

Melting point: 150-152 °C

NMR – spectroscopy of **L5**



^{1}H-NMR spectrum of **L5**:

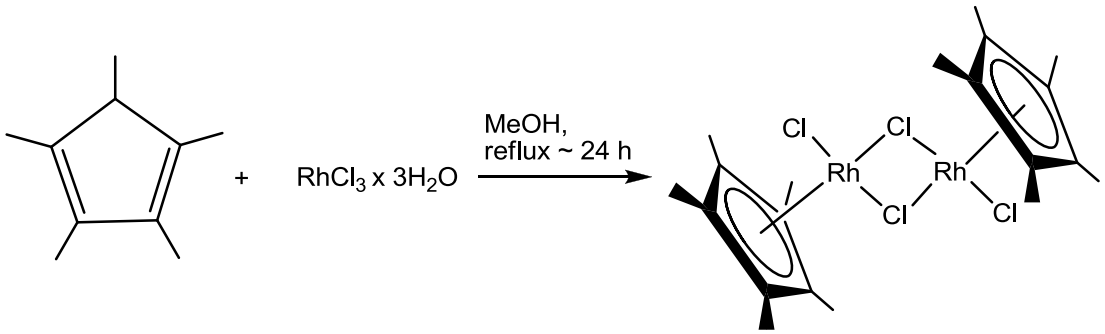
NMR (500.10 MHz, d_6-DMSO): δ = 9.71 (s, 1H, 3-OH), 8.30 (dd, ^{3}J(H,H) = 9.1, ^{4}J (F,H) = 5.5 Hz, 2H, H2'/H6'), 8.13 (dd, ^{3}J(H,H) = 7.9, ^{4}J(H,H) = 1.5 Hz, 1H, H5), 7.85-7.76 (m, 2H, H6/H8), 7.51-7.41 (m, 3H, H3'/H5'/H7).

^{13}C{^{1}H }-NMR spectrum of **L5**:

NMR (125.75 MHz, d_6-DMSO): δ = 173.0 (C4), 162.7 (d, ^{1}J(C,F) = 248.8 Hz, C4') 154.6 (C4a), 144.4 (C3), 138.9 (C1'), 133.8 (C6), 130.2 (d, ^{4}J(C,F) = 8.5 Hz, C2'/C6'), 127.9 (d, ^{2}J(C,H) = 3.3 Hz, C2), 124.8 (C5), 124.6 (C7), 121.3 (C8a), 118.4 (C8), 115.6 (d, ^{3}J(C,F) = 21.7 Hz, C3'/C5').

3.3 (η^5-Cp*)Rh(III) complexes with 3-hydroxyflavone ligands

3.3.1 Synthesis of Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)]



[135.23] $C_{10}H_{16}$ + [263.32] → [618.09] $C_{20}H_{30}Cl_4Rh_2$

Synthesis

$RhCl_3$ x 3 H_2O (1.7 g, 6.5 mmol, 0.45 eq) was suspended in methanol (50 mL) and pentamethylcyclopentadiene (1.1 mL, 7.1 mmol, 1.1 eq) was added. The mixture was refluxed for 24 hours. The red solid was filtered and used without further purification.

Yield: 1.5 g (75%), red solid

Melting point: 152-154°C

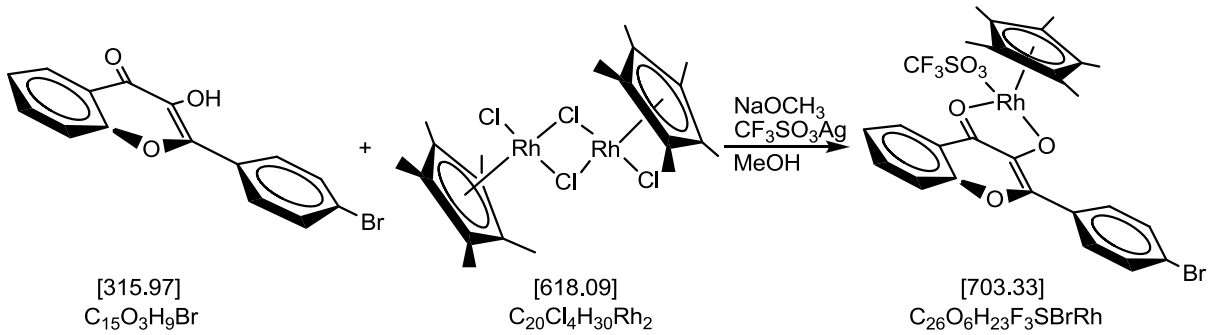
^{1}H-NMR spectrum of bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)]:

NMR (500.10 MHz, CD_3OD): δ = 1.71 (s, 30 H, 2 Cp*).

$^{13}C\{^1H\}$-NMR spectrum of bis[dichlorido(η^5-pentamethylcyclopentadienyl) rhodium(III)]:

NMR (125.75 MHz, $CDCl_3$): δ = 9.54 (10 C, CH_3 groups of Cp*), 94.3 (d, $^2J(C,H)$ = 9.5 Hz, 10 C, 2 Cp* rings)

3.3.2 Synthesis and characterization of trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-bromophenyl)-chromen-4-onato-κ*O*](η^5-pentamethylcyclopentadienyl)rhodium(III) C1



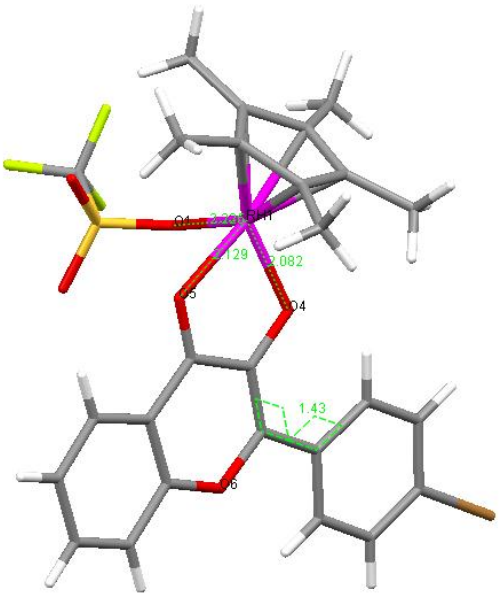
[315.97] $C_{15}O_3H_9Br$ + [618.09] $C_{20}Cl_4H_{30}Rh_2$ → [703.33] $C_{26}O_6H_{23}F_3SBrRh$

Synthesis of **C1**

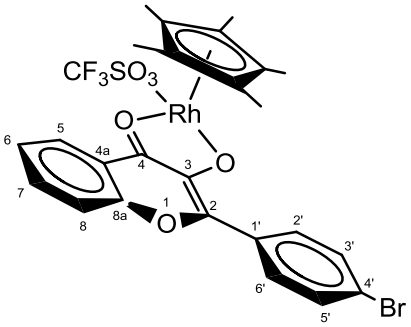
Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)] (50 mg, 0.081 mmol, 0.45 eq) was suspended in methanol (25 mL) and 3-hydroxy-2-(4-bromophenyl)-4H-chromen-4-one (57 mg, 0.18 mmol, 1 eq) and silver trifluoromethanesulfonate (102 mg, 0.395 mmol, 2.2 eq) were added. Sodium methoxide (11 mg, 0.198 mmol, 1.1 eq) was added for activation and the mixture was refluxed for 18 hours. Solid silver chloride was filtered off and the solvent was removed under vacuum. The product was dissolved in dichloromethane, filtered and recrystallized from methanol/diethyl ether by diffusion.

Yield: 47.0 mg (42 %), red needles

Melting point: 211-213°C



NMR – spectroscopy of **C1**



^{1}H-NMR spectrum of **C1**

NMR (500.10 MHz, CD_3OD): δ = 8.63 (d, $^{3}J(H,H)$ = 8.8 Hz, 2H, H2'/H6'), 8.26 (d, $^{3}J(H,H)$ = 9.7 Hz, 1H, H5), 7.79 – 7.84 (m, 2H, H6/H8), 7.71-7.74 (m, 2H, H3'/H5'), 7.54 – 7.50 (m, 1H, H7), 1.81 (s, 15H, Cp*).

$^{13}C\{^{1}H\}$-NMR spectrum of **C1**

NMR (125.75 MHz, CD_3OD): δ = 184.4 (C4), 155.6 (C4a), 155.1 (C3), 150.1 (C4'), 135.1 (C6), 132.8 (C3'/C5'), 132.4 (C1'), 130.2 (C2'/C6'), 126.3 (C7), 125.2 (C2), 125.0 (C5), 121.2 (C8a), 119.4 (C8), 94.3 (d, $^{2}J(C,H)$ = 10.1 Hz, 5 C, Cp*), 8.9 (5 CH_3, Cp*).

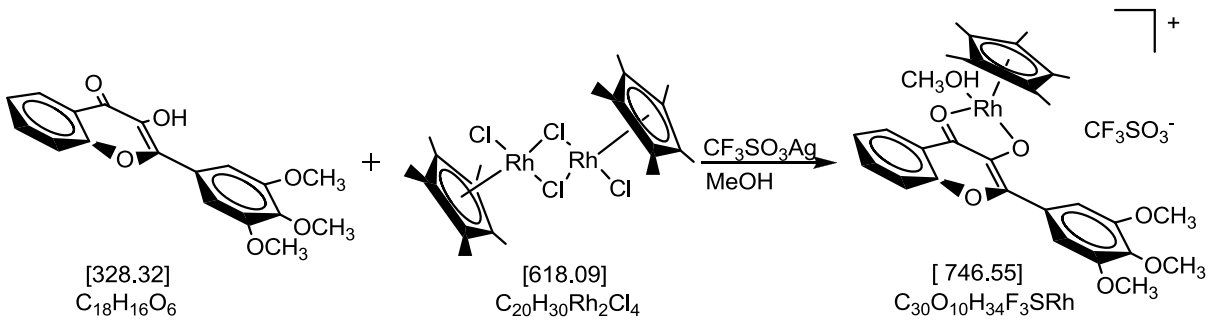
Elemental analysis of **C1**

	w-% C	w-% H	w-% N	w-% S	w-% O
Calculated	44.40	3.30	0	4.56	13.65
Found	44.37	3.36	<0.05	4.21	-
	44.36	3.26	<0.05	4.17	-
	-	-	-	-	13.70
	-	-	-	-	13.75

Crystal structure analysis of **C1**

Chemical formula	$C_{26}H_{23}BrF_3O_6RhS$
M [g□□·mol^{-1}]	703.32
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.3895(4)
b (Å)	21.2582(11)
c (Å)	14.8896(7)
ß (°)	99.497(3)
V (Å^3)	2619.1(2)
Z, Calculated density [mg/m^3]	4, 1.784
Absorption coefficient [mm^{-1}]	2.319
F(000)	1.400
Crystal size [mm]	0.40 x 0.13 x 0.03
Theta range for data collection [°]	2.37 to 26.00
Index ranges	-8<=h<=10, -26<=k<=26, -18<=l<=18
Reflections collected/unique	63337 / 5149
Total number of l.s. parameters	348
R_{int}	0.1307
R_σ	0.0728
R_1	0.0755
wR_2	0.1024
GOF on F^2	1.057
Largest diff. peak and hole [e·Å^{-3}]	0.896, -0.589

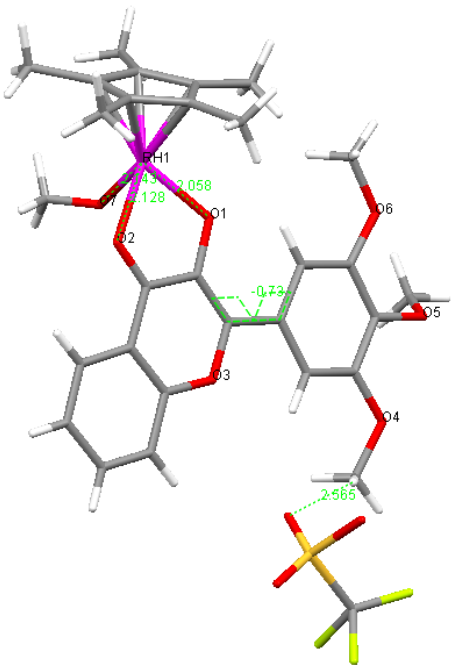
3.3.3 Synthesis and characterization of [{3-(oxo-κ*O*)-2-(3,4,5-trimethoxyphenyl)-chromen-4-onato-κ*O*}(methanol)(η^5-pentamethylcyclopentadienyl)rhodium(III)] trifluoromethanesulfonate C2



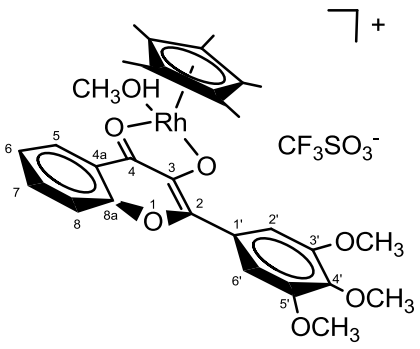
Synthesis of **C2**

Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)] (70 mg, 0.113 mmol, 0.45 eq) was suspended in methanol (25 mL) and 3-hydroxy-2-(3,4,5-trimethoxyphenyl)-4H-chromen-4-one (83 mg, 0.252 mmol, 1 eq) and silver trifluoromethanesulfonate (142 mg, 0.554 mmol, 2.2 eq) were added. The mixture was refluxed for 18 hours. Solid silver chloride was filtered off and the solvent was removed under pressure. The product was dissolved in dichloromethane, filtered and finally recrystallized from methanol/diethyl ether by diffusion.

Yield: 51.0 mg (30 %), red spicular crystals
Melting point: 166-168°C



NMR – spectroscopy of **C2**



^{1}H-NMR of **C2**

NMR (500.10 MHz, CD_3OD): δ = 8.25 (dd, $^{4}J(H,H)$ = 1.1 Hz, $^{3}J(H,H)$ = 8.2 Hz, 1H, H5,), 8.13 (s, 2H, H2'/H6'), 7.86-7.77 (m, 2H, H6/H8), 7.51 (ddd, $^{3}J(H,H)$ = 8.1 Hz, $^{3}J(H,H)$ = 6.6 Hz, $^{4}J(H,H)$ = 1.4 Hz, 1H, H7), 3.99 (s, 6H, 3'/5'-CH_3), 3.88 (s, 3H, 4'-CH_3), 1.82 (s, 15H, Cp*).

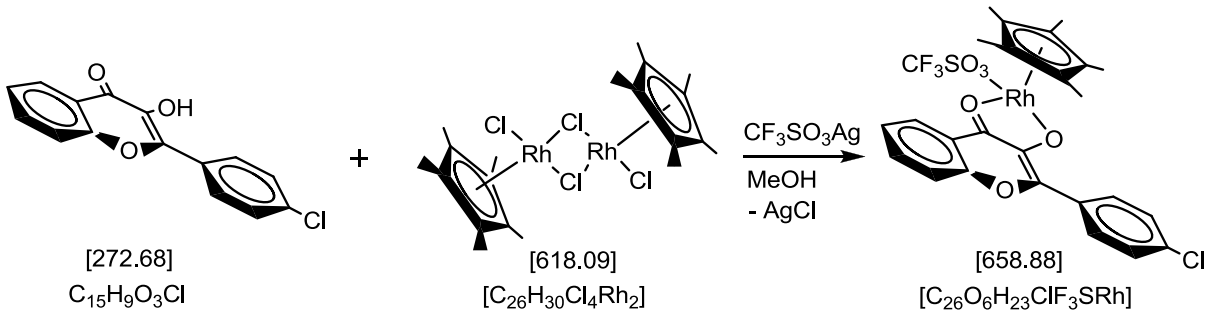
$^{13}C\{^{1}H\}$-NMR of **C2**

NMR (125.75 MHz, CD_3OD): δ = 183.8 (C4), 155.3 (C4a), 154.6 (C4'), 154.5 (C3'/5'), 151.1 (C3), 141.3 (C1'), 134.8 (C6), 128.8 (C2), 126.3 (C7), 124.9 (C5), 121.2 (C8a), 119.3 (C8), 106.6 (C2'/C6'), 94.10 (d, $^{2}J(C,H)$ = 10.1 Hz, 5 C, Cp*), 61.3 (4'-OCH_3), 56.8 (3'/5'-OCH_3), 8.9 (5 CH_3, Cp*).

Crystal structure analysis of **C2**

Chemical formula	$C_{30}H_{33}F_3O_{10}RhS$
M [g·mol^{-1}]	745.53
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.8123(9)
b (Å)	23.201(2)
c (Å)	12.3771(11)
ß (°)	91.737(4)
V (Å^3)	3103.4(5)
Z, Calculated density [mg/m^3]	4, 1.596
Absorption coefficient [mm^{-1}]	0.692
F(000)	1.524
Crystal size [mm]	0.20 x 0.15 x 0.10
Theta range for data collection [°]	2.08 to 25.36
Index ranges	-13<=h<=13, -27<=k<=27, -14<=l<=14
Reflections collected/unique	96775 / 5650
Total number of l.s. parameters	410
R_{int}	0.1556
R_σ	0.0714
R_1	0.1328
wR_2	0.2244
GOF on F^2	1.082
Largest diff. peak and hole [e·Å^{-3}]	1.794 and -1.171

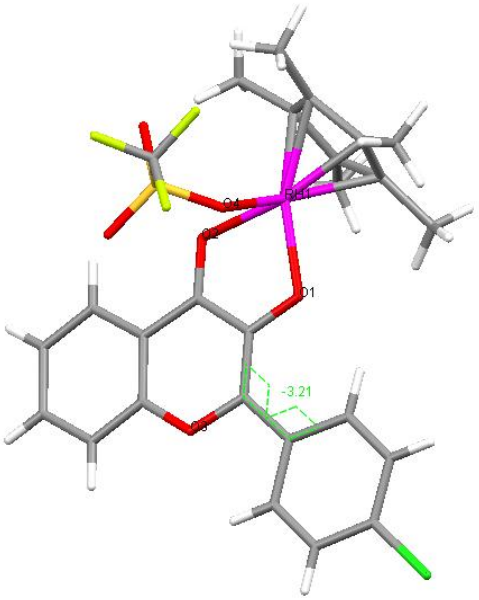
3.3.4 Synthesis and characterization of trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-chlorophenyl)-chromen-4-onato-κ*O*](η^5-pentamethylcyclopentadienyl)rhodium(III) C3



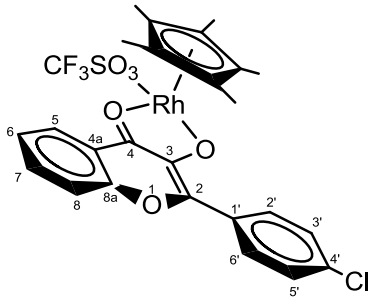
Synthesis of **C3**

Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)] (200 mg, 0.324 mmol, 0.45 eq) were suspended in methanol (100 mL) and 3-hydroxy-2-(4-chlorophenyl)-4H-chromen-4-one (252 mg, 0.0.719 mmol, 1 eq) and silver trifluoromethanesulfonate (406 mg, 1.582 mmol, 2.2 eq) were added. Sodium methoxide (43 mg, 0.0.791 mmol, 1.1 eq) was added for activation and the mixture was refluxed for 23 hours. Solid AgCl was filtered off and the solvent was removed under vacuum. The product was dissolved in dichloromethane, filtered and recrystallized from methanol/diethyl ether by diffusion.

Yield: 153.7 mg (36%), red crystals
Melting point: 142-144°C



NMR – spectroscopy of **C3**



^{1}H-NMR of **C3**

NMR (500.10 MHz, CD_3OD): δ = 8.70 (d, $^{3}J(H,H)$ = 8.9 Hz, 2H, H2'/H6'), 8.26 (d, $^{3}J(H,H)$ = 9.1 Hz, 1H, H5), 7.79-7.83 (m, 2H, H6/H8), 7.55-7.58 (m, 2H, H3'/H5'), 7.52 (t, $^{3}J(H,H)$ = 8.1 Hz, 1H, H7), 1.82 (s, 15H, Cp*).

$^{13}C\{^{1}H\}$-NMR of **C3**

NMR (125.75 MHz, CD_3OD): δ = 184.5 (C4), 155.6 (C4a), 155.0 (C3), 150.0 (C4'), 136.9 (C1'), 135.2 (C6), 132.1 (C2), 130.0 (C3'/C5'), 129.8 (C2'/6'), 126.3 (C7), 125.0 (C5), 121.2 (C8a), 119.4 (C8), 94.2 (d, $^{2}J(C,H)$ = 10.0 Hz, 5 C, Cp*), 8.9 (5 CH_3, Cp*).

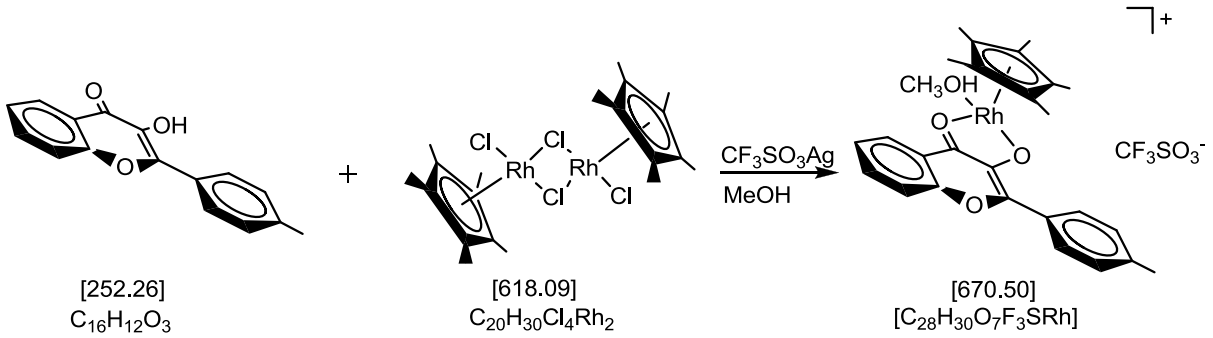
Elemental analysis of **C3**

	w-% C	w-% H	w-% N	w-% S	w-% O
Calculated	47.40	3.52	0	4.87	14.57
Found	47.14	3.45	< 0.05	4.82	-
	47.05	3.41	< 0.05	4.64	-
	-	-	-	-	14.69
	-	-	-	-	14.29

Crystal structure analysis of **C3**

Chemical formula	$C_{26}H_{23}ClF_3O_6RhS$
M [g·mol^{-1}]	658.86
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.3505(4)
b (Å)	20.8885(12)
c (Å)	14.7677(8)
ß (°)	98.438(2)
V (Å^3)	2548.0(2)
Z, Calculated density [mg/m^3]	4, 1.718
Absorption coefficient [mm^{-1}]	0.920
F(000)	1.328
Crystal size [mm]	0.15 x 0.12 x 0.12 mm
Theta range for data collection [°]	2.40 to 30.11
Index ranges	-11<=h<=11 -29<=k<=29 -20<=l<=20
Reflections collected/unique	92704 / 7472
Total number of l.s. parameters	348
R_{int}	0.0456
R_σ	0.0193
R_1	0.0256
wR_2	0.0573
GOF on F^2	0.998
Largest diff. peak and hole [e·Å^{-3}]	0.488 and -0.476

3.3.5 Synthesis and characterization of [{3-(oxo-κ*O*)-2-(4-methylphenyl)-chromen-4-onato- κ*O*}(methanol)(η^5-pentamethylcyclopentadienyl)rhodium(III)] trifluoromethanesulfonate C4



[252.26]
$C_{16}H_{12}O_3$

[618.09]
$C_{20}H_{30}Cl_4Rh_2$

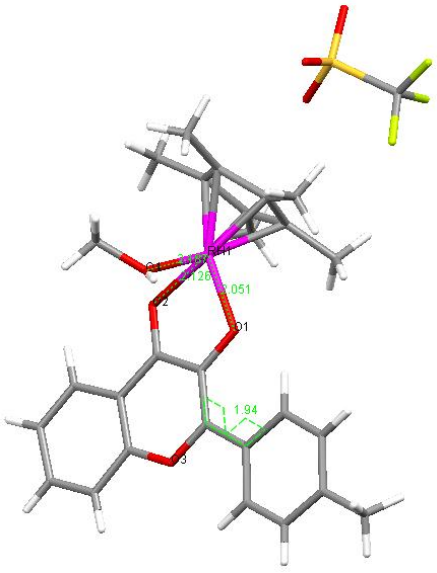
[670.50]
$[C_{28}H_{30}O_7F_3SRh]$

Synthesis of **C4**

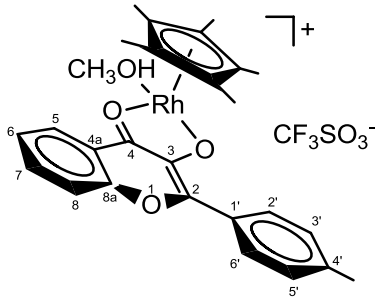
Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)] (50 mg, 0.081 mmol, 0.45 eq) was suspended in methanol (25 mL) and 3-hydroxy-2-(4-methylphenyl)-4H-chromen-4-one (45 mg, 0.18 mmol, 1 eq) and silver trifluoromethanesulfonate (102 mg, 0.395 mmol, 2.2 eq) were added. Sodium methoxide (11 mg, 0.198 mmol, 1.1 eq) was added for activation and the mixture was refluxed for 18 hours. Solid silver chloride was filtered off and the solvent was removed under vacuum. The product was dissolved in dichloromethane, filtered and recrystallized from methanol/diethyl ether by diffusion.

Yield: 80.0 mg (74%), red crystals

Melting point: 176-178°C



NMR – spectroscopy of **C4**



^{1}H-NMR of **C4**

NMR (500.10 MHz, CD_3OD): δ = 8.59 (d, $^{3}J(H,H)$ = 8.4 Hz, 2H, H2'/H6'), 8.24 (dt, $^{3}J(H,H)$ = 8.6 Hz, 1H, H5), 7.77-7.81 (m, 2H, H6/H8), 7.49-7.52 (m, 1H, H7), 7.38 (d, $^{3}J(H,H)$ = 8.2 Hz, 2H, H3'/H5'), 2.44 (s, 3H, 4'CH_3), 1.81 (s, 15H, Cp*).

$^{13}C\{^{1}H\}$-NMR of **C4**

NMR (125.75 MHz, CD_3OD): δ = 183.7 (C4), 155.3 (C4a), 154.5 (C3), 151.9 (C4'), 142.0 (C1'), 134.6 (C6), 130.6 (C2), 130.3 (C3'/C5'), 128.8 (C2'/C6'), 126.2 (C7), 124.8 (C5), 121.3 (C8a), 119.2 (C8), 94.1 (d, $^{2}J(C,H)$ = 10.0 Hz, 5C, Cp*), 21.6 (4'-CH_3), 8.9 (5 CH_3, Cp*).

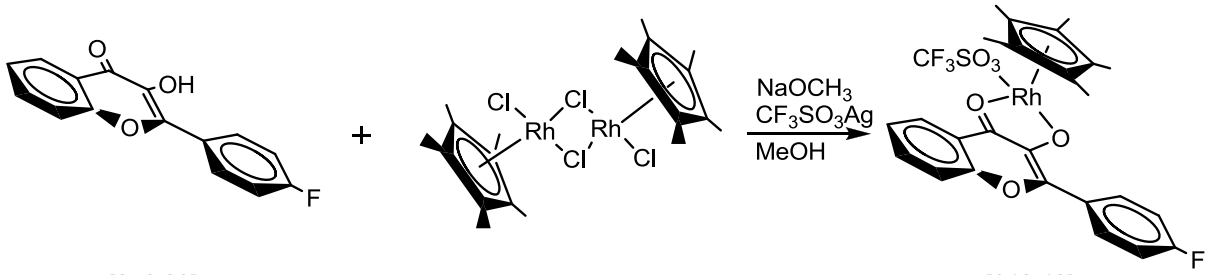
Elemental analysis of **C4**

	w-% C	w-% H	w-% N	w-% S
Calculated	50.16	4.51	-	4.78
Found	50.09	4.19	< 0.05	4.51
	50.05	4.33	< 0.05	4.79

Crystal structure analysis of **C4**

Chemical formula	$C_{28.5}H_{32}F_3O_{7.5}RhS$
M [g·mol^{-1}]	686.51
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	?
Space group	?
a (Å)	a = 8.3638(4)
b (Å)	12.7551(7)
c (Å)	13.4080(7)
α (°)	82.061(3)
ß (°)	88.640(3)
γ (°)	89.160(3)
V (Å^3)	1416.18(13)
Z, Calculated density [mg/m^3]	2, 1.610
Absorption coefficient [mm^{-1}]	0.744
F(000)	702
Crystal size [mm]	0.15 x 0.15 x 0.15
Theta range for data collection [°]	2.85 to 30.15
Index ranges	-11<=h<=11, -18<=k<=17, -18<=l<=18
Reflections collected/unique	39430 / 8311
Total number of l.s. parameters	380
R_{int}	0.0899
R_σ	0.0629
R_1	0.0413
wR_2	0.1003
GOF on F^2	0.987
Largest diff. peak and hole [e·Å^{-3}]	0.603 and -0.700

3.3.6 Synthesis and characterization of trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-fluorophenyl)-chromen-4-onato-κ*O*](η^5-pentamethylcyclopentadienyl)rhodium(III) C5



[256.23]
$C_{15}H_9O_3F$

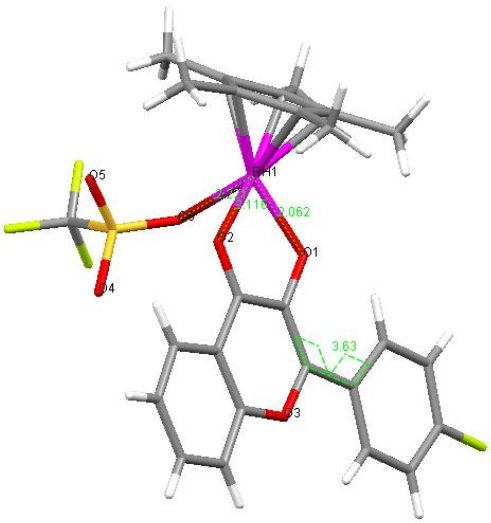
[618.09]
$C_{20}H_{30}Cl_4Rh_2$

[642.42]
$C_{26}H_{23}O_6F_4SRh$

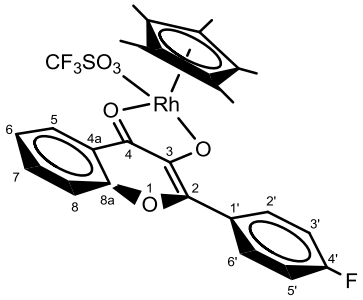
Synthesis of **C5**

Bis[dichlorido(η^5-pentamethylcyclopentadienyl)rhodium(III)] (50 mg, 0.081 mmol, 0.45 eq) was suspended in methanol (25 mL) and 3-hydroxy-2-(4-fluorophenyl)-4H-chromen-4-one (46 mg, 0.18 mmol, 1 eq) and silver trifluoromethanesulfonate (102 mg, 0.395 mmol, 2.2 eq) were added. Sodium methoxide (11 mg, 0.198 mmol, 1.1 eq) was added for activation and the mixture was refluxed for 18 hours. Solid silver chloride was filtered off and the solvent was removed under vacuum. The product was dissolved in dichloromethane, filtered and recrystallized from methanol/diethyl ether by diffusion.

Yield: 46.3 mg (41%), red crystals
Melting point: 147-149°C



NMR – spectroscopy of **C5**



^{1}H-NMR of **C5**

NMR (500.10 MHz, CD_3OD): δ = 8.70-8.73 (m, 2H, H2'/H6'), 8.21 (d, $^{3}J(H,H)$ = 8.0 Hz, 1H, H5), 7.72-7.78 (m, 2H, H6/H8), 7.46 (t, $^{3}J(H,H)$ = 6.7 Hz, 1H, H7), 7.26 (t, $^{3}J(H,H)$ = 8.9 Hz, 2H, H3'H5'), 1.79 (s, 15H, Cp*).

$^{13}C\{^{1}H\}$-NMR of **C5**

NMR (125.75 MHz, d_6-DMSO): δ = 182.0 (C4), 162.1 (d, ^{1}J (C,F) = 249.2 Hz, C4'), 153.5 (d, $^{1}J(C,C)$ = 45.7 Hz, C3), 146.0 (C4a), 133.2 (C6), 129.1 (C2), 128.8 (d, $^{4}J(C,F)$ = 8.1 Hz, C2'/C6'), 124.5 (C5), 123.9 (C7), 119.6 (C8a), 118.3 (d, $^{3}J(C,H)$ = 18.6 Hz, C8), 115.4 (d, $^{2}J(C,F)$ = 21.5 Hz, C3'/C5'), 98.8 (d, $^{2}J(C,H)$ = 9.2 Hz, 5 C, Cp*), 8.6 (5 CH_3, Cp*).

Crystal structure analysis of **C5**

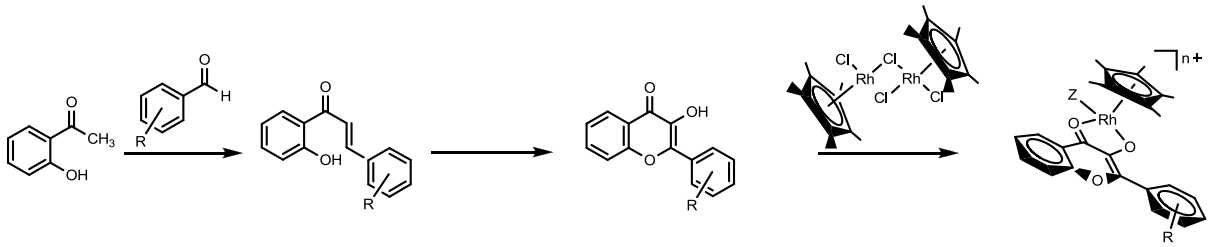
Chemical formula	$C_{26}H_{23}F_4O_6RhS$
M [g·mol^{-1}]	642.41
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	8.3551(3)
b (Å)	20.4778(8
c (Å)	14.7587(5)
ß (°)	96.201(2)
V (Å^3)	2510.35(16)
Z, Calculated density [mg/m^3]	4, 1.700
Absorption coefficient [mm^{-1}]	0.834
F(000)	1.296
Crystal size [mm]	0.13 x 0.10 x 0.01
Theta range for data collection [°]	2.43 to 30.11
Index ranges	-11<=h<=11 -28<=k<=28 -20<=l<=20
Reflections collected/unique	46924 / 7373
Total number of l.s. parameters	348
R_{int}	0.0895
R_σ	0.0737
R_1	0.0785
wR_2	0.0892
GOF on F^2	0.989
Largest diff. peak and hole [e·Å^{-3}]	0.856 and -0.640

4. CONCLUSIONS AND OUTLOOK

As cancer remains one of the most common causes of death, further research on the development of new anticancer drugs is essential. Increasing knowledge about the mechanism of action of currently applied drugs leads to more specific and better tolerable chemotherapeutics. Since the ruthenium compounds KP1019 and NAMI-A passed phase I of clinical trials, the interest in the development of new ruthenium compounds as anticancer agents is increasing. As rhodium parallels some of the physicochemical properties of ruthenium such as its ionic radius, many rhodium complexes exhibiting cytotoxicity have been synthesized in the last years.

Within this diploma thesis, five (η^5-Cp*)rhodium(III) complexes with different substituted 3-hydroxyflavone ligands have been synthesized and characterized. All of the compounds were characterized by crystal structure analysis showing the expected pseudo octahedral piano-stool configuration. Furthermore, the red crystals were characterized by ^{1}H, ^{13}C{^{1}H} and 2D NMR spectroscopy methods the latter comprising ^{1}H,^{1}H-COSY, HMBC and HSQC 2D NMR spectroscopy.

Flavonoids, a class of secondary metabolites of plants, show properties which make them interesting for the use as ligands in chemotherapeutics as they have antiinflammatory, antiallergic, antifungal, antiviral, antibacterial, antimicrobial, antidiarrheal, estrogenic, antioxidant, vascular and anticancer activity. The 3-hydroxyflavone ligands were synthesized in an aldol condensation, according to an established synthetic route reported in literature (Scheme 1). The second step is an Algar-Flynn-Oyamada reaction to yield the desired product in moderate to good yields. The purity and characterization of the ligands was done by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.



Scheme 1: Synthetic strategy pursued in this diploma thesis.

The Rh(Cp*) complexes were obtained by reaction of the ligands with bis[dichlorido(η^5-pentamethylcyclopentadiene)rhodium(III)] in methanolic solution. According to the HSAB (hard and soft acids and bases) theory, rhodium is a hard

acid with a high charge density while oxygen is considered a hard base. The HSAB theory states that bonds between hard acids and hard bases are very stable. Therefore, the coordination of the O-O-chelating 3-hydroxyflavones to the metal center results in stable complexes. Further investigations on the rate of ligand exchange and stability should therefore demonstrate the potential of the compounds for intravenous administration. Unfortunately, the (η^5-Cp*)rhodium(III) complexes exhibit only limited solubility in aqueous solutions and therefore *in* vitro anticancer activity assays are not accessible and IC_{50} values cannot be established under standard conditions. This demands modifications on the ligands of these complexes in order to provide more hydrophilic compounds or optimization of the formulation. On the other hand, the high stability of these complexes might qualify them for the use as oral drugs.

5. SUPPLEMENT

5.1 X-ray diffraction analysis data

Trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-bromophenyl)-chromen-4-onato κ*O*](*η*^{5}-pentamethylcyclopentadienyl)rhodium(III) C1

Bond lengths [Å]

Atom1	Atom2	Length	Atom1	Atom2	Length
Rh1	O1	2.2246(1)	C16	H16	0.9500
Rh1	O4	2.0817(1)	C17	C18	1.4590(1)
Rh1	O5	2.1290(1)	C17	C21	1.4389(1)
Rh1	C17	2.1001(1)	C17	C22	1.5022(1)
Rh1	C18	2.1416(1)	C18	C19	1.4219
Rh1	C19	2.1588(1)	C18	C23	1.4961(1)
Rh1	C20	2.1254(1)	C19	C20	1.4522(1)
Rh1	C21	2.1300(1)	C19	C24	1.4991(1)
Br1	C14	1.9104(1)	C20	C21	1.4390(1)
S1	O1	1.4677(1)	C20	C25	1.5149(1)
S1	O2	1.4357(1)	C21	C26	1.5096(1)
S1	O3	1.4287(1)	C22	H22A	0.9800
S1	C1	1.8267(1)	C22	H22B	0.9800
O4	C2	1.3243	C22	H22C	0.9800
O5	C3	1.2765	C23	H23A	0.9800
O6	C9	1.3572(1)	C23	H23B	0.9800
O6	C10	1.3782	C23	H23C	0.9800
F1	C1	1.3525(1)	C24	H24A	0.9800
F2	C1	1.3212(1)	C24	H24B	0.9800
F3	C1	1.3469(1)	C24	H24C	0.9800
C2	C3	1.4543(1)	C25	H25A	0.9800
C2	C10	1.3824(1)	C25	H25B	0.9800
C3	C4	1.4506(1)	C25	H25C	0.9800
C4	C5	1.3995(1)	C26	H26A	0.9800
C4	C9	1.4107	C26	H26B	0.9800
C5	H5	0.9500	C26	H26C	0.9800
C5	C6	1.3652(1)	C13	H13	0.9500
C6	H6	0.9500	C13	C14	1.4008(1)
C6	C7	1.4046	C14	C15	1.3783
C7	H7	0.9500	C15	H15	0.9500
C7	C8	1.3772(1)	C15	C16	1.3734(1)
C8	H8	0.9500	C12	C13	1.3820(1)
C8	C9	1.4055(1)			
C10	C11	1.4634(1)			
C11	C12	1.4227(1)			
C11	C16	1.4053(1)			
C12	H12	0.9500			

Bond angles [°]

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
O1	Rh1	O4	83.03	F2	C1	F3	107.66
O1	Rh1	O5	82.72	O4	C2	C3	117.25
O1	Rh1	C17	162.76	O4	C2	C10	123.92
O1	Rh1	C18	123.29	C3	C2	C10	118.81
O1	Rh1	C19	97.29	O5	C3	C2	119.13
O1	Rh1	C20	103.93	O5	C3	C4	121.80
O1	Rh1	C21	139.39	C2	C3	C4	119.06
O4	Rh1	O5	79.15	C3	C4	C5	123.90
O4	Rh1	C17	113.82	C3	C4	C9	117.18
O4	Rh1	C18	153.52	C5	C4	C9	118.87
O4	Rh1	C19	152.52	C4	C5	H5	119.64
O4	Rh1	C20	113.46	C4	C5	C6	120.72
O4	Rh1	C21	96.06	H5	C5	C6	119.64
O5	Rh1	C17	103.36	C5	C6	H6	119.81
O5	Rh1	C18	99.77	C5	C6	C7	120.39
O5	Rh1	C19	128.26	H6	C6	C7	119.81
O5	Rh1	C20	166.12	C6	C7	H7	119.78
O5	Rh1	C21	137.22	C6	C7	C8	120.44
C17	Rh1	C18	40.22	H7	C7	C8	119.78
C17	Rh1	C19	66.16	C7	C8	H8	120.30
C17	Rh1	C20	66.89	C7	C8	C9	119.40
C17	Rh1	C21	39.76	H8	C8	C9	120.30
C18	Rh1	C19	38.61	O6	C9	C4	122.26
C18	Rh1	C20	66.37	O6	C9	C8	117.57
C18	Rh1	C21	66.55	C4	C9	C8	120.17
C19	Rh1	C20	39.62	O6	C10	C2	121.31
C19	Rh1	C21	65.90	O6	C10	C11	111.19
C20	Rh1	C21	39.53	C2	C10	C11	127.50
O1	S1	O2	114.33	C10	C11	C12	122.46
O1	S1	O3	114.28	C10	C11	C16	120.26
O1	S1	C1	100.06	C12	C11	C16	117.27
O2	S1	O3	117.07	C11	C12	H12	119.23
O2	S1	C1	104.65	C11	C12	C13	121.54
O3	S1	C1	103.62	H12	C12	C13	119.23
Rh1	O1	S1	125.32	C12	C13	H13	120.66
Rh1	O4	C2	112.32	C12	C13	C14	118.68
Rh1	O5	C3	111.58	H13	C13	C14	120.66
C9	O6	C10	121.30	Br1	C14	C13	118.77
S1	C1	F1	110.64	Br1	C14	C15	120.33
S1	C1	F2	112.91	C13	C14	C15	120.90
S1	C1	F3	111.49	C14	C15	H15	119.85
F1	C1	F2	107.57	C14	C15	C16	120.29
F1	C1	F3	106.25	H15	C15	C16	119.85

Bond angles [°]

Atom1	Atom2	Atom3	Angle
C11	C16	C15	121.30
C11	C16	H16	119.35
C15	C16	H16	119.35
Rh1	C17	C18	71.42
Rh1	C17	C21	71.24
Rh1	C17	C22	126.65
C18	C17	C21	107.94
C18	C17	C22	125.29
C21	C17	C22	126.60
Rh1	C18	C17	68.36
Rh1	C18	C19	71.35
Rh1	C18	C23	123.50
C17	C18	C19	107.62
C17	C18	C23	125.85
C19	C18	C23	126.47
Rh1	C19	C18	70.04
Rh1	C19	C20	68.95
Rh1	C19	C24	127.13
C18	C19	C20	108.70
C18	C19	C24	126.27
C20	C19	C24	125.03
Rh1	C20	C19	71.43
Rh1	C20	C21	70.40
Rh1	C20	C25	124.94
C19	C20	C21	107.58
C19	C20	C25	125.42
C21	C20	C25	126.98
Rh1	C21	C17	69.00
Rh1	C21	C20	70.07
Rh1	C21	C26	123.62
C17	C21	C20	108.05
C17	C21	C26	124.69
C20	C21	C26	127.16
C17	C22	H22A	109.47
C17	C22	H22B	109.47
C17	C22	H22C	109.47
H22A	C22	H22B	109.47
H22A	C22	H22C	109.47
H22B	C22	H22C	109.47
C18	C23	H23A	109.47
C18	C23	H23B	109.47
C18	C23	H23C	109.47
H23A	C23	H23B	109.47
H23A	C23	H23C	109.47
H23B	C23	H23C	109.47
C19	C24	H24A	109.47
C19	C24	H24B	109.47
C19	C24	H24C	109.47
H24A	C24	H24B	109.47
H24A	C24	H24C	109.47
H24B	C24	H24C	109.47
C20	C25	H25A	109.47
C20	C25	H25B	109.47
C20	C25	H25C	109.47
H25A	C25	H25B	109.47
H25A	C25	H25C	109.47
H25B	C25	H25C	109.47
C21	C26	H26A	109.47
C21	C26	H26B	109.47
C21	C26	H26C	109.47
H26A	C26	H26B	109.47
H26A	C26	H26C	109.47
H26B	C26	H26C	109.47

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O4	Rh1	O1	S1	129.02
O5	Rh1	O1	S1	49.13
C17	Rh1	O1	S1	-62.84
C18	Rh1	O1	S1	-47.81
C19	Rh1	O1	S1	-78.67
C20	Rh1	O1	S1	-118.47
C21	Rh1	O1	S1	-139.79
O1	Rh1	O4	C2	-77.51
O5	Rh1	O4	C2	6.38
C17	Rh1	O4	C2	106.31
C18	Rh1	O4	C2	96.54
C19	Rh1	O4	C2	-169.92
C20	Rh1	O4	C2	-179.71
C21	Rh1	O4	C2	143.36
O1	Rh1	O5	C3	78.21
O4	Rh1	O5	C3	-6.05
C17	Rh1	O5	C3	-118.21
C18	Rh1	O5	C3	-159.14
C19	Rh1	O5	C3	171.78
C20	Rh1	O5	C3	-162.11
C21	Rh1	O5	C3	-93.25
O1	Rh1	C17	C18	19.62
O1	Rh1	C17	C21	-97.60
O1	Rh1	C17	C22	140.25
O4	Rh1	C17	C18	-173.27
O4	Rh1	C17	C21	69.50
O4	Rh1	C17	C22	-52.64
O5	Rh1	C17	C18	-89.39
O5	Rh1	C17	C21	153.38
O5	Rh1	C17	C22	31.24
C18	Rh1	C17	C21	-117.22
C18	Rh1	C17	C22	120.63
C19	Rh1	C17	C18	36.83
C19	Rh1	C17	C21	-80.40
C19	Rh1	C17	C22	157.46
C20	Rh1	C17	C18	80.19
C20	Rh1	C17	C21	-37.04
C20	Rh1	C17	C22	-159.18
C21	Rh1	C17	C18	117.22
C21	Rh1	C17	C22	-122.14
O1	Rh1	C18	C17	-173.16
O1	Rh1	C18	C19	-54.63
O1	Rh1	C18	C23	67.30
O4	Rh1	C18	C17	13.91
O4	Rh1	C18	C19	132.43
O4	Rh1	C18	C23	-105.64
O5	Rh1	C18	C17	99.17
O5	Rh1	C18	C19	-142.30
O5	Rh1	C18	C23	-20.37
C17	Rh1	C18	C19	118.53
C17	Rh1	C18	C23	-119.54
C19	Rh1	C18	C17	-118.53
C19	Rh1	C18	C23	121.93
C20	Rh1	C18	C17	-81.61
C20	Rh1	C18	C19	36.92
C20	Rh1	C18	C23	158.85
C21	Rh1	C18	C17	-38.31
C21	Rh1	C18	C19	80.21
C21	Rh1	C18	C23	-157.86
O1	Rh1	C19	C18	136.59
O1	Rh1	C19	C20	-103.07
O1	Rh1	C19	C24	15.62
O4	Rh1	C19	C18	-134.51
O4	Rh1	C19	C20	-14.16
O4	Rh1	C19	C24	104.53
O5	Rh1	C19	C18	50.12
O5	Rh1	C19	C20	170.47
O5	Rh1	C19	C24	-70.84
C17	Rh1	C19	C18	-38.34
C17	Rh1	C19	C20	82.01
C17	Rh1	C19	C24	-159.30
C18	Rh1	C19	C20	120.34
C18	Rh1	C19	C24	-120.97
C20	Rh1	C19	C18	-120.34
C20	Rh1	C19	C24	118.69
C21	Rh1	C19	C18	-82.04
C21	Rh1	C19	C20	38.31
C21	Rh1	C19	C24	157.00
O1	Rh1	C20	C19	84.57
O1	Rh1	C20	C21	-158.18
O1	Rh1	C20	C25	-36.16
O4	Rh1	C20	C19	172.93
O4	Rh1	C20	C21	-69.82
O4	Rh1	C20	C25	52.19
O5	Rh1	C20	C19	-32.82
O5	Rh1	C20	C21	84.43

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O5	Rh1	C20	C25	-153.55
C17	Rh1	C20	C19	-80.00
C17	Rh1	C20	C21	37.25
C17	Rh1	C20	C25	159.27
C18	Rh1	C20	C19	-36.01
C18	Rh1	C20	C21	81.24
C18	Rh1	C20	C25	-156.74
C19	Rh1	C20	C21	117.25
C19	Rh1	C20	C25	-120.74
C21	Rh1	C20	C19	-117.25
C21	Rh1	C20	C25	122.01
O1	Rh1	C21	C17	153.16
O1	Rh1	C21	C20	33.67
O1	Rh1	C21	C26	-88.36
O4	Rh1	C21	C17	-120.49
O4	Rh1	C21	C20	120.02
O4	Rh1	C21	C26	-2.02
O5	Rh1	C21	C17	-39.92
O5	Rh1	C21	C20	-159.42
O5	Rh1	C21	C26	78.55
C17	Rh1	C21	C20	-119.49
C17	Rh1	C21	C26	118.48
C18	Rh1	C21	C17	38.75
C18	Rh1	C21	C20	-80.74
C18	Rh1	C21	C26	157.23
C19	Rh1	C21	C17	81.10
C19	Rh1	C21	C20	-38.39
C19	Rh1	C21	C26	-160.42
C20	Rh1	C21	C17	119.49
C20	Rh1	C21	C26	-122.03
O2	S1	O1	Rh1	33.15
O3	S1	O1	Rh1	-105.59
C1	S1	O1	Rh1	144.38
O1	S1	C1	F1	179.66
O1	S1	C1	F2	59.03
O1	S1	C1	F3	-62.33
O2	S1	C1	F1	-61.73
O2	S1	C1	F2	177.64
O2	S1	C1	F3	56.29
O3	S1	C1	F1	61.45
O3	S1	C1	F2	-59.18
O3	S1	C1	F3	179.47
Rh1	O4	C2	C3	-5.98
Rh1	O4	C2	C10	172.68
Rh1	O5	C3	C2	4.87
Rh1	O5	C3	C4	-176.38
C10	O6	C9	C4	2.08
C10	O6	C9	C8	-177.41
C9	O6	C10	C2	-0.49
C9	O6	C10	C11	179.28
O4	C2	C3	O5	0.67
O4	C2	C3	C4	-178.11
C10	C2	C3	O5	-178.06
C10	C2	C3	C4	3.16
O4	C2	C10	O6	179.24
O4	C2	C10	C11	-0.48
C3	C2	C10	O6	-2.12
C3	C2	C10	C11	178.15
O5	C3	C4	C5	-2.84
O5	C3	C4	C9	179.58
C2	C3	C4	C5	175.91
C2	C3	C4	C9	-1.67
C3	C4	C5	H5	2.01
C3	C4	C5	C6	-177.98
C9	C4	C5	H5	179.56
C9	C4	C5	C6	-0.44
C3	C4	C9	O6	-0.92
C3	C4	C9	C8	178.56
C5	C4	C9	O6	-178.63
C5	C4	C9	C8	0.85
C4	C5	C6	H6	179.80
C4	C5	C6	C7	-0.20
H5	C5	C6	H6	-0.20
H5	C5	C6	C7	179.80
C5	C6	C7	H7	-179.55
C5	C6	C7	C8	0.45
H6	C6	C7	H7	0.45
H6	C6	C7	C8	-179.55
C6	C7	C8	H8	179.96
C6	C7	C8	C9	-0.03
H7	C7	C8	H8	-0.04
H7	C7	C8	C9	179.97
C7	C8	C9	O6	178.89
C7	C8	C9	C4	-0.61
H8	C8	C9	O6	-1.11
H8	C8	C9	C4	179.39

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O6	C10	C11	C12	-178.32
O6	C10	C11	C16	2.80
C2	C10	C11	C12	1.43
C2	C10	C11	C16	-177.45
C10	C11	C12	H12	0.59
C10	C11	C12	C13	-179.41
C16	C11	C12	H12	179.51
C16	C11	C12	C13	-0.49
C10	C11	C16	C15	-179.95
C10	C11	C16	H16	0.05
C12	C11	C16	C15	1.11
C12	C11	C16	H16	-178.89
C11	C12	C13	H13	179.47
C11	C12	C13	C14	-0.53
H12	C12	C13	H13	-0.53
H12	C12	C13	C14	179.47
C12	C13	C14	Br1	-178.49
C12	C13	C14	C15	0.99
H13	C13	C14	Br1	1.51
H13	C13	C14	C15	-179.01
Br1	C14	C15	H15	-0.93
Br1	C14	C15	C16	179.07
C13	C14	C15	H15	179.60
C13	C14	C15	C16	-0.40
C14	C15	C16	C11	-0.68
C14	C15	C16	H16	179.32
H15	C15	C16	C11	179.32
H15	C15	C16	H16	-0.68
Rh1	C17	C18	C19	-60.86
Rh1	C17	C18	C23	116.48
C21	C17	C18	Rh1	62.25
C21	C17	C18	C19	1.39
C21	C17	C18	C23	178.73
C22	C17	C18	Rh1	-122.25
C22	C17	C18	C19	176.89
C22	C17	C18	C23	-5.77
Rh1	C17	C21	C20	59.39
Rh1	C17	C21	C26	-117.10
C18	C17	C21	Rh1	-62.37
C18	C17	C21	C20	-2.98
C18	C17	C21	C26	-179.47
C22	C17	C21	Rh1	122.21
C22	C17	C21	C20	-178.40
C22	C17	C21	C26	5.11
Rh1	C17	C22	H22A	61.38
Rh1	C17	C22	H22B	-58.61
Rh1	C17	C22	H22C	-178.62
C18	C17	C22	H22A	153.68
C18	C17	C22	H22B	33.68
C18	C17	C22	H22C	-86.32
C21	C17	C22	H22A	-31.66
C21	C17	C22	H22B	-151.66
C21	C17	C22	H22C	88.34
Rh1	C18	C19	C20	-58.25
Rh1	C18	C19	C24	122.00
C17	C18	C19	Rh1	58.96
C17	C18	C19	C20	0.72
C17	C18	C19	C24	-179.03
C23	C18	C19	Rh1	-118.35
C23	C18	C19	C20	-176.60
C23	C18	C19	C24	3.65
Rh1	C18	C23	H23A	-126.70
Rh1	C18	C23	H23B	113.30
Rh1	C18	C23	H23C	-6.70
C17	C18	C23	H23A	147.16
C17	C18	C23	H23B	27.16
C17	C18	C23	H23C	-92.84
C19	C18	C23	H23A	-36.00
C19	C18	C23	H23B	-156.00
C19	C18	C23	H23C	84.01
Rh1	C19	C20	C21	-61.47
Rh1	C19	C20	C25	120.16
C18	C19	C20	Rh1	58.91
C18	C19	C20	C21	-2.56
C18	C19	C20	C25	179.07
C24	C19	C20	Rh1	-121.34
C24	C19	C20	C21	177.19
C24	C19	C20	C25	-1.18
Rh1	C19	C24	H24A	56.34
Rh1	C19	C24	H24B	-63.66
Rh1	C19	C24	H24C	176.34
C18	C19	C24	H24A	-35.06
C18	C19	C24	H24B	-155.06
C18	C19	C24	H24C	84.94
C20	C19	C24	H24A	145.22
C20	C19	C24	H24B	25.22

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C20	C19	C24	H24C	-94.78
Rh1	C20	C21	C17	-58.72
Rh1	C20	C21	C26	117.65
C19	C20	C21	Rh1	62.13
C19	C20	C21	C17	3.41
C19	C20	C21	C26	179.78
C25	C20	C21	Rh1	-119.53
C25	C20	C21	C17	-178.25
C25	C20	C21	C26	-1.88
Rh1	C20	C25	H25A	-73.39
Rh1	C20	C25	H25B	166.61
Rh1	C20	C25	H25C	46.61
C19	C20	C25	H25A	-164.54
C19	C20	C25	H25B	75.46
C19	C20	C25	H25C	-44.54
C21	C20	C25	H25A	17.41
C21	C20	C25	H25B	-102.59
C21	C20	C25	H25C	137.41
Rh1	C21	C26	H26A	76.72
Rh1	C21	C26	H26B	-43.28
Rh1	C21	C26	H26C	-163.28
C17	C21	C26	H26A	163.10
C17	C21	C26	H26B	43.10
C17	C21	C26	H26C	-76.90
C20	C21	C26	H26A	-12.71
C20	C21	C26	H26B	-132.71
C20	C21	C26	H26C	107.29

[{3-(oxo-κ*O*)-2-(3,4,5-trimethoxyphenyl)-chromen-4-onato-κ*O*}(methanol)(η^5-pentamethylcyclopentadienyl)rhodium(III)] trifluoromethanesulfonate C2

Bond lengths [Å]

Atom1	Atom2	Length	Atom1	Atom2	Length
Rh1	O1	2.0581(1)	C17	H17A	0.9800(1)
Rh1	O2	2.1283(1)	C17	H17B	0.9800(1)
Rh1	O7	2.1427(2)	C17	H17C	0.9800(1)
Rh1	C20	2.1544(1)	C18	H18A	0.9800(1)
Rh1	C21	2.1324(2)	C18	H18B	0.9800(1)
Rh1	C22	2.1152(1)	C18	H18C	0.9800(1)
Rh1	C23	2.0857(2)	O7	C19	1.2628(1)
Rh1	C24	2.1389(1)	C19	H19A	0.9800(1)
O1	C1	1.3380(1)	C19	H19B	0.9800(1)
O2	C2	1.2681(1)	C19	H19C	0.9800(1)
O3	C8	1.3582(1)	C20	C21	1.4621(1)
O3	C9	1.3745(1)	C20	C24	1.4102(1)
O4	C12	1.3785(1)	C20	C25	1.5195(1)
O4	C16	1.4271(1)	C21	C22	1.4176(1)
O5	C13	1.3847(1)	C21	C26	1.5077(1)
O5	C17	1.4212(1)	C22	C23	1.4376(1)
O6	C14	1.3855(1)	C22	C27	1.4966(1)
O6	C18	1.4443(1)	C23	C24	1.4213(1)
C1	C2	1.4411(1)	C23	C28	1.5121(1)
C1	C9	1.3713(1)	C24	C29	1.5158(1)
C2	C3	1.4485(1)	C25	H25A	0.9800(1)
C3	C4	1.4209(1)	C25	H25B	0.9800(1)
C3	C8	1.3976(1)	C25	H25C	0.9800(1)
C4	H4	0.9500(1)	C26	H26A	0.9800(1)
C4	C5	1.3646(1)	C26	H26B	0.9800(1)
C5	H5	0.9500(1)	C26	H26C	0.9800(1)
C5	C6	1.4189(1)	C27	H27A	0.9800(1)
C6	H6	0.9500(1)	C27	H27B	0.9800(1)
C6	C7	1.3707(1)	C27	H27C	0.9800(1)
C7	H7	0.9500(1)	C28	H28A	0.9800(1)
C7	C8	1.4005(1)	C28	H28B	0.9800(1)
C9	C10	1.4926(1)	C28	H28C	0.9800(1)
C10	C11	1.3970(1)	C29	H29A	0.9800(1)
C10	C15	1.4070(1)	C29	H29B	0.9800(1)
C11	H11	0.9500(1)	C29	H29C	0.9800(1)
C11	C12	1.3951(1)	S1	O8	1.3826(1)
C12	C13	1.3995(1)	S1	O9	1.5967(1)
C13	C14	1.3939(1)	S1	O10	1.3455(1)
C14	C15	1.3975(1)	S1	C30	1.7949(1)
C15	H15	0.9500(1)	C30	F1	1.3313(1)
C16	H16A	0.9800(1)	C30	F2	1.3307(1)
C16	H16B	0.9800(1)	C30	F3	1.3313(1)
C16	H16C	0.9800(1)			

Bond angles [°]

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
O1	Rh1	O2	78.82	C3	C4	H4	120.19
O1	Rh1	O7	79.64	C3	C4	C5	119.63
O1	Rh1	C20	159.97	H4	C4	C5	120.19
O1	Rh1	C21	122.08	C4	C5	H5	119.81
O1	Rh1	C22	93.73	C4	C5	C6	120.38
O1	Rh1	C23	100.88	H5	C5	C6	119.81
O1	Rh1	C24	136.76	C5	C6	H6	119.54
O2	Rh1	O7	81.10	C5	C6	C7	120.92
O2	Rh1	C20	119.81	H6	C6	C7	119.54
O2	Rh1	C21	159.02	C6	C7	H7	120.61
O2	Rh1	C22	152.62	C6	C7	C8	118.78
O2	Rh1	C23	115.05	H7	C7	C8	120.61
O2	Rh1	C24	101.37	O3	C8	C3	122.06
O7	Rh1	C20	108.96	O3	C8	C7	116.60
O7	Rh1	C21	99.84	C3	C8	C7	121.21
O7	Rh1	C22	123.83	O3	C9	C1	121.21
O7	Rh1	C23	163.74	O3	C9	C10	111.03
O7	Rh1	C24	143.55	C1	C9	C10	127.72
C20	Rh1	C21	39.88	C9	C10	C11	119.40
C20	Rh1	C22	66.36	C9	C10	C15	120.31
C20	Rh1	C23	65.71	C11	C10	C15	120.29
C20	Rh1	C24	38.35	C10	C11	H11	119.92
C21	Rh1	C22	38.99	C10	C11	C12	120.16
C21	Rh1	C23	65.91	H11	C11	C12	119.92
C21	Rh1	C24	65.46	O4	C12	C11	123.85
C22	Rh1	C23	40.01	O4	C12	C13	116.01
C22	Rh1	C24	66.22	C11	C12	C13	120.13
C23	Rh1	C24	39.29	O5	C13	C12	119.39
Rh1	O1	C1	112.19	O5	C13	C14	121.27
Rh1	O2	C2	110.89	C12	C13	C14	119.30
C8	O3	C9	120.88	O6	C14	C13	114.75
C12	O4	C16	116.30	O6	C14	C15	123.83
C13	O5	C17	115.40	C13	C14	C15	121.42
C14	O6	C18	116.99	C10	C15	C14	118.67
O1	C1	C2	116.26	C10	C15	H15	120.67
O1	C1	C9	123.93	C14	C15	H15	120.67
C2	C1	C9	119.81	O4	C16	H16A	109.47
O2	C2	C1	119.45	O4	C16	H16B	109.47
O2	C2	C3	122.45	O4	C16	H16C	109.47
C1	C2	C3	118.06	H16A	C16	H16B	109.47
C2	C3	C4	123.02	H16A	C16	H16C	109.47
C2	C3	C8	117.97	H16B	C16	H16C	109.47
C4	C3	C8	119.01	O5	C17	H17A	109.47

Bond angles [°]

Atom1	Atom2	Atom3	Angle
O5	C17	H17B	109.47
O5	C17	H17C	109.47
H17A	C17	H17B	109.47
H17A	C17	H17C	109.47
H17B	C17	H17C	109.47
O6	C18	H18A	109.47
O6	C18	H18B	109.47
O6	C18	H18C	109.47
H18A	C18	H18B	109.47
H18A	C18	H18C	109.47
H18B	C18	H18C	109.47
Rh1	O7	C19	123.04
O7	C19	H19A	109.47
O7	C19	H19B	109.47
O7	C19	H19C	109.47
H19A	C19	H19B	109.47
H19A	C19	H19C	109.47
H19B	C19	H19C	109.47
Rh1	C20	C21	69.25
Rh1	C20	C24	70.23
Rh1	C20	C25	130.01
C21	C20	C24	107.01
C21	C20	C25	125.80
C24	C20	C25	126.94
Rh1	C21	C20	70.87
Rh1	C21	C22	69.85
Rh1	C21	C26	123.90
C20	C21	C22	108.48
C20	C21	C26	124.94
C22	C21	C26	126.56
Rh1	C22	C21	71.16
Rh1	C22	C23	68.89
Rh1	C22	C27	121.91
C21	C22	C23	106.99
C21	C22	C27	125.22
C23	C22	C27	127.66
Rh1	C23	C22	71.10
Rh1	C23	C24	72.37
Rh1	C23	C28	122.27
C22	C23	C24	108.77
C22	C23	C28	123.37
C24	C23	C28	127.86
Rh1	C24	C20	71.42
Rh1	C24	C23	68.33
Rh1	C24	C29	125.19
C20	C24	C23	108.72
C20	C24	C29	125.13
C23	C24	C29	126.13
C20	C25	H25A	109.47
C20	C25	H25B	109.47
C20	C25	H25C	109.47
H25A	C25	H25B	109.47
H25A	C25	H25C	109.47
H25B	C25	H25C	109.47
C21	C26	H26A	109.47
C21	C26	H26B	109.47
C21	C26	H26C	109.47
H26A	C26	H26B	109.47
H26A	C26	H26C	109.47
H26B	C26	H26C	109.47
C22	C27	H27A	109.47
C22	C27	H27B	109.47
C22	C27	H27C	109.47
H27A	C27	H27B	109.47
H27A	C27	H27C	109.47
H27B	C27	H27C	109.47
C23	C28	H28A	109.47
C23	C28	H28B	109.47
C23	C28	H28C	109.47
H28A	C28	H28B	109.47
H28A	C28	H28C	109.47
H28B	C28	H28C	109.47
C24	C29	H29A	109.47
C24	C29	H29B	109.47
C24	C29	H29C	109.47
H29A	C29	H29B	109.47
H29A	C29	H29C	109.47
H29B	C29	H29C	109.47
O8	S1	O9	108.63
O8	S1	O10	126.22
O8	S1	C30	105.20
O9	S1	O10	106.71
O9	S1	C30	101.05
O10	S1	C30	106.24
S1	C30	F1	112.13
S1	C30	F2	112.13

Bond angles [°]

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
S1	C30	F3	112.06	F1	C30	F3	106.70
F1	C30	F2	106.75	F2	C30	F3	106.68

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion	Atom1	Atom2	Atom3	Atom4	Torsion
O2	Rh1	O1	C1	13.15	C21	Rh1	C20	C24	-117.95
O7	Rh1	O1	C1	-69.71	C21	Rh1	C20	C25	119.91
C20	Rh1	O1	C1	172.74	C22	Rh1	C20	C21	36.92
C21	Rh1	O1	C1	-164.89	C22	Rh1	C20	C24	-81.02
C22	Rh1	O1	C1	166.56	C22	Rh1	C20	C25	156.83
C23	Rh1	O1	C1	126.83	C23	Rh1	C20	C21	80.90
C24	Rh1	O1	C1	107.92	C23	Rh1	C20	C24	-37.05
O1	Rh1	O2	C2	-12.77	C23	Rh1	C20	C25	-159.19
O7	Rh1	O2	C2	68.34	C24	Rh1	C20	C21	117.95
C20	Rh1	O2	C2	175.15	C24	Rh1	C20	C25	-122.14
C21	Rh1	O2	C2	162.60	O1	Rh1	C21	C20	-168.27
C22	Rh1	O2	C2	-89.03	O1	Rh1	C21	C22	-49.28
C23	Rh1	O2	C2	-109.66	O1	Rh1	C21	C26	71.91
C24	Rh1	O2	C2	-148.63	O2	Rh1	C21	C20	17.09
O1	Rh1	O7	C19	170.88	O2	Rh1	C21	C22	136.08
O2	Rh1	O7	C19	90.72	O2	Rh1	C21	C26	-102.73
C20	Rh1	O7	C19	-27.85	O7	Rh1	C21	C20	107.86
C21	Rh1	O7	C19	-68.03	O7	Rh1	C21	C22	-133.15
C22	Rh1	O7	C19	-101.57	O7	Rh1	C21	C26	-11.96
C23	Rh1	O7	C19	-95.77	C20	Rh1	C21	C22	118.99
C24	Rh1	O7	C19	-6.38	C20	Rh1	C21	C26	-119.82
O1	Rh1	C20	C21	30.19	C22	Rh1	C21	C20	-118.99
O1	Rh1	C20	C24	-87.76	C22	Rh1	C21	C26	121.19
O1	Rh1	C20	C25	150.10	C23	Rh1	C21	C20	-80.35
O2	Rh1	C20	C21	-173.03	C23	Rh1	C21	C22	38.64
O2	Rh1	C20	C24	69.02	C23	Rh1	C21	C26	159.83
O2	Rh1	C20	C25	-53.12	C24	Rh1	C21	C20	-37.05
O7	Rh1	C20	C21	-82.57	C24	Rh1	C21	C22	81.94
O7	Rh1	C20	C24	159.48	C24	Rh1	C21	C26	-156.87
O7	Rh1	C20	C25	37.34	O1	Rh1	C22	C21	139.94

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O1	Rh1	C22	C23	-102.50
O1	Rh1	C22	C27	19.59
O2	Rh1	C22	C21	-147.31
O2	Rh1	C22	C23	-29.75
O2	Rh1	C22	C27	92.33
O7	Rh1	C22	C21	59.92
O7	Rh1	C22	C23	177.48
O7	Rh1	C22	C27	-60.44
C20	Rh1	C22	C21	-37.75
C20	Rh1	C22	C23	79.81
C20	Rh1	C22	C27	-158.11
C21	Rh1	C22	C23	117.56
C21	Rh1	C22	C27	-120.36
C23	Rh1	C22	C21	-117.56
C23	Rh1	C22	C27	122.08
C24	Rh1	C22	C21	-79.79
C24	Rh1	C22	C23	37.77
C24	Rh1	C22	C27	159.85
O1	Rh1	C23	C22	82.77
O1	Rh1	C23	C24	-159.48
O1	Rh1	C23	C28	-35.36
O2	Rh1	C23	C22	165.41
O2	Rh1	C23	C24	-76.84
O2	Rh1	C23	C28	47.28
O7	Rh1	C23	C22	-7.50
O7	Rh1	C23	C24	110.25
O7	Rh1	C23	C28	-125.63
C20	Rh1	C23	C22	-81.57
C20	Rh1	C23	C24	36.18
C20	Rh1	C23	C28	160.31
C21	Rh1	C23	C22	-37.66
C21	Rh1	C23	C24	80.09
C21	Rh1	C23	C28	-155.79
C22	Rh1	C23	C24	117.75
C22	Rh1	C23	C28	-118.13
C24	Rh1	C23	C22	-117.75
C24	Rh1	C23	C28	124.12
O1	Rh1	C24	C20	150.02
O1	Rh1	C24	C23	30.17
O1	Rh1	C24	C29	-89.59
O2	Rh1	C24	C20	-124.27
O2	Rh1	C24	C23	115.87
O2	Rh1	C24	C29	-3.88
O7	Rh1	C24	C20	-33.91
O7	Rh1	C24	C23	-153.76
O7	Rh1	C24	C29	86.48
C20	Rh1	C24	C23	-119.86
C20	Rh1	C24	C29	120.39
C21	Rh1	C24	C20	38.51
C21	Rh1	C24	C23	-81.35
C21	Rh1	C24	C29	158.90
C22	Rh1	C24	C20	81.41
C22	Rh1	C24	C23	-38.45
C22	Rh1	C24	C29	-158.20
C23	Rh1	C24	C20	119.86
C23	Rh1	C24	C29	-119.75
Rh1	O1	C1	C2	-12.06
Rh1	O1	C1	C9	167.25
Rh1	O2	C2	C1	10.52
Rh1	O2	C2	C3	-167.13
C9	O3	C8	C3	0.38
C9	O3	C8	C7	176.36
C8	O3	C9	C1	0.16
C8	O3	C9	C10	-177.91
C16	O4	C12	C11	9.53
C16	O4	C12	C13	-170.18
C12	O4	C16	H16A	179.49
C12	O4	C16	H16B	59.49
C12	O4	C16	H16C	-60.51
C17	O5	C13	C12	112.62
C17	O5	C13	C14	-69.69
C13	O5	C17	H17A	179.63
C13	O5	C17	H17B	59.63
C13	O5	C17	H17C	-60.37
C18	O6	C14	C13	-178.75
C18	O6	C14	C15	0.74
C14	O6	C18	H18A	-179.64
C14	O6	C18	H18B	60.36
C14	O6	C18	H18C	-59.64
O1	C1	C2	O2	0.74
O1	C1	C2	C3	178.49
C9	C1	C2	O2	-178.60
C9	C1	C2	C3	-0.85
O1	C1	C9	O3	-179.19
O1	C1	C9	C10	-1.47
C2	C1	C9	O3	0.11

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C2	C1	C9	C10	177.82
O2	C2	C3	C4	-0.85
O2	C2	C3	C8	179.01
C1	C2	C3	C4	-178.53
C1	C2	C3	C8	1.33
C2	C3	C4	H4	-2.76
C2	C3	C4	C5	177.24
C8	C3	C4	H4	177.38
C8	C3	C4	C5	-2.62
C2	C3	C8	O3	-1.13
C2	C3	C8	C7	-176.93
C4	C3	C8	O3	178.74
C4	C3	C8	C7	2.94
C3	C4	C5	H5	-178.17
C3	C4	C5	C6	1.83
H4	C4	C5	H5	1.83
H4	C4	C5	C6	-178.17
C4	C5	C6	H6	178.66
C4	C5	C6	C7	-1.34
H5	C5	C6	H6	-1.34
H5	C5	C6	C7	178.66
C5	C6	C7	H7	-178.41
C5	C6	C7	C8	1.59
H6	C6	C7	H7	1.59
H6	C6	C7	C8	-178.41
C6	C7	C8	O3	-178.45
C6	C7	C8	C3	-2.44
H7	C7	C8	O3	1.55
H7	C7	C8	C3	177.57
O3	C9	C10	C11	-2.60
O3	C9	C10	C15	177.18
C1	C9	C10	C11	179.49
C1	C9	C10	C15	-0.73
C9	C10	C11	H11	-1.71
C9	C10	C11	C12	178.29
C15	C10	C11	H11	178.50
C15	C10	C11	C12	-1.49
C9	C10	C15	C14	-179.13
C9	C10	C15	H15	0.87
C11	C10	C15	C14	0.65
C11	C10	C15	H15	-179.35
C10	C11	C12	O4	-179.19
C10	C11	C12	C13	0.50
H11	C11	C12	O4	0.81
H11	C11	C12	C13	-179.50
O4	C12	C13	O5	-1.23
O4	C12	C13	C14	-178.97
C11	C12	C13	O5	179.05
C11	C12	C13	C14	1.31
O5	C13	C14	O6	-0.38
O5	C13	C14	C15	-179.88
C12	C13	C14	O6	177.31
C12	C13	C14	C15	-2.19
O6	C14	C15	C10	-178.25
O6	C14	C15	H15	1.75
C13	C14	C15	C10	1.21
C13	C14	C15	H15	-178.80
Rh1	O7	C19	H19A	-56.22
Rh1	O7	C19	H19B	-176.22
Rh1	O7	C19	H19C	63.78
Rh1	C20	C21	C22	-59.98
Rh1	C20	C21	C26	118.54
C24	C20	C21	Rh1	60.38
C24	C20	C21	C22	0.40
C24	C20	C21	C26	178.93
C25	C20	C21	Rh1	-125.05
C25	C20	C21	C22	174.97
C25	C20	C21	C26	-6.51
Rh1	C20	C24	C23	58.32
Rh1	C20	C24	C29	-120.45
C21	C20	C24	Rh1	-59.75
C21	C20	C24	C23	-1.43
C21	C20	C24	C29	179.79
C25	C20	C24	Rh1	125.76
C25	C20	C24	C23	-175.92
C25	C20	C24	C29	5.31
Rh1	C20	C25	H25A	57.05
Rh1	C20	C25	H25B	-62.95
Rh1	C20	C25	H25C	177.05
C21	C20	C25	H25A	149.05
C21	C20	C25	H25B	29.05
C21	C20	C25	H25C	-90.95
C24	C20	C25	H25A	-37.45
C24	C20	C25	H25B	-157.45
C24	C20	C25	H25C	82.55
Rh1	C21	C22	C23	-59.86

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
Rh1	C21	C22	C27	116.28
C20	C21	C22	Rh1	60.62
C20	C21	C22	C23	0.76
C20	C21	C22	C27	176.90
C26	C21	C22	Rh1	-117.87
C26	C21	C22	C23	-177.73
C26	C21	C22	C27	-1.59
Rh1	C21	C26	H26A	-166.62
Rh1	C21	C26	H26B	73.38
Rh1	C21	C26	H26C	-46.62
C20	C21	C26	H26A	104.07
C20	C21	C26	H26B	-15.93
C20	C21	C26	H26C	-135.93
C22	C21	C26	H26A	-77.67
C22	C21	C26	H26B	162.33
C22	C21	C26	H26C	42.33
Rh1	C22	C23	C24	-62.98
Rh1	C22	C23	C28	116.75
C21	C22	C23	Rh1	61.32
C21	C22	C23	C24	-1.65
C21	C22	C23	C28	178.08
C27	C22	C23	Rh1	-114.69
C27	C22	C23	C24	-177.66
C27	C22	C23	C28	2.06
Rh1	C22	C27	H27A	61.53
Rh1	C22	C27	H27B	-58.47
Rh1	C22	C27	H27C	-178.47
C21	C22	C27	H27A	-26.98
C21	C22	C27	H27B	-146.98
C21	C22	C27	H27C	93.02
C23	C22	C27	H27A	148.35
C23	C22	C27	H27B	28.35
C23	C22	C27	H27C	-91.65
Rh1	C23	C24	C20	-60.23
Rh1	C23	C24	C29	118.53
C22	C23	C24	Rh1	62.16
C22	C23	C24	C20	1.94
C22	C23	C24	C29	-179.30
C28	C23	C24	Rh1	-117.55
C28	C23	C24	C20	-177.78
C28	C23	C24	C29	0.98
Rh1	C23	C28	H28A	-100.44
Rh1	C23	C28	H28B	139.56
Rh1	C23	C28	H28C	19.56
C22	C23	C28	H28A	172.02
C22	C23	C28	H28B	52.02
C22	C23	C28	H28C	-67.98
C24	C23	C28	H28A	-8.31
C24	C23	C28	H28B	-128.31
C24	C23	C28	H28C	111.69
Rh1	C24	C29	H29A	-172.66
Rh1	C24	C29	H29B	67.33
Rh1	C24	C29	H29C	-52.66
C20	C24	C29	H29A	-81.55
C20	C24	C29	H29B	158.45
C20	C24	C29	H29C	38.45
C23	C24	C29	H29A	99.89
C23	C24	C29	H29B	-20.11
C23	C24	C29	H29C	-140.11
O8	S1	C30	F1	-31.56
O8	S1	C30	F2	-151.65
O8	S1	C30	F3	88.41
O9	S1	C30	F1	-144.54
O9	S1	C30	F2	95.37
O9	S1	C30	F3	-24.57
O10	S1	C30	F1	104.24
O10	S1	C30	F2	-15.85
O10	S1	C30	F3	-135.79

Trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-chlorophenyl)-chromen-4-onato-κ*O*](*η*^{5}-pentamethylcyclopentadienyl)rhodium(III) C3

Bond lengths [Å]

Atom1	Atom2	Length	Atom1	Atom2	Length
Rh1	O1	2.0678(1)	C10	H10	0.9500
Rh1	O2	2.1200(1)	C10	C11	1.3769(1)
Rh1	O4	2.2176(1)	C11	H11	0.9500
Rh1	C16	2.1523(1)	C11	C12	1.4055(1)
Rh1	C17	2.1288(1)	C12	H12	0.9500
Rh1	C18	2.0961(1)	C12	C13	1.3744(1)
Rh1	C19	2.1184(1)	C13	H13	0.9500
Rh1	C20	2.1164(1)	C13	C14	1.4087(1)
Cl1	C6	1.7415(1)	C14	C15	1.4355(1)
S1	O4	1.4676(1)	C16	C17	1.4205(1)
S1	O5	1.4329(1)	C16	C20	1.4492(1)
S1	O6	1.4320(1)	C16	C21	1.4884(1)
S1	C26	1.8232(1)	C17	C18	1.4485(1)
O1	C1	1.3153(1)	C17	C22	1.4946(1)
O2	C15	1.2662(1)	C18	C19	1.4403(1)
O3	C2	1.3734(1)	C18	C23	1.4904(1)
O3	C9	1.3543(1)	C19	C20	1.4374(1)
F1	C26	1.3270(1)	C19	C24	1.4921(1)
F2	C26	1.3367(1)	C20	C25	1.4944(1)
F3	C26	1.3356(1)	C21	H21A	0.9800
C1	C2	1.3822(1)	C21	H21B	0.9800(1)
C1	C15	1.4453(1)	C21	H21C	0.9800
C2	C3	1.4628(1)	C22	H22A	0.9800
C3	C4	1.4034(1)	C22	H22B	0.9800
C3	C8	1.4013(1)	C22	H22C	0.9800
C4	H4	0.9500	C23	H23A	0.9800
C4	C5	1.3922(1)	C23	H23B	0.9800
C5	H5	0.9500	C23	H23C	0.9800
C5	C6	1.3826(1)	C24	H24A	0.9800
C6	C7	1.3824(1)	C24	H24B	0.9800(1)
C7	H7	0.9500	C24	H24C	0.9800
C7	C8	1.3839(1)	C25	H25A	0.9800
C8	H8	0.9500	C25	H25B	0.9800
C9	C10	1.3975(1)	C25	H25C	0.9800
C9	C14	1.3935(1)			

Bond angles [°]

Atom1	Atom2	Atom3	Angle
O1	Rh1	O2	78.99
O1	Rh1	O4	83.01
O1	Rh1	C16	152.30
O1	Rh1	C17	153.99
O1	Rh1	C18	114.39
O1	Rh1	C19	96.12
O1	Rh1	C20	113.28
O2	Rh1	O4	82.36
O2	Rh1	C16	128.64
O2	Rh1	C17	99.68
O2	Rh1	C18	102.64
O2	Rh1	C19	136.34
O2	Rh1	C20	166.16
O4	Rh1	C16	97.33
O4	Rh1	C17	122.78
O4	Rh1	C18	162.43
O4	Rh1	C19	140.64
O4	Rh1	C20	104.83
C16	Rh1	C17	38.75
C16	Rh1	C18	66.26
C16	Rh1	C19	66.16
C16	Rh1	C20	39.68
C17	Rh1	C18	40.09
C17	Rh1	C19	66.70
C17	Rh1	C20	66.48
C18	Rh1	C19	39.96
C18	Rh1	C20	67.06
C19	Rh1	C20	39.68
O4	S1	O5	114.31
O4	S1	O6	114.63
O4	S1	C26	100.27
O5	S1	O6	117.01
O5	S1	C26	103.68
O6	S1	C26	104.02
Rh1	O1	C1	112.33
Rh1	O2	C15	111.62
C2	O3	C9	121.47
Rh1	O4	S1	124.07
O1	C1	C2	123.80
O1	C1	C15	117.32
C2	C1	C15	118.88
O3	C2	C1	120.84
O3	C2	C3	111.58
C1	C2	C3	127.56
C2	C3	C4	122.34
C2	C3	C8	119.21
C4	C3	C8	118.44
C3	C4	H4	119.68
C3	C4	C5	120.65
H4	C4	C5	119.68
C4	C5	H5	120.41
C4	C5	C6	119.17
H5	C5	C6	120.41
Cl1	C6	C5	119.48
Cl1	C6	C7	119.05
C5	C6	C7	121.46
C6	C7	H7	120.36
C6	C7	C8	119.27
H7	C7	C8	120.36
C3	C8	C7	121.00
C3	C8	H8	119.50
C7	C8	H8	119.50
O3	C9	C10	116.80
O3	C9	C14	121.79
C10	C9	C14	121.41
C9	C10	H10	120.69
C9	C10	C11	118.61
H10	C10	C11	120.69
C10	C11	H11	119.56
C10	C11	C12	120.89
H11	C11	C12	119.56
C11	C12	H12	119.87
C11	C12	C13	120.26
H12	C12	C13	119.87
C12	C13	H13	120.09
C12	C13	C14	119.82
H13	C13	C14	120.09
C9	C14	C13	119.00
C9	C14	C15	118.11
C13	C14	C15	122.88
O2	C15	C1	119.01
O2	C15	C14	122.15
C1	C15	C14	118.83
Rh1	C16	C17	69.73
Rh1	C16	C20	68.83
Rh1	C16	C21	127.18

Bond angles [°]

Atom1	Atom2	Atom3	Angle
C17	C16	C20	108.37
C17	C16	C21	126.29
C20	C16	C21	125.34
Rh1	C17	C16	71.52
Rh1	C17	C18	68.74
Rh1	C17	C22	123.39
C16	C17	C18	108.08
C16	C17	C22	126.04
C18	C17	C22	125.84
Rh1	C18	C17	71.17
Rh1	C18	C19	70.85
Rh1	C18	C23	126.01
C17	C18	C19	107.85
C17	C18	C23	125.91
C19	C18	C23	126.16
Rh1	C19	C18	69.19
Rh1	C19	C20	70.09
Rh1	C19	C24	123.87
C18	C19	C20	107.91
C18	C19	C24	125.11
C20	C19	C24	126.91
Rh1	C20	C16	71.49
Rh1	C20	C19	70.23
Rh1	C20	C25	125.55
C16	C20	C19	107.71
C16	C20	C25	125.02
C19	C20	C25	127.23
C16	C21	H21A	109.47
C16	C21	H21B	109.47
C16	C21	H21C	109.47
H21A	C21	H21B	109.47
H21A	C21	H21C	109.47
H21B	C21	H21C	109.47
C17	C22	H22A	109.47
C17	C22	H22B	109.47
C17	C22	H22C	109.47
H22A	C22	H22B	109.47
H22A	C22	H22C	109.47
H22B	C22	H22C	109.47
C18	C23	H23A	109.47
C18	C23	H23B	109.47
C18	C23	H23C	109.47
H23A	C23	H23B	109.47
H23A	C23	H23C	109.47
H23B	C23	H23C	109.47
C19	C24	H24A	109.47
C19	C24	H24B	109.47
C19	C24	H24C	109.47
H24A	C24	H24B	109.47
H24A	C24	H24C	109.47
H24B	C24	H24C	109.47
C20	C25	H25A	109.47
C20	C25	H25B	109.47
C20	C25	H25C	109.47
H25A	C25	H25B	109.47
H25A	C25	H25C	109.47
H25B	C25	H25C	109.47
S1	C26	F1	111.82
S1	C26	F2	110.62
S1	C26	F3	111.30
F1	C26	F2	107.74
F1	C26	F3	107.57
F2	C26	F3	107.61

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O2	Rh1	O1	C1	-7.50
O4	Rh1	O1	C1	76.03
C16	Rh1	O1	C1	168.52
C17	Rh1	O1	C1	-97.03
C18	Rh1	O1	C1	-106.51
C19	Rh1	O1	C1	-143.59
C20	Rh1	O1	C1	179.21
O1	Rh1	O2	C15	6.84
O4	Rh1	O2	C15	-77.48
C16	Rh1	O2	C15	-170.79
C17	Rh1	O2	C15	160.43
C18	Rh1	O2	C15	119.64
C19	Rh1	O2	C15	94.16
C20	Rh1	O2	C15	160.17
O1	Rh1	O4	S1	-129.07
O2	Rh1	O4	S1	-49.31
C16	Rh1	O4	S1	78.85
C17	Rh1	O4	S1	47.32
C18	Rh1	O4	S1	58.61
C19	Rh1	O4	S1	139.79
C20	Rh1	O4	S1	118.62
O1	Rh1	C16	C17	135.70
O1	Rh1	C16	C20	15.48
O1	Rh1	C16	C21	-103.52
O2	Rh1	C16	C17	-49.31
O2	Rh1	C16	C20	-169.52
O2	Rh1	C16	C21	71.48
O4	Rh1	C16	C17	-135.37
O4	Rh1	C16	C20	104.41
O4	Rh1	C16	C21	-14.58
C17	Rh1	C16	C20	-120.22
C17	Rh1	C16	C21	120.79
C18	Rh1	C16	C17	38.08
C18	Rh1	C16	C20	-82.14
C18	Rh1	C16	C21	158.87
C19	Rh1	C16	C17	81.94
C19	Rh1	C16	C20	-38.28
C19	Rh1	C16	C21	-157.27
C20	Rh1	C16	C17	120.22
C20	Rh1	C16	C21	-119.00
O1	Rh1	C17	C16	-132.23
O1	Rh1	C17	C18	-13.46
O1	Rh1	C17	C22	106.27
O2	Rh1	C17	C16	143.07
O2	Rh1	C17	C18	-98.16
O2	Rh1	C17	C22	21.57
O4	Rh1	C17	C16	55.97
O4	Rh1	C17	C18	174.73
O4	Rh1	C17	C22	-65.54
C16	Rh1	C17	C18	118.76
C16	Rh1	C17	C22	-121.50
C18	Rh1	C17	C16	-118.76
C18	Rh1	C17	C22	119.73
C19	Rh1	C17	C16	-80.41
C19	Rh1	C17	C18	38.35
C19	Rh1	C17	C22	158.09
C20	Rh1	C17	C16	-37.00
C20	Rh1	C17	C18	81.77
C20	Rh1	C17	C22	-158.50
O1	Rh1	C18	C17	173.56
O1	Rh1	C18	C19	-68.97
O1	Rh1	C18	C23	52.35
O2	Rh1	C18	C17	90.07
O2	Rh1	C18	C19	-152.46
O2	Rh1	C18	C23	-31.15
O4	Rh1	C18	C17	-14.82
O4	Rh1	C18	C19	102.65
O4	Rh1	C18	C23	-136.03
C16	Rh1	C18	C17	-36.83
C16	Rh1	C18	C19	80.64
C16	Rh1	C18	C23	-158.04
C17	Rh1	C18	C19	117.47
C17	Rh1	C18	C23	-121.21
C19	Rh1	C18	C17	-117.47
C19	Rh1	C18	C23	121.32
C20	Rh1	C18	C17	-80.21
C20	Rh1	C18	C19	37.25
C20	Rh1	C18	C23	158.57
O1	Rh1	C19	C18	121.24
O1	Rh1	C19	C20	-119.57
O1	Rh1	C19	C24	2.18
O2	Rh1	C19	C18	40.80
O2	Rh1	C19	C20	159.99
O2	Rh1	C19	C24	-78.27
O4	Rh1	C19	C18	-152.33
O4	Rh1	C19	C20	-33.14

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O4	Rh1	C19	C24	88.61
C16	Rh1	C19	C18	-80.91
C16	Rh1	C19	C20	38.28
C16	Rh1	C19	C24	160.02
C17	Rh1	C19	C18	-38.47
C17	Rh1	C19	C20	80.72
C17	Rh1	C19	C24	-157.54
C18	Rh1	C19	C20	119.19
C18	Rh1	C19	C24	-119.07
C20	Rh1	C19	C18	-119.19
C20	Rh1	C19	C24	121.75
O1	Rh1	C20	C16	-172.24
O1	Rh1	C20	C19	70.30
O1	Rh1	C20	C25	-51.93
O2	Rh1	C20	C16	36.43
O2	Rh1	C20	C19	-81.03
O2	Rh1	C20	C25	156.73
O4	Rh1	C20	C16	-83.56
O4	Rh1	C20	C19	158.98
O4	Rh1	C20	C25	36.74
C16	Rh1	C20	C19	-117.46
C16	Rh1	C20	C25	120.30
C17	Rh1	C20	C16	36.15
C17	Rh1	C20	C19	-81.31
C17	Rh1	C20	C25	156.45
C18	Rh1	C20	C16	79.95
C18	Rh1	C20	C19	-37.51
C18	Rh1	C20	C25	-159.75
C19	Rh1	C20	C16	117.46
C19	Rh1	C20	C25	-122.24
O5	S1	O4	Rh1	104.56
O6	S1	O4	Rh1	-34.49
C26	S1	O4	Rh1	-145.22
O4	S1	C26	F1	-58.83
O4	S1	C26	F2	-178.92
O4	S1	C26	F3	61.50
O5	S1	C26	F1	59.51
O5	S1	C26	F2	-60.58
O5	S1	C26	F3	179.84
O6	S1	C26	F1	-177.64
O6	S1	C26	F2	62.28
O6	S1	C26	F3	-57.30
Rh1	O1	C1	C2	-172.81
Rh1	O1	C1	C15	7.31
Rh1	O2	C15	C1	-5.22
Rh1	O2	C15	C14	175.72
C9	O3	C2	C1	2.42
C9	O3	C2	C3	-178.96
C2	O3	C9	C10	176.93
C2	O3	C9	C14	-2.64
O1	C1	C2	O3	-179.87
O1	C1	C2	C3	1.74
C15	C1	C2	O3	0.00
C15	C1	C2	C3	-178.38
O1	C1	C15	O2	-1.34
O1	C1	C15	C14	177.75
C2	C1	C15	O2	178.78
C2	C1	C15	C14	-2.13
O3	C2	C3	C4	178.28
O3	C2	C3	C8	-1.52
C1	C2	C3	C4	-3.21
C1	C2	C3	C8	176.99
C2	C3	C4	H4	0.11
C2	C3	C4	C5	-179.89
C8	C3	C4	H4	179.91
C8	C3	C4	C5	-0.09
C2	C3	C8	C7	179.74
C2	C3	C8	H8	-0.26
C4	C3	C8	C7	-0.07
C4	C3	C8	H8	179.94
C3	C4	C5	H5	-179.69
C3	C4	C5	C6	0.31
H4	C4	C5	H5	0.31
H4	C4	C5	C6	-179.69
C4	C5	C6	Cl1	178.53
C4	C5	C6	C7	-0.38
H5	C5	C6	Cl1	-1.47
H5	C5	C6	C7	179.62
Cl1	C6	C7	H7	1.31
Cl1	C6	C7	C8	-178.69
C5	C6	C7	H7	-179.77
C5	C6	C7	C8	0.23
C6	C7	C8	C3	0.00
C6	C7	C8	H8	180.00
H7	C7	C8	C3	-180.00
H7	C7	C8	H8	-0.00

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O3	C9	C10	H10	1.54
O3	C9	C10	C11	-178.46
C14	C9	C10	H10	-178.89
C14	C9	C10	C11	1.11
O3	C9	C14	C13	178.97
O3	C9	C14	C15	0.41
C10	C9	C14	C13	-0.58
C10	C9	C14	C15	-179.14
C9	C10	C11	H11	179.46
C9	C10	C11	C12	-0.54
H10	C10	C11	H11	-0.54
H10	C10	C11	C12	179.46
C10	C11	C12	H12	179.44
C10	C11	C12	C13	-0.56
H11	C11	C12	H12	-0.56
H11	C11	C12	C13	179.44
C11	C12	C13	H13	-178.90
C11	C12	C13	C14	1.09
H12	C12	C13	H13	1.10
H12	C12	C13	C14	-178.90
C12	C13	C14	C9	-0.54
C12	C13	C14	C15	177.95
H13	C13	C14	C9	179.46
H13	C13	C14	C15	-2.05
C9	C14	C15	O2	-179.01
C9	C14	C15	C1	1.93
C13	C14	C15	O2	2.49
C13	C14	C15	C1	-176.57
Rh1	C16	C17	C18	-59.25
Rh1	C16	C17	C22	118.32
C20	C16	C17	Rh1	58.11
C20	C16	C17	C18	-1.14
C20	C16	C17	C22	176.43
C21	C16	C17	Rh1	-121.88
C21	C16	C17	C18	178.88
C21	C16	C17	C22	-3.55
Rh1	C16	C20	C19	61.23
Rh1	C16	C20	C25	-120.94
C17	C16	C20	Rh1	-58.67
C17	C16	C20	C19	2.56
C17	C16	C20	C25	-179.61
C21	C16	C20	Rh1	121.32
C21	C16	C20	C19	-177.45
C21	C16	C20	C25	0.38
Rh1	C16	C21	H21A	178.40
Rh1	C16	C21	H21B	58.40
Rh1	C16	C21	H21C	-61.60
C17	C16	C21	H21A	-90.59
C17	C16	C21	H21B	149.41
C17	C16	C21	H21C	29.41
C20	C16	C21	H21A	89.42
C20	C16	C21	H21B	-30.58
C20	C16	C21	H21C	-150.58
Rh1	C17	C18	C19	-61.71
Rh1	C17	C18	C23	121.34
C16	C17	C18	Rh1	60.99
C16	C17	C18	C19	-0.72
C16	C17	C18	C23	-177.67
C22	C17	C18	Rh1	-116.58
C22	C17	C18	C19	-178.29
C22	C17	C18	C23	4.75
Rh1	C17	C22	H22A	14.91
Rh1	C17	C22	H22B	-105.09
Rh1	C17	C22	H22C	134.91
C16	C17	C22	H22A	-75.66
C16	C17	C22	H22B	164.34
C16	C17	C22	H22C	44.34
C18	C17	C22	H22A	101.49
C18	C17	C22	H22B	-18.51
C18	C17	C22	H22C	-138.51
Rh1	C18	C19	C20	-59.61
Rh1	C18	C19	C24	117.49
C17	C18	C19	Rh1	61.92
C17	C18	C19	C20	2.30
C17	C18	C19	C24	179.40
C23	C18	C19	Rh1	-121.14
C23	C18	C19	C20	179.25
C23	C18	C19	C24	-3.66
Rh1	C18	C23	H23A	57.01
Rh1	C18	C23	H23B	-62.99
Rh1	C18	C23	H23C	177.01
C17	C18	C23	H23A	-34.92
C17	C18	C23	H23B	-154.92
C17	C18	C23	H23C	85.08
C19	C18	C23	H23A	148.67
C19	C18	C23	H23B	28.67

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C19	C18	C23	H23C	-91.33
Rh1	C19	C20	C16	-62.04
Rh1	C19	C20	C25	120.19
C18	C19	C20	Rh1	59.05
C18	C19	C20	C16	-2.99
C18	C19	C20	C25	179.24
C24	C19	C20	Rh1	-117.98
C24	C19	C20	C16	179.98
C24	C19	C20	C25	2.21
Rh1	C19	C24	H24A	162.06
Rh1	C19	C24	H24B	42.06
Rh1	C19	C24	H24C	-77.94
C18	C19	C24	H24A	75.00
C18	C19	C24	H24B	-45.00
C18	C19	C24	H24C	-165.00
C20	C19	C24	H24A	-108.46
C20	C19	C24	H24B	131.54
C20	C19	C24	H24C	11.54
Rh1	C20	C25	H25A	72.46
Rh1	C20	C25	H25B	-47.55
Rh1	C20	C25	H25C	-167.55
C16	C20	C25	H25A	163.85
C16	C20	C25	H25B	43.85
C16	C20	C25	H25C	-76.15
C19	C20	C25	H25A	-18.75
C19	C20	C25	H25B	-138.75
C19	C20	C25	H25C	101.25

[{3-(oxo-κ*O*)-2-(4-methylphenyl)-chromen-4-onato- κ*O*}(methanol)(η^5-pentamethylcyclopentadienyl)rhodium(III)] trifluoromethanesulfonate C4

Bond lengths [Å]

Atom1	Atom2	Length	Atom1	Atom2	Length
Rh1	O1	2.0511(1)	C17	C18	1.4218(1)
Rh1	O2	2.1264(1)	C17	C21	1.4440(1)
Rh1	C17	2.1343(1)	C17	C22	1.4899(1)
Rh1	C18	2.1500(1)	C18	C19	1.4358(1)
Rh1	C19	2.1162(1)	C18	C23	1.4923(1)
Rh1	C20	2.1144(1)	C19	C20	1.4373(1)
Rh1	C21	2.1066(1)	C19	C24	1.4879(1)
Rh1	O4	2.1874(1)	C20	C21	1.4266(1)
O1	C1	1.3176(1)	C20	C25	1.4866(1)
O2	C2	1.2757(1)	C21	C26	1.4890(1)
O3	C8	1.3592(1)	C22	H22A	0.9800
O3	C9	1.3626(1)	C22	H22B	0.9800(1)
C1	C2	1.4393(1)	C22	H22C	0.9800
C1	C9	1.3828(1)	C23	H23A	0.9800
C2	C3	1.4263(1)	C23	H23B	0.9800
C3	C4	1.4068(1)	C23	H23C	0.9800
C3	C8	1.3865(1)	C24	H24A	0.9800
C4	H4	0.9500	C24	H24B	0.9800
C4	C5	1.3731(1)	C24	H24C	0.9800
C5	H5	0.9500	C25	H25A	0.9800(1)
C5	C6	1.3965(1)	C25	H25B	0.9800
C6	H6	0.9500	C25	H25C	0.9800
C6	C7	1.3743(1)	C26	H26A	0.9800
C7	H7	0.9500	C26	H26B	0.9800
C7	C8	1.4005(1)	C26	H26C	0.9800(1)
C9	C10	1.4605(1)	O4	H40	0.7253
C10	C11	1.3975(1)	O4	C27	1.4125(1)
C10	C15	1.3996(1)	C27	H27A	0.9800
C11	H11	0.9500	C27	H27B	0.9800
C11	C12	1.3895(1)	C27	H27C	0.9800
C12	H12	0.9500	S1	O5	1.4382(1)
C12	C13	1.3926(1)	S1	O6	1.4376(1)
C13	C14	1.3814(1)	S1	O7	1.4515(1)
C13	C16	1.5087(1)	S1	C28	1.8225(1)
C14	H14	0.9500	C28	F1	1.3258(1)
C14	C15	1.3863(1)	C28	F2	1.3248(1)
C15	H15	0.9500	C28	F3	1.3332(1)
C16	H16A	0.9800	O8	C29	1.4503(1)
C16	H16B	0.9800	C29	C29	1.6799(1)
C16	H16C	0.9800	O8	C29	1.4503(1)

Bond angles [°]

Atom1	Atom2	Atom3	Angle
O1	Rh1	O2	79.11
O1	Rh1	C17	160.00
O1	Rh1	C18	144.58
O1	Rh1	C19	107.60
O1	Rh1	C20	96.30
O1	Rh1	C21	120.26
O1	Rh1	O4	82.06
O2	Rh1	C17	103.91
O2	Rh1	C18	135.99
O2	Rh1	C19	167.70
O2	Rh1	C20	130.71
O2	Rh1	C21	101.32
O2	Rh1	O4	78.62
C17	Rh1	C18	38.76
C17	Rh1	C19	66.22
C17	Rh1	C20	66.49
C17	Rh1	C21	39.81
C17	Rh1	O4	117.94
C18	Rh1	C19	39.32
C18	Rh1	C20	65.91
C18	Rh1	C21	65.70
C18	Rh1	O4	98.43
C19	Rh1	C20	39.72
C19	Rh1	C21	66.43
C19	Rh1	O4	112.14
C20	Rh1	C21	39.51
C20	Rh1	O4	150.02
C21	Rh1	O4	157.47
Rh1	O1	C1	112.78
Rh1	O2	C2	110.71
C8	O3	C9	121.27
O1	C1	C2	116.97
O1	C1	C9	123.87
C2	C1	C9	119.15
O2	C2	C1	119.25
O2	C2	C3	122.25
C1	C2	C3	118.49
C2	C3	C4	122.91
C2	C3	C8	118.59
C4	C3	C8	118.50
C3	C4	H4	120.02
C3	C4	C5	119.96
H4	C4	C5	120.02
C4	C5	H5	119.77
C4	C5	C6	120.46
H5	C5	C6	119.77
C5	C6	H6	119.55
C5	C6	C7	120.90
H6	C6	C7	119.55
C6	C7	H7	120.88
C6	C7	C8	118.23
H7	C7	C8	120.88
O3	C8	C3	121.63
O3	C8	C7	116.47
C3	C8	C7	121.90
O3	C9	C1	120.82
O3	C9	C10	112.12
C1	C9	C10	127.04
C9	C10	C11	121.51
C9	C10	C15	120.49
C11	C10	C15	117.99
C10	C11	H11	119.66
C10	C11	C12	120.68
H11	C11	C12	119.66
C11	C12	H12	119.43
C11	C12	C13	121.14
H12	C12	C13	119.43
C12	C13	C14	117.98
C12	C13	C16	119.81
C14	C13	C16	122.21
C13	C14	H14	119.15
C13	C14	C15	121.69
H14	C14	C15	119.15
C10	C15	C14	120.50
C10	C15	H15	119.75
C14	C15	H15	119.75
C13	C16	H16A	109.47
C13	C16	H16B	109.47
C13	C16	H16C	109.47
H16A	C16	H16B	109.47
H16A	C16	H16C	109.47
H16B	C16	H16C	109.47
Rh1	C17	C18	71.22
Rh1	C17	C21	69.06
Rh1	C17	C22	125.32
C18	C17	C21	107.37

Bond angles [°]

Atom1	Atom2	Atom3	Angle
C18	C17	C22	127.97
C21	C17	C22	124.66
Rh1	C18	C17	70.02
Rh1	C18	C19	69.07
Rh1	C18	C23	127.23
C17	C18	C19	108.68
C17	C18	C23	127.59
C19	C18	C23	123.73
Rh1	C19	C18	71.61
Rh1	C19	C20	70.07
Rh1	C19	C24	126.30
C18	C19	C20	107.71
C18	C19	C24	125.47
C20	C19	C24	126.74
Rh1	C20	C19	70.21
Rh1	C20	C21	69.95
Rh1	C20	C25	123.44
C19	C20	C21	107.74
C19	C20	C25	126.23
C21	C20	C25	125.99
Rh1	C21	C17	71.13
Rh1	C21	C20	70.54
Rh1	C21	C26	126.44
C17	C21	C20	108.46
C17	C21	C26	124.97
C20	C21	C26	126.51
C17	C22	H22A	109.47
C17	C22	H22B	109.47
C17	C22	H22C	109.47
H22A	C22	H22B	109.47
H22A	C22	H22C	109.47
H22B	C22	H22C	109.47
C18	C23	H23A	109.47
C18	C23	H23B	109.47
C18	C23	H23C	109.47
H23A	C23	H23B	109.47
H23A	C23	H23C	109.47
H23B	C23	H23C	109.47
C19	C24	H24A	109.47
C19	C24	H24B	109.47
C19	C24	H24C	109.47
H24A	C24	H24B	109.47
H24A	C24	H24C	109.47
H24B	C24	H24C	109.47
C20	C25	H25A	109.47
C20	C25	H25B	109.47
C20	C25	H25C	109.47
H25A	C25	H25B	109.47
H25A	C25	H25C	109.47
H25B	C25	H25C	109.47
C21	C26	H26A	109.47
C21	C26	H26B	109.47
C21	C26	H26C	109.47
H26A	C26	H26B	109.47
H26A	C26	H26C	109.47
H26B	C26	H26C	109.47
Rh1	O4	H40	121.25
Rh1	O4	C27	122.30
H40	O4	C27	108.97
O4	C27	H27A	109.47
O4	C27	H27B	109.47
O4	C27	H27C	109.47
H27A	C27	H27B	109.47
H27A	C27	H27C	109.47
H27B	C27	H27C	109.47
O5	S1	O6	116.14
O5	S1	O7	114.62
O5	S1	C28	103.93
O6	S1	O7	113.95
O6	S1	C28	103.59
O7	S1	C28	102.22
S1	C28	F1	111.10
S1	C28	F2	111.45
S1	C28	F3	110.81
F1	C28	F2	107.87
F1	C28	F3	107.71
F2	C28	F3	107.75
O8	C29	C29	74.89
C29	C29	O8	74.89

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O2	Rh1	O1	C1	-9.31
C17	Rh1	O1	C1	-110.10
C18	Rh1	O1	C1	163.95
C19	Rh1	O1	C1	-178.66
C20	Rh1	O1	C1	-139.63
C21	Rh1	O1	C1	-106.16
O4	Rh1	O1	C1	70.55
O1	Rh1	O2	C2	8.96
C17	Rh1	O2	C2	168.71
C18	Rh1	O2	C2	-165.42
C19	Rh1	O2	C2	133.18
C20	Rh1	O2	C2	97.93
C21	Rh1	O2	C2	127.96
O4	Rh1	O2	C2	-75.02
O1	Rh1	C17	C18	-112.56
O1	Rh1	C17	C21	5.32
O1	Rh1	C17	C22	123.69
O2	Rh1	C17	C18	151.04
O2	Rh1	C17	C21	-91.07
O2	Rh1	C17	C22	27.30
C18	Rh1	C17	C21	117.88
C18	Rh1	C17	C22	-123.74
C19	Rh1	C17	C18	-36.73
C19	Rh1	C17	C21	81.15
C19	Rh1	C17	C22	-160.48
C20	Rh1	C17	C18	-80.27
C20	Rh1	C17	C21	37.61
C20	Rh1	C17	C22	155.98
C21	Rh1	C17	C18	-117.88
C21	Rh1	C17	C22	118.37
O4	Rh1	C17	C18	66.71
O4	Rh1	C17	C21	-175.41
O4	Rh1	C17	C22	-57.04
O1	Rh1	C18	C17	146.98
O1	Rh1	C18	C19	26.72
O1	Rh1	C18	C23	-90.41
O2	Rh1	C18	C17	-42.56
O2	Rh1	C18	C19	-162.83
O2	Rh1	C18	C23	80.04
C17	Rh1	C18	C19	-120.27
C17	Rh1	C18	C23	122.61
C19	Rh1	C18	C17	120.27
C19	Rh1	C18	C23	-117.13
C20	Rh1	C18	C17	81.88
C20	Rh1	C18	C19	-38.39
C20	Rh1	C18	C23	-155.52
C21	Rh1	C18	C17	38.38
C21	Rh1	C18	C19	-81.88
C21	Rh1	C18	C23	160.99
O4	Rh1	C18	C17	-124.89
O4	Rh1	C18	C19	114.85
O4	Rh1	C18	C23	-2.28
O1	Rh1	C19	C18	-164.14
O1	Rh1	C19	C20	78.38
O1	Rh1	C19	C24	-43.17
O2	Rh1	C19	C18	74.28
O2	Rh1	C19	C20	-43.21
O2	Rh1	C19	C24	-164.76
C17	Rh1	C19	C18	36.22
C17	Rh1	C19	C20	-81.26
C17	Rh1	C19	C24	157.19
C18	Rh1	C19	C20	-117.49
C18	Rh1	C19	C24	120.97
C20	Rh1	C19	C18	117.49
C20	Rh1	C19	C24	-121.55
C21	Rh1	C19	C18	79.87
C21	Rh1	C19	C20	-37.62
C21	Rh1	C19	C24	-159.17
O4	Rh1	C19	C18	-75.71
O4	Rh1	C19	C20	166.80
O4	Rh1	C19	C24	45.26
O1	Rh1	C20	C19	-110.06
O1	Rh1	C20	C21	131.52
O1	Rh1	C20	C25	10.94
O2	Rh1	C20	C19	168.90
O2	Rh1	C20	C21	50.48
O2	Rh1	C20	C25	-70.10
C17	Rh1	C20	C19	80.53
C17	Rh1	C20	C21	-37.89
C17	Rh1	C20	C25	-158.47
C18	Rh1	C20	C19	38.01
C18	Rh1	C20	C21	-80.42
C18	Rh1	C20	C25	159.01
C19	Rh1	C20	C21	-118.42
C19	Rh1	C20	C25	121.00
C21	Rh1	C20	C19	118.42

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C21	Rh1	C20	C25	-120.58
O4	Rh1	C20	C19	-25.03
O4	Rh1	C20	C21	-143.46
O4	Rh1	C20	C25	95.97
O1	Rh1	C21	C17	-177.90
O1	Rh1	C21	C20	-59.49
O1	Rh1	C21	C26	62.07
O2	Rh1	C21	C17	98.21
O2	Rh1	C21	C20	-143.39
O2	Rh1	C21	C26	-21.82
C17	Rh1	C21	C20	118.40
C17	Rh1	C21	C26	-120.03
C18	Rh1	C21	C17	-37.39
C18	Rh1	C21	C20	81.01
C18	Rh1	C21	C26	-157.42
C19	Rh1	C21	C17	-80.58
C19	Rh1	C21	C20	37.82
C19	Rh1	C21	C26	159.39
C20	Rh1	C21	C17	-118.40
C20	Rh1	C21	C26	121.57
O4	Rh1	C21	C17	10.63
O4	Rh1	C21	C20	129.03
O4	Rh1	C21	C26	-109.40
O1	Rh1	O4	H40	51.34
O1	Rh1	O4	C27	-162.20
O2	Rh1	O4	H40	131.76
O2	Rh1	O4	C27	-81.79
C17	Rh1	O4	H40	-128.40
C17	Rh1	O4	C27	18.05
C18	Rh1	O4	H40	-92.86
C18	Rh1	O4	C27	53.59
C19	Rh1	O4	H40	-54.48
C19	Rh1	O4	C27	91.97
C20	Rh1	O4	H40	-37.51
C20	Rh1	O4	C27	108.94
C21	Rh1	O4	H40	-136.09
C21	Rh1	O4	C27	10.37
Rh1	O1	C1	C2	8.52
Rh1	O1	C1	C9	-171.57
Rh1	O2	C2	C1	-7.43
Rh1	O2	C2	C3	171.61
C9	O3	C8	C3	1.14
C9	O3	C8	C7	-179.00
C8	O3	C9	C1	-2.40
C8	O3	C9	C10	176.22
O1	C1	C2	O2	-0.49
O1	C1	C2	C3	-179.56
C9	C1	C2	O2	179.60
C9	C1	C2	C3	0.53
O1	C1	C9	O3	-178.39
O1	C1	C9	C10	3.21
C2	C1	C9	O3	1.52
C2	C1	C9	C10	-176.88
O2	C2	C3	C4	-1.82
O2	C2	C3	C8	179.24
C1	C2	C3	C4	177.22
C1	C2	C3	C8	-1.71
C2	C3	C4	H4	0.54
C2	C3	C4	C5	-179.46
C8	C3	C4	H4	179.48
C8	C3	C4	C5	-0.52
C2	C3	C8	O3	0.93
C2	C3	C8	C7	-178.92
C4	C3	C8	O3	-178.05
C4	C3	C8	C7	2.10
C3	C4	C5	H5	178.51
C3	C4	C5	C6	-1.49
H4	C4	C5	H5	-1.48
H4	C4	C5	C6	178.52
C4	C5	C6	H6	-178.00
C4	C5	C6	C7	2.00
H5	C5	C6	H6	2.00
H5	C5	C6	C7	-178.00
C5	C6	C7	H7	179.54
C5	C6	C7	C8	-0.46
H6	C6	C7	H7	-0.46
H6	C6	C7	C8	179.54
C6	C7	C8	O3	178.53
C6	C7	C8	C3	-1.61
H7	C7	C8	O3	-1.47
H7	C7	C8	C3	178.39
O3	C9	C10	C11	-176.58
O3	C9	C10	C15	2.85
C1	C9	C10	C11	1.94
C1	C9	C10	C15	-178.63
C9	C10	C11	H11	-0.27

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C9	C10	C11	C12	179.73
C15	C10	C11	H11	-179.72
C15	C10	C11	C12	0.29
C9	C10	C15	C14	-179.56
C9	C10	C15	H15	0.44
C11	C10	C15	C14	-0.10
C11	C10	C15	H15	179.90
C10	C11	C12	H12	-179.64
C10	C11	C12	C13	0.36
H11	C11	C12	H12	0.36
H11	C11	C12	C13	-179.64
C11	C12	C13	C14	-1.16
C11	C12	C13	C16	179.21
H12	C12	C13	C14	178.83
H12	C12	C13	C16	-0.80
C12	C13	C14	H14	-178.64
C12	C13	C14	C15	1.36
C16	C13	C14	H14	0.97
C16	C13	C14	C15	-179.03
C12	C13	C16	H16A	75.87
C12	C13	C16	H16B	-44.13
C12	C13	C16	H16C	-164.13
C14	C13	C16	H16A	-103.74
C14	C13	C16	H16B	136.26
C14	C13	C16	H16C	16.26
C13	C14	C15	C10	-0.74
C13	C14	C15	H15	179.26
H14	C14	C15	C10	179.26
H14	C14	C15	H15	-0.74
Rh1	C17	C18	C19	58.38
Rh1	C17	C18	C23	-122.17
C21	C17	C18	Rh1	-59.88
C21	C17	C18	C19	-1.50
C21	C17	C18	C23	177.95
C22	C17	C18	Rh1	120.61
C22	C17	C18	C19	178.99
C22	C17	C18	C23	-1.56
Rh1	C17	C21	C20	-60.97
Rh1	C17	C21	C26	121.79
C18	C17	C21	Rh1	61.26
C18	C17	C21	C20	0.29
C18	C17	C21	C26	-176.95
C22	C17	C21	Rh1	-119.21
C22	C17	C21	C20	179.82
C22	C17	C21	C26	2.58
Rh1	C17	C22	H22A	75.99
Rh1	C17	C22	H22B	-44.01
Rh1	C17	C22	H22C	-164.01
C18	C17	C22	H22A	-17.02
C18	C17	C22	H22B	-137.02
C18	C17	C22	H22C	102.98
C21	C17	C22	H22A	163.55
C21	C17	C22	H22B	43.55
C21	C17	C22	H22C	-76.45
Rh1	C18	C19	C20	61.10
Rh1	C18	C19	C24	-121.95
C17	C18	C19	Rh1	-58.97
C17	C18	C19	C20	2.14
C17	C18	C19	C24	179.08
C23	C18	C19	Rh1	121.56
C23	C18	C19	C20	-177.33
C23	C18	C19	C24	-0.39
Rh1	C18	C23	H23A	164.20
Rh1	C18	C23	H23B	44.20
Rh1	C18	C23	H23C	-75.80
C17	C18	C23	H23A	-103.32
C17	C18	C23	H23B	136.69
C17	C18	C23	H23C	16.69
C19	C18	C23	H23A	76.05
C19	C18	C23	H23B	-43.95
C19	C18	C23	H23C	-163.95
Rh1	C19	C20	C21	60.16
Rh1	C19	C20	C25	-117.53
C18	C19	C20	Rh1	-62.09
C18	C19	C20	C21	-1.94
C18	C19	C20	C25	-179.62
C24	C19	C20	Rh1	121.01
C24	C19	C20	C21	-178.83
C24	C19	C20	C25	3.48
Rh1	C19	C24	H24A	59.05
Rh1	C19	C24	H24B	-60.95
Rh1	C19	C24	H24C	179.05
C18	C19	C24	H24A	151.50
C18	C19	C24	H24B	31.50
C18	C19	C24	H24C	-88.50
C20	C19	C24	H24A	-32.13

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C20	C19	C24	H24B	-152.13
C20	C19	C24	H24C	87.87
Rh1	C20	C21	C17	61.34
Rh1	C20	C21	C26	-121.48
C19	C20	C21	Rh1	-60.32
C19	C20	C21	C17	1.03
C19	C20	C21	C26	178.21
C25	C20	C21	Rh1	117.38
C25	C20	C21	C17	178.72
C25	C20	C21	C26	-4.10
Rh1	C20	C25	H25A	60.06
Rh1	C20	C25	H25B	-59.94
Rh1	C20	C25	H25C	-179.94
C19	C20	C25	H25A	148.95
C19	C20	C25	H25B	28.95
C19	C20	C25	H25C	-91.05
C21	C20	C25	H25A	-28.33
C21	C20	C25	H25B	-148.33
C21	C20	C25	H25C	91.67
Rh1	C21	C26	H26A	172.18
Rh1	C21	C26	H26B	52.18
Rh1	C21	C26	H26C	-67.82
C17	C21	C26	H26A	80.70
C17	C21	C26	H26B	-39.29
C17	C21	C26	H26C	-159.29
C20	C21	C26	H26A	-96.03
C20	C21	C26	H26B	143.97
C20	C21	C26	H26C	23.97
Rh1	O4	C27	H27A	-113.92
Rh1	O4	C27	H27B	126.08
Rh1	O4	C27	H27C	6.08
H40	O4	C27	H27A	36.11
H40	O4	C27	H27B	-83.89
H40	O4	C27	H27C	156.11
O5	S1	C28	F1	-62.98
O5	S1	C28	F2	57.34
O5	S1	C28	F3	177.32
O6	S1	C28	F1	175.22
O6	S1	C28	F2	-64.46
O6	S1	C28	F3	55.52
O7	S1	C28	F1	56.55
O7	S1	C28	F2	176.87
O7	S1	C28	F3	-63.15
O8	C29	C29	O8	180.00

Synthesis and characterization of trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-fluorophenyl)-chromen-4-onato-κ*O*](*η*^{5}-pentamethylcyclopentadienyl)rhodium(III) C5

Bond lengths [Å]

Atom1	Atom2	Length	Atom1	Atom2	Length
Rh1	O1	2.0616(1)	C14	C15	1.3722
Rh1	O2	2.1155(1)	C15	H15	0.9500
Rh1	C16	2.1492(1)	C16	C17	1.4415
Rh1	C17	2.1121(1)	C16	C20	1.4164
Rh1	C18	2.1085(1)	C16	C21	1.4840
Rh1	C19	2.0925(1)	C17	C18	1.4284
Rh1	C20	2.1182(1)	C17	C22	1.4884
Rh1	O6	2.2208(1)	C18	C19	1.4300
O1	C1	1.3230	C18	C23	1.4986
O2	C2	1.2684	C19	C20	1.4405
O3	C8	1.3634	C19	C24	1.4916
O3	C9	1.3710	C20	C25	1.4985
F4	C13	1.3705	C21	H21A	0.9800
C1	C2	1.4301	C21	H21B	0.9800
C1	C9	1.3746	C21	H21C	0.9800
C2	C3	1.4382	C22	H22A	0.9800
C3	C4	1.3995	C22	H22B	0.9800
C3	C8	1.3901	C22	H22C	0.9800
C4	H4	0.9500	C23	H23A	0.9800
C4	C5	1.3654	C23	H23B	0.9800
C5	H5	0.9500	C23	H23C	0.9800
C5	C6	1.3944	C24	H24A	0.9800
C6	H6	0.9500	C24	H24B	0.9800
C6	C7	1.3790	C24	H24C	0.9800
C7	H7	0.9500	C25	H25A	0.9800
C7	C8	1.3876	C25	H25B	0.9800
C9	C10	1.4618	C25	H25C	0.9800
C10	C11	1.4017	S1	O4	1.4247
C10	C15	1.3919	S1	O5	1.4277
C11	H11	0.9500	S1	O6	1.4625(1)
C11	C12	1.3917	S1	C26	1.8172
C12	H12	0.9500	F1	C26	1.3221
C12	C13	1.3609	F2	C26	1.3378
C13	C14	1.3614	F3	C26	1.3279
C14	H14	0.9500			

Bond angles [°]

Atom1	Atom2	Atom3	Angle
O1	Rh1	O2	79.12
O1	Rh1	C16	151.17
O1	Rh1	C17	112.55
O1	Rh1	C18	96.35
O1	Rh1	C19	115.43
O1	Rh1	C20	155.11
O1	Rh1	O6	83.41
O2	Rh1	C16	129.63
O2	Rh1	C17	165.79
O2	Rh1	C18	134.39
O2	Rh1	C19	101.33
O2	Rh1	C20	99.63
O2	Rh1	O6	82.20
C16	Rh1	C17	39.53
C16	Rh1	C18	65.96
C16	Rh1	C19	66.10
C16	Rh1	C20	38.76
C16	Rh1	O6	97.24
C17	Rh1	C18	39.56
C17	Rh1	C19	66.80
C17	Rh1	C20	66.33
C17	Rh1	O6	106.52
C18	Rh1	C19	39.80
C18	Rh1	C20	66.53
C18	Rh1	O6	142.90
C19	Rh1	C20	40.00
C19	Rh1	O6	161.15
C20	Rh1	O6	121.26
Rh1	O1	C1	112.10
Rh1	O2	C2	111.26
C8	O3	C9	121.30
O1	C1	C2	117.26
O1	C1	C9	123.23
C2	C1	C9	119.50
O2	C2	C1	119.45
O2	C2	C3	121.66
C1	C2	C3	118.88
C2	C3	C4	123.16
C2	C3	C8	118.03
C4	C3	C8	118.80
C3	C4	H4	120.06
C3	C4	C5	119.88
H4	C4	C5	120.06
C4	C5	H5	119.66
C4	C5	C6	120.68
H5	C5	C6	119.66
C5	C6	H6	119.74
C5	C6	C7	120.51
H6	C6	C7	119.75
C6	C7	H7	120.74
C6	C7	C8	118.53
H7	C7	C8	120.74
O3	C8	C3	121.50
O3	C8	C7	116.93
C3	C8	C7	121.57
O3	C9	C1	120.73
O3	C9	C10	110.95
C1	C9	C10	128.30
C9	C10	C11	122.08
C9	C10	C15	119.87
C11	C10	C15	118.05
C10	C11	H11	119.78
C10	C11	C12	120.44
H11	C11	C12	119.78
C11	C12	H12	120.87
C11	C12	C13	118.27
H12	C12	C13	120.87
F4	C13	C12	118.37
F4	C13	C14	118.25
C12	C13	C14	123.38
C13	C14	H14	120.86
C13	C14	C15	118.29
H14	C14	C15	120.86
C10	C15	C14	121.58
C10	C15	H15	119.21
C14	C15	H15	119.21
Rh1	C16	C17	68.85
Rh1	C16	C20	69.43
Rh1	C16	C21	127.16
C17	C16	C20	108.13
C17	C16	C21	125.25
C20	C16	C21	126.61
Rh1	C17	C16	71.62
Rh1	C17	C18	70.08
Rh1	C17	C22	125.69
C16	C17	C18	107.74

Bond angles [°]

Atom1	Atom2	Atom3	Angle
C16	C17	C22	125.03
C18	C17	C22	127.18
Rh1	C18	C17	70.36
Rh1	C18	C19	69.50
Rh1	C18	C23	123.61
C17	C18	C19	108.15
C17	C18	C23	126.79
C19	C18	C23	125.00
Rh1	C19	C18	70.70
Rh1	C19	C20	70.96
Rh1	C19	C24	125.38
C18	C19	C20	107.74
C18	C19	C24	126.44
C20	C19	C24	125.79
Rh1	C20	C16	71.81
Rh1	C20	C19	69.04
Rh1	C20	C25	123.79
C16	C20	C19	108.18
C16	C20	C25	125.68
C19	C20	C25	126.13
C16	C21	H21A	109.47
C16	C21	H21B	109.47
C16	C21	H21C	109.47
H21A	C21	H21B	109.47
H21A	C21	H21C	109.47
H21B	C21	H21C	109.47
C17	C22	H22A	109.47
C17	C22	H22B	109.47
C17	C22	H22C	109.47
H22A	C22	H22B	109.47
H22A	C22	H22C	109.47
H22B	C22	H22C	109.47
C18	C23	H23A	109.47
C18	C23	H23B	109.47
C18	C23	H23C	109.47
H23A	C23	H23B	109.47
H23A	C23	H23C	109.47
H23B	C23	H23C	109.47
C19	C24	H24A	109.47
C19	C24	H24B	109.47
C19	C24	H24C	109.47
H24A	C24	H24B	109.47
H24A	C24	H24C	109.47
H24B	C24	H24C	109.47
C20	C25	H25A	109.47
C20	C25	H25B	109.47
C20	C25	H25C	109.47
H25A	C25	H25B	109.47
H25A	C25	H25C	109.47
H25B	C25	H25C	109.47
O4	S1	O5	117.02
O4	S1	O6	114.92
O4	S1	C26	103.37
O5	S1	O6	113.98
O5	S1	C26	104.03
O6	S1	C26	100.64
Rh1	O6	S1	122.64
S1	C26	F1	112.06
S1	C26	F2	110.35
S1	C26	F3	111.52
F1	C26	F2	107.24
F1	C26	F3	107.55
F2	C26	F3	107.92

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
O2	Rh1	O1	C1	7.75
C16	Rh1	O1	C1	-168.57
C17	Rh1	O1	C1	179.27
C18	Rh1	O1	C1	141.80
C19	Rh1	O1	C1	105.22
C20	Rh1	O1	C1	97.21
O6	Rh1	O1	C1	-75.54
O1	Rh1	O2	C2	-7.34
C16	Rh1	O2	C2	170.36
C17	Rh1	O2	C2	-153.66
C18	Rh1	O2	C2	-95.60
C19	Rh1	O2	C2	-121.39
C20	Rh1	O2	C2	-162.07
O6	Rh1	O2	C2	77.40
O1	Rh1	C16	C17	-17.79
O1	Rh1	C16	C20	-137.89
O1	Rh1	C16	C21	101.12
O2	Rh1	C16	C17	166.91
O2	Rh1	C16	C20	46.80
O2	Rh1	C16	C21	-74.19
C17	Rh1	C16	C20	-120.10
C17	Rh1	C16	C21	118.90
C18	Rh1	C16	C17	38.21
C18	Rh1	C16	C20	-81.89
C18	Rh1	C16	C21	157.11
C19	Rh1	C16	C17	81.95
C19	Rh1	C16	C20	-38.15
C19	Rh1	C16	C21	-159.15
C20	Rh1	C16	C17	120.10
C20	Rh1	C16	C21	-120.99
O6	Rh1	C16	C17	-107.25
O6	Rh1	C16	C20	132.65
O6	Rh1	C16	C21	11.65
O1	Rh1	C17	C16	170.82
O1	Rh1	C17	C18	-71.67
O1	Rh1	C17	C22	50.42
O2	Rh1	C17	C16	-45.31
O2	Rh1	C17	C18	72.20
O2	Rh1	C17	C22	-165.72
C16	Rh1	C17	C18	117.51
C16	Rh1	C17	C22	-120.41
C18	Rh1	C17	C16	-117.51
C18	Rh1	C17	C22	122.08
C19	Rh1	C17	C16	-80.03
C19	Rh1	C17	C18	37.48
C19	Rh1	C17	C22	159.56
C20	Rh1	C17	C16	-36.26
C20	Rh1	C17	C18	81.25
C20	Rh1	C17	C22	-156.66
O6	Rh1	C17	C16	81.20
O6	Rh1	C17	C18	-161.29
O6	Rh1	C17	C22	-39.21
O1	Rh1	C18	C17	118.11
O1	Rh1	C18	C19	-122.78
O1	Rh1	C18	C23	-3.65
O2	Rh1	C18	C17	-160.91
O2	Rh1	C18	C19	-41.80
O2	Rh1	C18	C23	77.33
C16	Rh1	C18	C17	-38.18
C16	Rh1	C18	C19	80.93
C16	Rh1	C18	C23	-159.94
C17	Rh1	C18	C19	119.11
C17	Rh1	C18	C23	-121.76
C19	Rh1	C18	C17	-119.11
C19	Rh1	C18	C23	119.13
C20	Rh1	C18	C17	-80.69
C20	Rh1	C18	C19	38.42
C20	Rh1	C18	C23	157.55
O6	Rh1	C18	C17	30.65
O6	Rh1	C18	C19	149.76
O6	Rh1	C18	C23	-91.11
O1	Rh1	C19	C18	67.70
O1	Rh1	C19	C20	-174.76
O1	Rh1	C19	C24	-53.84
O2	Rh1	C19	C18	150.94
O2	Rh1	C19	C20	-91.53
O2	Rh1	C19	C24	29.39
C16	Rh1	C19	C18	-80.55
C16	Rh1	C19	C20	36.99
C16	Rh1	C19	C24	157.90
C17	Rh1	C19	C18	-37.26
C17	Rh1	C19	C20	80.28
C17	Rh1	C19	C24	-158.81
C18	Rh1	C19	C20	117.54
C18	Rh1	C19	C24	-121.55
C20	Rh1	C19	C18	-117.54

Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C20	Rh1	C19	C24	120.92
O6	Rh1	C19	C18	-109.94
O6	Rh1	C19	C20	7.59
O6	Rh1	C19	C24	128.51
O1	Rh1	C20	C16	129.83
O1	Rh1	C20	C19	11.30
O1	Rh1	C20	C25	-108.93
O2	Rh1	C20	C16	-145.29
O2	Rh1	C20	C19	96.19
O2	Rh1	C20	C25	-24.04
C16	Rh1	C20	C19	-118.52
C16	Rh1	C20	C25	121.25
C17	Rh1	C20	C16	36.96
C17	Rh1	C20	C19	-81.57
C17	Rh1	C20	C25	158.21
C18	Rh1	C20	C16	80.30
C18	Rh1	C20	C19	-38.23
C18	Rh1	C20	C25	-158.45
C19	Rh1	C20	C16	118.52
C19	Rh1	C20	C25	-120.23
O6	Rh1	C20	C16	-58.61
O6	Rh1	C20	C19	-177.14
O6	Rh1	C20	C25	62.64
O1	Rh1	O6	S1	128.45
O2	Rh1	O6	S1	48.58
C16	Rh1	O6	S1	-80.58
C17	Rh1	O6	S1	-119.93
C18	Rh1	O6	S1	-139.73
C19	Rh1	O6	S1	-53.69
C20	Rh1	O6	S1	-47.99
Rh1	O1	C1	C2	-7.29
Rh1	O1	C1	C9	173.66
Rh1	O2	C2	C1	5.90
Rh1	O2	C2	C3	-174.61
C9	O3	C8	C3	2.31
C9	O3	C8	C7	-177.79
C8	O3	C9	C1	-3.13
C8	O3	C9	C10	178.51
O1	C1	C2	O2	0.83
O1	C1	C2	C3	-178.67
C9	C1	C2	O2	179.91
C9	C1	C2	C3	0.41
O1	C1	C9	O3	-179.25
O1	C1	C9	C10	-1.20
C2	C1	C9	O3	1.73
C2	C1	C9	C10	179.78
O2	C2	C3	C4	-2.05
O2	C2	C3	C8	179.31
C1	C2	C3	C4	177.45
C1	C2	C3	C8	-1.19
C2	C3	C4	H4	1.85
C2	C3	C4	C5	-178.15
C8	C3	C4	H4	-179.52
C8	C3	C4	C5	0.48
C2	C3	C8	O3	-0.13
C2	C3	C8	C7	179.97
C4	C3	C8	O3	-178.83
C4	C3	C8	C7	1.27
C3	C4	C5	H5	178.47
C3	C4	C5	C6	-1.53
H4	C4	C5	H5	-1.53
H4	C4	C5	C6	178.47
C4	C5	C6	H6	-179.14
C4	C5	C6	C7	0.86
H5	C5	C6	H6	0.86
H5	C5	C6	C7	-179.14
C5	C6	C7	H7	-179.15
C5	C6	C7	C8	0.85
H6	C6	C7	H7	0.85
H6	C6	C7	C8	-179.15
C6	C7	C8	O3	178.17
C6	C7	C8	C3	-1.92
H7	C7	C8	O3	-1.83
H7	C7	C8	C3	178.08
O3	C9	C10	C11	-178.16
O3	C9	C10	C15	1.71
C1	C9	C10	C11	3.63
C1	C9	C10	C15	-176.50
C9	C10	C11	H11	-0.01
C9	C10	C11	C12	179.99
C15	C10	C11	H11	-179.88
C15	C10	C11	C12	0.12
C9	C10	C15	C14	-179.97
C9	C10	C15	H15	0.03
C11	C10	C15	C14	-0.10
C11	C10	C15	H15	179.90

Torsion angles [°]

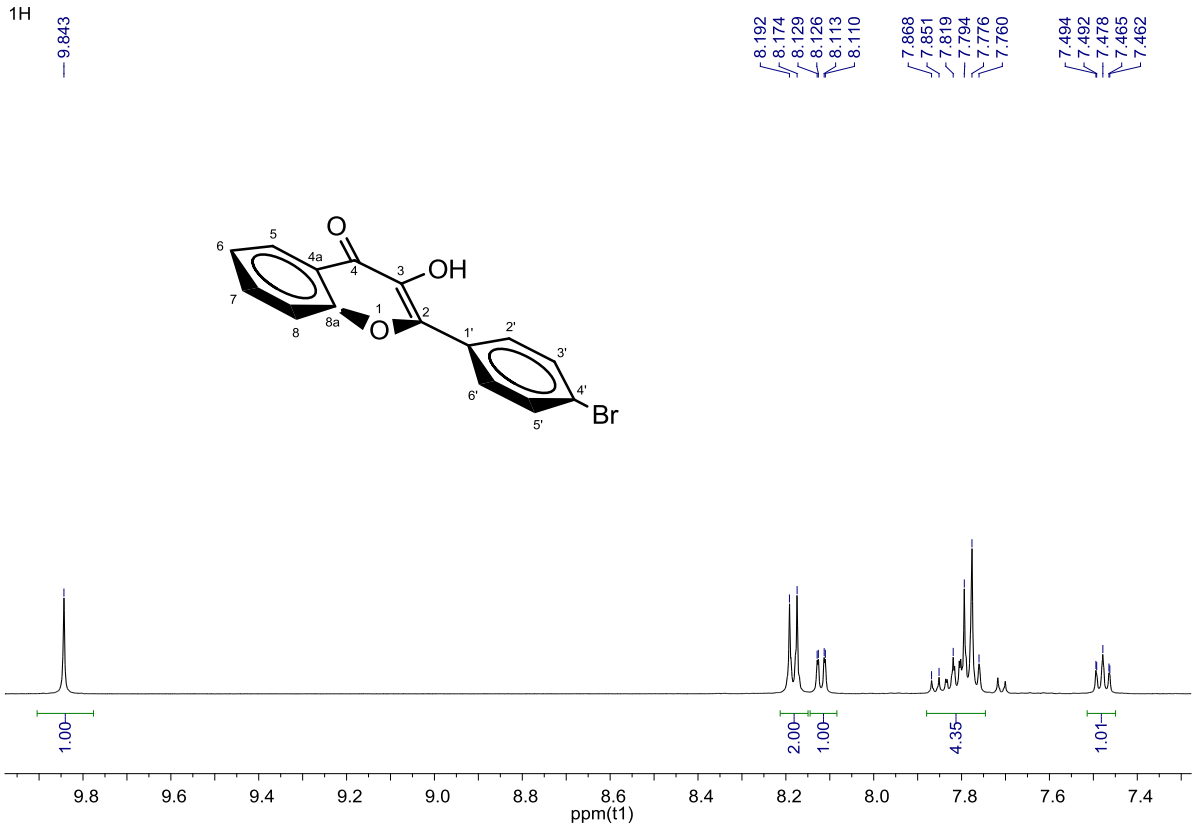
Atom1	Atom2	Atom3	Atom4	Torsion
C10	C11	C12	H12	179.99
C10	C11	C12	C13	-0.01
H11	C11	C12	H12	-0.01
H11	C11	C12	C13	179.99
C11	C12	C13	F4	-179.62
C11	C12	C13	C14	-0.14
H12	C12	C13	F4	0.38
H12	C12	C13	C14	179.86
F4	C13	C14	H14	-0.35
F4	C13	C14	C15	179.65
C12	C13	C14	H14	-179.83
C12	C13	C14	C15	0.17
C13	C14	C15	C10	-0.04
C13	C14	C15	H15	179.96
H14	C14	C15	C10	179.96
H14	C14	C15	H15	-0.04
Rh1	C16	C17	C18	-61.10
Rh1	C16	C17	C22	121.19
C20	C16	C17	Rh1	58.46
C20	C16	C17	C18	-2.64
C20	C16	C17	C22	179.65
C21	C16	C17	Rh1	-121.30
C21	C16	C17	C18	177.59
C21	C16	C17	C22	-0.11
Rh1	C16	C20	C19	59.72
Rh1	C16	C20	C25	-119.00
C17	C16	C20	Rh1	-58.10
C17	C16	C20	C19	1.62
C17	C16	C20	C25	-177.10
C21	C16	C20	Rh1	121.66
C21	C16	C20	C19	-178.62
C21	C16	C20	C25	2.66
Rh1	C16	C21	H21A	65.46
Rh1	C16	C21	H21B	-54.54
Rh1	C16	C21	H21C	-174.54
C17	C16	C21	H21A	154.38
C17	C16	C21	H21B	34.38
C17	C16	C21	H21C	-85.62
C20	C16	C21	H21A	-25.34
C20	C16	C21	H21B	-145.34
C20	C16	C21	H21C	94.66
Rh1	C17	C18	C19	-59.45
Rh1	C17	C18	C23	117.84
C16	C17	C18	Rh1	62.09
C16	C17	C18	C19	2.65
C16	C17	C18	C23	179.93
C22	C17	C18	Rh1	-120.27
C22	C17	C18	C19	-179.71
C22	C17	C18	C23	-2.43
Rh1	C17	C22	H22A	176.77
Rh1	C17	C22	H22B	56.77
Rh1	C17	C22	H22C	-63.23
C16	C17	C22	H22A	85.08
C16	C17	C22	H22B	-34.92
C16	C17	C22	H22C	-154.92
C18	C17	C22	H22A	-92.18
C18	C17	C22	H22B	147.82
C18	C17	C22	H22C	27.82
Rh1	C18	C19	C20	-61.64
Rh1	C18	C19	C24	120.27
C17	C18	C19	Rh1	59.99
C17	C18	C19	C20	-1.66
C17	C18	C19	C24	-179.75
C23	C18	C19	Rh1	-117.36
C23	C18	C19	C20	-179.00
C23	C18	C19	C24	2.91
Rh1	C18	C23	H23A	78.98
Rh1	C18	C23	H23B	-41.02
Rh1	C18	C23	H23C	-161.02
C17	C18	C23	H23A	-10.62
C17	C18	C23	H23B	-130.61
C17	C18	C23	H23C	109.38
C19	C18	C23	H23A	166.23
C19	C18	C23	H23B	46.23
C19	C18	C23	H23C	-73.77
Rh1	C19	C20	C16	-61.46
Rh1	C19	C20	C25	117.25
C18	C19	C20	Rh1	61.48
C18	C19	C20	C16	0.02
C18	C19	C20	C25	178.73
C24	C19	C20	Rh1	-120.41
C24	C19	C20	C16	178.12
C24	C19	C20	C25	-3.17
Rh1	C19	C24	H24A	-171.03
Rh1	C19	C24	H24B	68.97
Rh1	C19	C24	H24C	-51.03

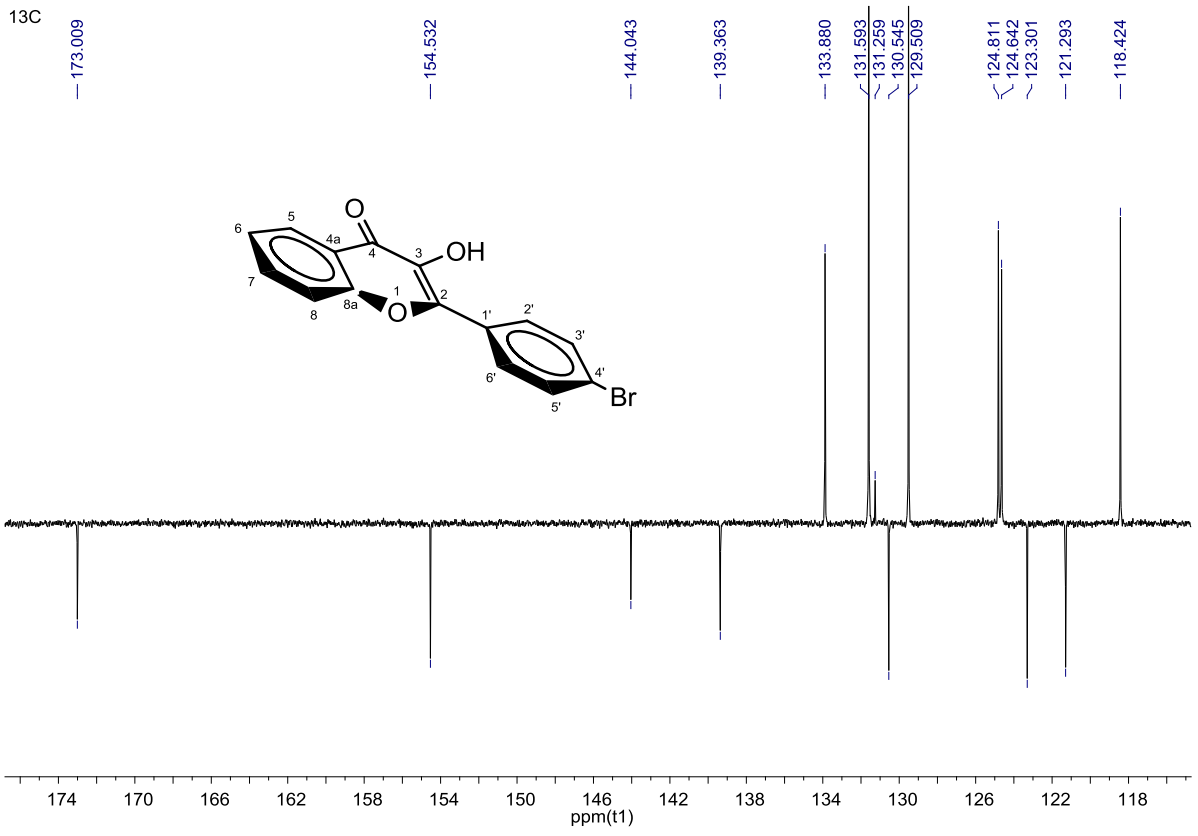
Torsion angles [°]

Atom1	Atom2	Atom3	Atom4	Torsion
C18	C19	C24	H24A	97.80
C18	C19	C24	H24B	-22.20
C18	C19	C24	H24C	-142.20
C20	C19	C24	H24A	-79.96
C20	C19	C24	H24B	160.05
C20	C19	C24	H24C	40.04
Rh1	C20	C25	H25A	-161.84
Rh1	C20	C25	H25B	78.16
Rh1	C20	C25	H25C	-41.84
C16	C20	C25	H25A	-70.81
C16	C20	C25	H25B	169.19
C16	C20	C25	H25C	49.19
C19	C20	C25	H25A	110.70
C19	C20	C25	H25B	-9.30
C19	C20	C25	H25C	-129.30
O4	S1	O6	Rh1	-101.31
O5	S1	O6	Rh1	37.71
C26	S1	O6	Rh1	148.41
O4	S1	C26	F1	-59.17
O4	S1	C26	F2	60.27
O4	S1	C26	F3	-179.81
O5	S1	C26	F1	178.10
O5	S1	C26	F2	-62.46
O5	S1	C26	F3	57.46
O6	S1	C26	F1	59.86
O6	S1	C26	F2	179.30
O6	S1	C26	F3	-60.78

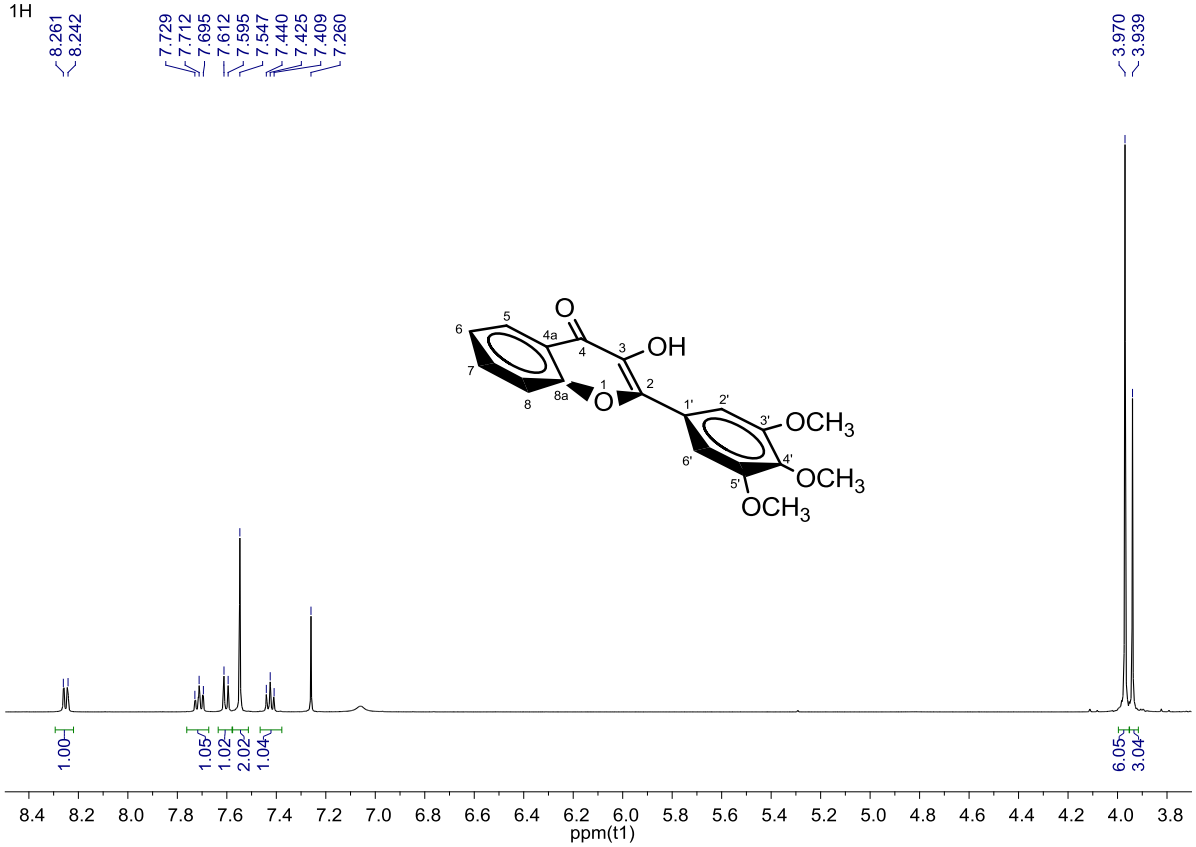
5.2 ^{1}H and ^{13}C NMR spectroscopy

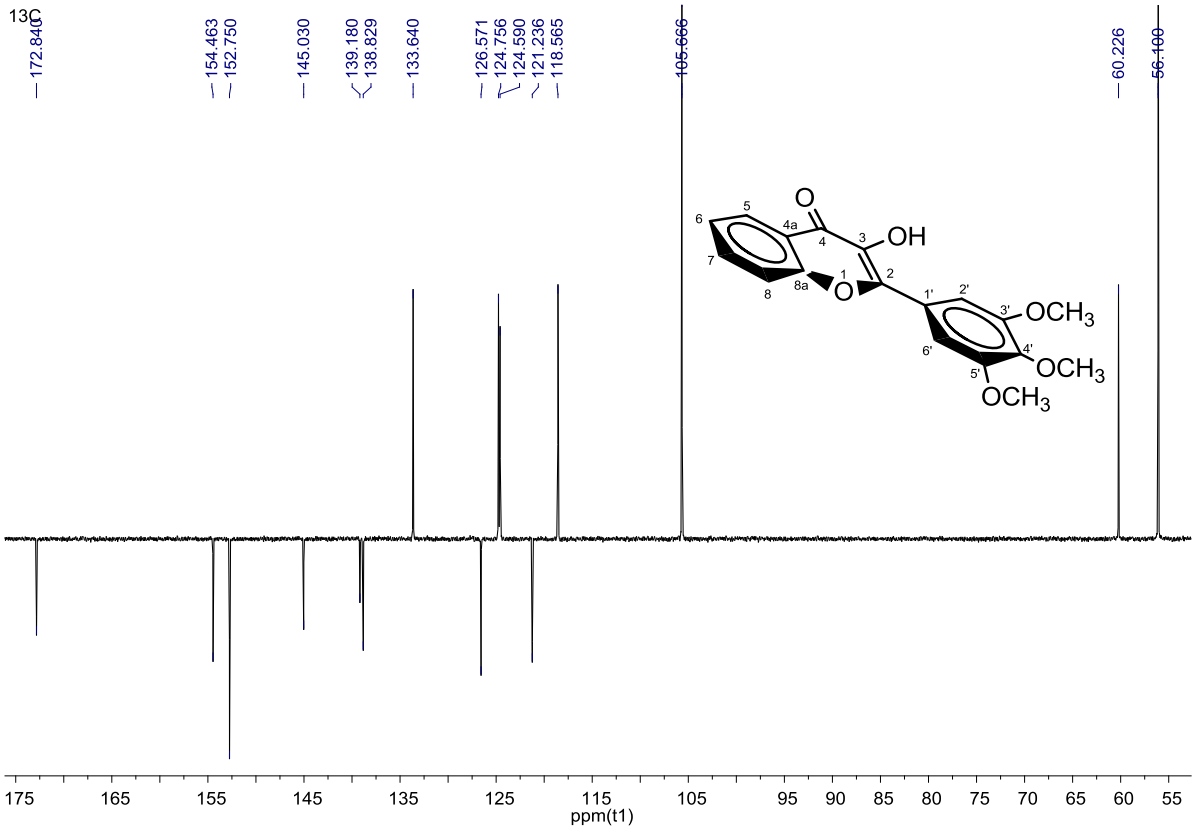
3-Hydroxy-2-(4-bromophenyl)-4H-chromen-4-one L1



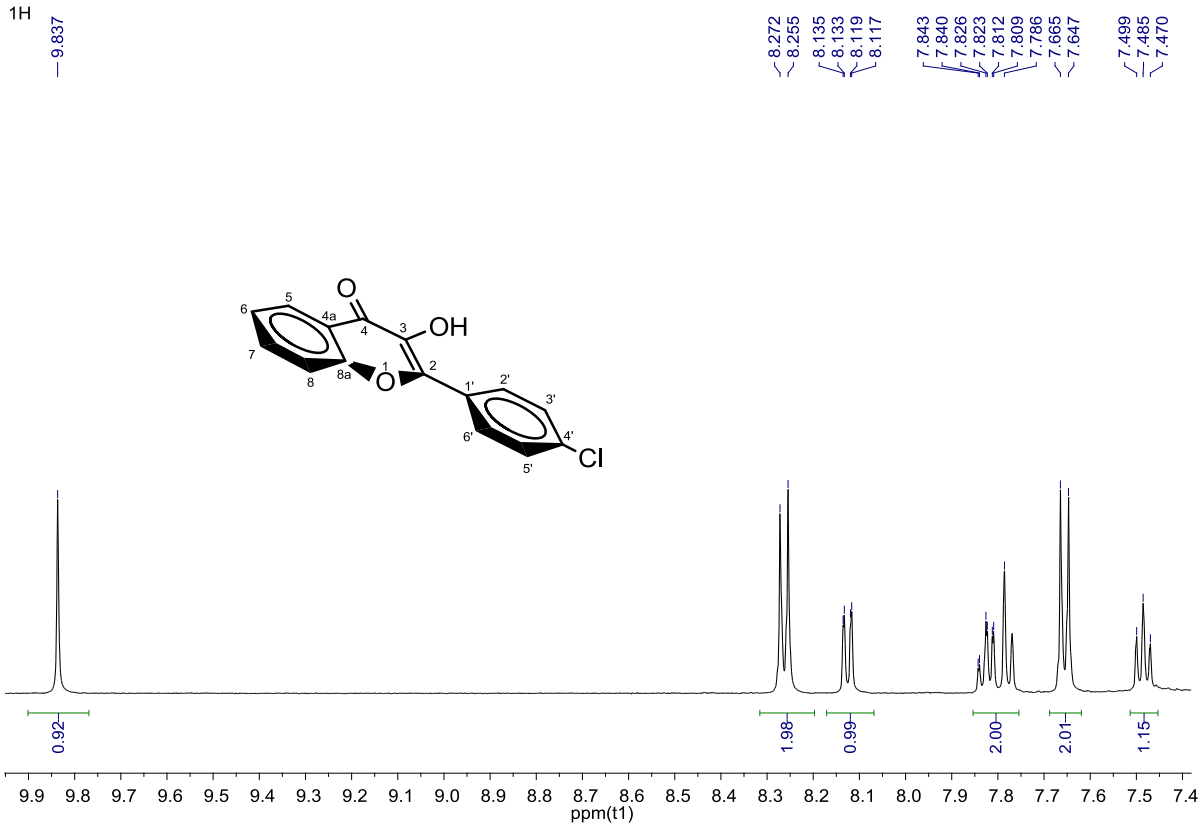


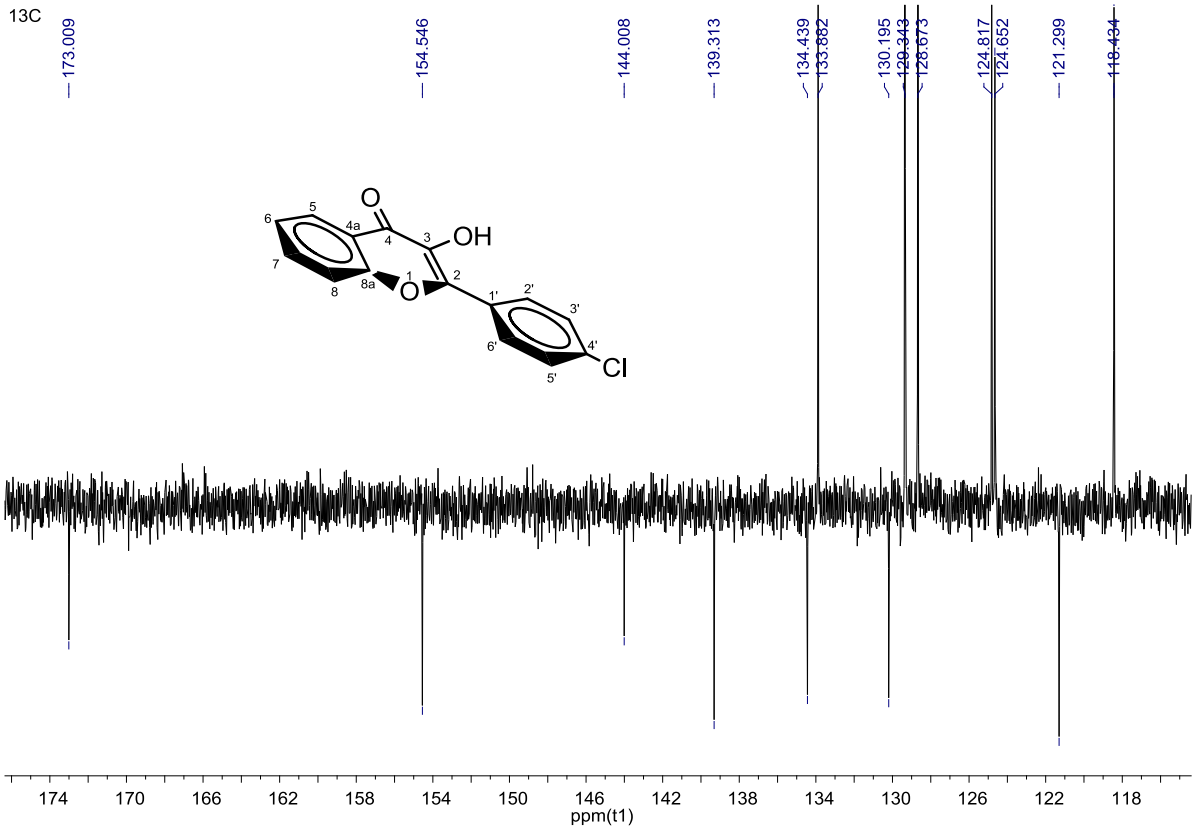
3-Hydroxy-2-(3,4,5-trimethoxyphenyl)-4H-chromen-4-one L2



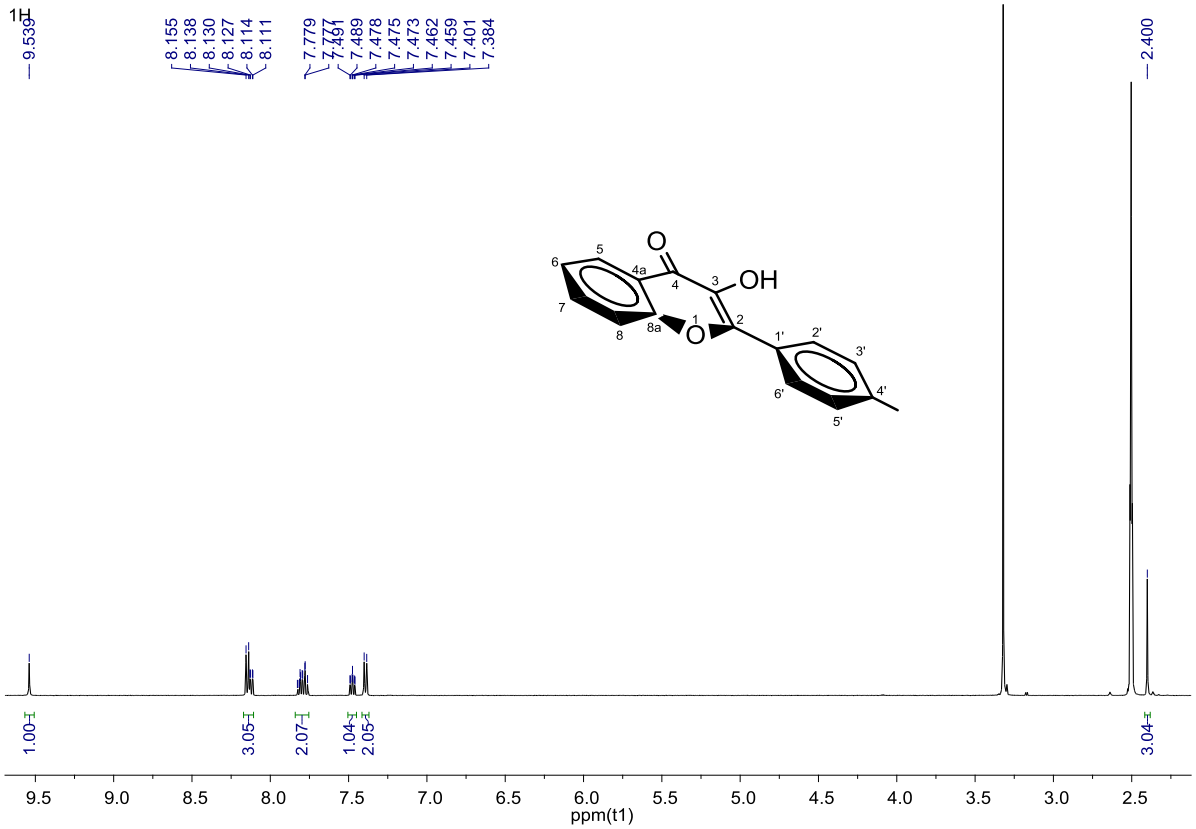


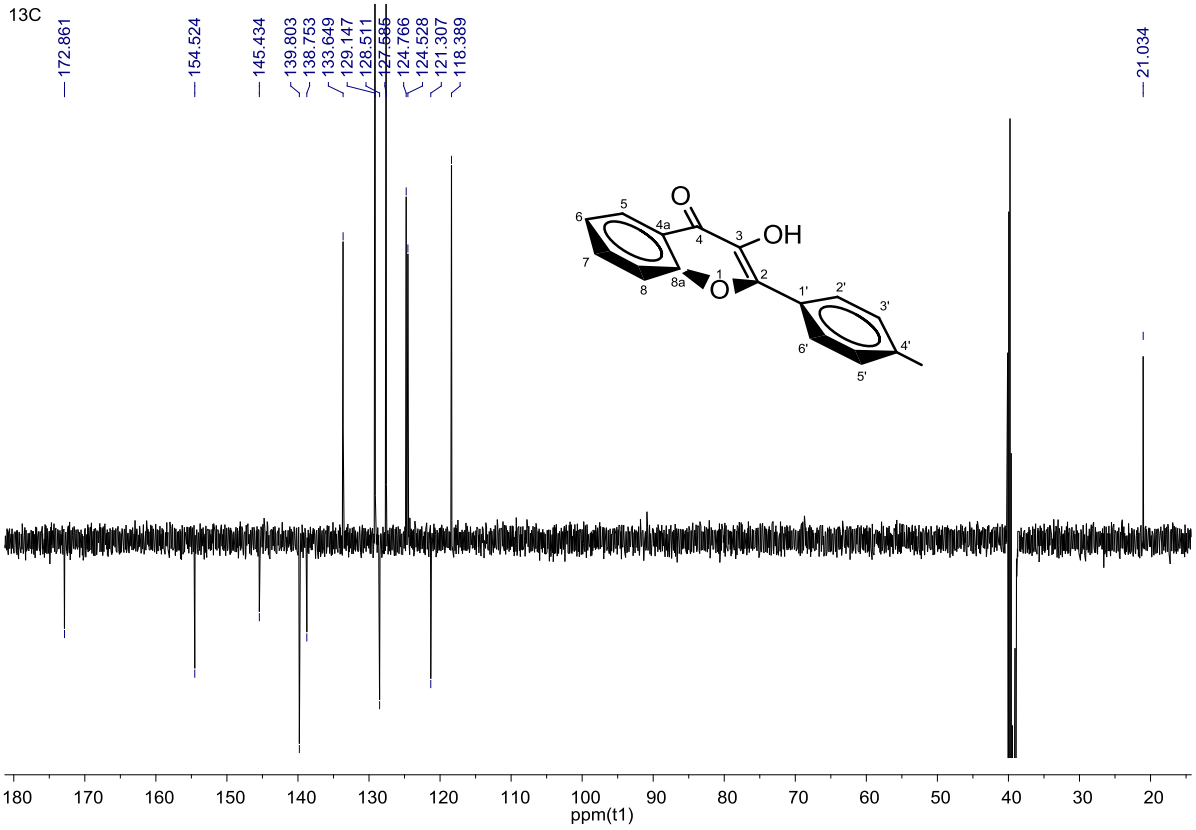
3-Hydroxy-2-(4-chlorophenyl)-4H-chromen-4-one L3



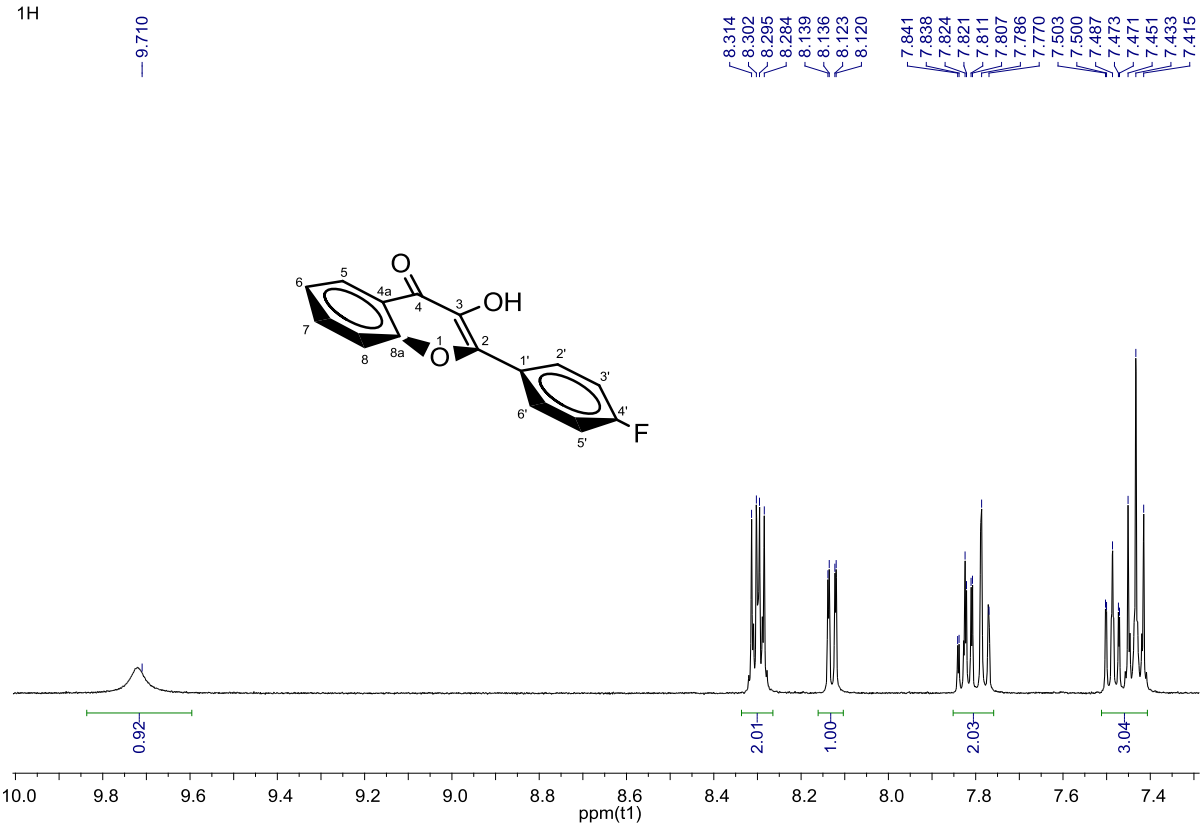


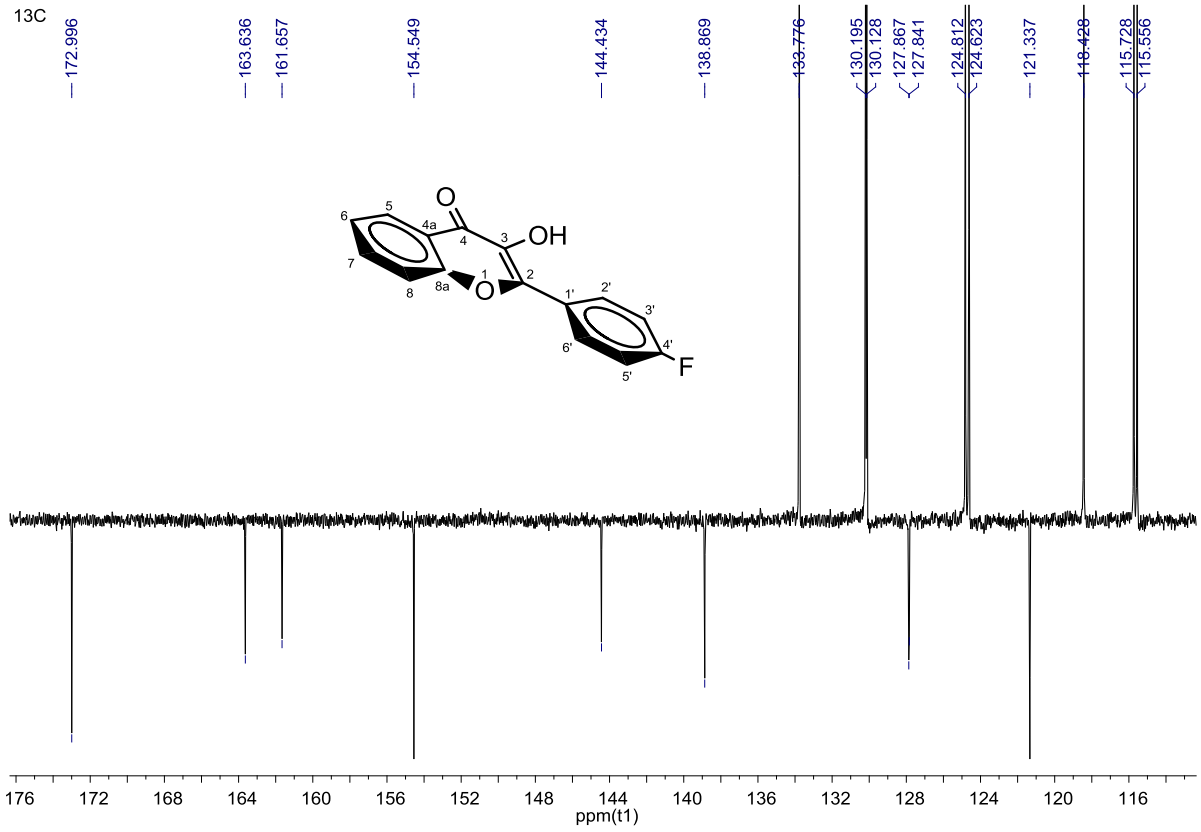
3-Hydroxy-2-(4-methylphenyl)-4H-chromen-4-one L4



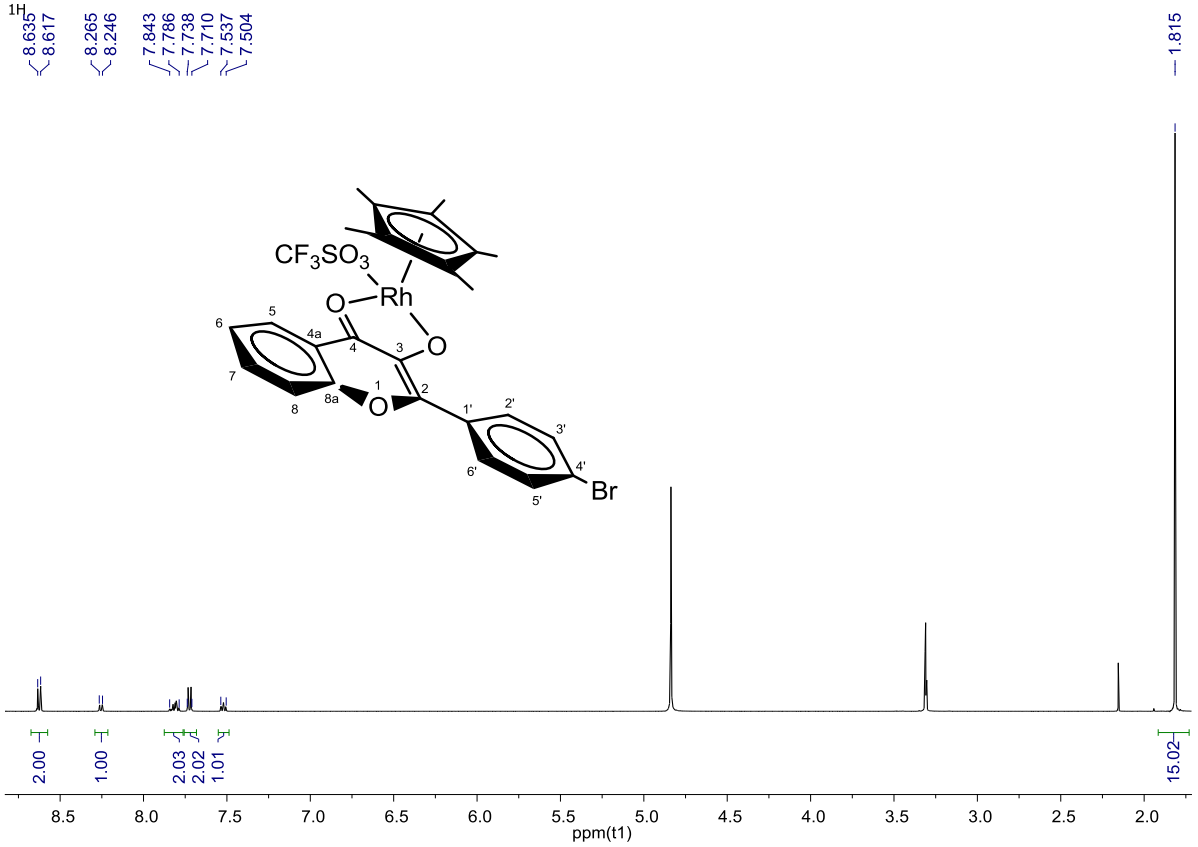


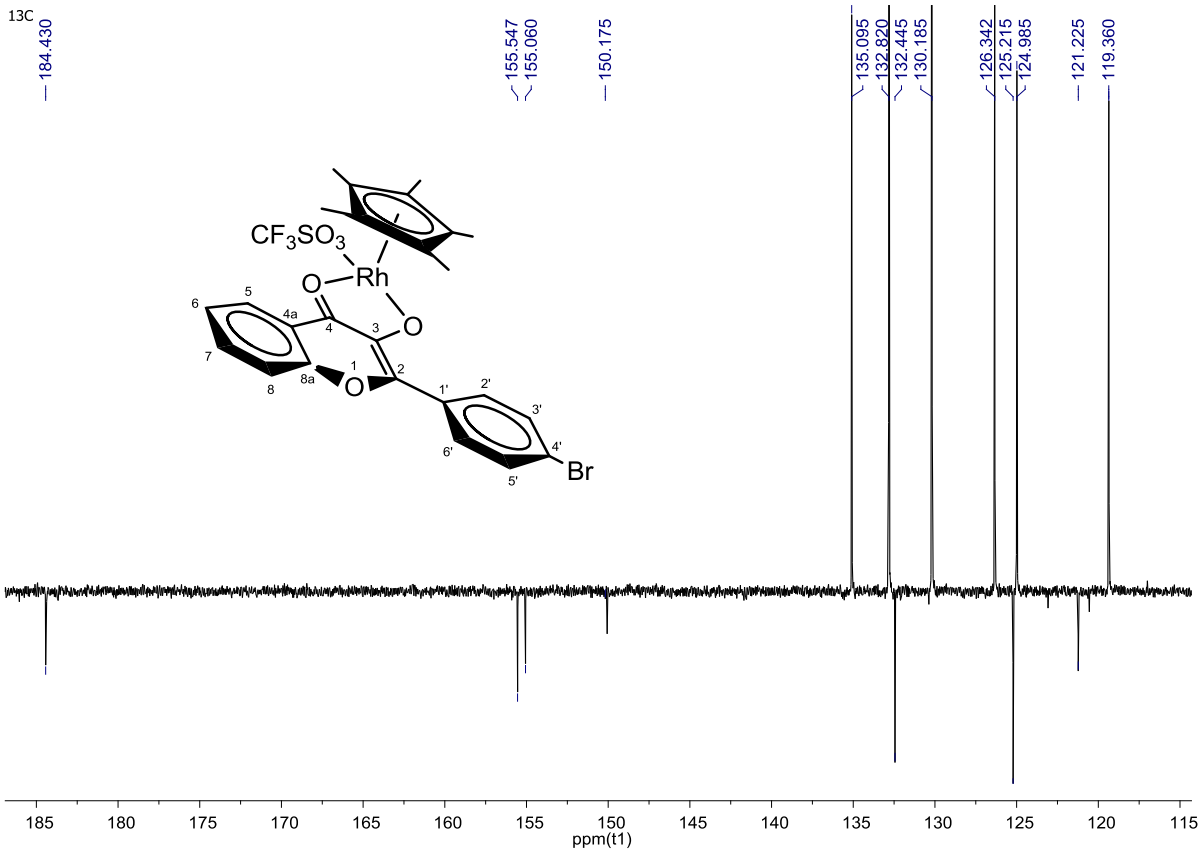
3-Hydroxy-2-(4-fluorophenyl)-4H-chromen-4-one L5



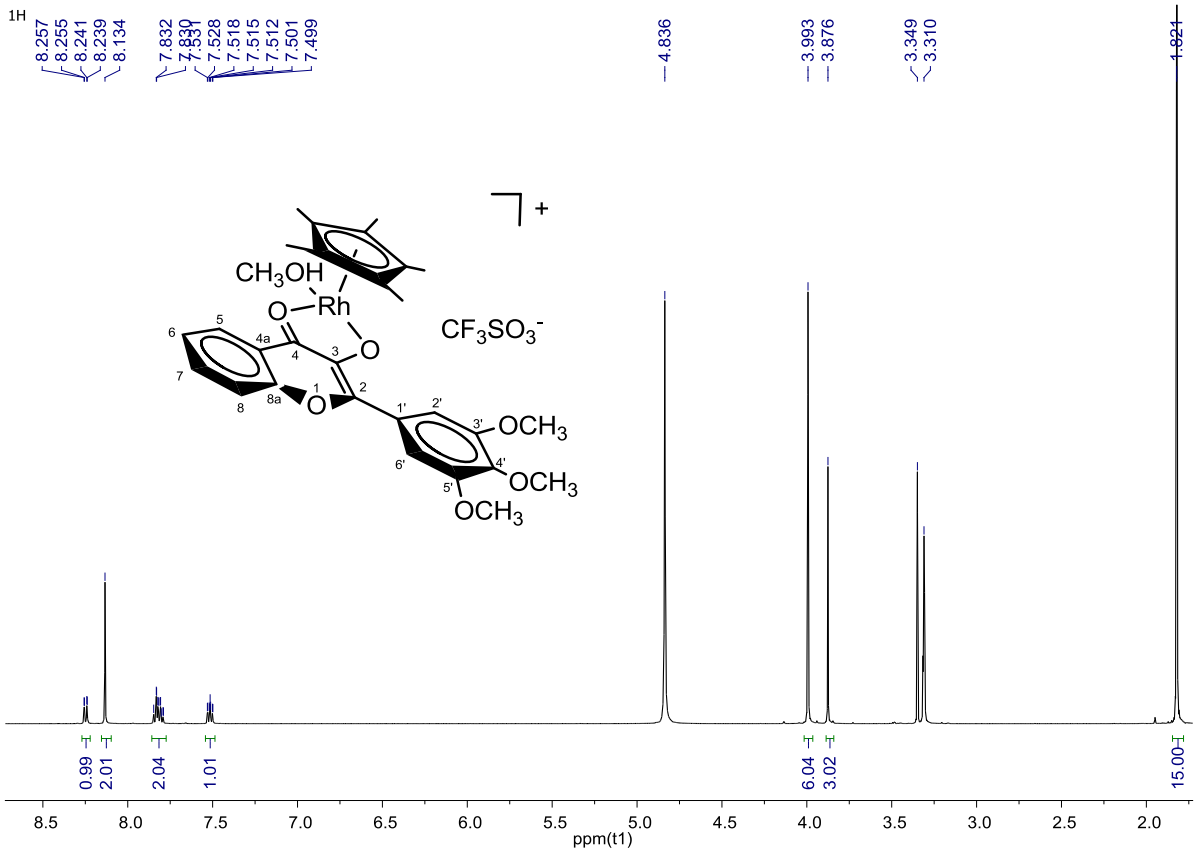


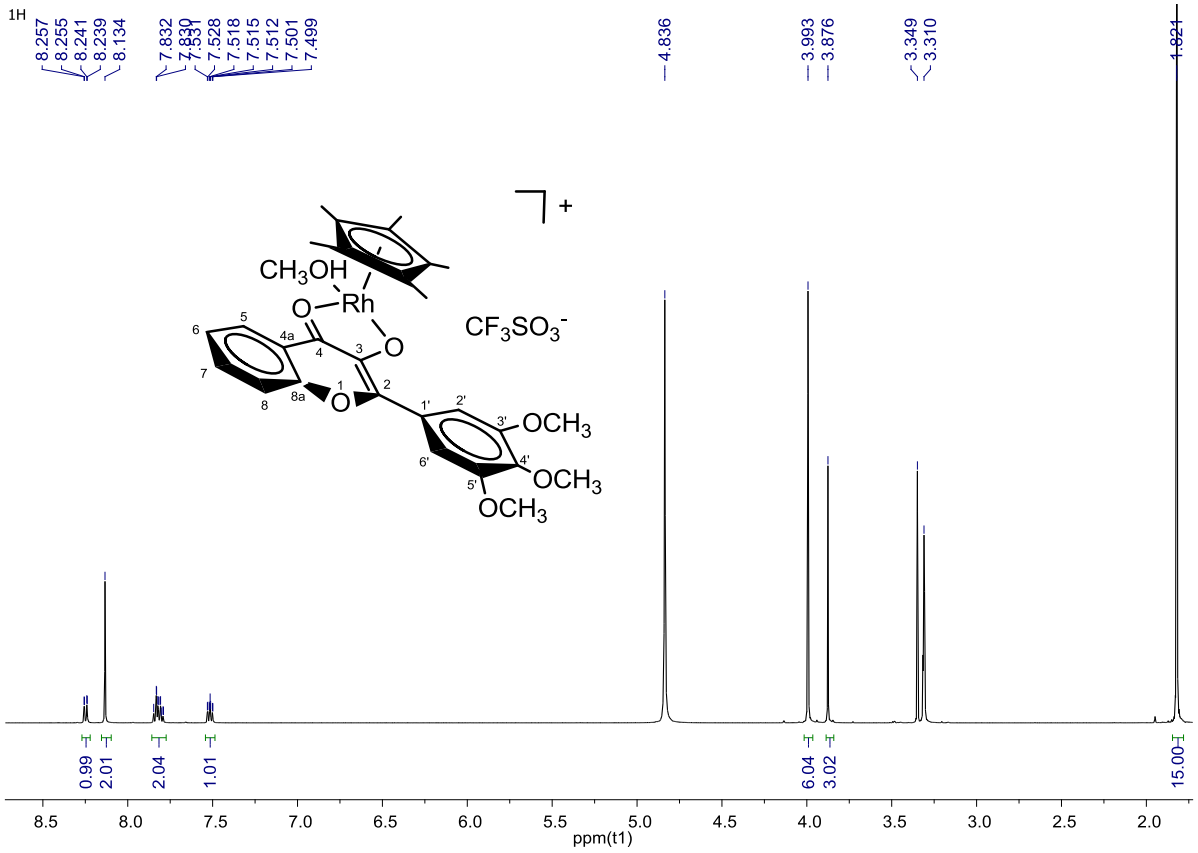
Trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-bromophenyl)-chromen-4-onato-κ*O*](η^5-pentamethylcyclopentadienyl)rhodium(III) C1



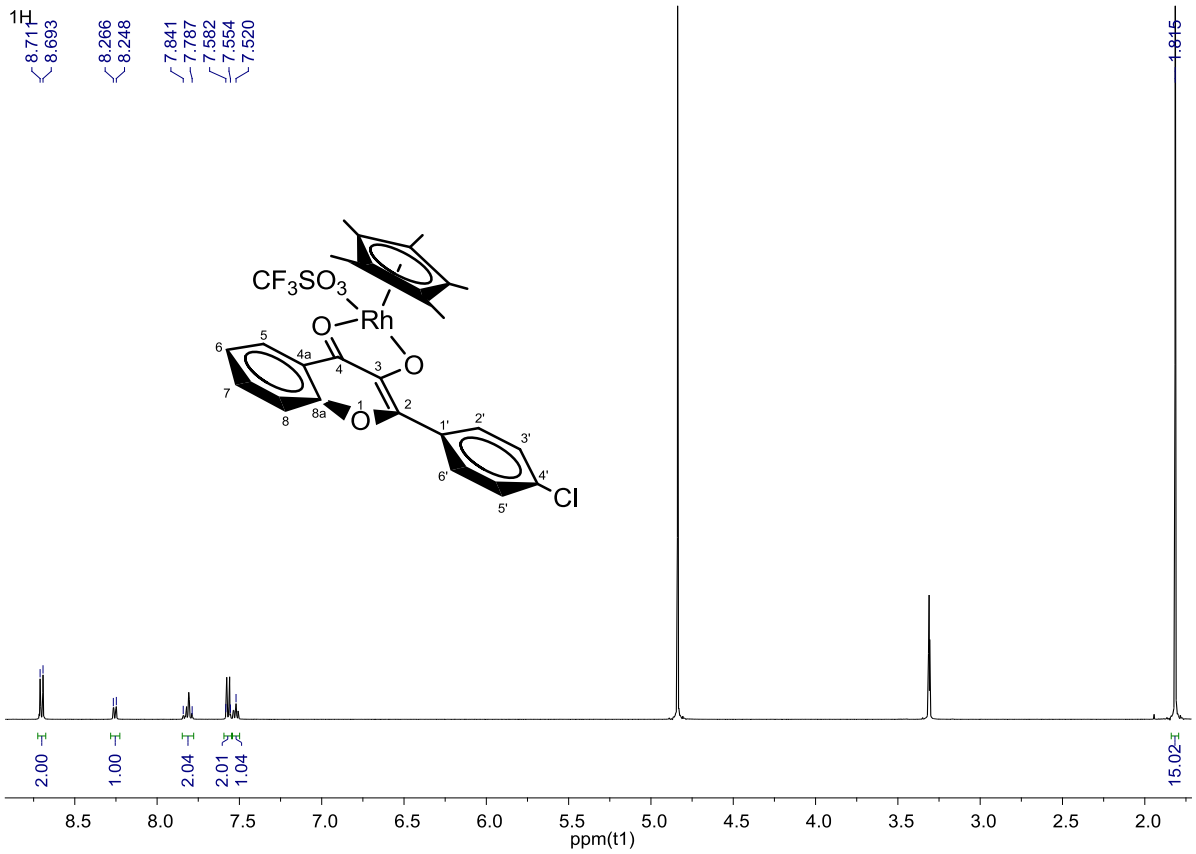


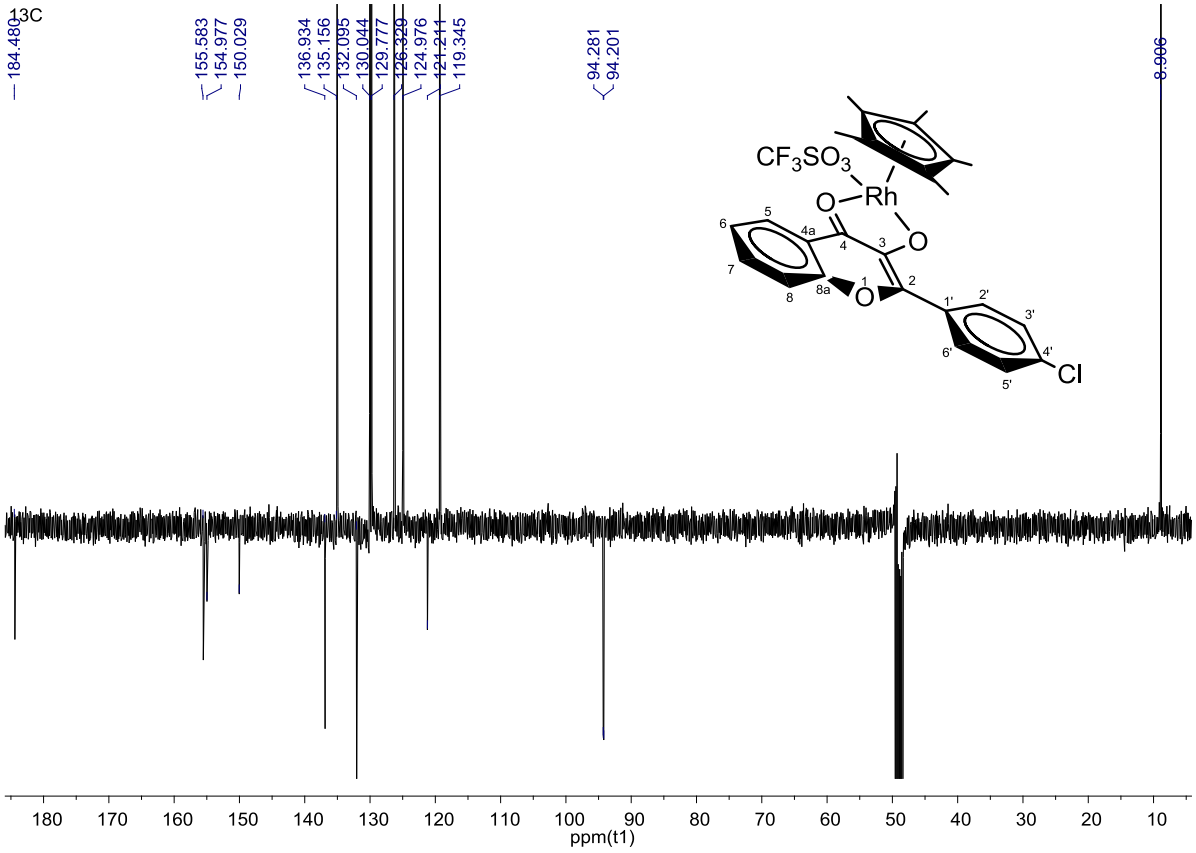
[{3-(oxo-κ*O*)-2-(3,4,5-trimethoxyphenyl)-chromen-4-onato-κ*O*}(methanol)(η^5-pentamethylcyclopentadienyl)rhodium(III)] trifluoromethanesulfonate C2



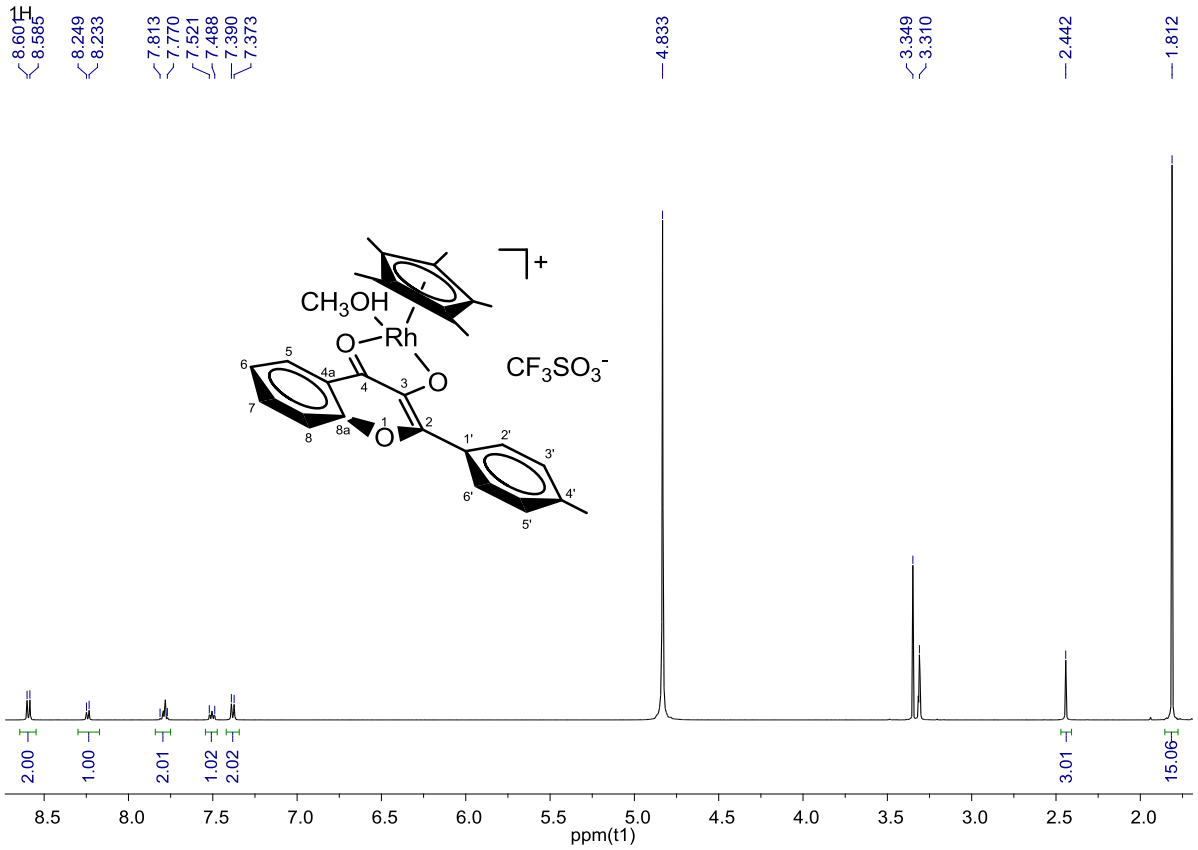


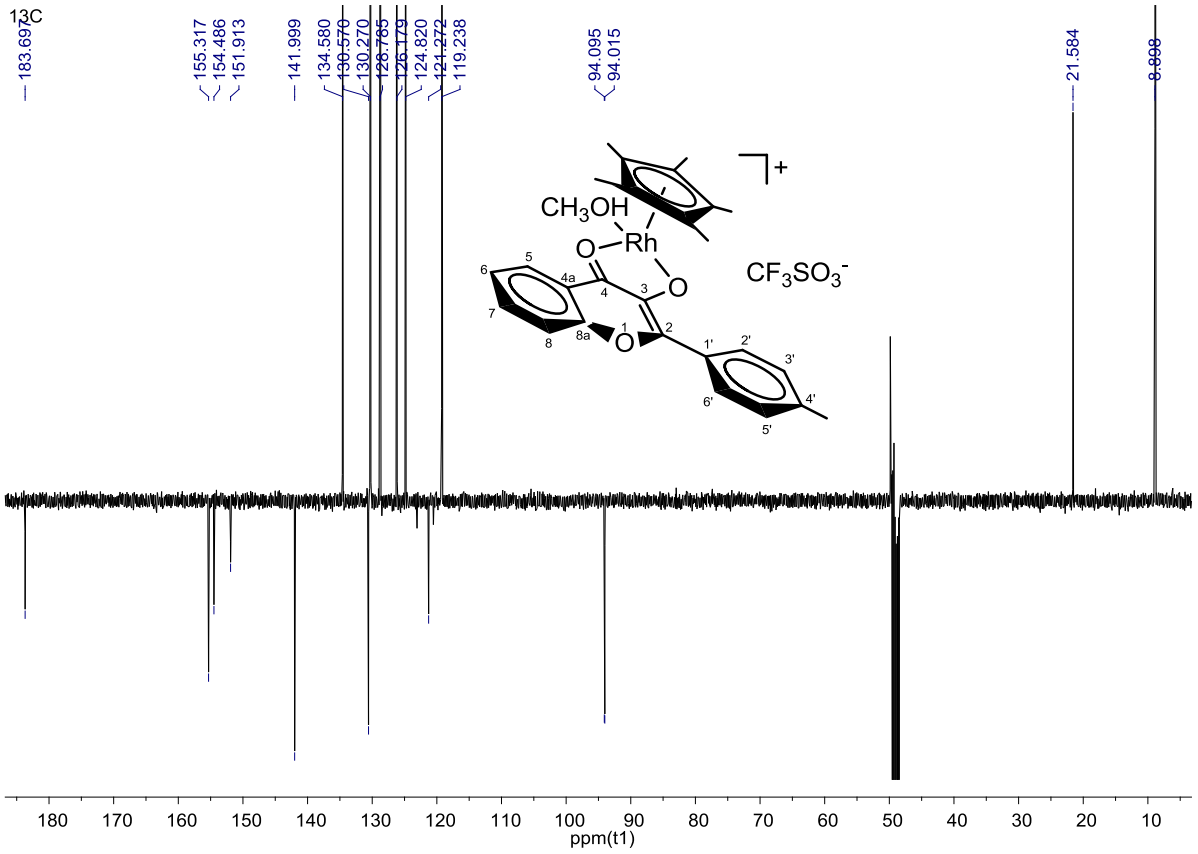
Trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-chlorophenyl)-chromen-4-onato-κ*O*](η^5-pentamethylcyclopentadienyl)rhodium(III) C3



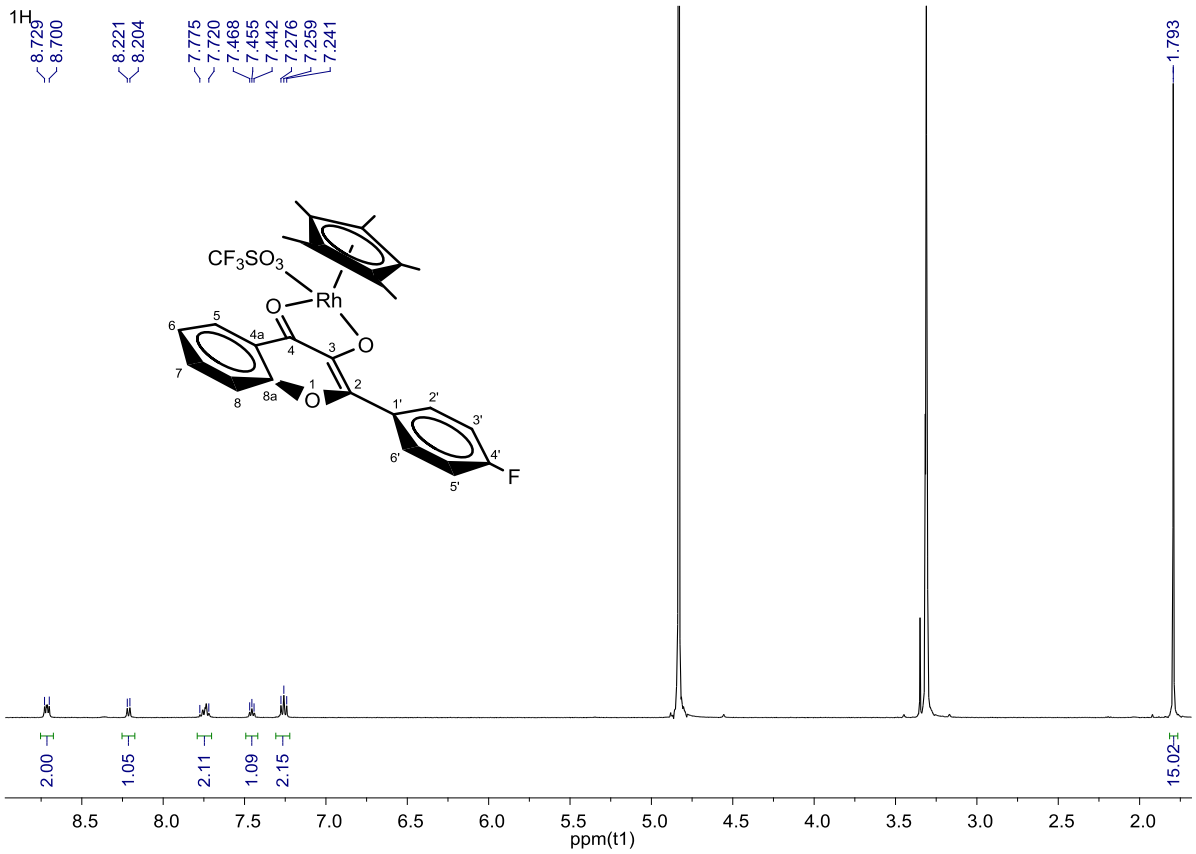


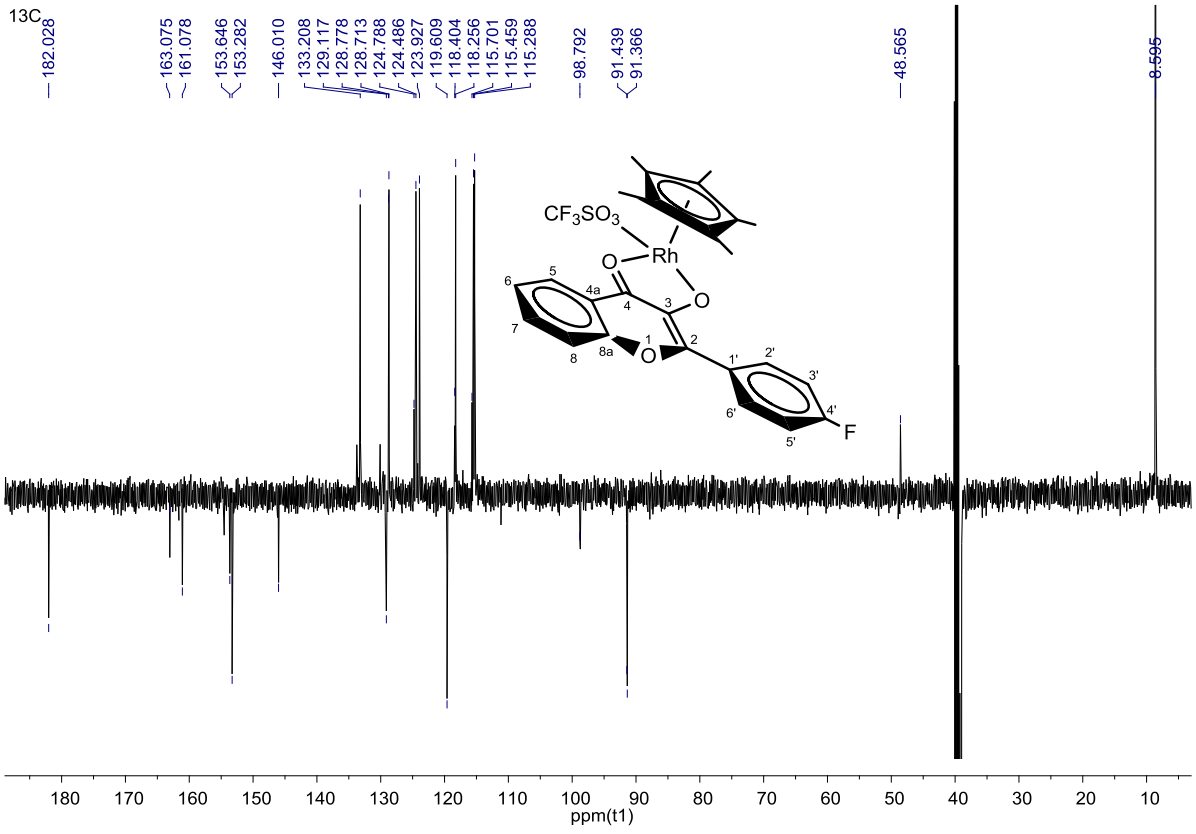
[{3-(oxo-κ*O*)-2-(4-methylphenyl)-chromen-4-onato- κ*O*}(methanol)(η^5-pentamethylcyclopentadienyl)rhodium(III)] trifluoromethanesulfonate C4





Trifluoromethanesulfonato[3-(oxo-κ*O*)-2-(4-fluorophenyl)-chromen-4-onato-κ*O*](η^{5}pentamethylcyclopentadienyl)rhodium(III) C5





6. CURRICULUM VITAE

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Nationality	**Austria**

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Mobile phone	**0676/ 54 50 459**
Mailing address	**martina.barasits@gmail.com**

Education

09.1994 to 06.2002	**Grammar school**
	1100 Vienna, Ettenreichgasse
	Specialized paper: „Die Beeinträchtigung der Nervenreizleitung durch Anästhetika, Narkotika und Opiate“
	School leaving examination passed with distinction

10.2002 to 09.2011	**University studies - chemistry**
	University of Vienna Diploma thesis – Institute of Inorganic Chemistry

Work Experience

Summer 1999	**Telekom Austria, 1010 Vienna**
	Internship

07/08.2001 to 2004 and 07.2006	**Gemeinde Wien, Magistratsabteilung 44, 1100 Vienna**
	Internships

2003	**Air Liquide, 2320 Schwechat**
	Freelance - Quality Management

08.2006	**Baxter, 1220 Vienna**
	Internship– Licensing Support Management

07.2007	**Sanofi – Aventis, 1220 Vienna**
	Internship – Communication/Reception

08.2007	**Baxter, 1220 Vienna**
	Internship – Receiving and Inspection

07/08.2008	**Baxter, 1220 Vienna**
	Internship – Biophysical Product Characterization

07/08.2009	**Baxter, 1220 Vienna**
	Internship – Pharmaceutical Formulation and Technology

Skills

Skills	MS Office
	Englisch (fluent)
	French (basic)
	German (mother tongue)
	…