Supporting Information for

Bimetallic Complexes with Xanthene-4,5-diNHC Ligands

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2,3,6,7,9,9-Hexamethylxanthene (**2**)

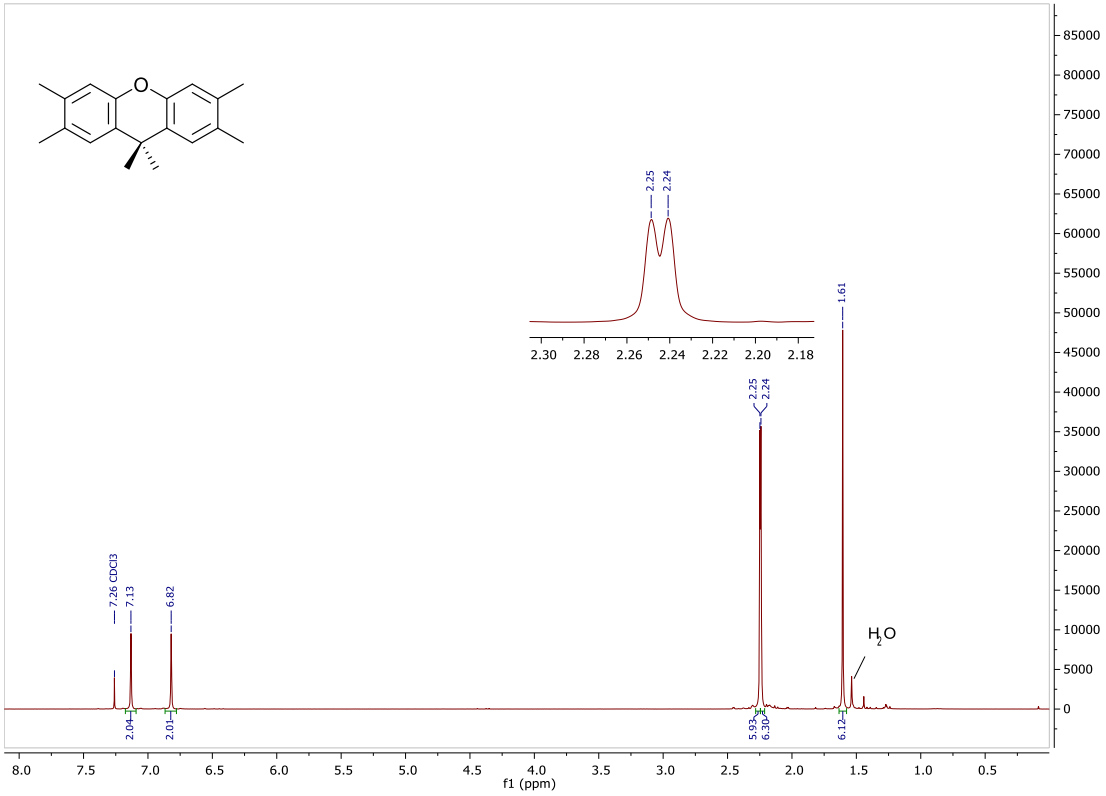


Figure 1: ^{1}H NMR of 2,3,6,7,9,9-hexamethylxanthene in $CDCl_3$.

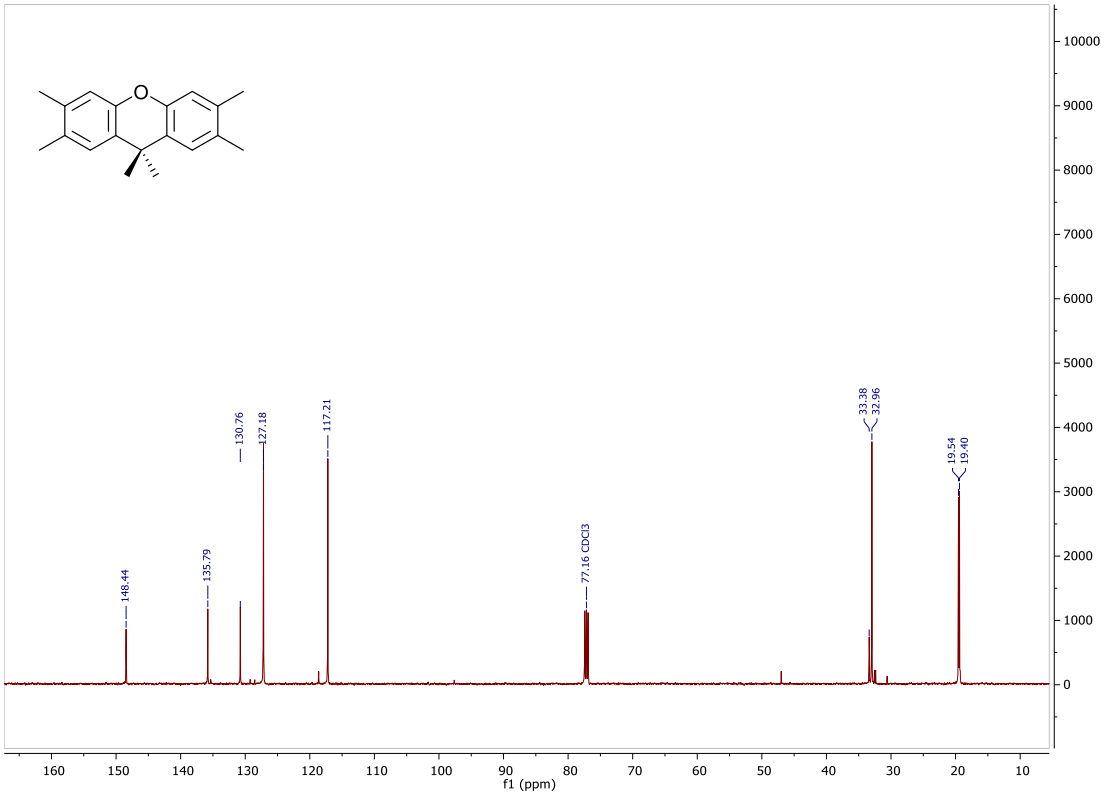


Figure 2: ^{13}C NMR of 2,3,6,7,9,9-hexamethylxanthene in $CDCl_3$.

4,5-Dibromo-2,3,6,7,9,9-hexamethylxanthene (**3**)

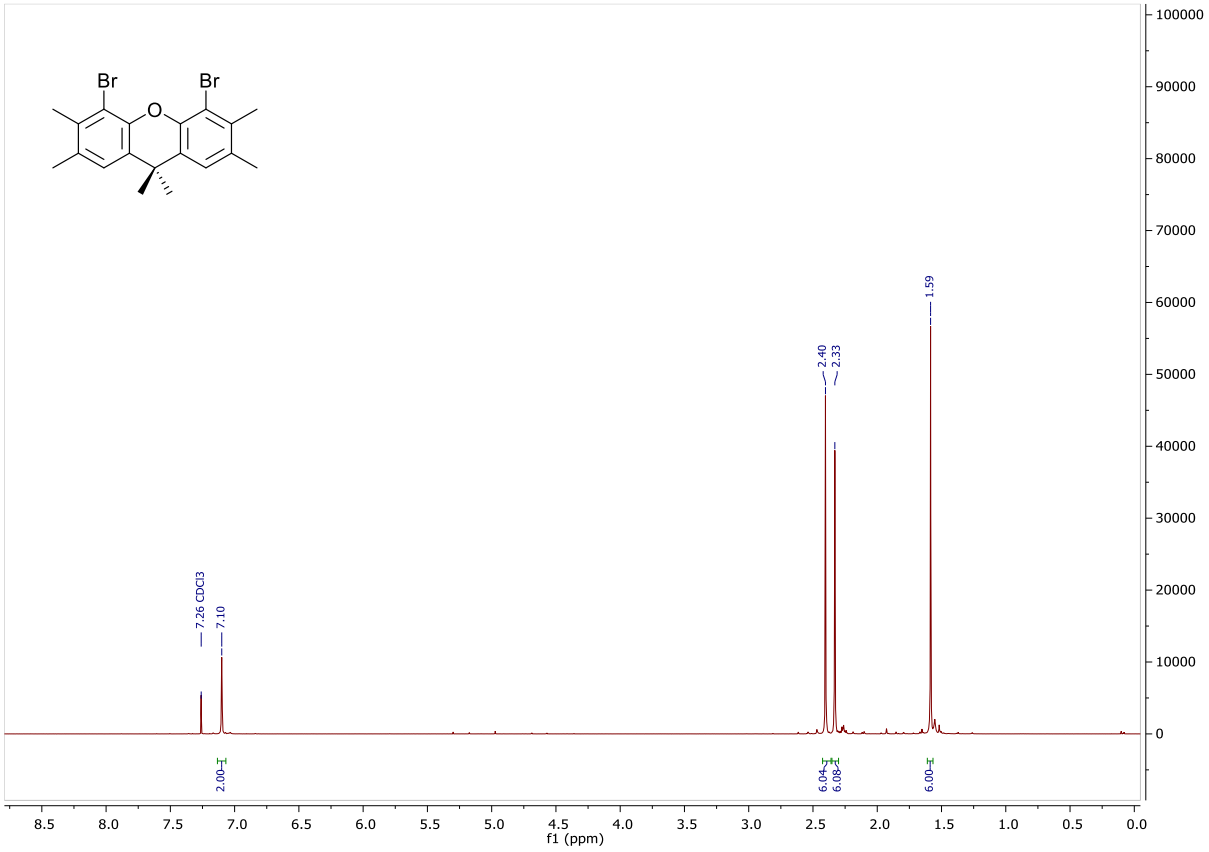


Figure 3: ^{1}H NMR of 4,5-dibromo-2,3,6,7,9,9-hexamethylxanthene in $CDCl_3$.

2,3,6,7,9,9-hexamethylxanthene-4,5-dicarboxylic acid (**4**)

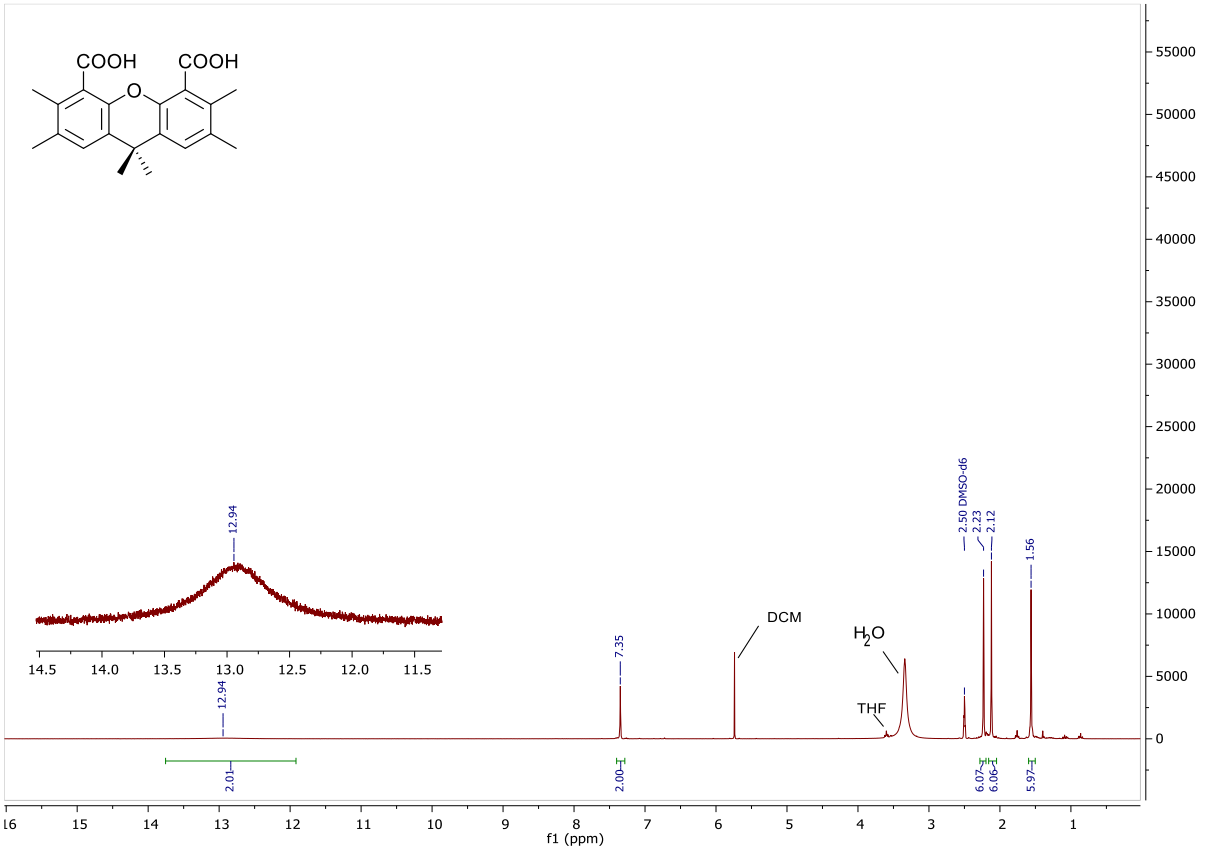


Figure 4: [1]H NMR of 2,3,6,7,9,9-hexamethylxanthene-4,5-dicarboxylic acid in DMSO-d_6.

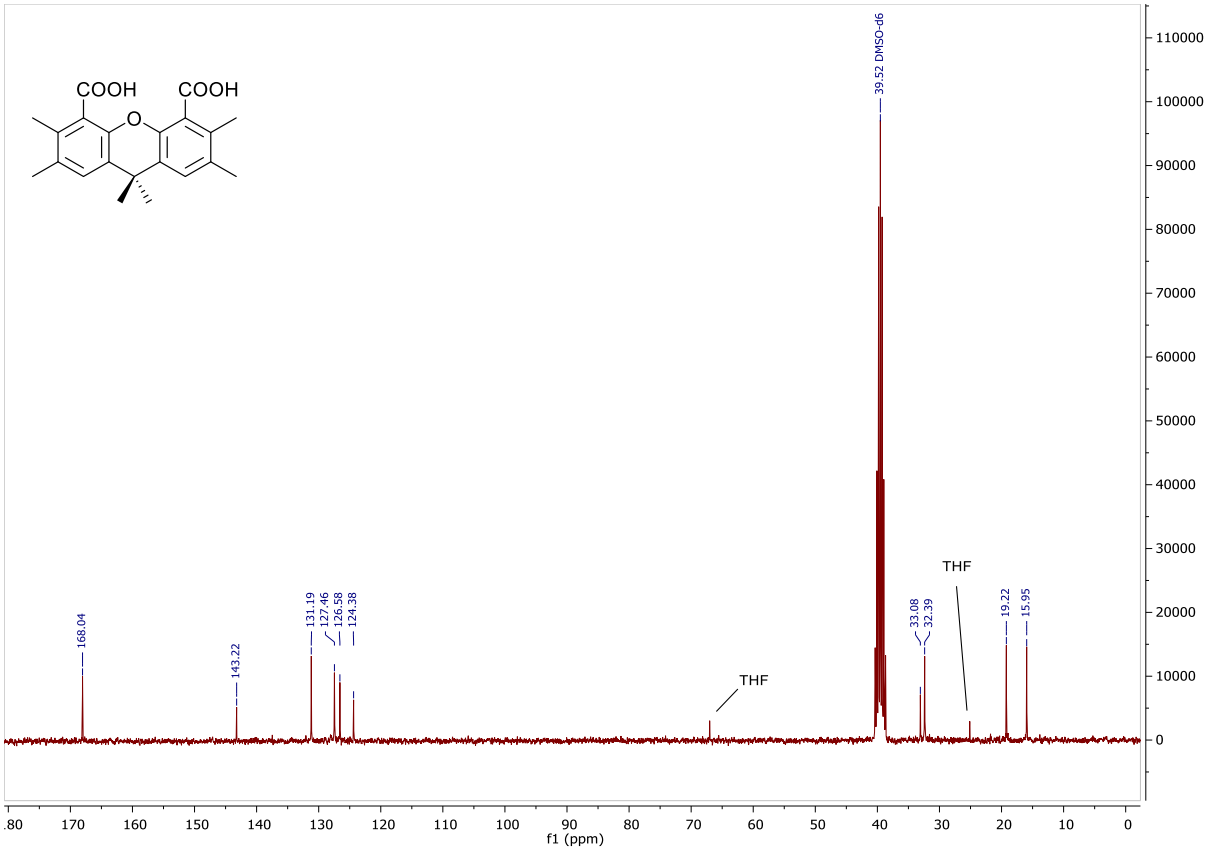


Figure 5: [13]C-NMR of 2,3,6,7,9,9-hexamethylxanthene-4,5-dicarboxylic acid in DMSO-d_6.

Dibenzyl(2,3,6,7,9,9-hexamethylxanthene-4,5-diyl)dicarbamate (**5**)

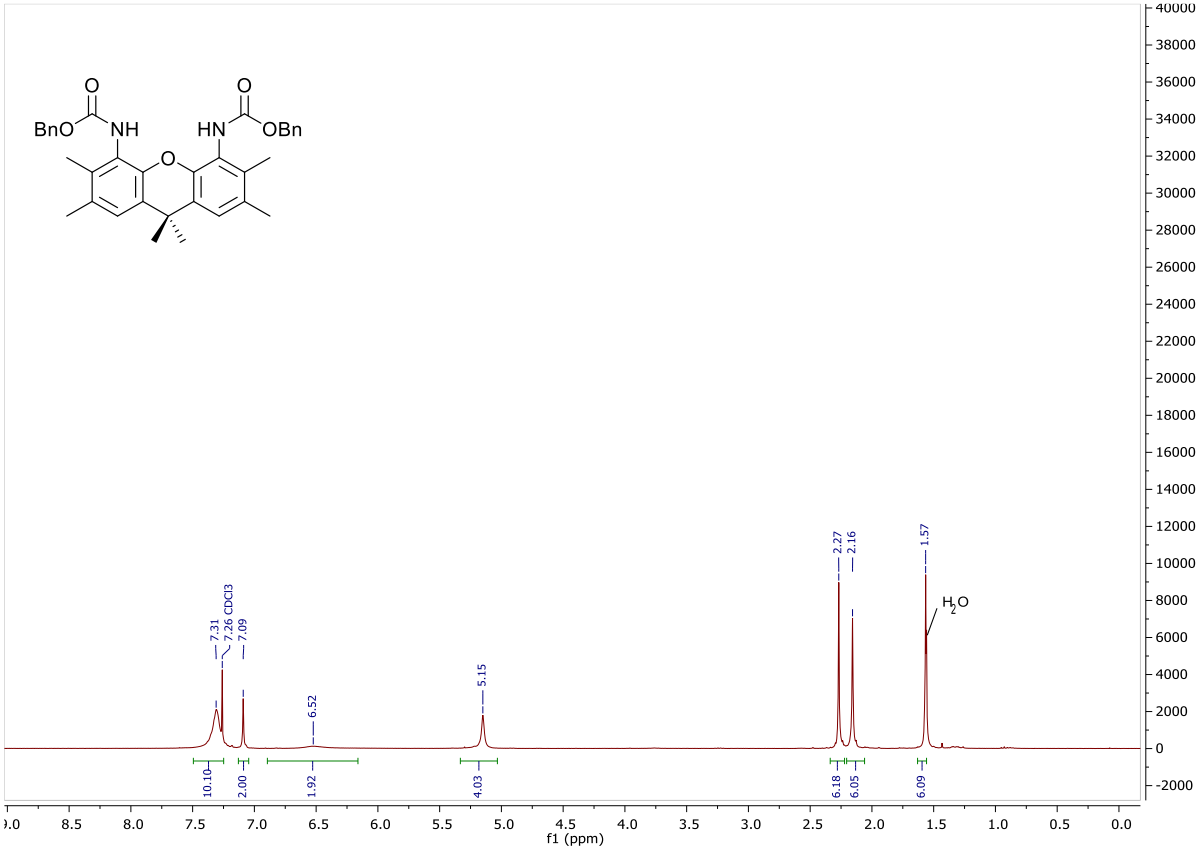


Figure 6: ^{1}H-NMR of dibenzyl(2,3,6,7,9,9-hexamethylxanthene-4,5-diyl)dicarbamate in $CDCl_3$.

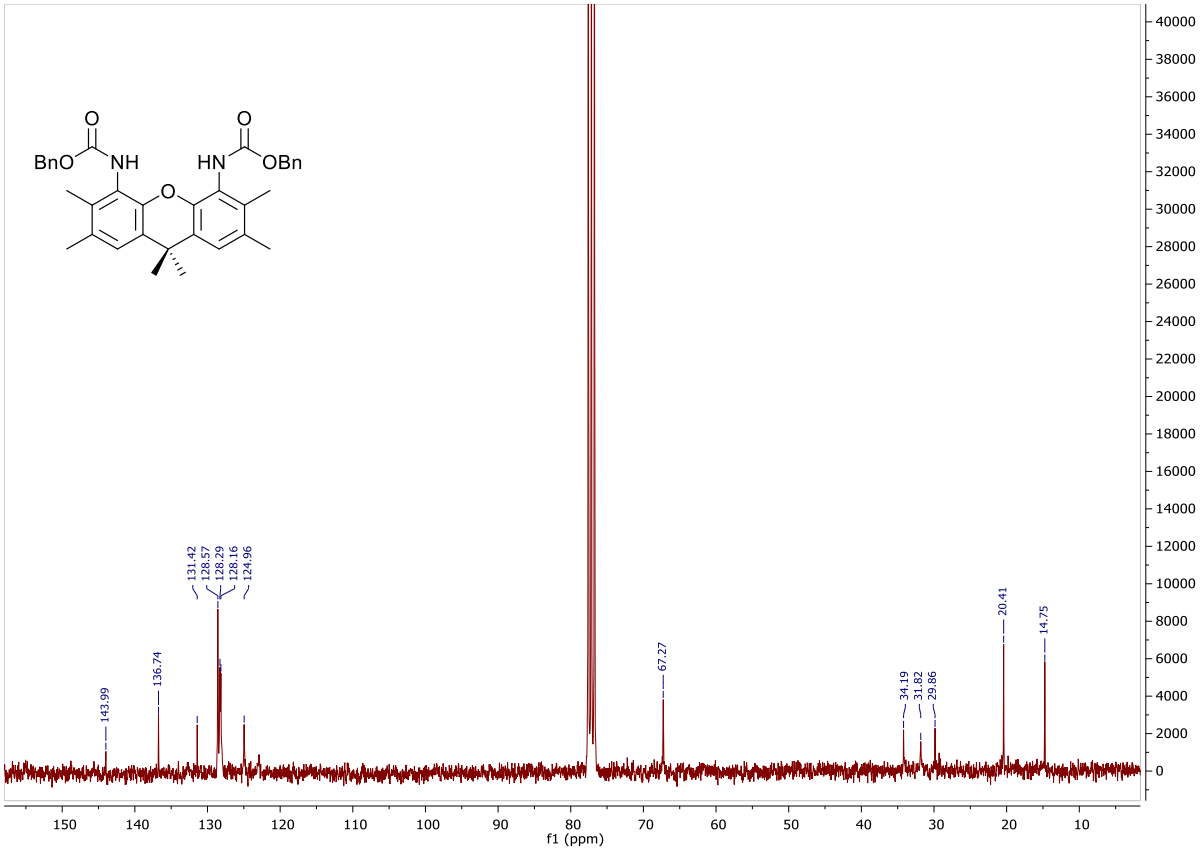


Figure 7: ^{13}C-NMR of dibenzyl(2,3,6,7,9,9-hexamethylxanthene-4,5-diyl)dicarbamate in $CDCl_3$.

4,5-Diamino-2,3,6,7,9,9-hexamethylxanthene (**6**)

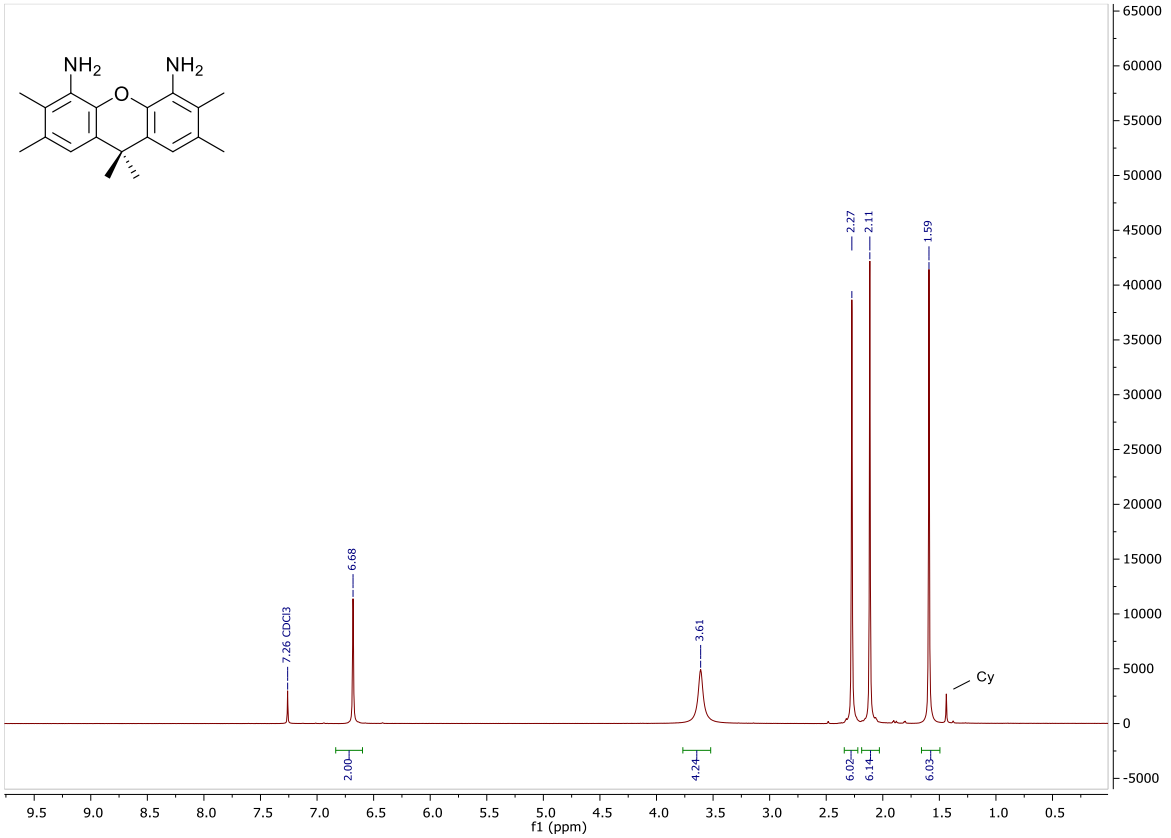


Figure 8: ^{1}H-NMR of 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene in $CDCl_3$.

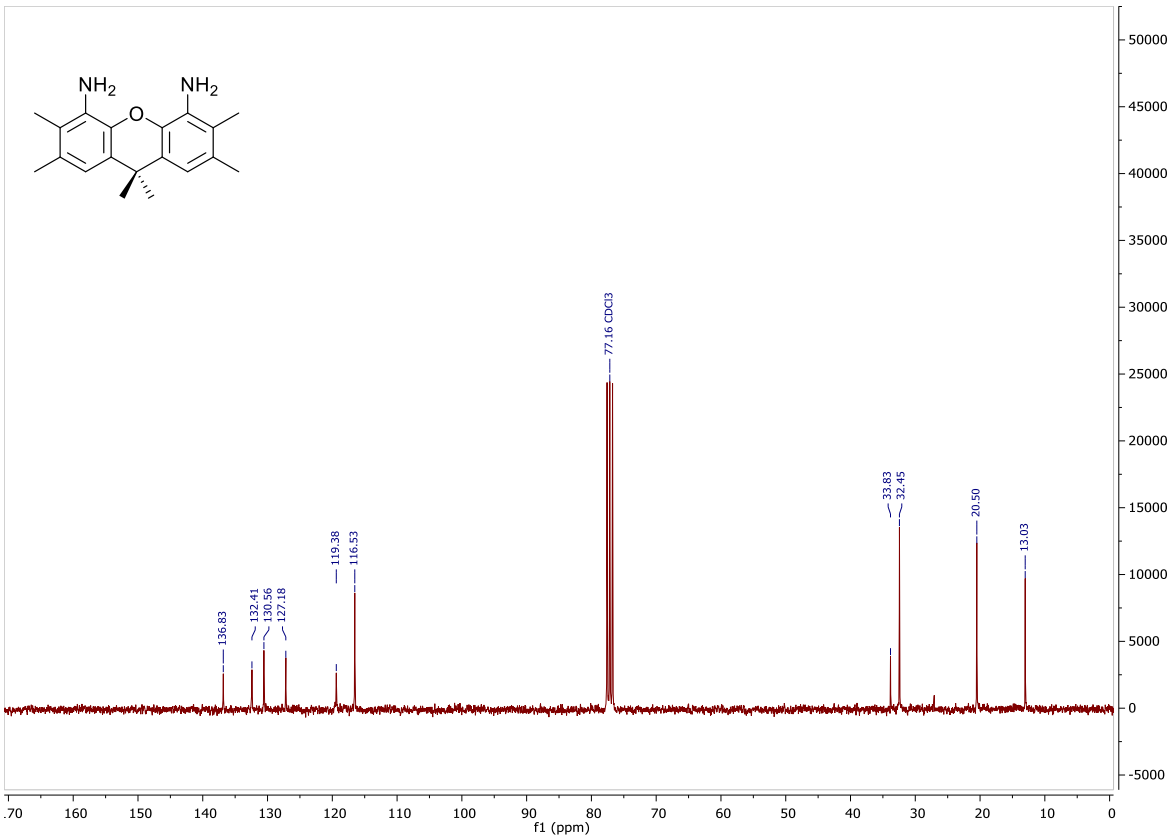


Figure 9: ^{13}C-NMR of 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene in $CDCl_3$.

4-Amino-2,3,6,7,9,9-hexamethylxanthene (**7**)

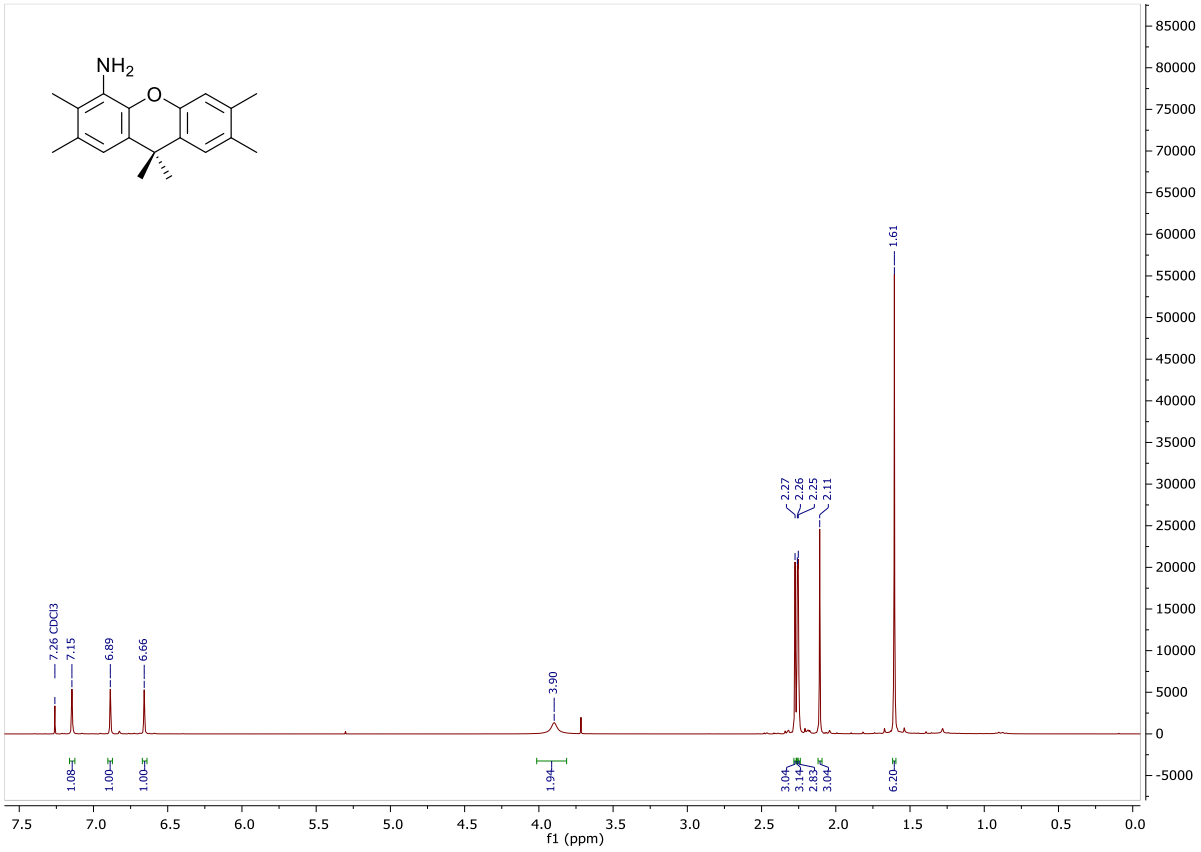


Figure 10: ^{1}H-NMR of 4-amino-2,3,6,7,9,9-hexamethylxanthene in $CDCl_3$.

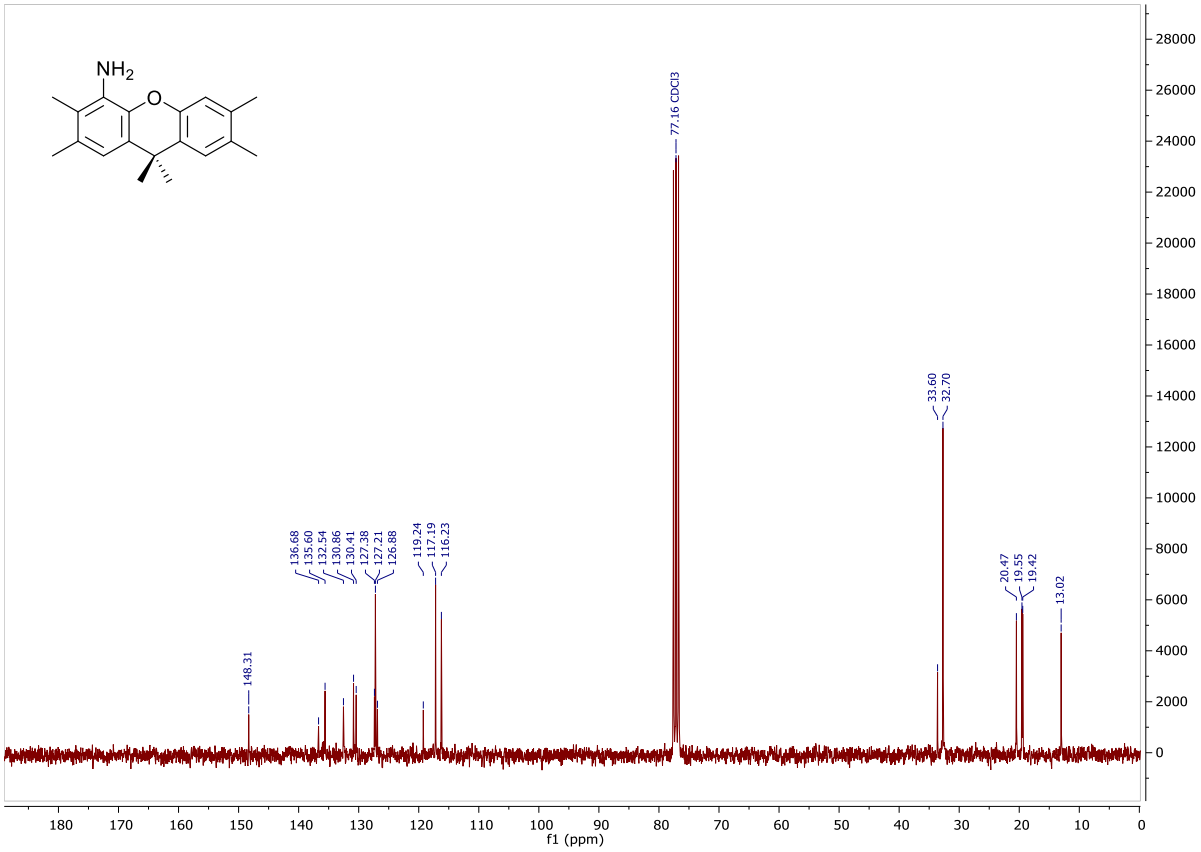


Figure 11: ^{13}C-NMR of 4-amino-2,3,6,7,9,9-hexamethylxanthene in $CDCl_3$.

Xanthene diimine (**8**)

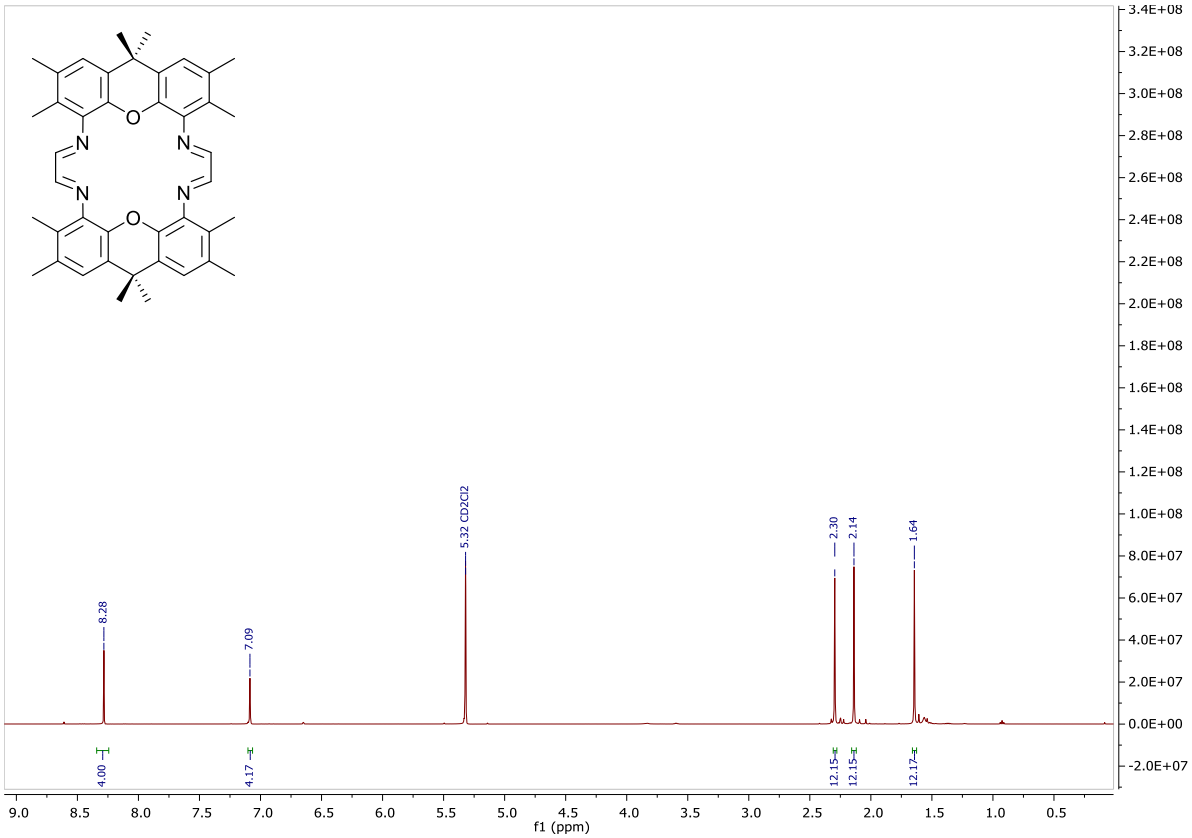


*Figure 12: ^{1}H-NMR of xanthene diimine (**8**) in CD_2Cl_2.*

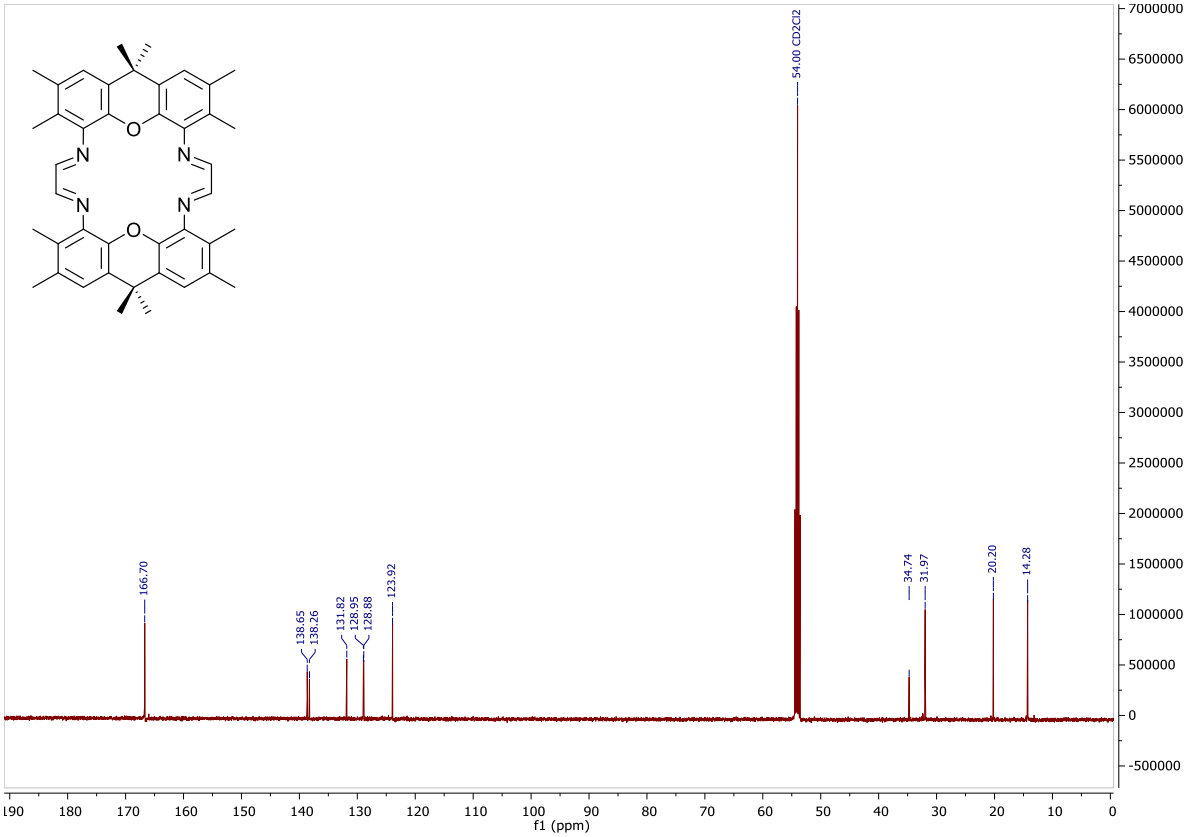


*Figure 13: ^{13}C-NMR of xanthene diimine (**8**) in CD_2Cl_2.*

Xanthene imidazolium salt (**9** · 2 HCl)

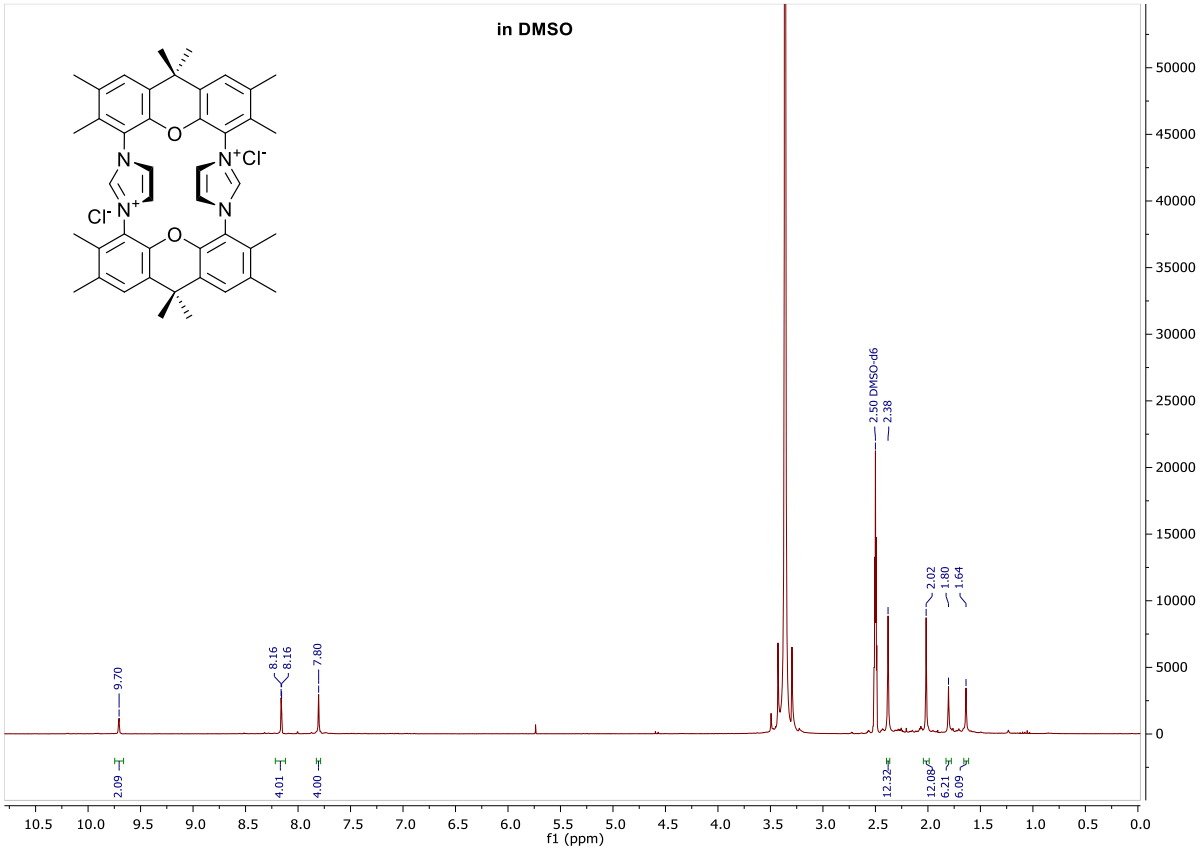


*Figure 14: ^{1}H-NMR of **9** · 2 HCl in DMSO-d_6.*

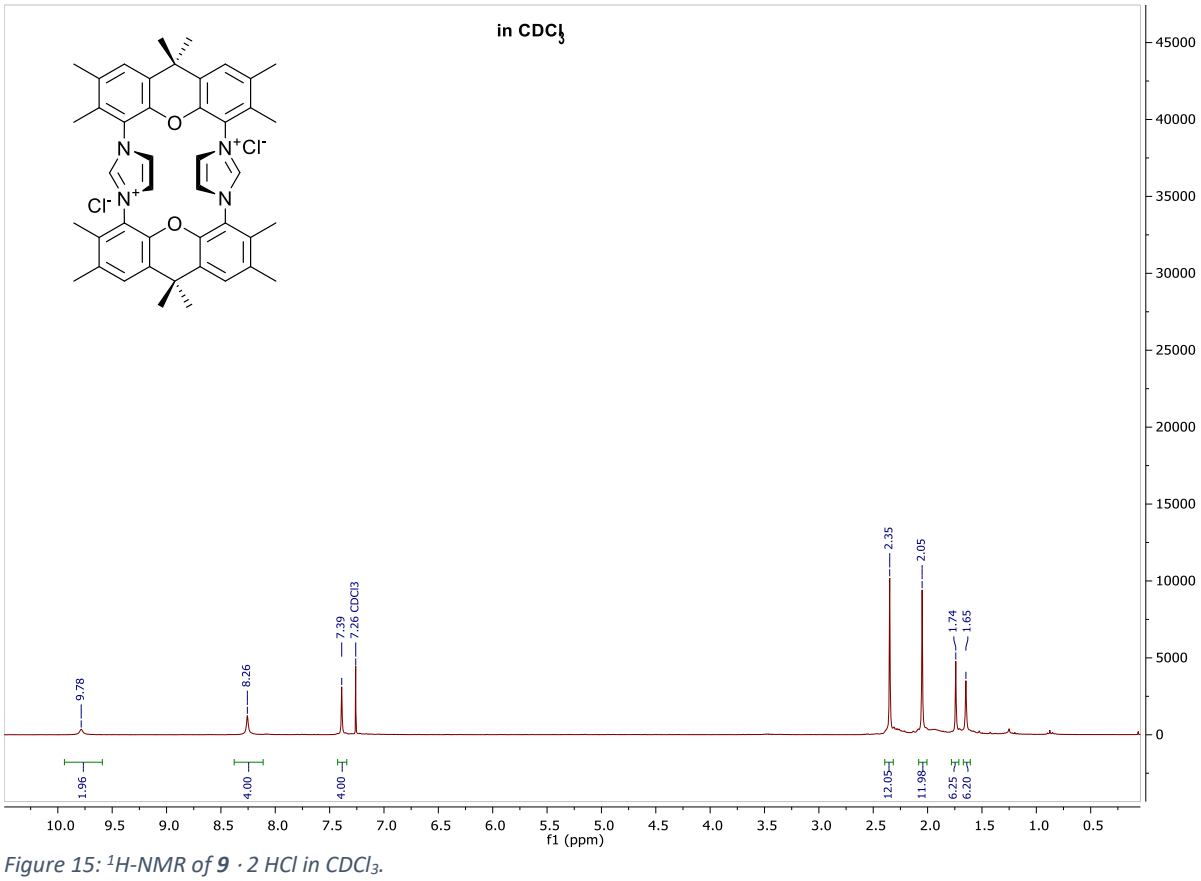


*Figure 15: ^{1}H-NMR of **9** · 2 HCl in $CDCl_3$.*

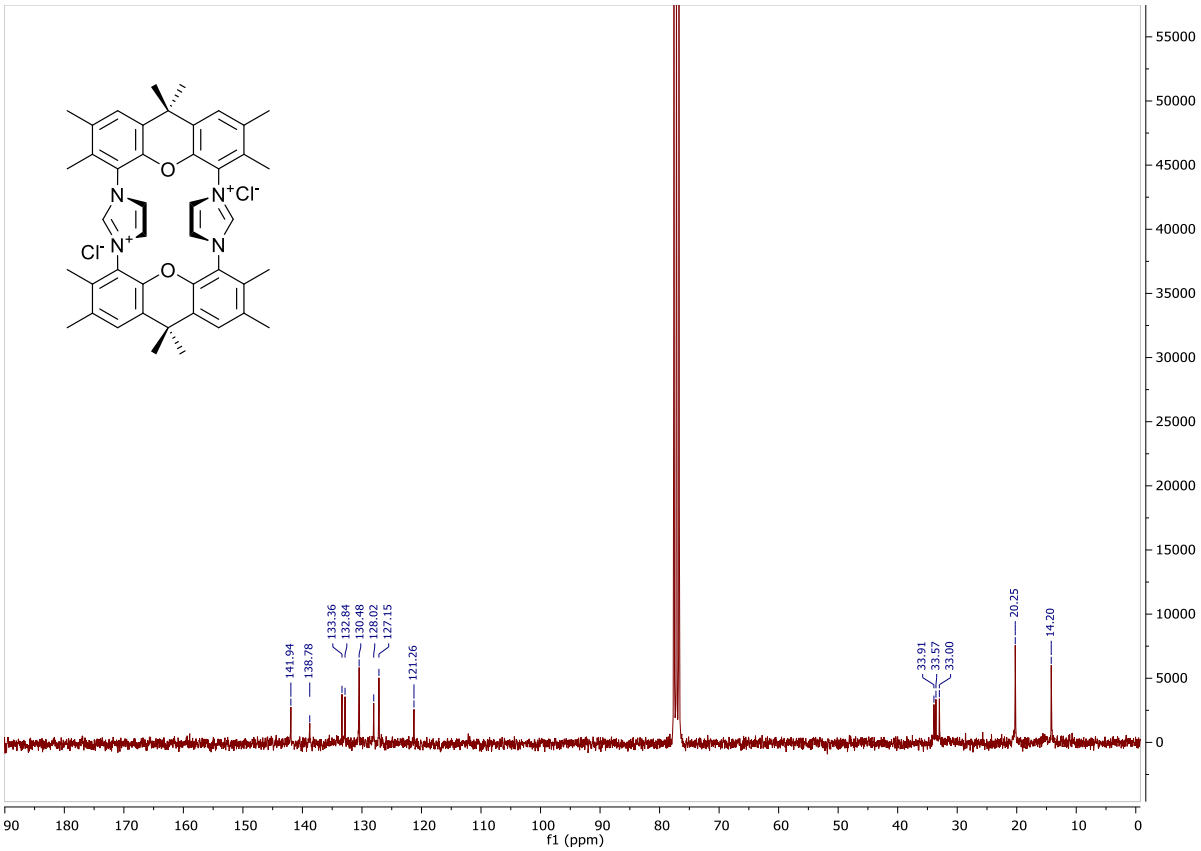


*Figure 16: ^{13}C-NMR of **9** · 2 HCl in $CDCl_3$.*

Xanthene imidazolium salt (**9** · 2 HBF_4)

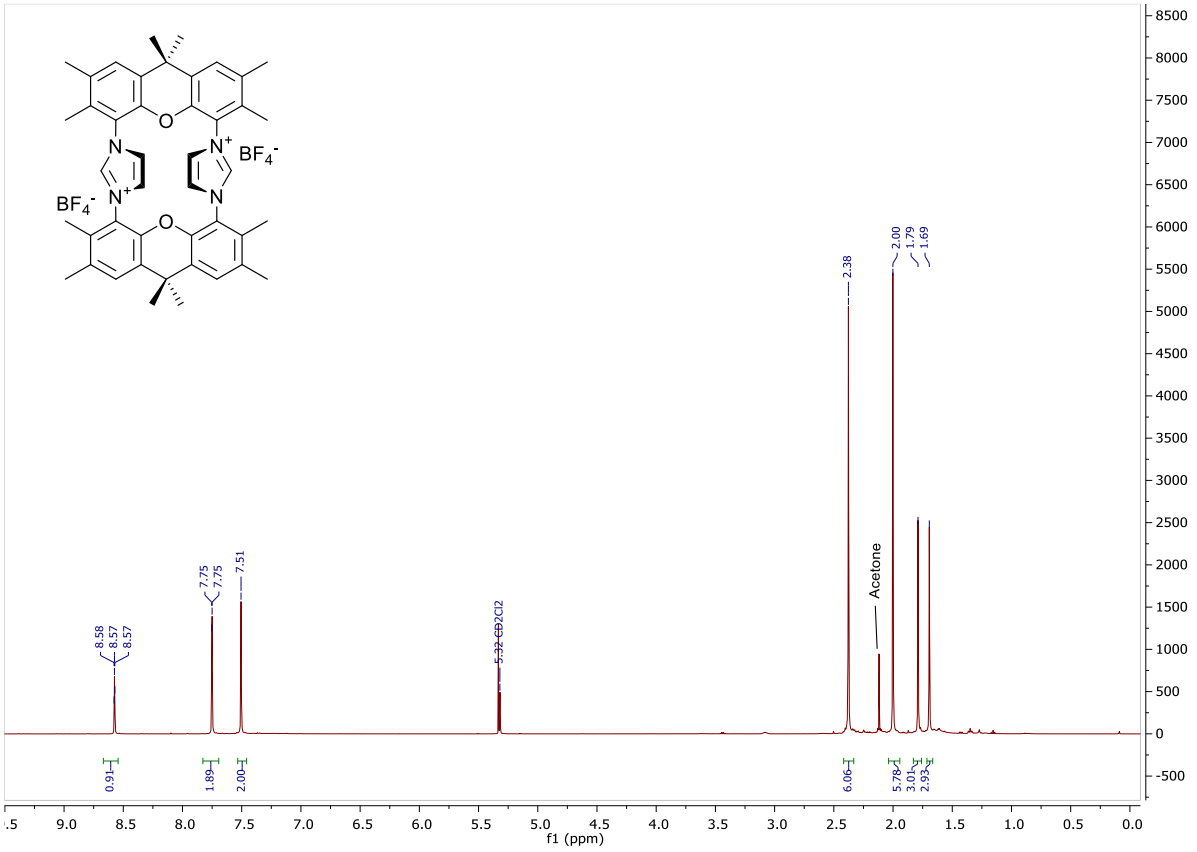


*Figure 17: ^{1}H-NMR **9** · 2 HBF_4 in CD_2Cl_2.*

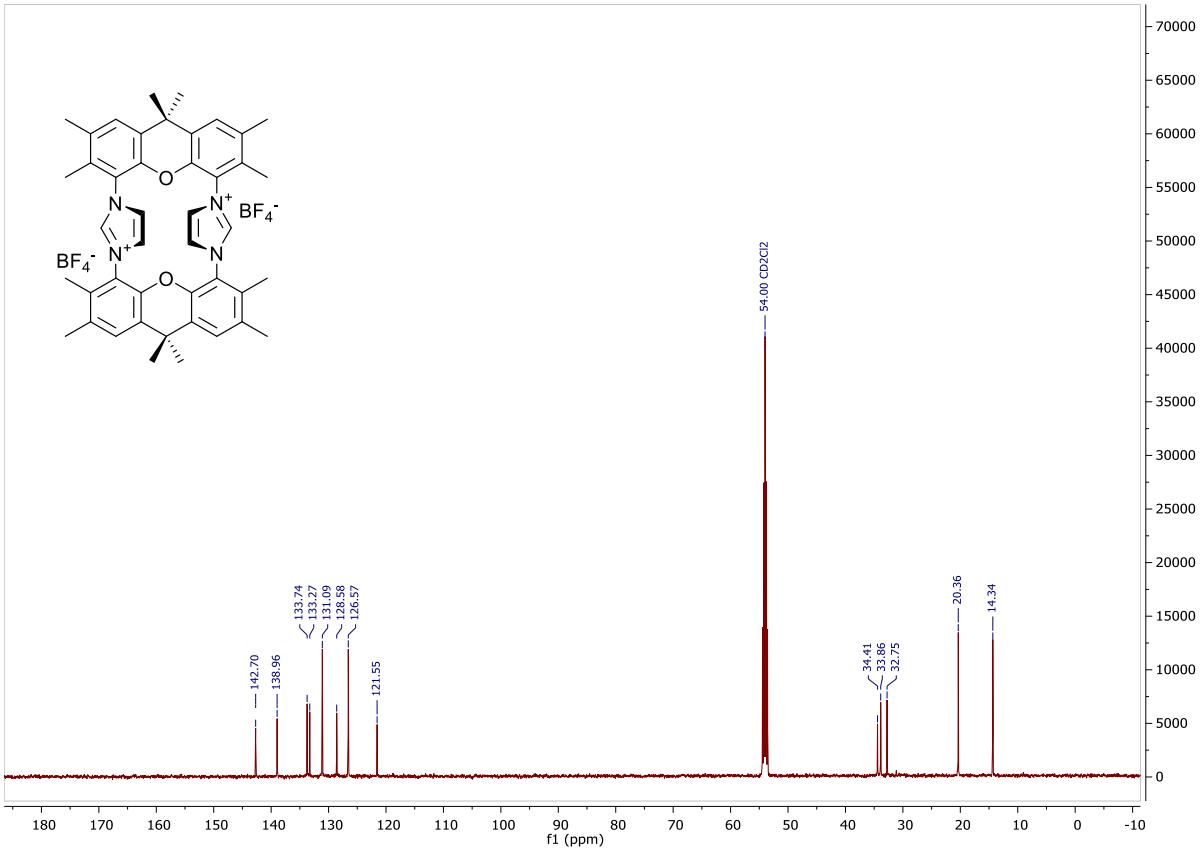


*Figure 18: ^{13}C-NMR of **9** · 2 HBF_4 in CD_2Cl_2.*

[(IrCl(cod))$_2$(**9**)]

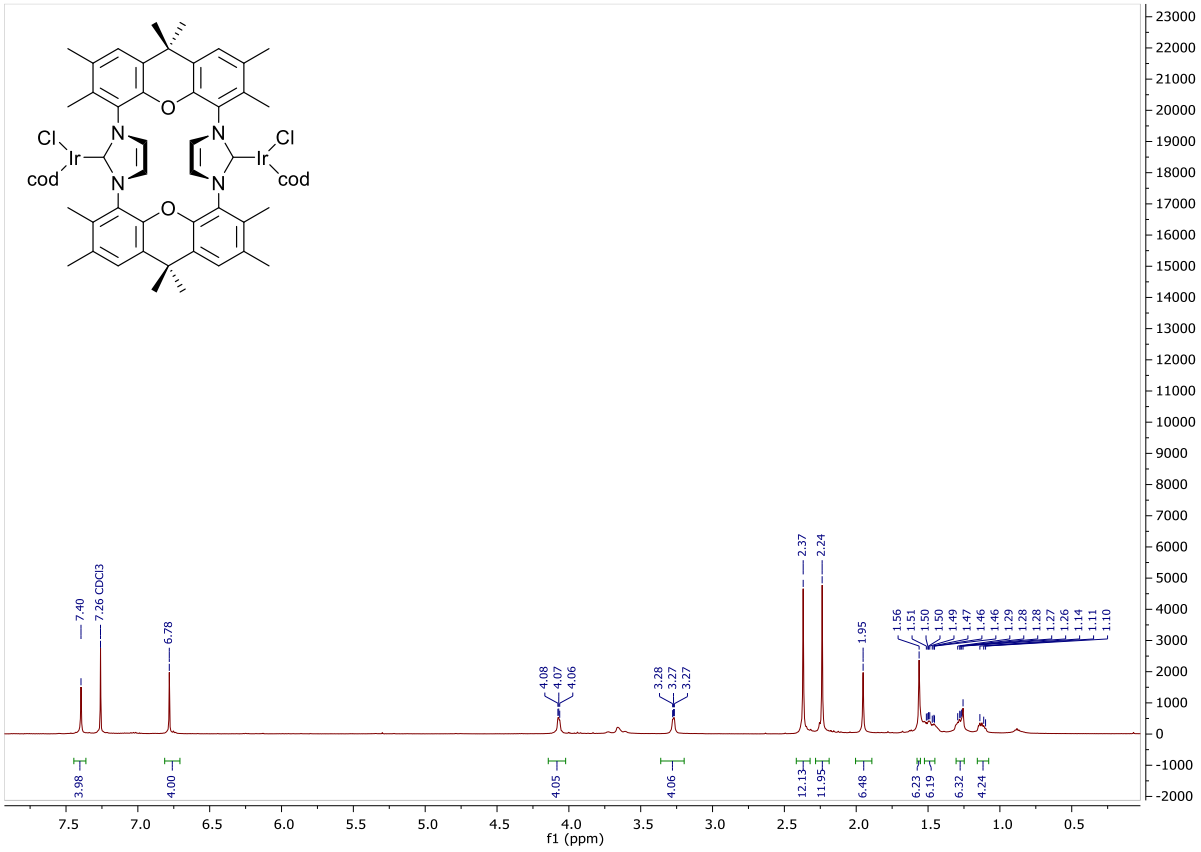


*Figure 19: ^{1}H-NMR of [(IrCl(cod))$_2$(**9**)] in $CDCl_3$.*

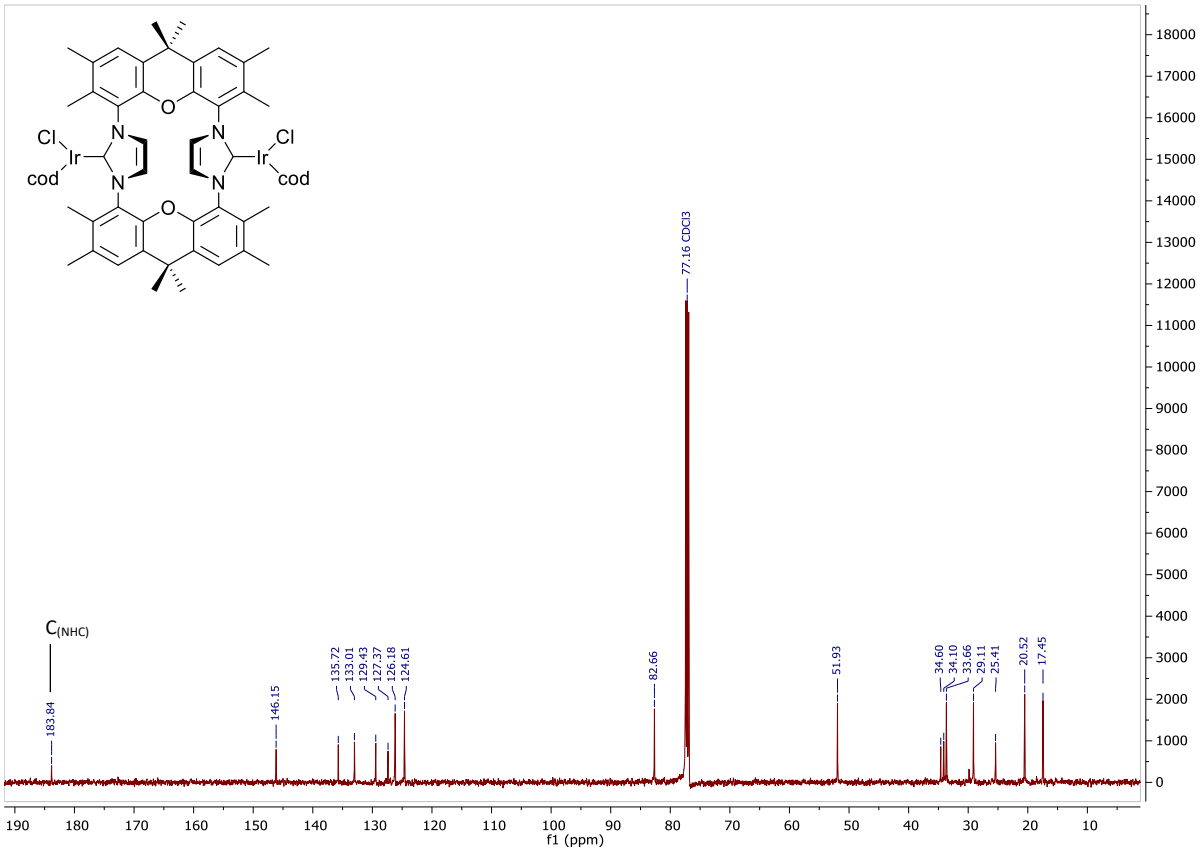


*Figure 20: ^{13}C-NMR of [(IrCl(cod))$_2$(**9**)] in $CDCl_3$.*

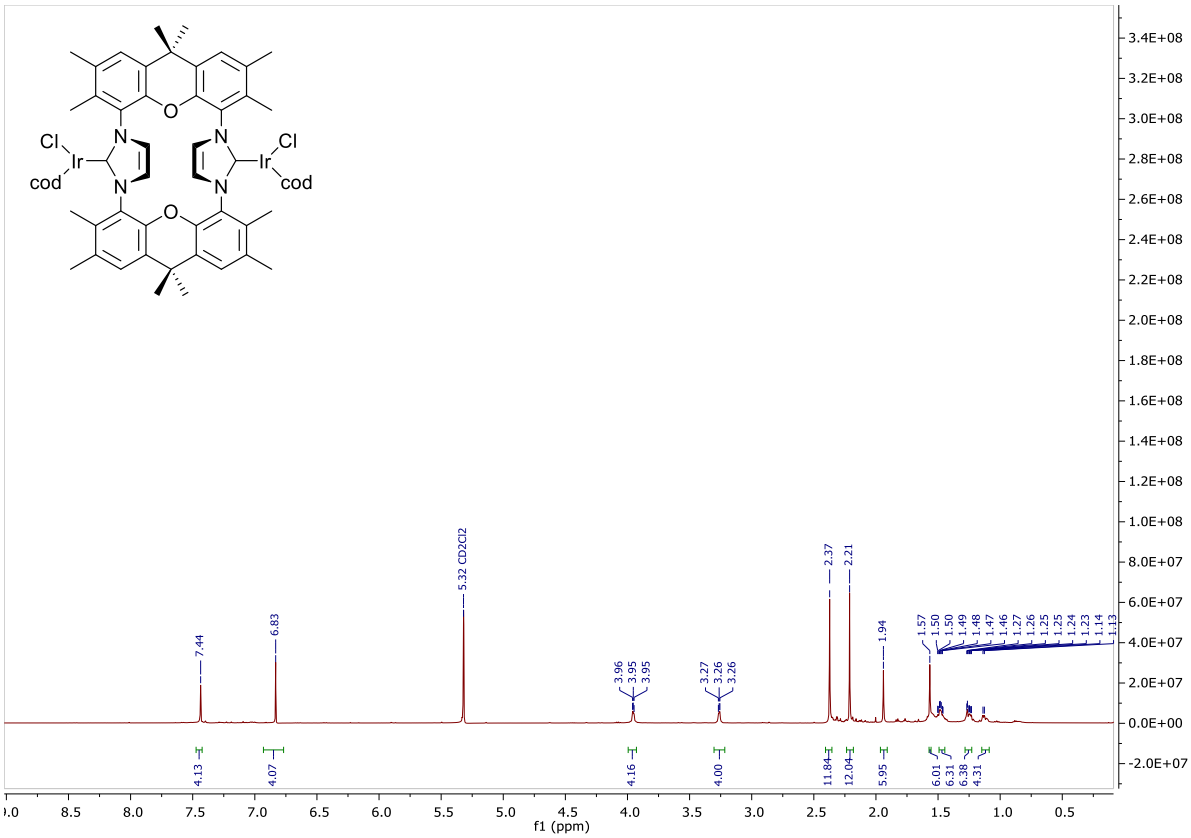


*Figure 21: ^{1}H-NMR of [(IrCl(cod))$_2$(**9**)] in CD_2Cl_2.*

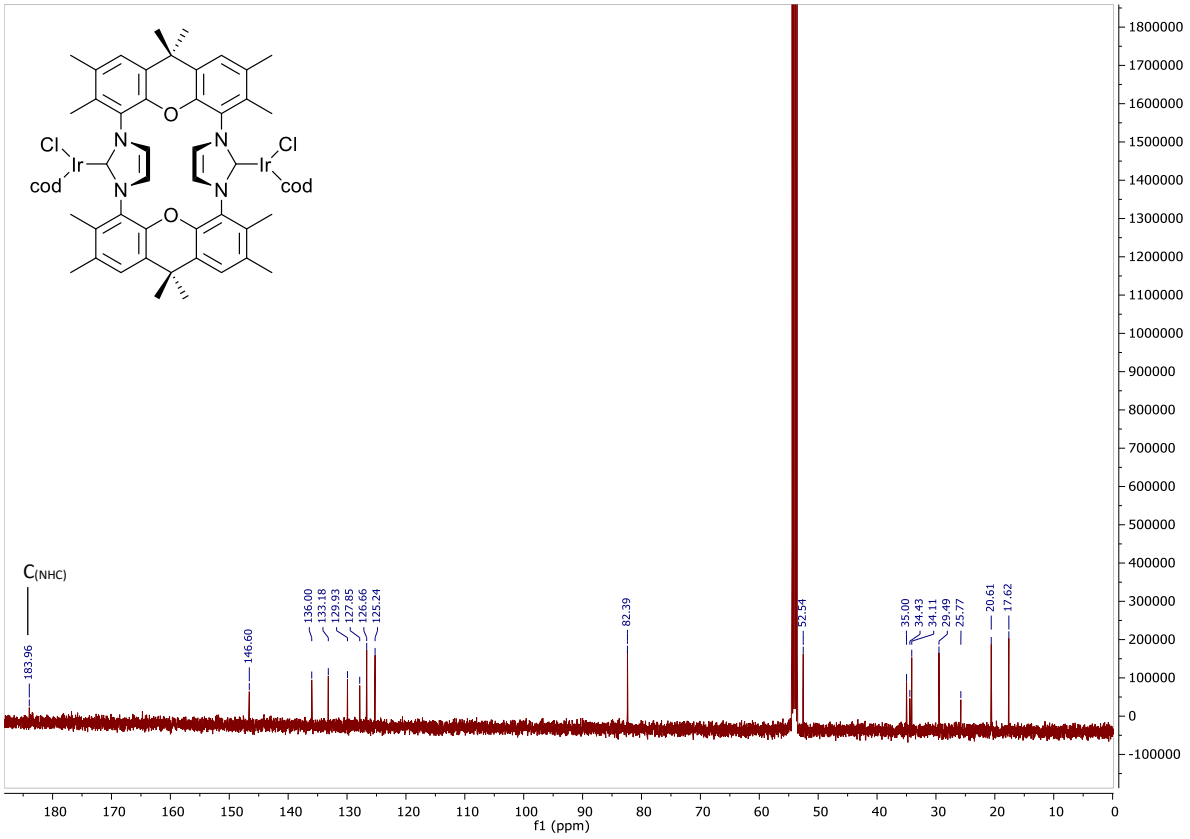


*Figure 22: ^{13}C-NMR of [(IrCl(cod))$_2$(**9**)] in CD_2Cl_2.*

[(IrCl(cod))$_2$(**9**)] + AgOTf - experiment

An NMR-Tube was charged with 5 mg [(IrCl(cod))$_2$(**9**)] and 1 mg (1 eq) AgOTf in CD_2Cl_2.

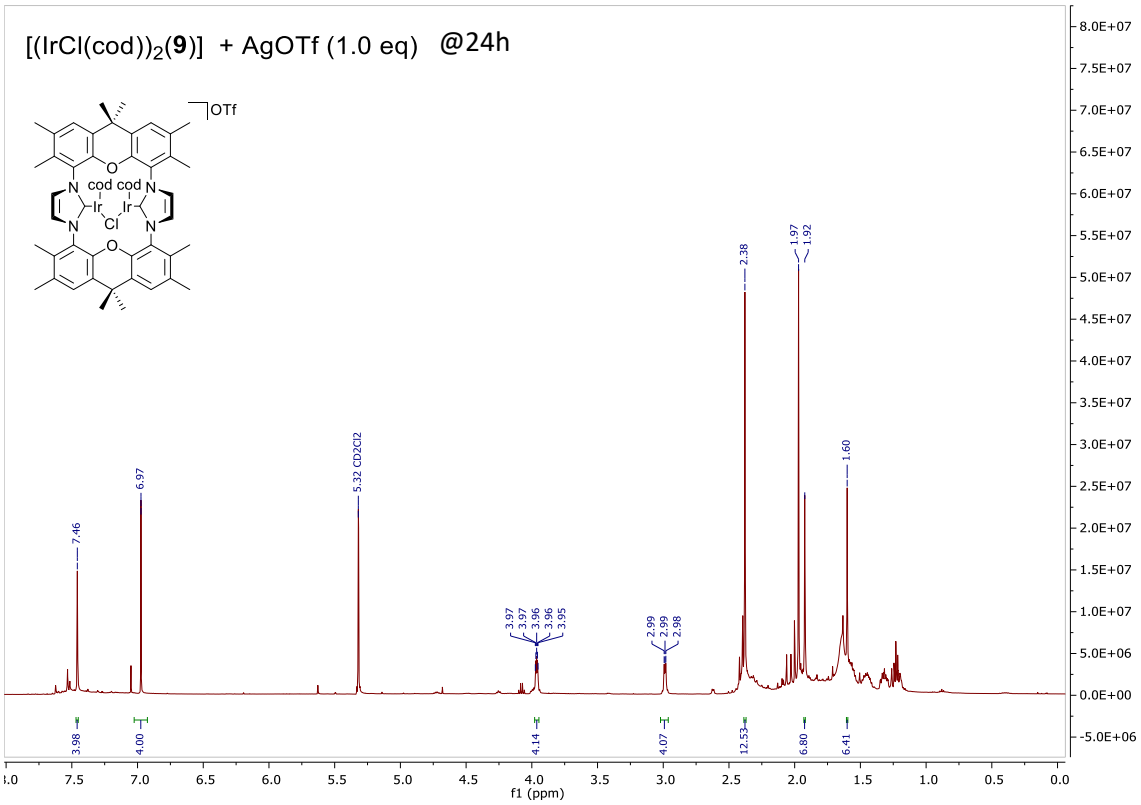


*Figure 23: ^{1}H-NMR of [(IrCl(cod))$_2$(**9**)] + AgOTf @24h in CD_2Cl_2. NMR sample was prepared from a pure substance according to TLC.*

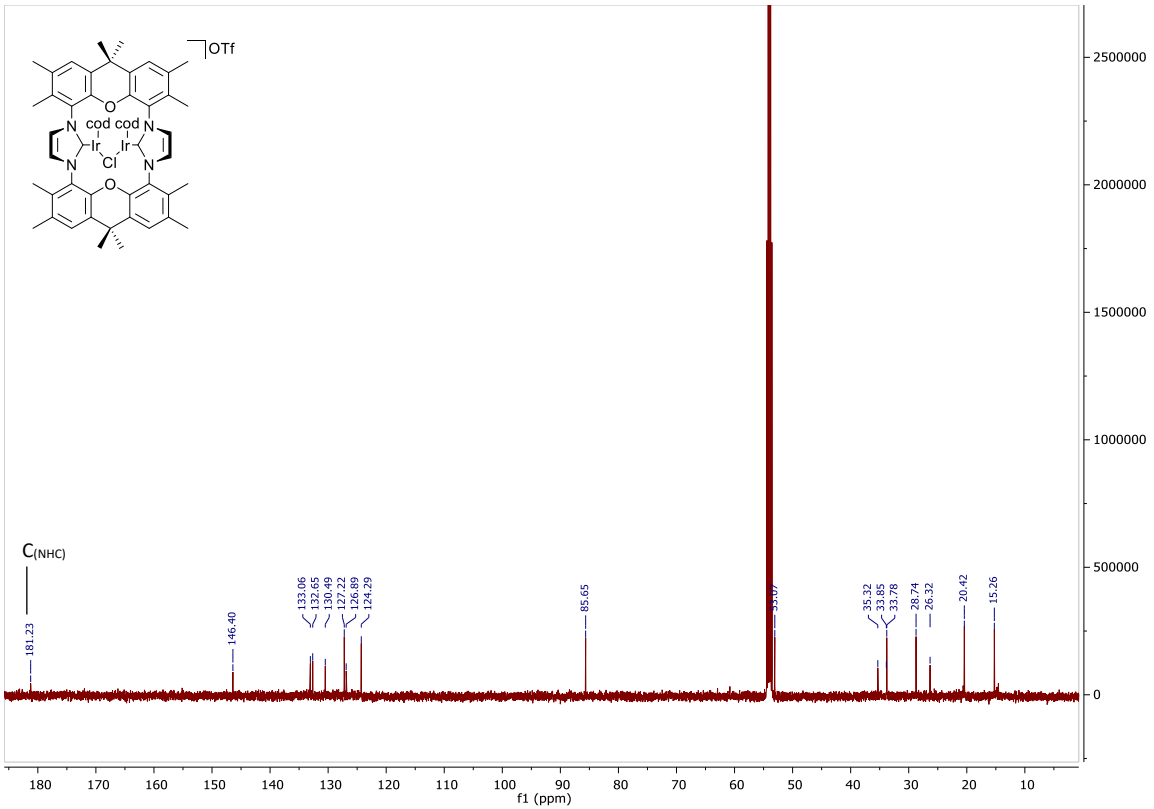


*Figure 24: ^{13}C-NMR of [(IrCl(cod))$_2$(**9**)] + AgOTf @24h in CD_2Cl_2. NMR sample was prepared from a pure substance according to TLC.*

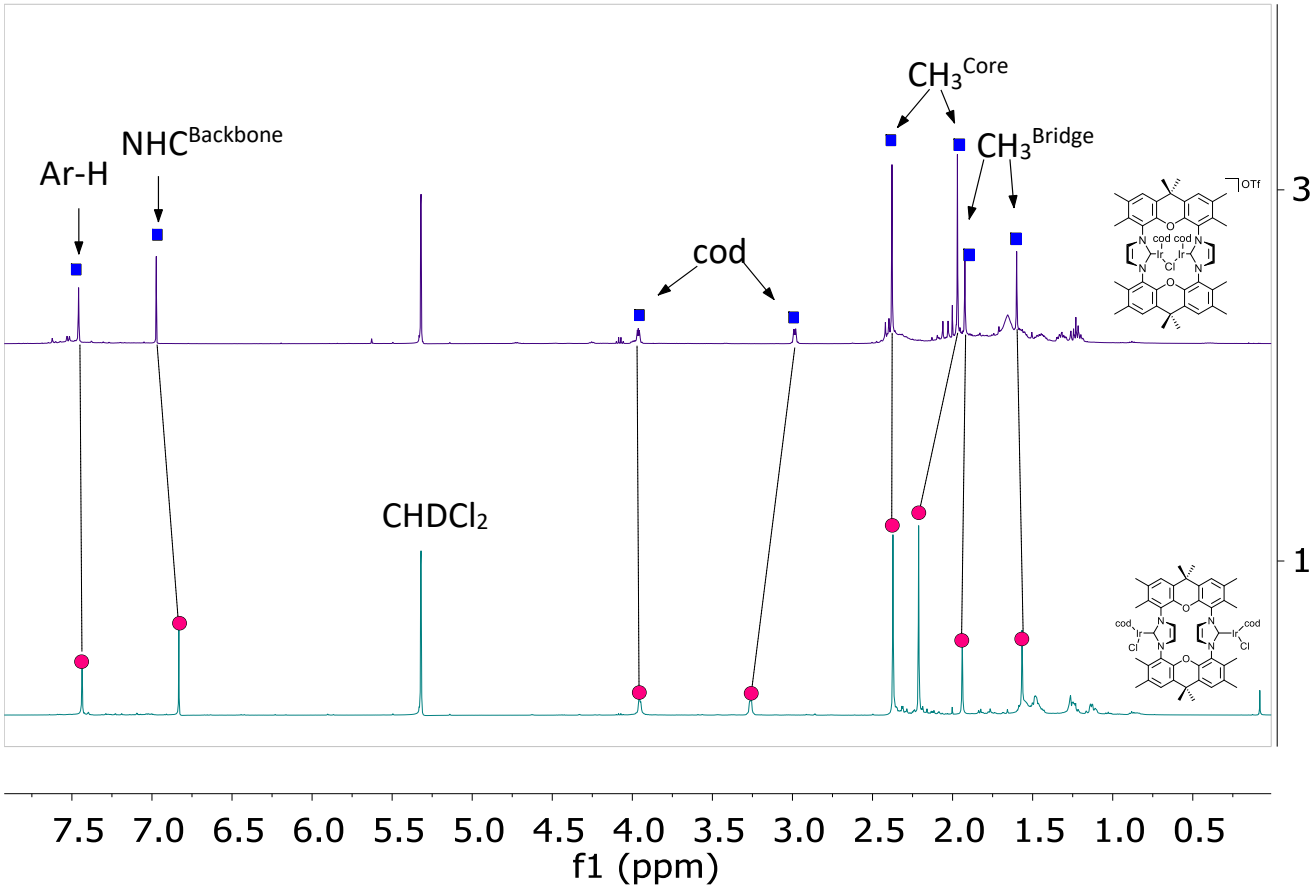


Figure 25: Stacked ^{1}H spectra *of [(IrCl(cod))$_2$(**9**)] (below), [(IrCl(cod))$_2$(**9**)] + AgOTf @24h (above) in CD_2Cl_2.*

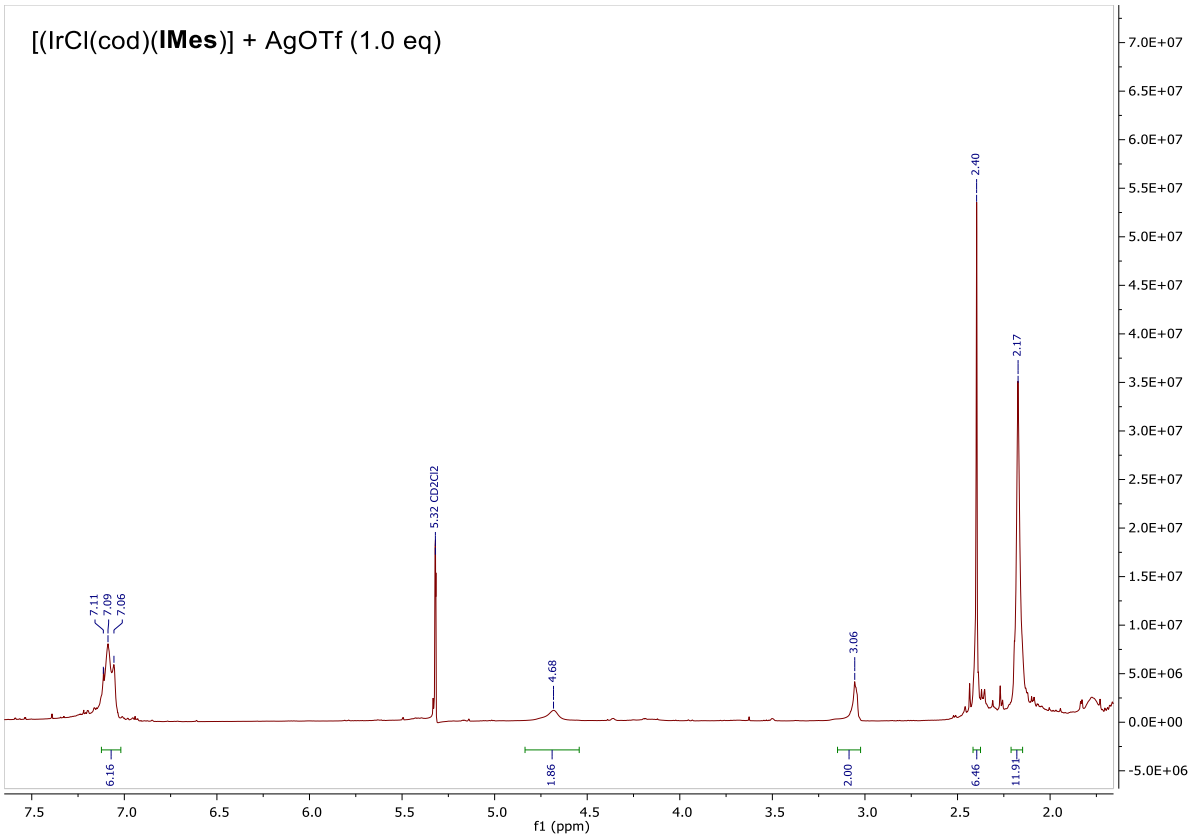


*Figure 26: ^{1}H-NMR of [(IrCl(cod))$_2$(**IMes**)] + AgOTf in CD_2Cl_2 NMR sample was prepared from a pure substance according to TLC.*

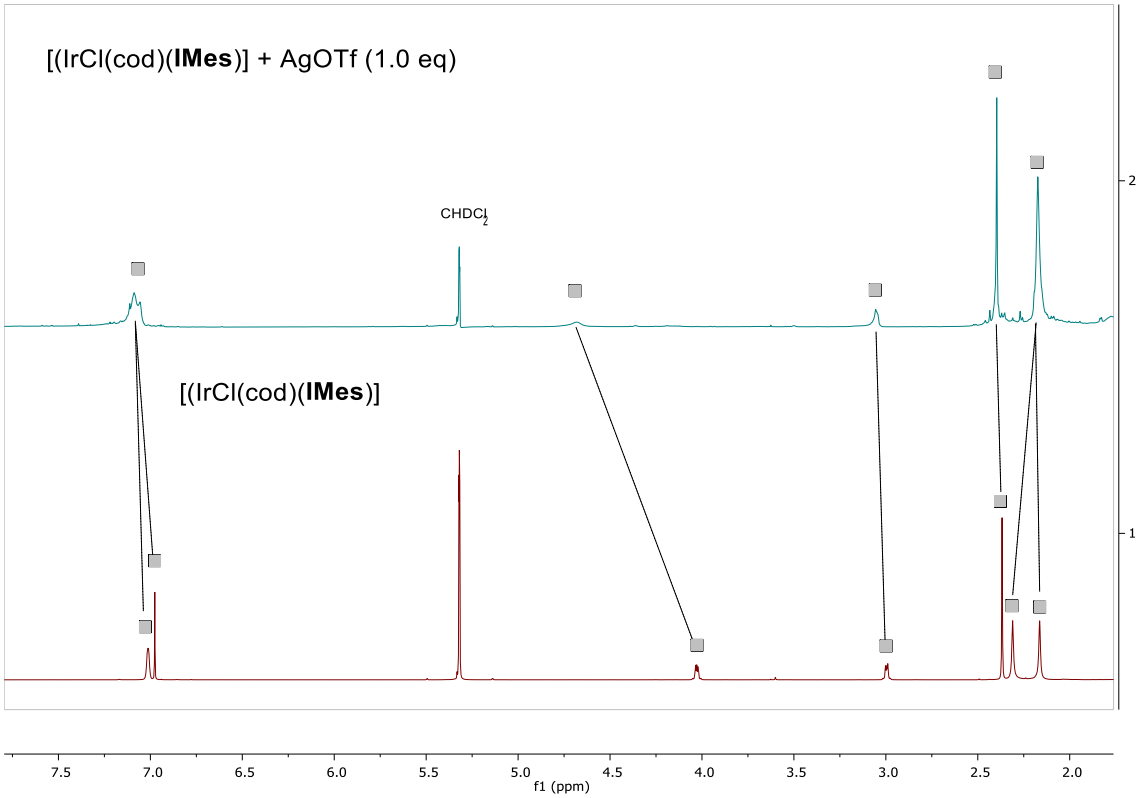


Figure 27: Stacked ^{1}H spectra *of [(IrCl(cod))$_2$(**IMes**)] (below), [(IrCl(cod))$_2$(**IMes**)] + AgOTf (above) in CD_2Cl_2.*

[(IrCl(CO)$_2$)$_2$(**9**)]

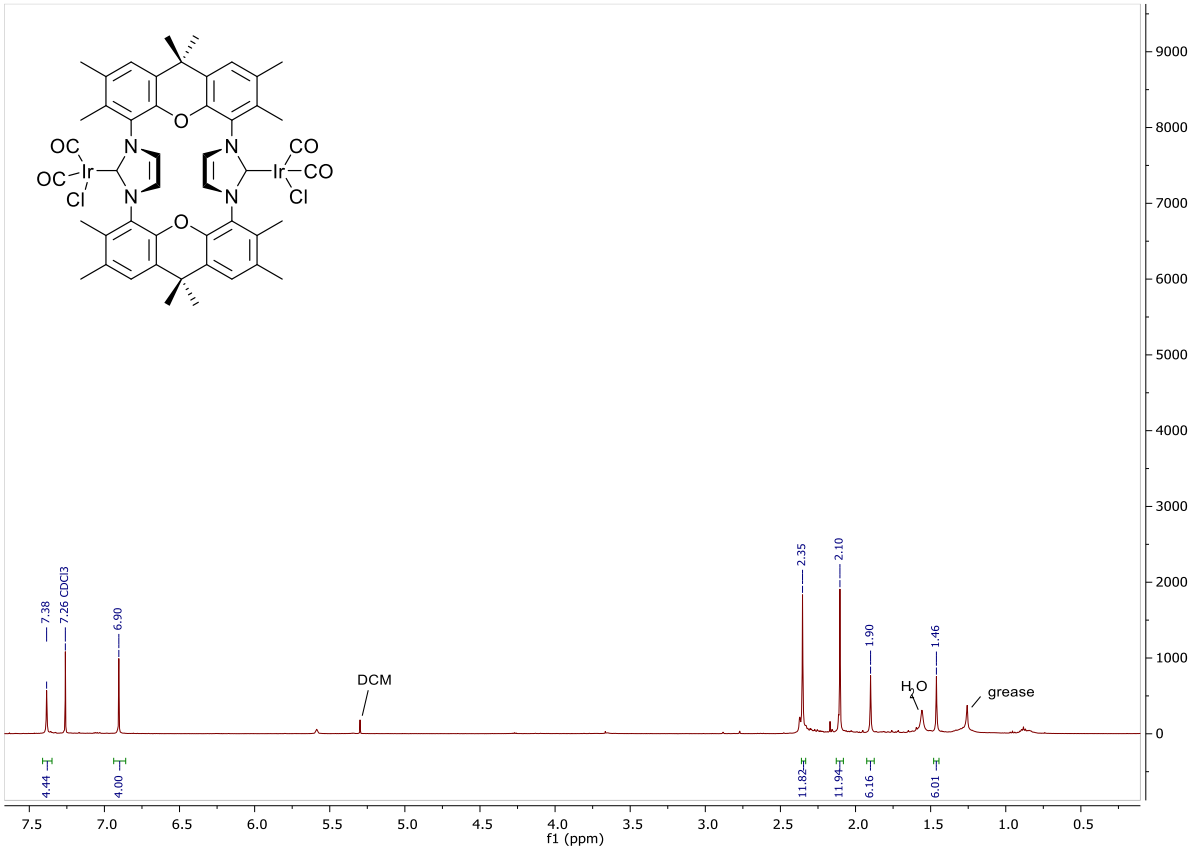


*Figure 28: ^{1}H-NMR of [(IrCl(CO)$_2$)$_2$(**9**)] in $CDCl_3$.*

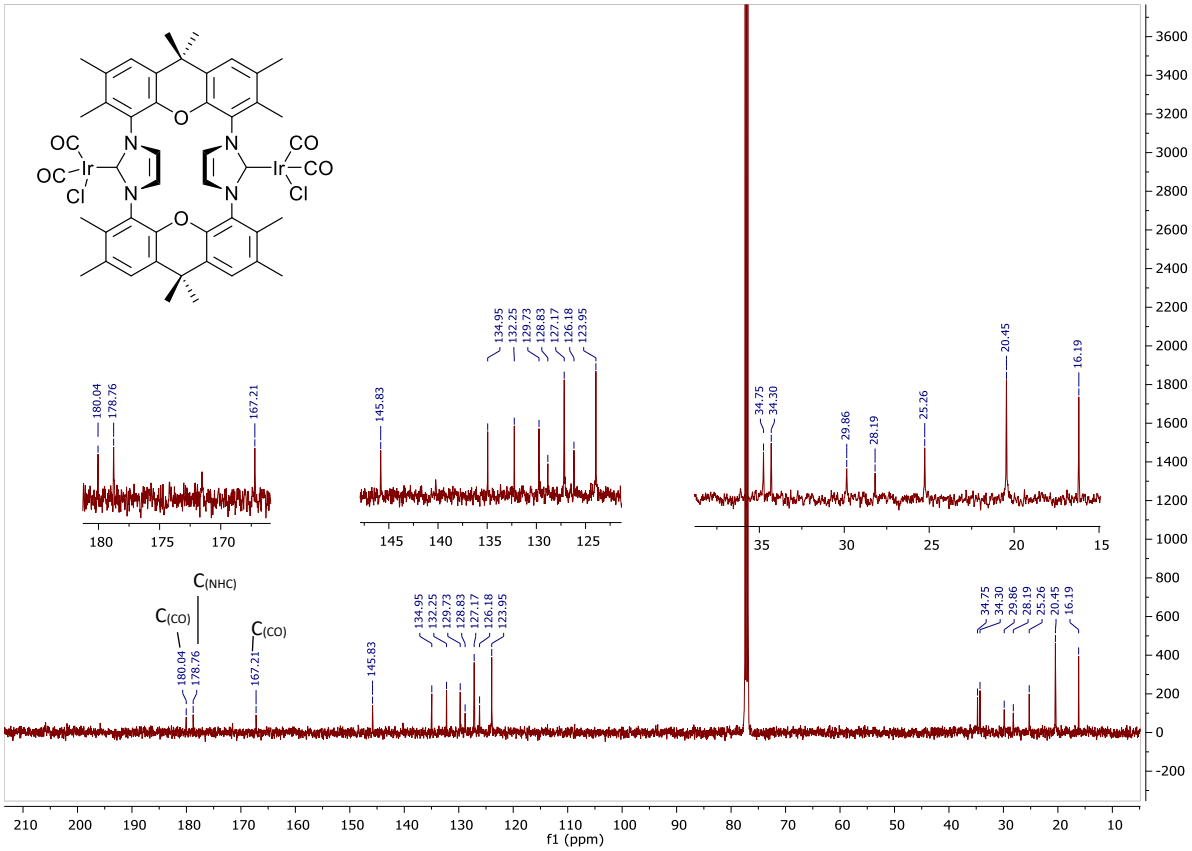


*Figure 29: ^{13}C-NMR of [(IrCl(CO)$_2$)$_2$(**9**)] in $CDCl_3$.*

[(RhCl(CO)$_2$)$_2$(**9**)]

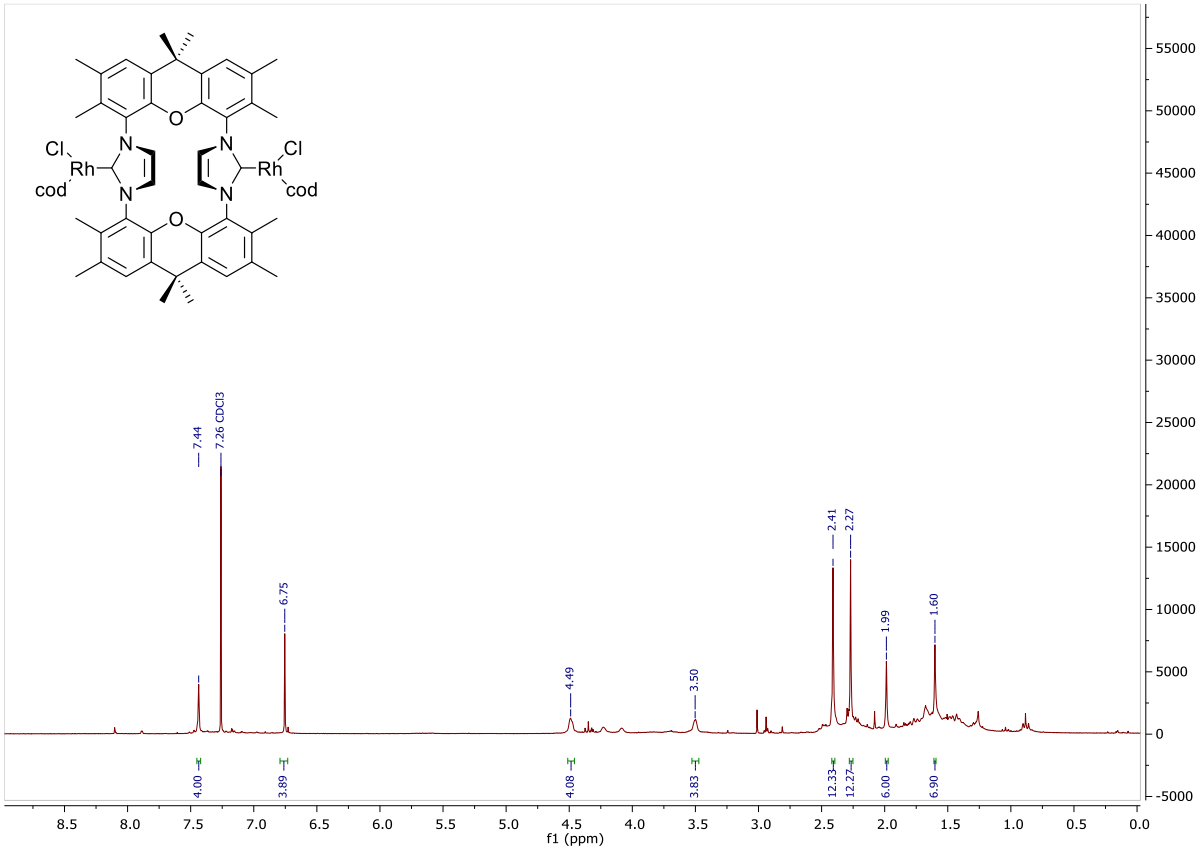


*Figure 30: ^{1}H-NMR of **crude** [(RhCl(CO)$_2$)$_2$(**9**)] in CDCl$_3$.*

[(AuCl)$_2$(**9**)]

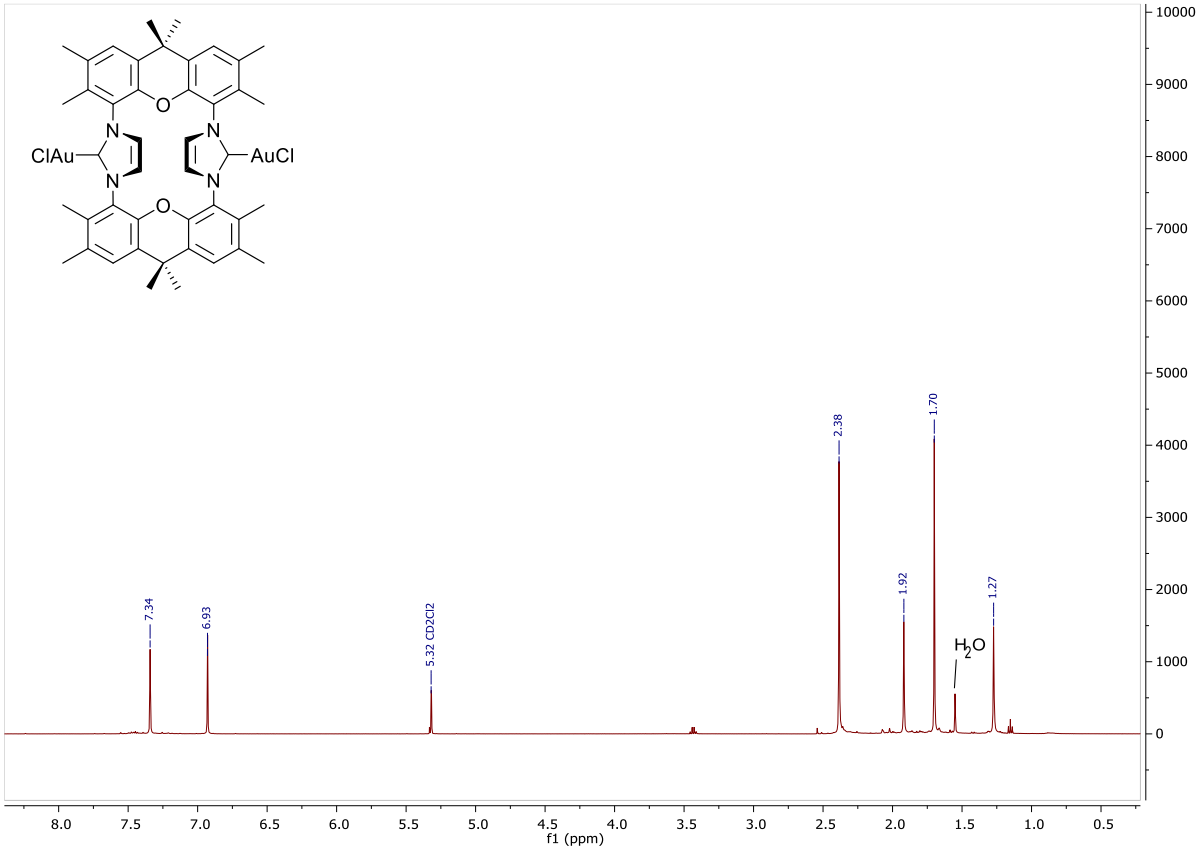


*Figure 31: ^{1}H-NMR of [(AuCl)$_2$(**9**)] in CD_2Cl_2.*

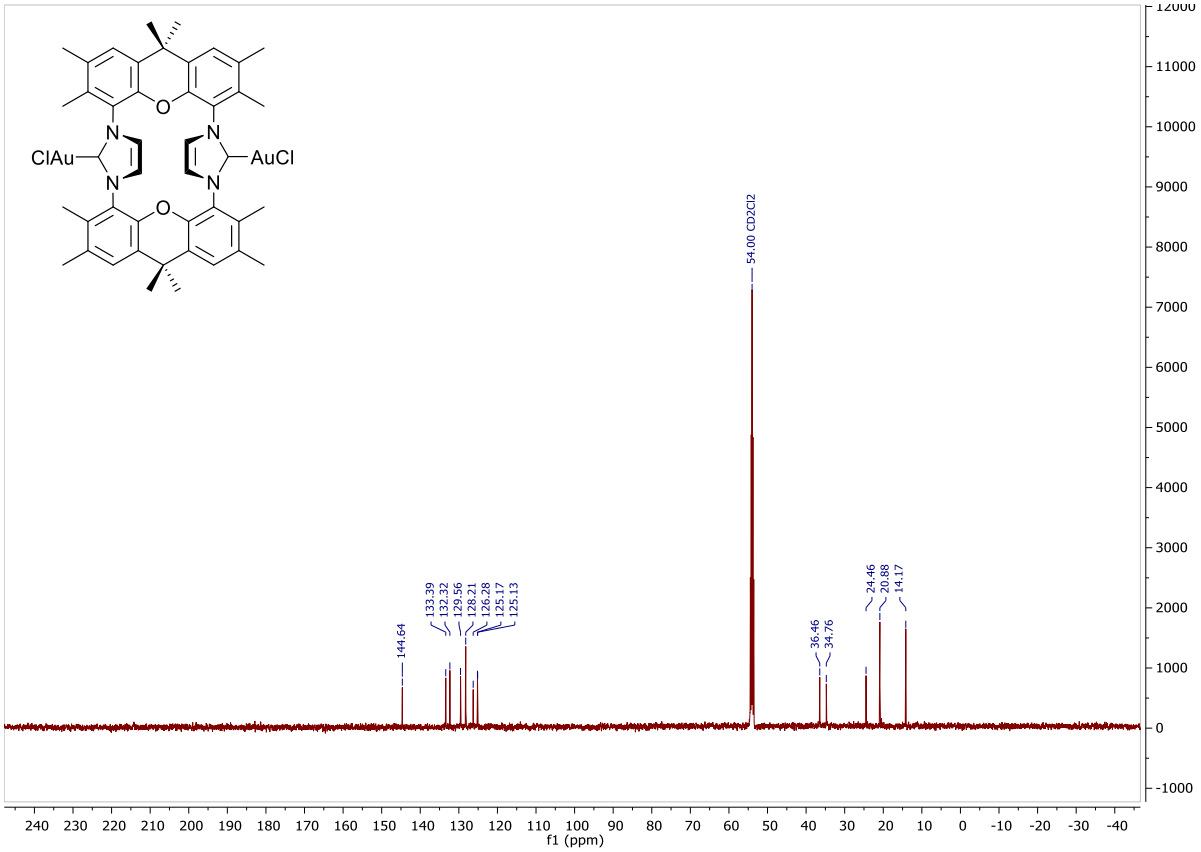


*Figure 32: ^{13}C-NMR of [(AuCl)$_2$(**9**)] in CD_2Cl_2.*

Xanthene diimine (**10**)

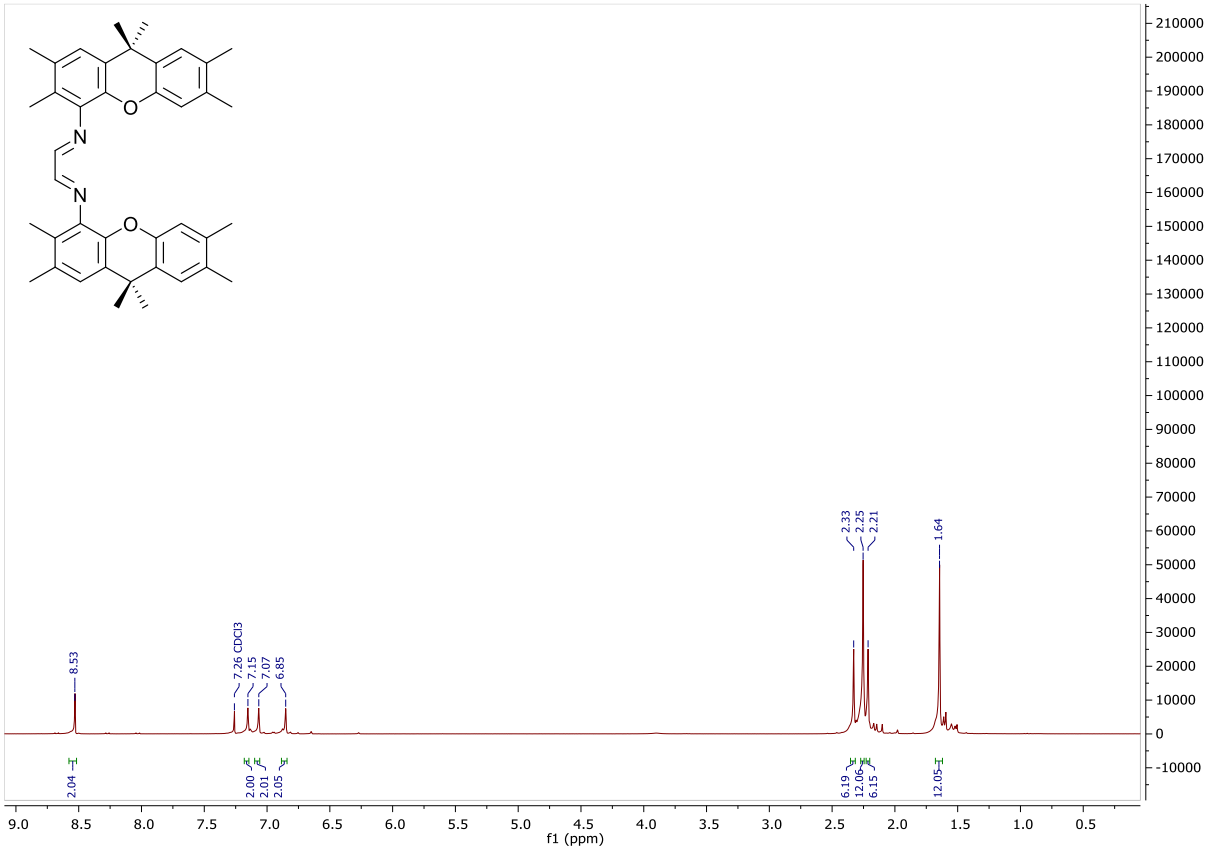


*Figure 33: ^{1}H-NMR of xanthene diimine (**10**) in $CDCl_3$.*

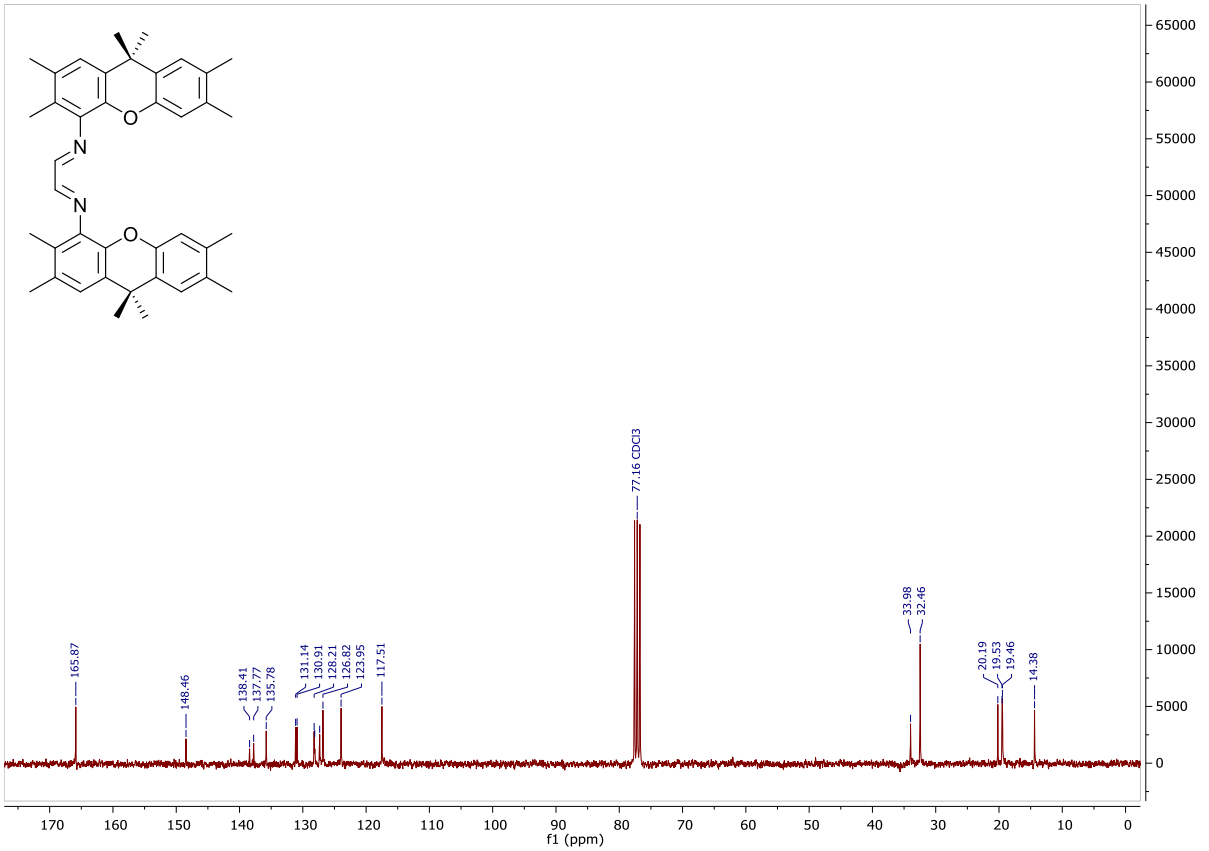


*Figure 34: ^{13}C-NMR of xanthene diimine (**10**) in $CDCl_3$.*

Xanthene imidazolium salt (**11** · HCl)

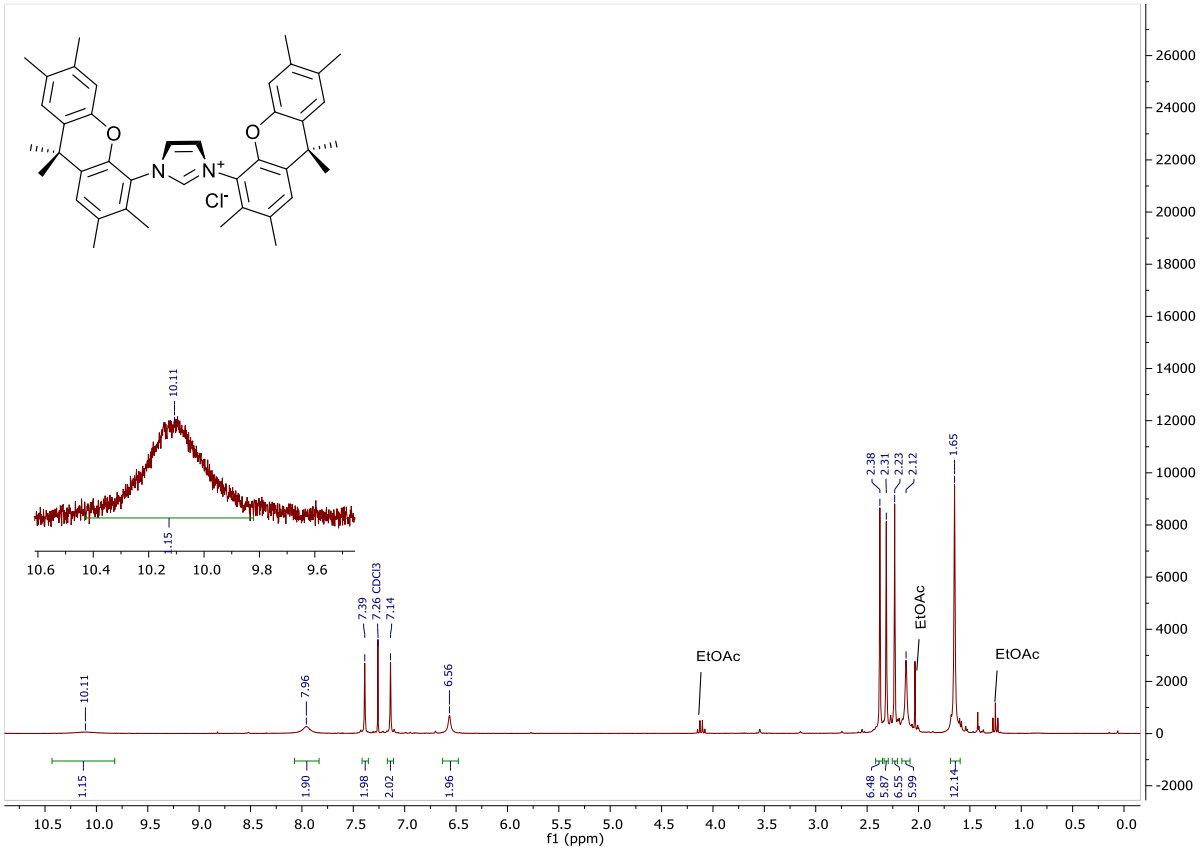


*Figure 35: ^{1}H-NMR of **11** · HCl in $CDCl_3$.*

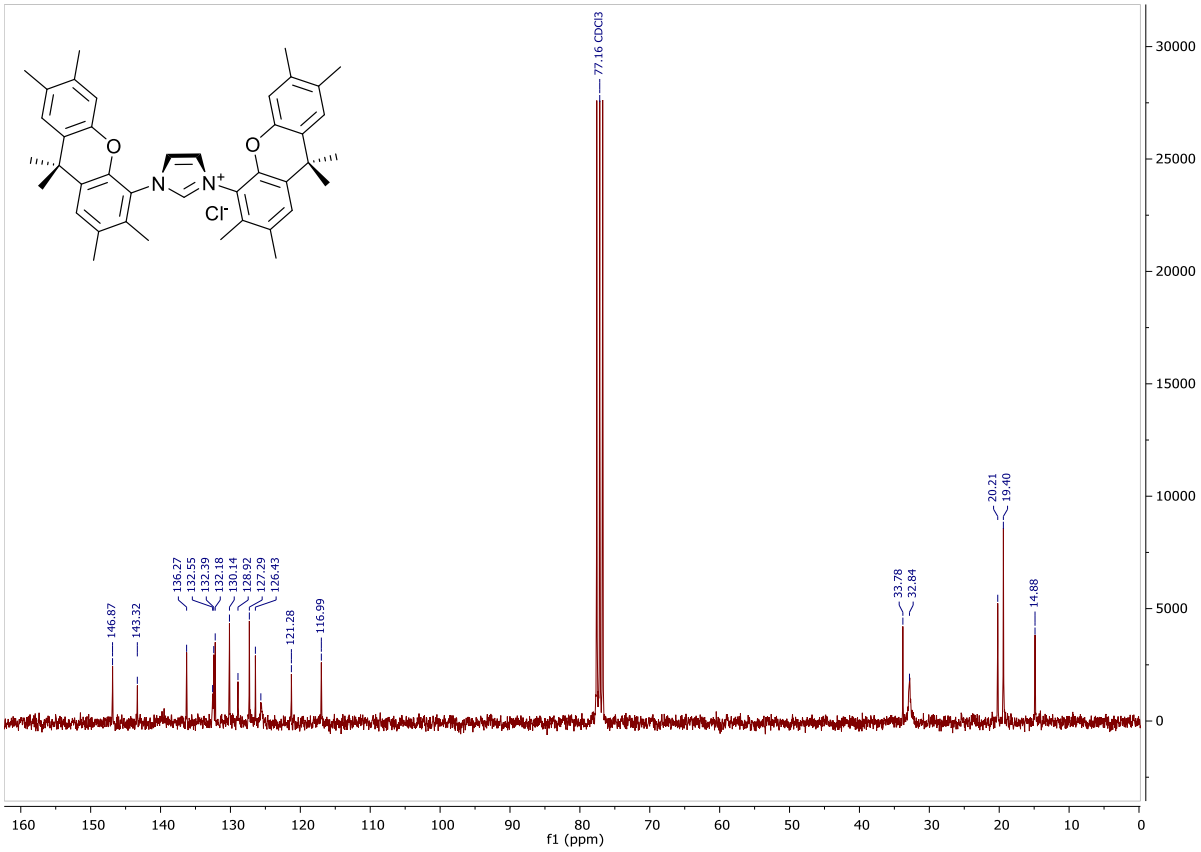


*Figure 36: ^{13}C-NMR of **11** · HCl in $CDCl_3$.*

[(AuCl)(**11**)]

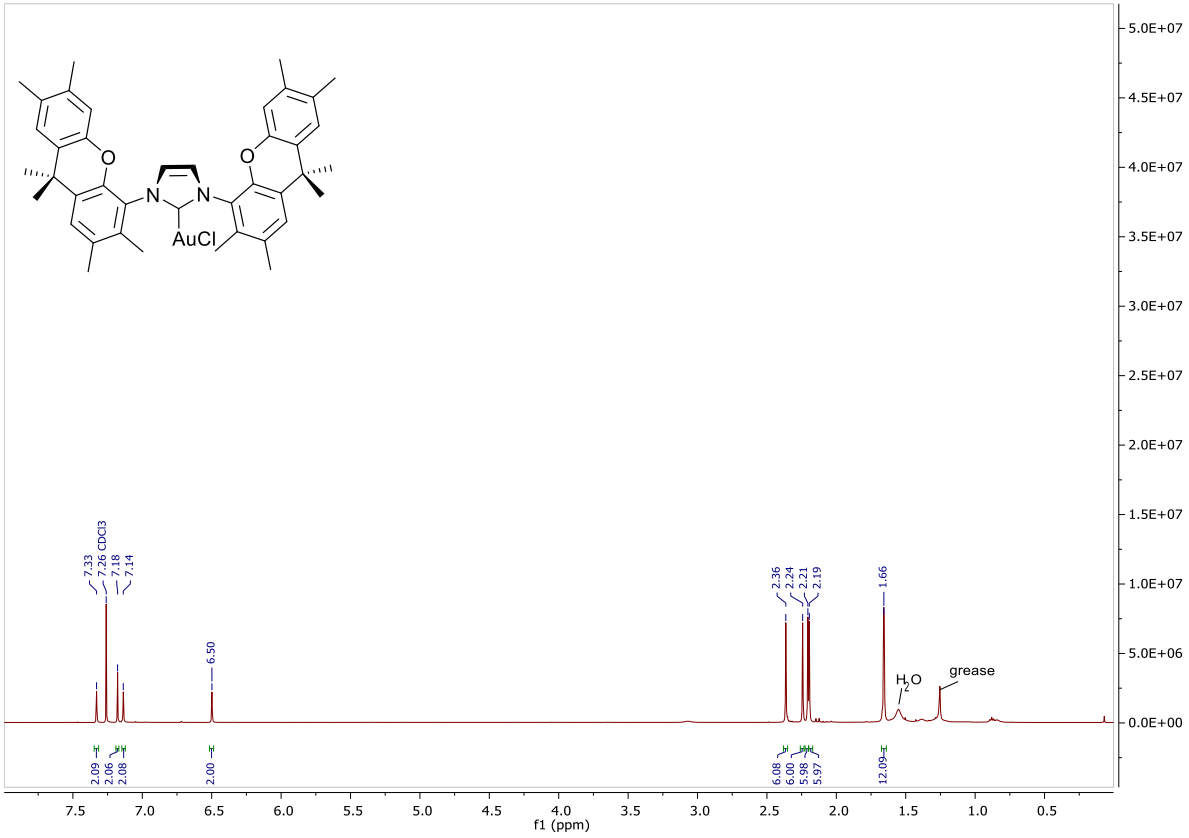


*Figure 37: ^{1}H-NMR of [(AuCl)(**11**)] in $CDCl_3$.*

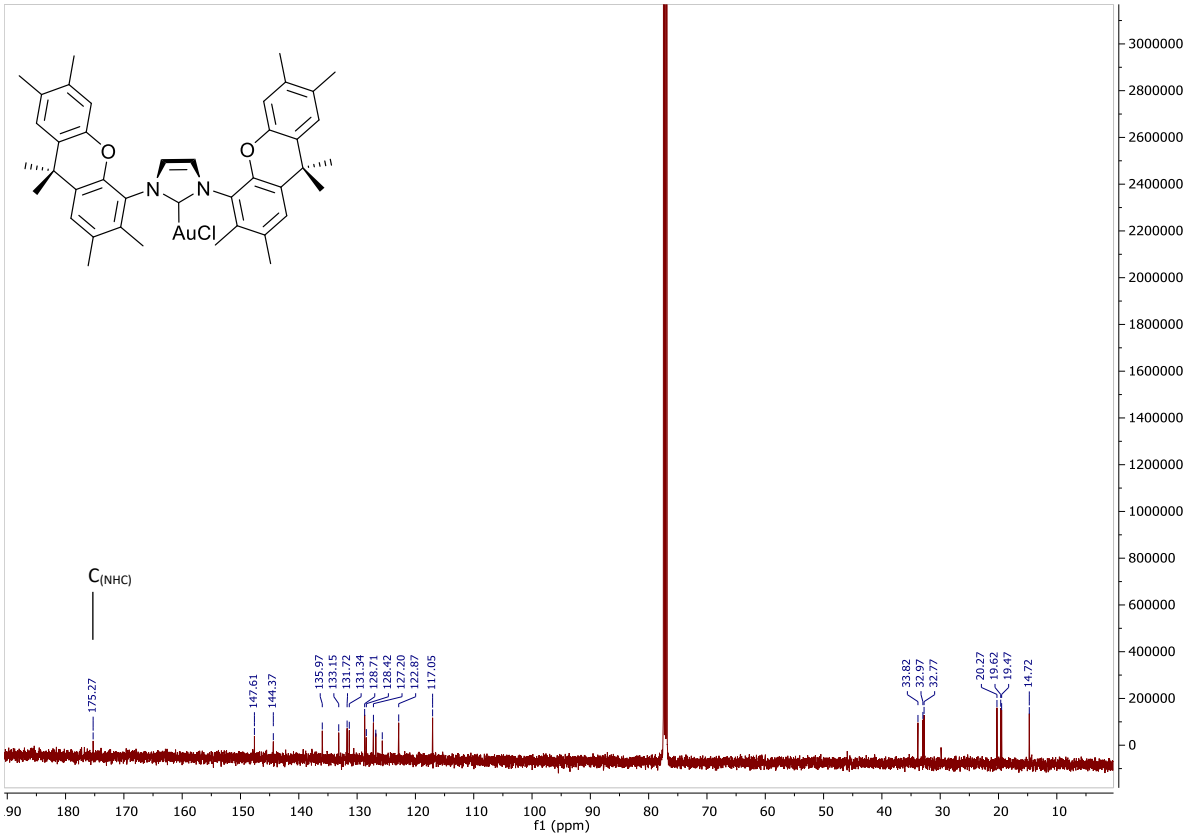


*Figure 38: ^{13}C-NMR of [(AuCl)(**11**)] in $CDCl_3$.*

[(IrCl(cod))(**11**)]

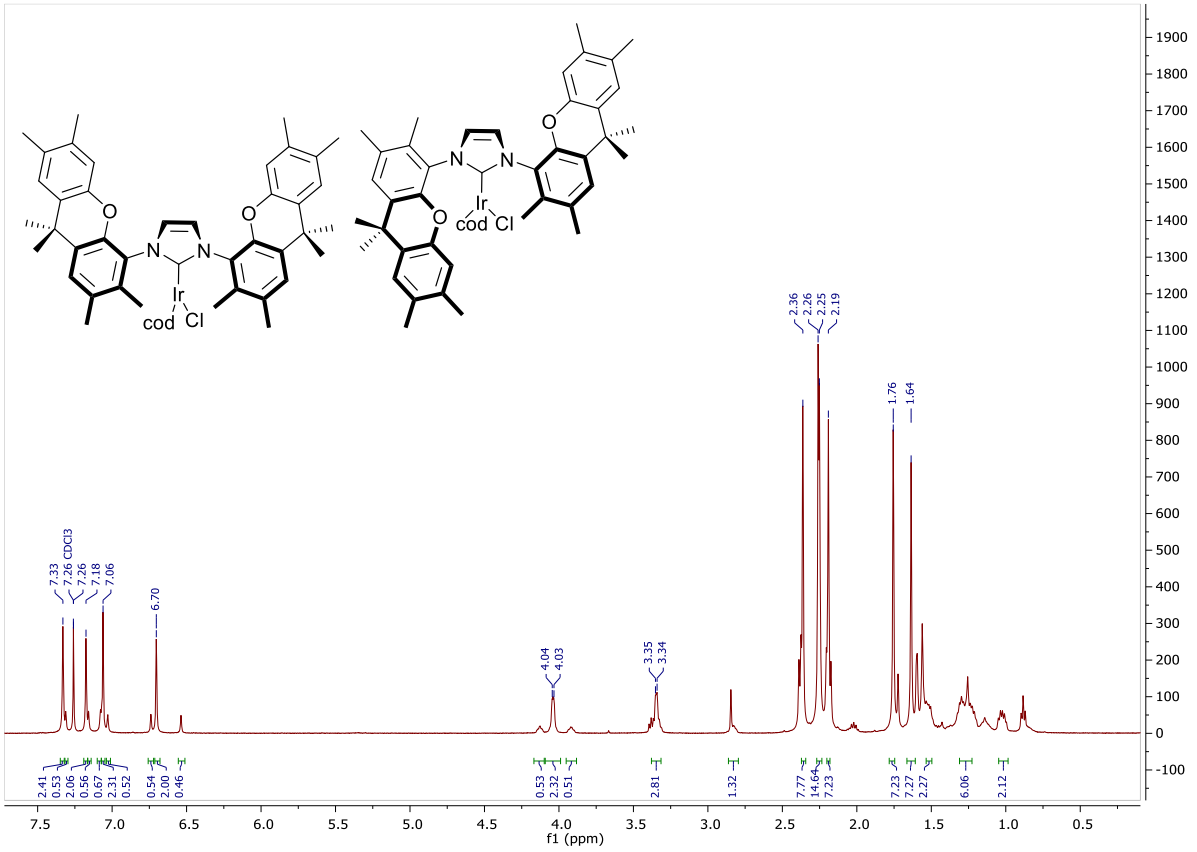


*Figure 39: ^{1}H-NMR of [(IrCl(cod))(**11**)] syn/anti in $CDCl_3$. Isomer mixture ratio approximately 70:30 (major/minor).*

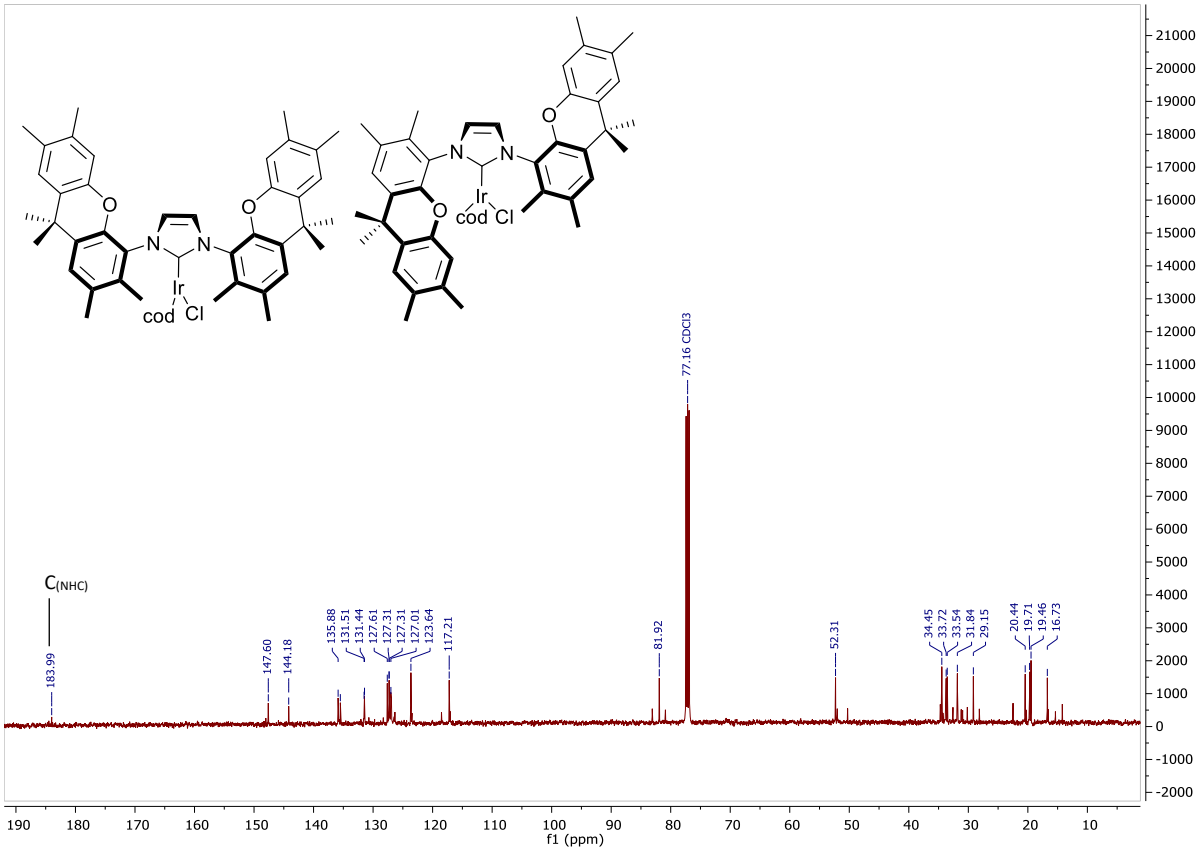


*Figure 40: ^{13}C-NMR of [(IrCl(cod))(**11**)] syn/anti in $CDCl_3$. Isomer mixture ratio approximately 70:30 (major/minor).*

[(IrCl(CO)$_2$)(**11**)]

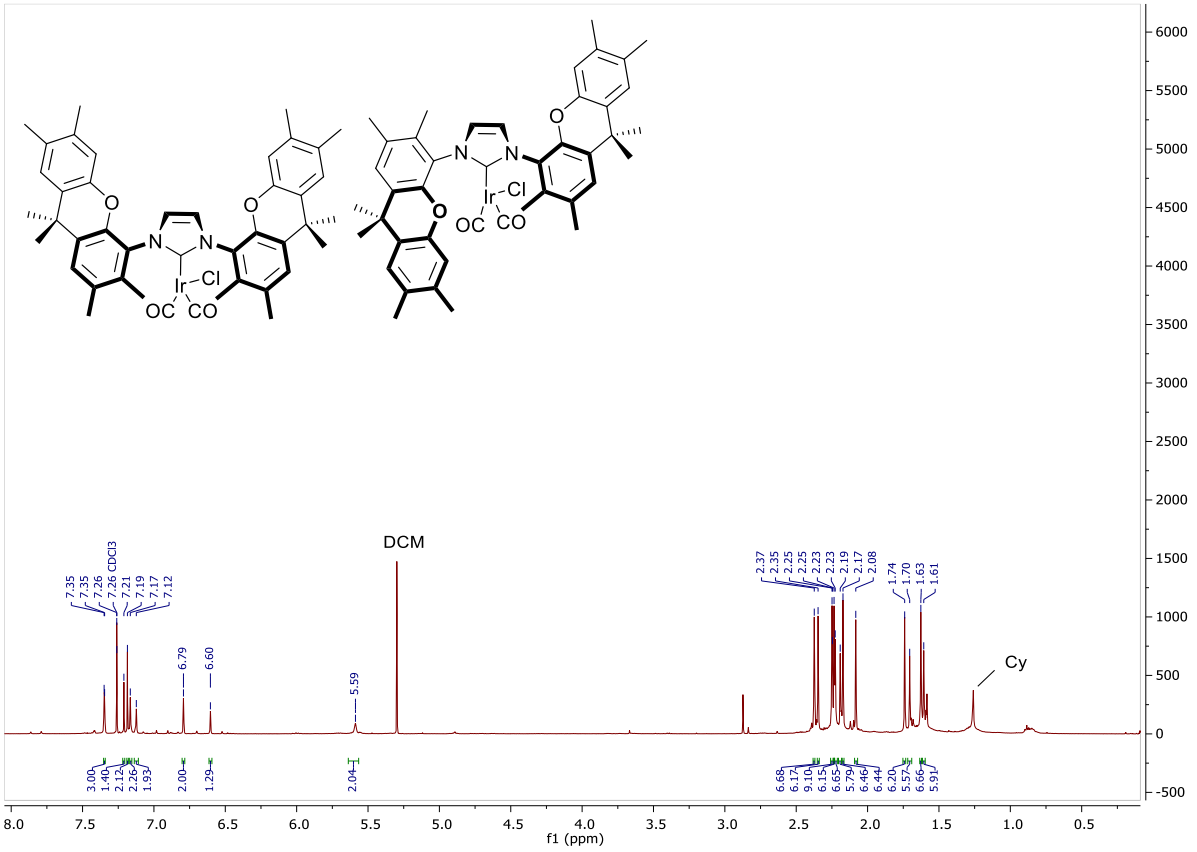


*Figure 41: ^{1}H-NMR of [(IrCl(CO)$_2$)(**11**)] syn/anti in CDCl$_3$. Isomer mixture ratio approximately 50:50.*

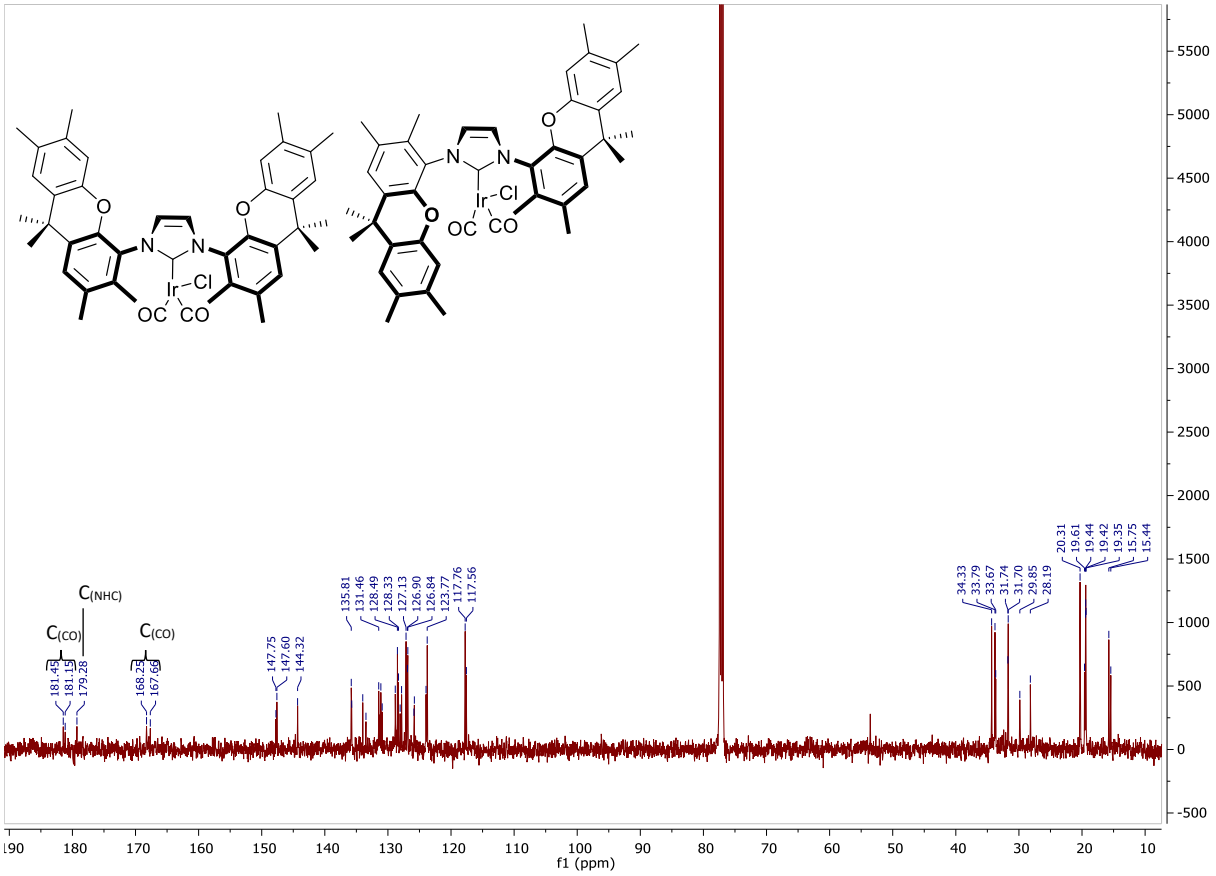


*Figure 42: ^{13}C-NMR of [(IrCl(CO)$_2$)(**11**)] syn/anti in CDCl$_3$. Isomer mixture ratio approximately 50:50.*

Xanthene tetraamide (**12**)

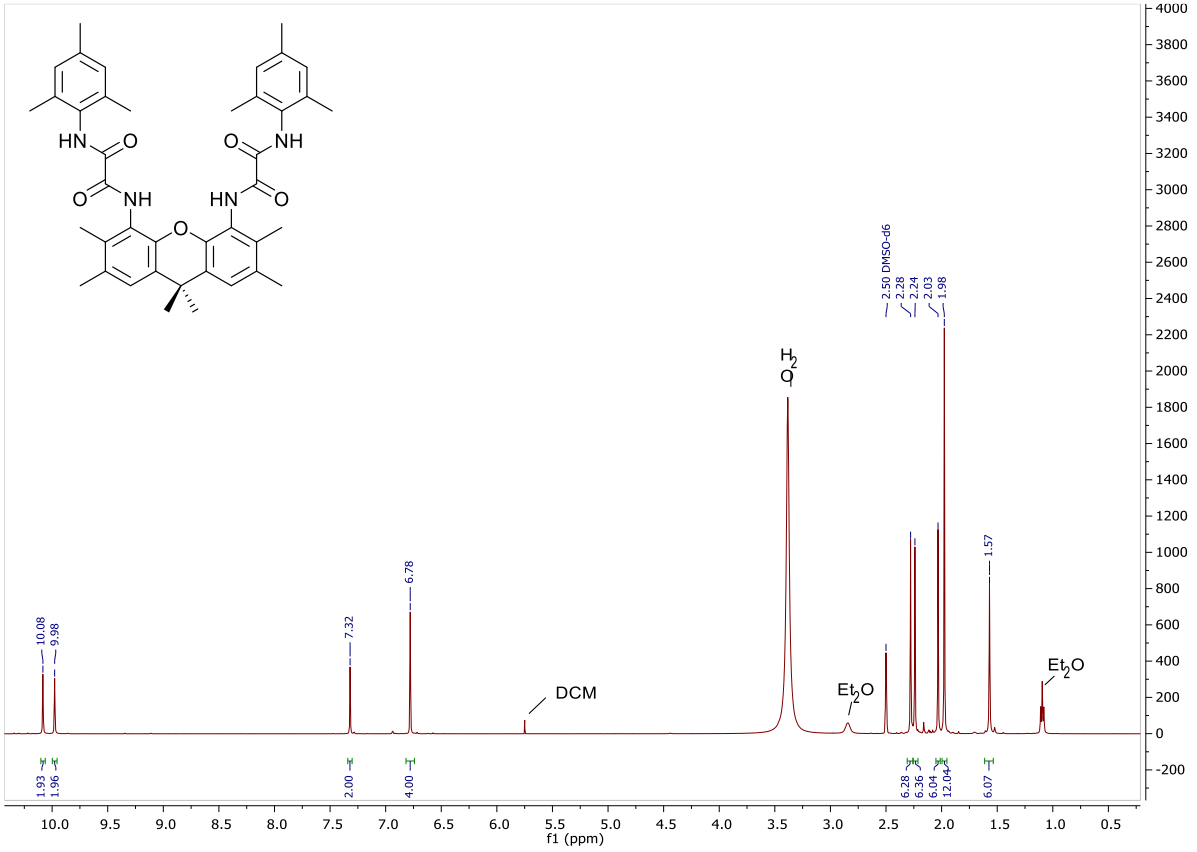


*Figure 43: ^{1}H-NMR of of xanthene tetraamide (**12**) in DMSO-d_6.*

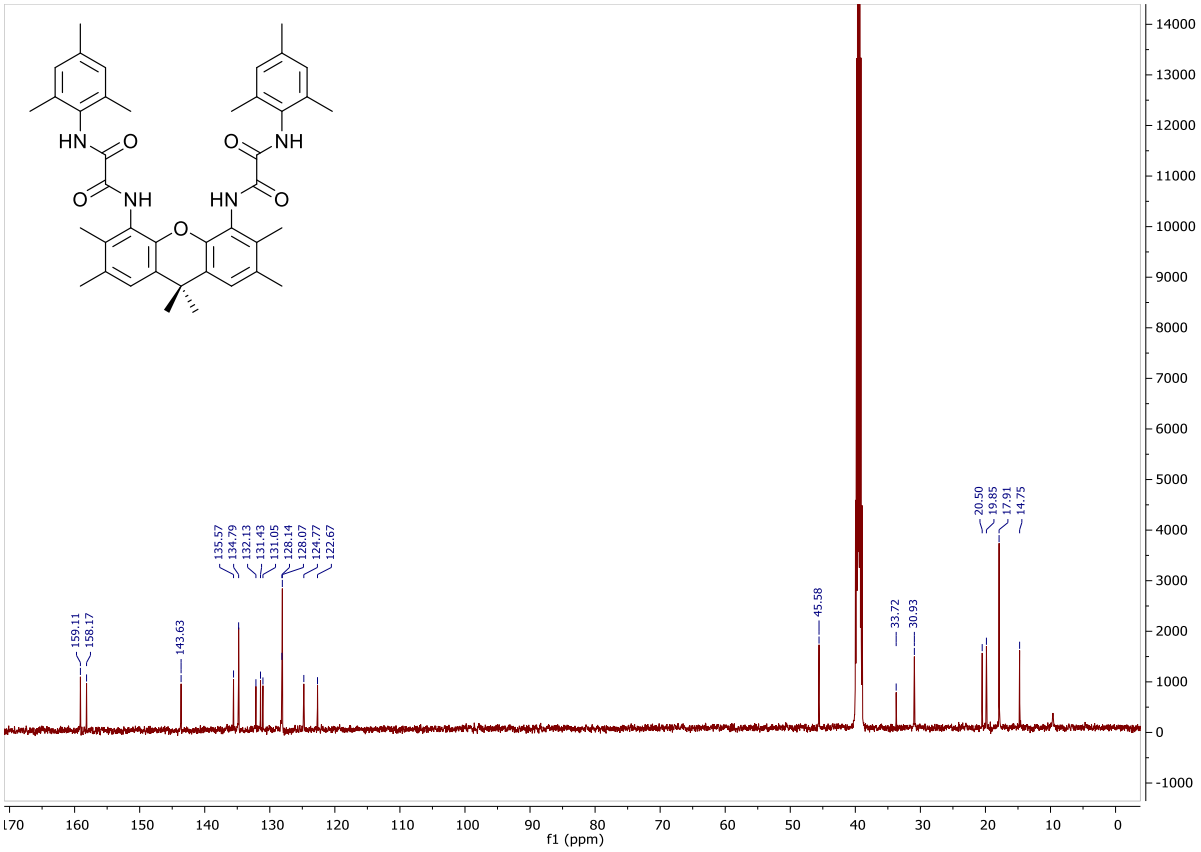


*Figure 44: ^{13}C-NMR of xanthene tetraamide (**12**) in DMSO-d_6.*

Xanthene tetramine (**13**)

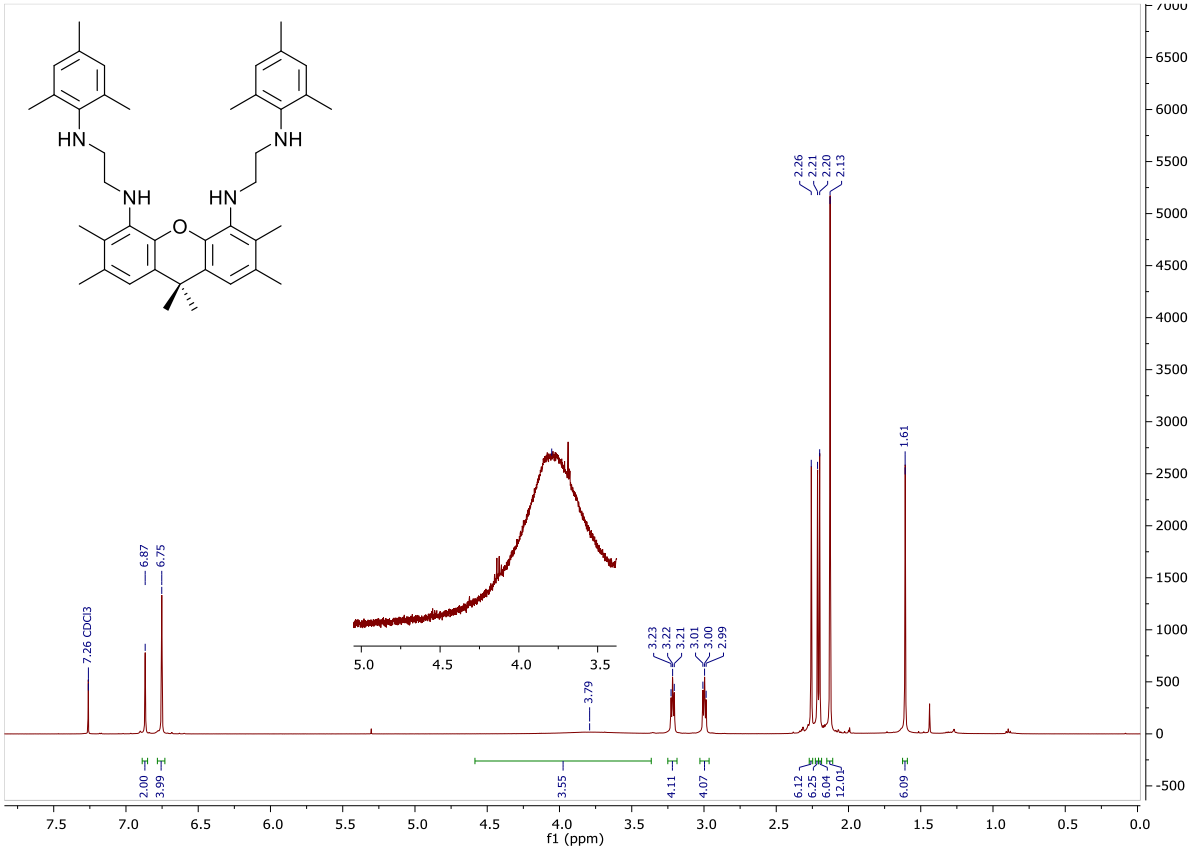


*Figure 45: ^{1}H-NMR of xanthene tetramine (**13**) in $CDCl_3$.*

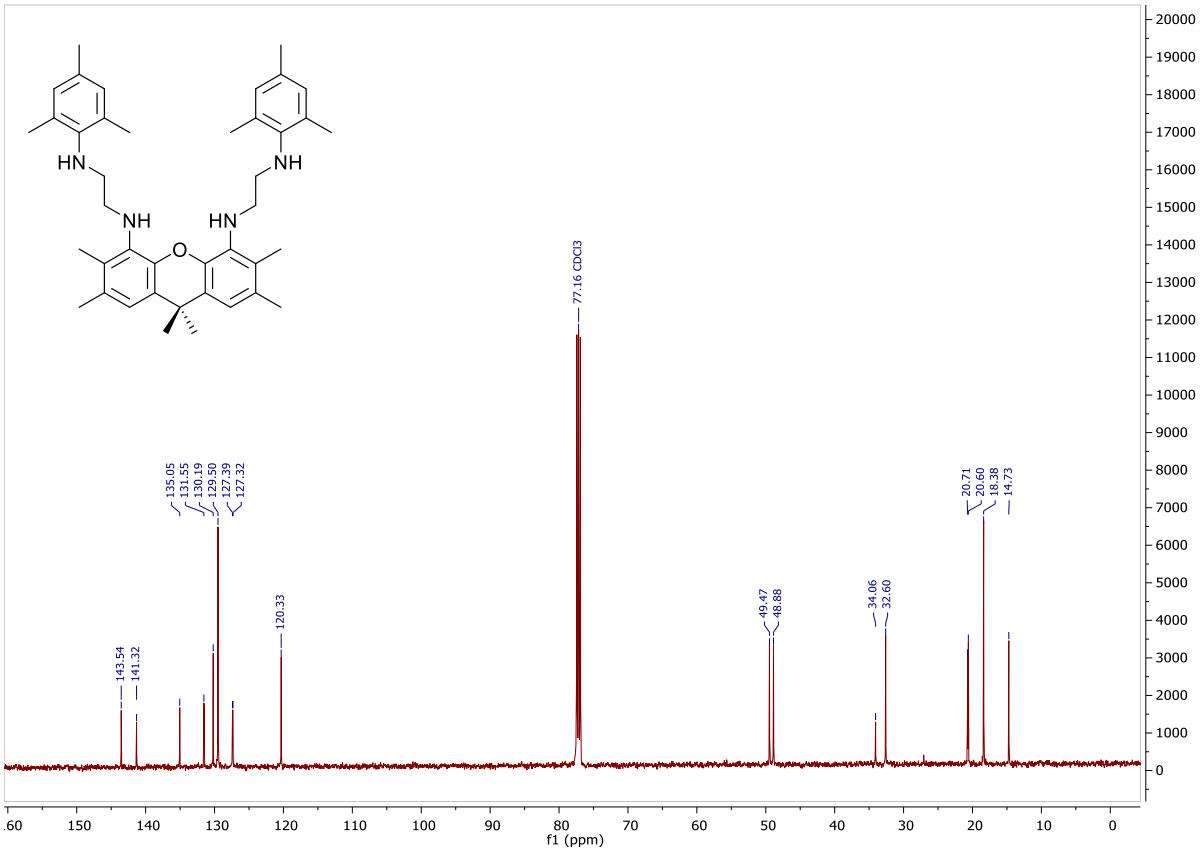


*Figure 46: ^{13}C-NMR of xanthene tetramine (**13**) in $CDCl_3$.*

Imidazolinium salt (**14** · 2 HCl)

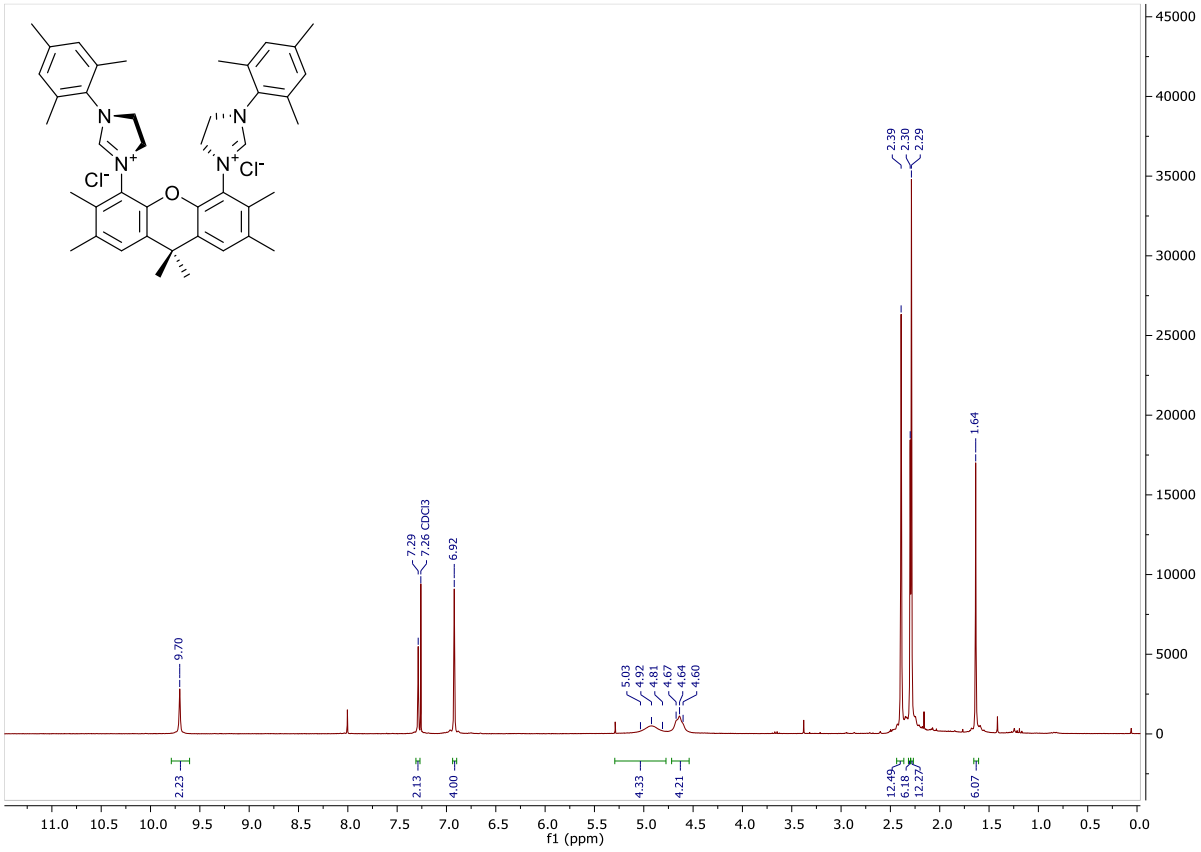


*Figure 47: ^{1}H-NMR of **14** · 2 HCl in $CDCl_3$.*

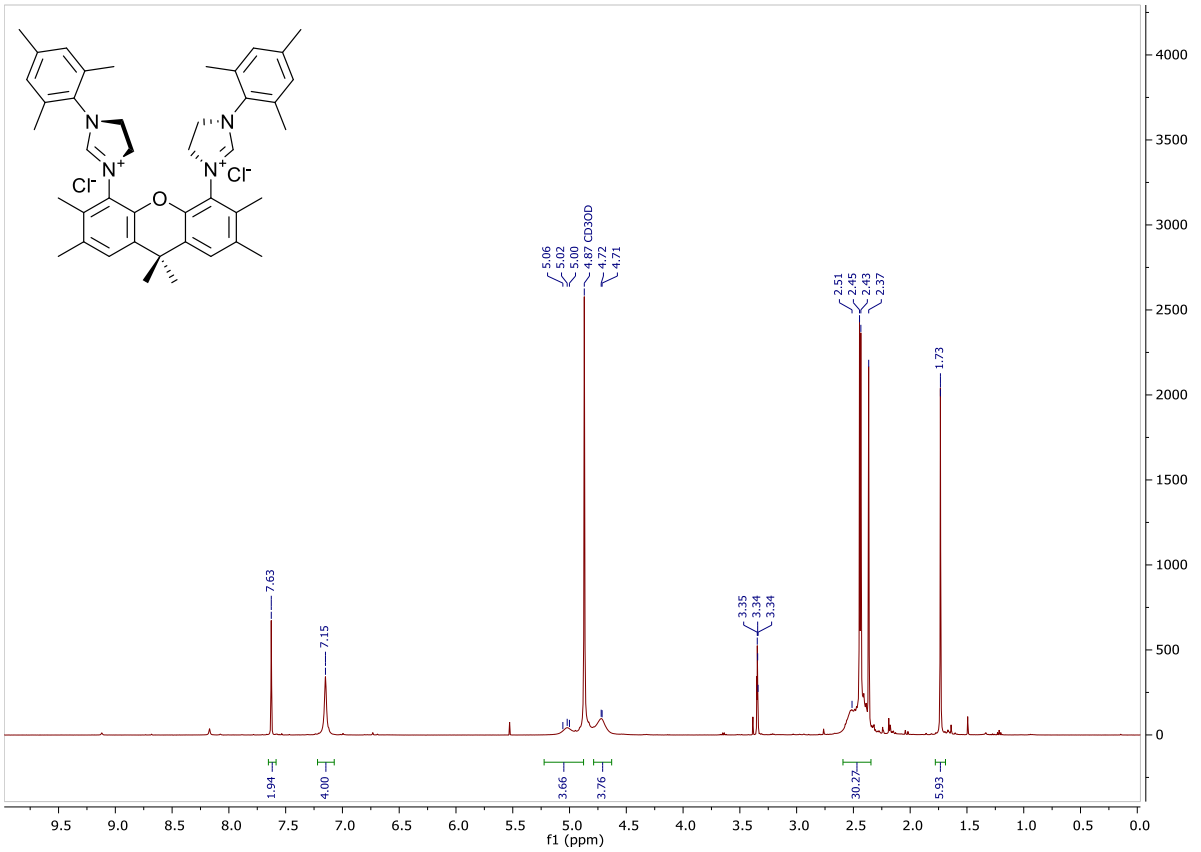


*Figure 48: ^{1}H-NMR of **14** · 2 HCl in MeOD.*

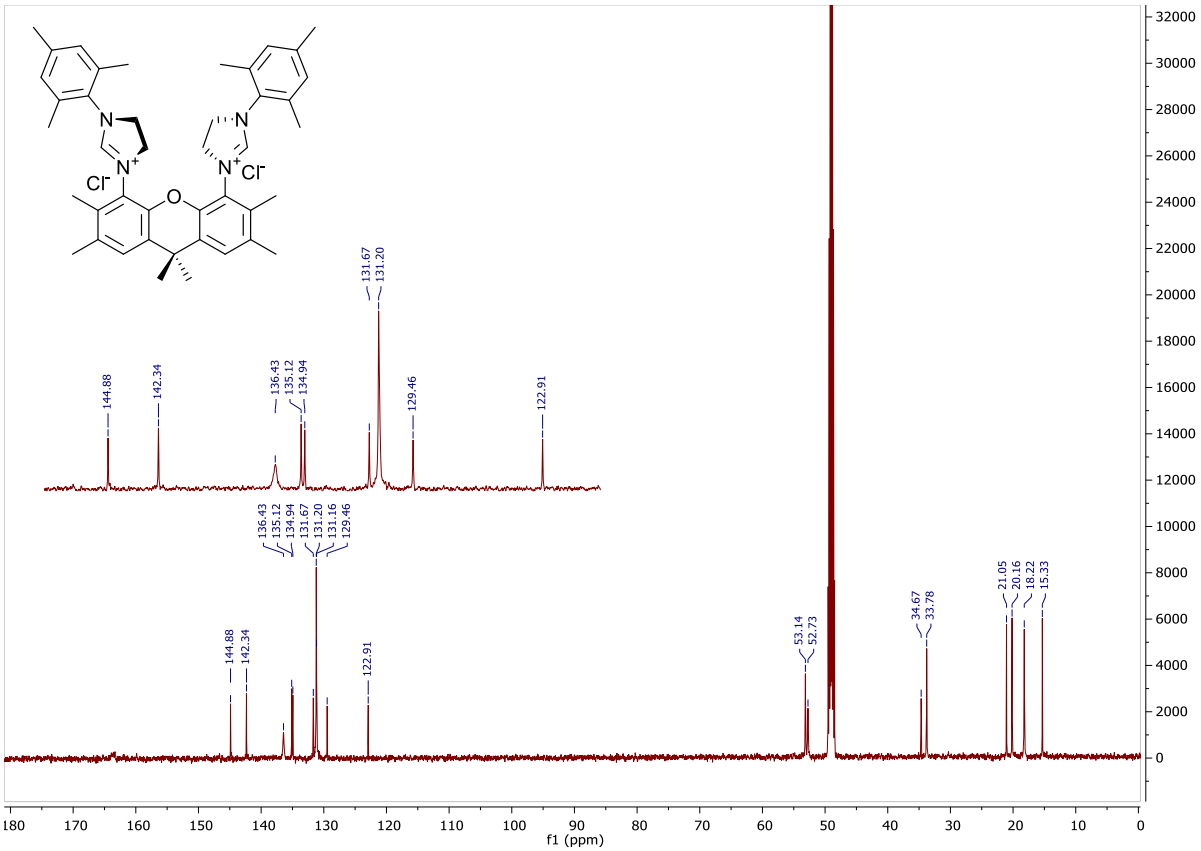


*Figure 49: ^{13}C-NMR of xanthene **14** · 2 HCl in MeOD.*

[(IrCl(cod))$_2$(**14**)]

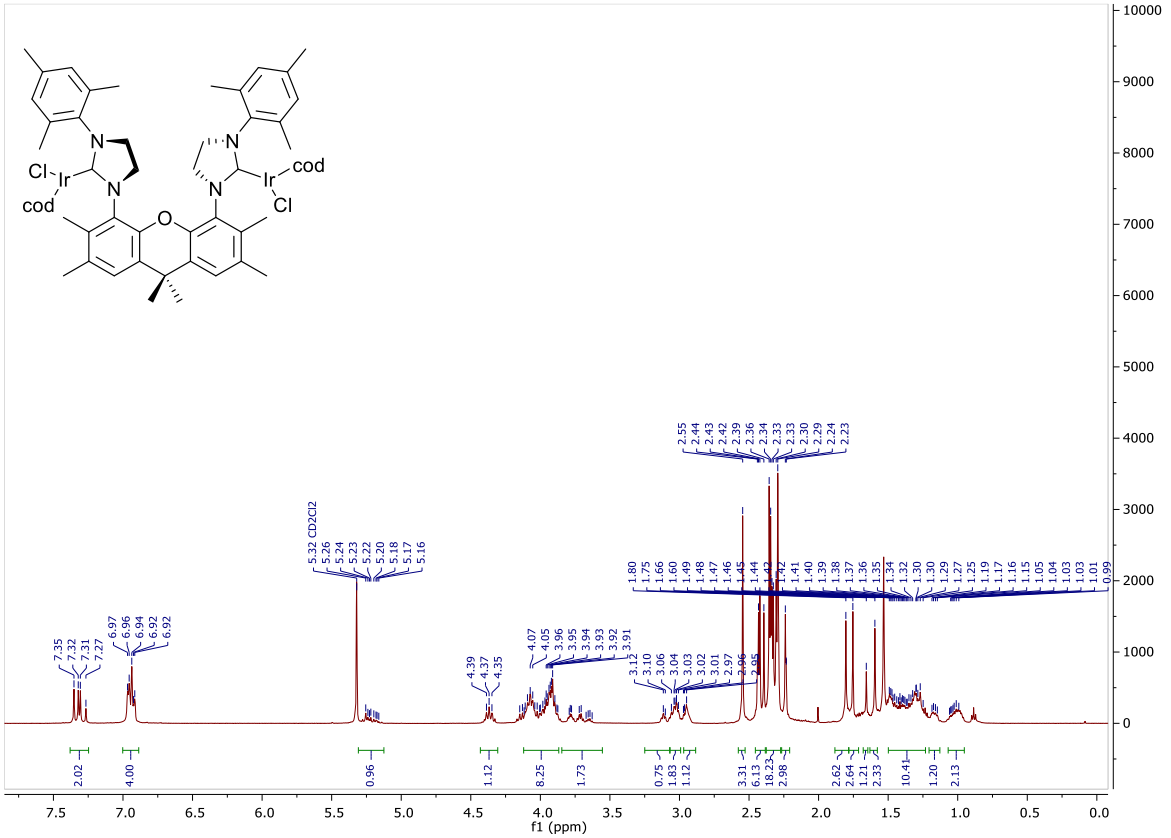


*Figure 50: ^{1}H-NMR of [(IrCl(cod))$_2$(**14**)] in CD_2Cl_2. NMR sample was prepared from a pure substance according to TLC.*

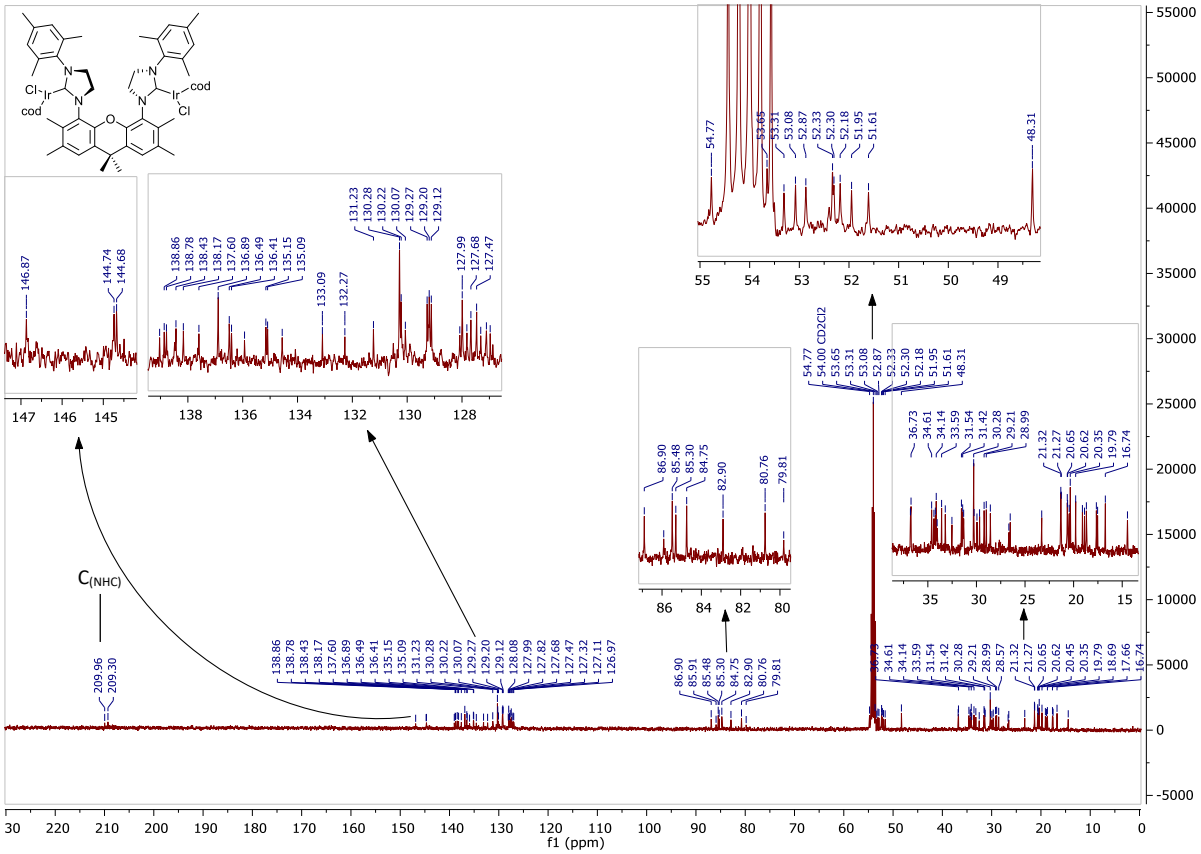


*Figure 51: ^{1}H-NMR of [(IrCl(cod))$_2$(**14**)] in CD_2Cl_2. NMR sample was prepared from a pure substance according to TLC*

[(IrCl(CO)$_2$)$_2$(**14**)]

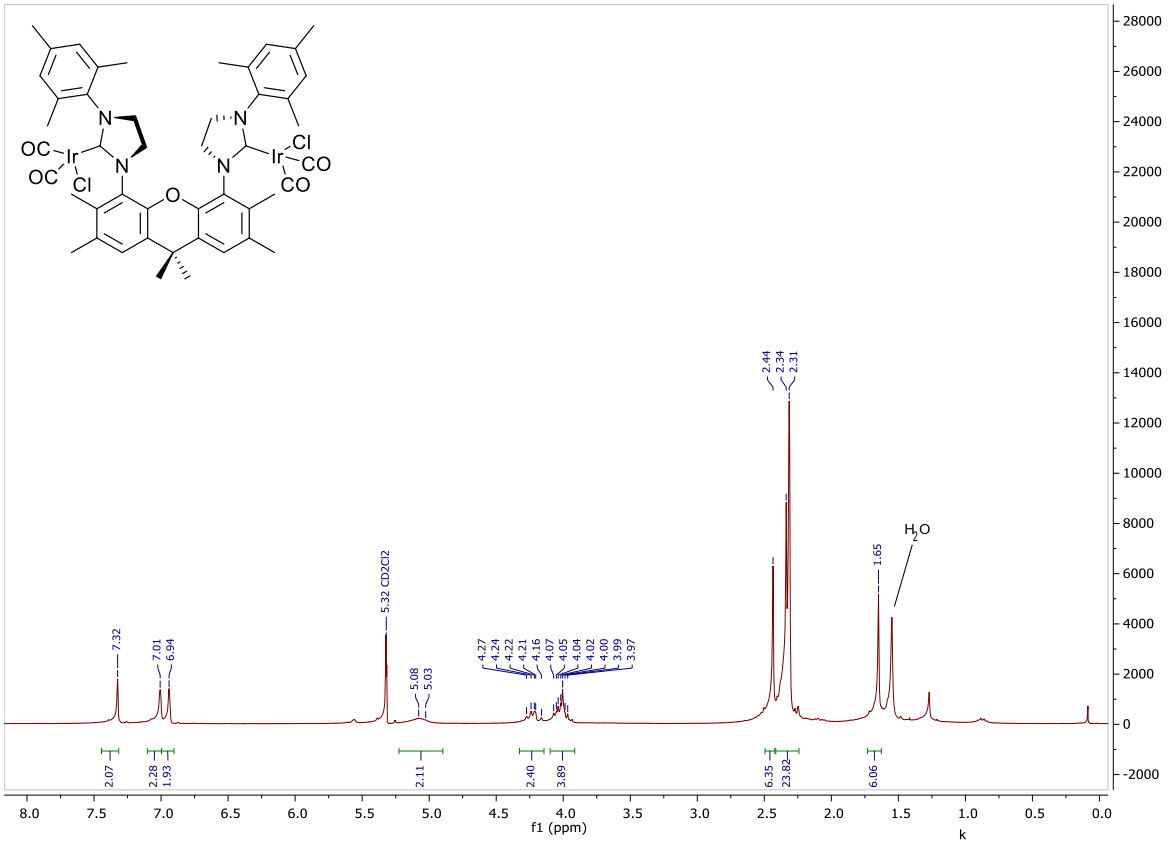


*Figure 52: ^{1}H-NMR of [(IrCl(CO)$_2$)$_2$(**14**)] in CD_2Cl_2.*

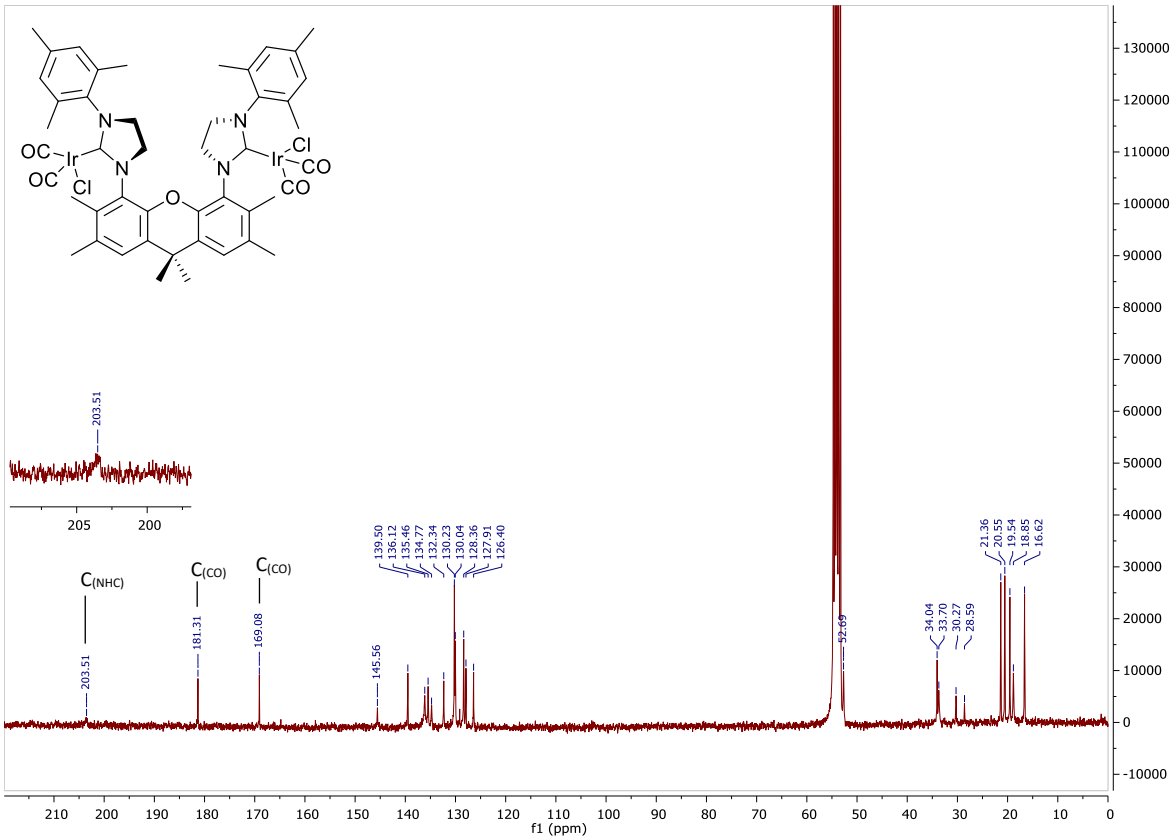


*Figure 53: ^{1}H-NMR of [(IrCl(CO)$_2$)$_2$(**14**)] in CD_2Cl_2.*

$[AuCl)_2$(**14**)]

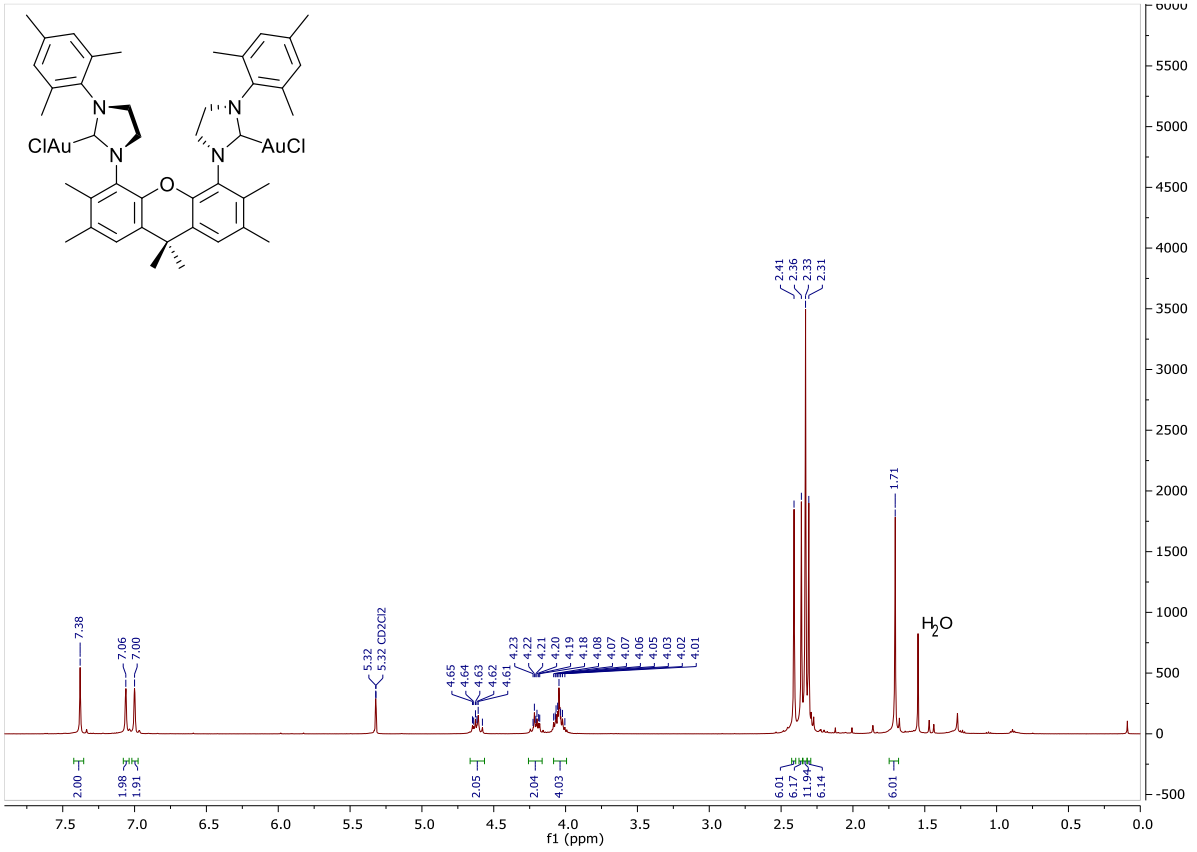


*Figure 54: ^{1}H-NMR of $[AuCl)_2$(**14**)] in CD_2Cl_2.*

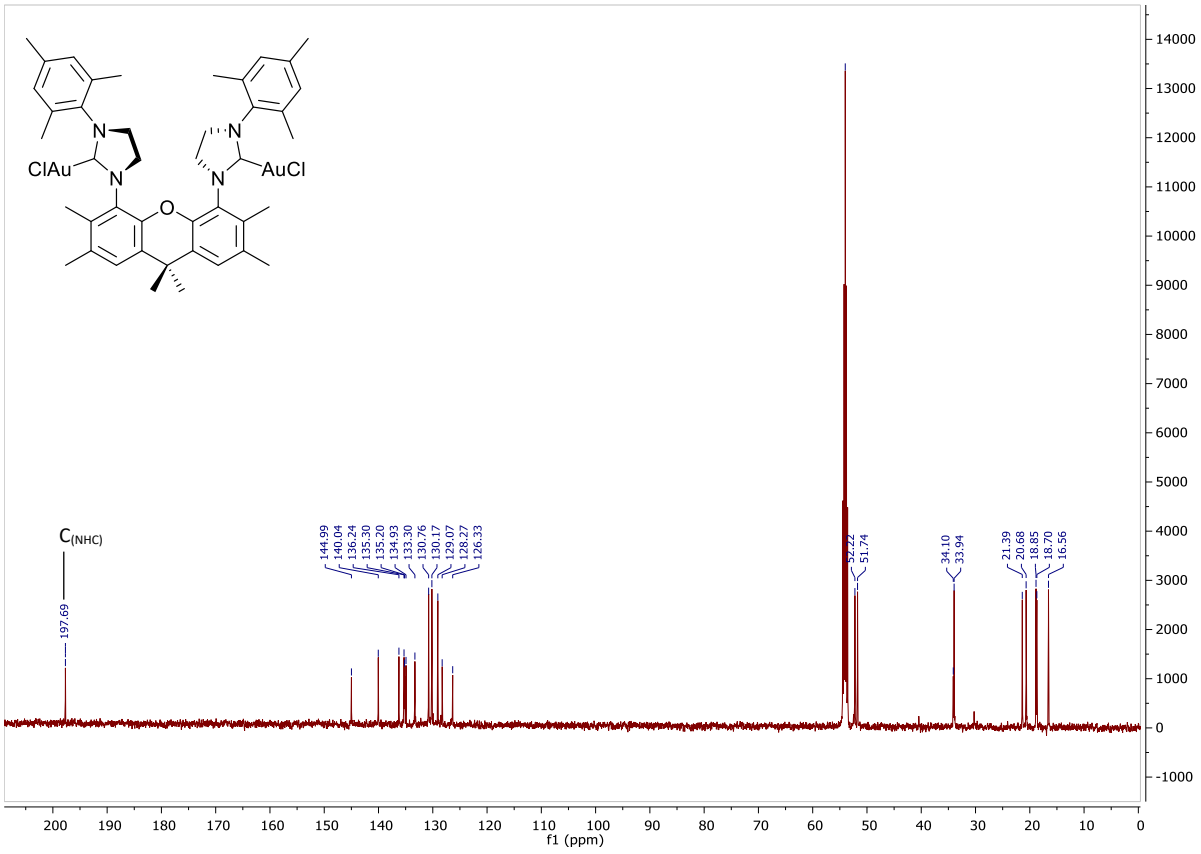


*Figure 55: ^{13}C-NMR of $[AuCl)_2$(**14**)] in CD_2Cl_2.*

1,1'-(2,3,6,7,9,9-hexamethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (**15**)

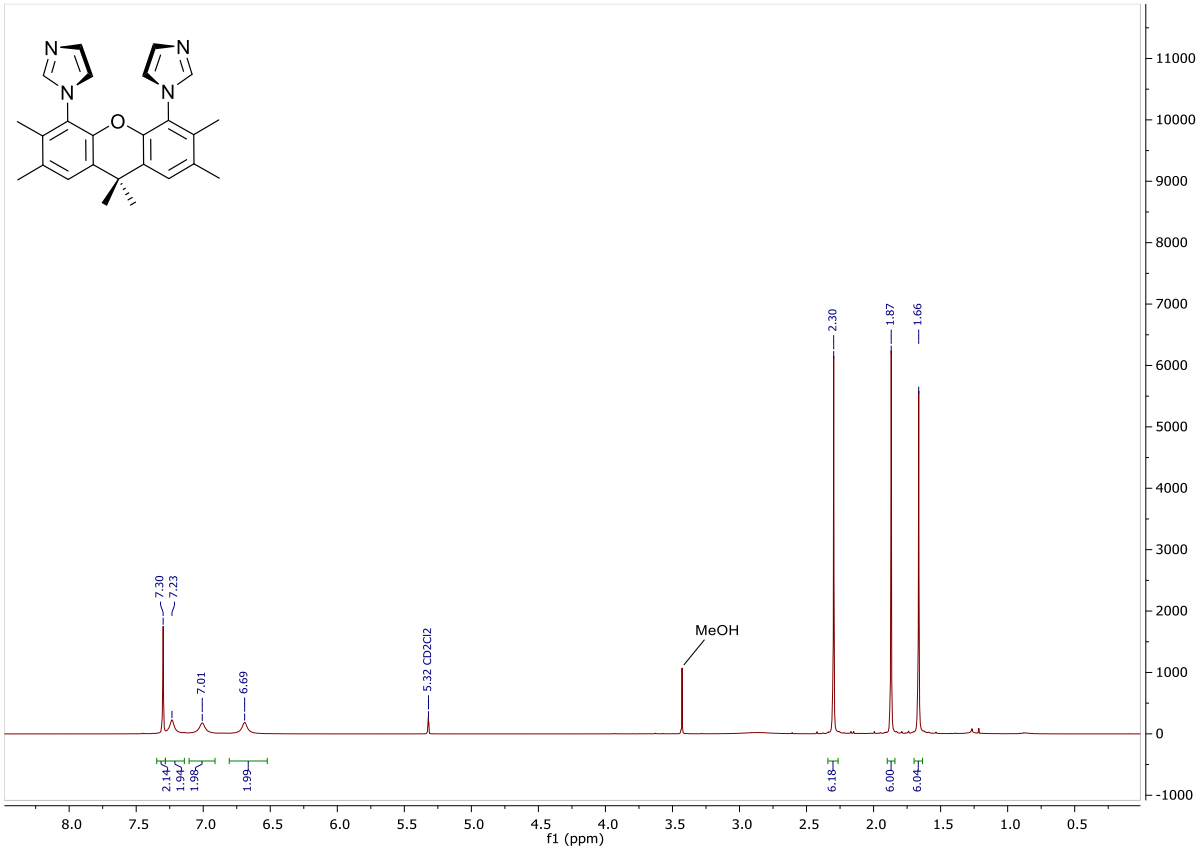


*Figure 56: ^{1}H-NMR of 1,1'-(2,3,6,7,9,9-hexamethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (**15**) in CD_2Cl_2.*

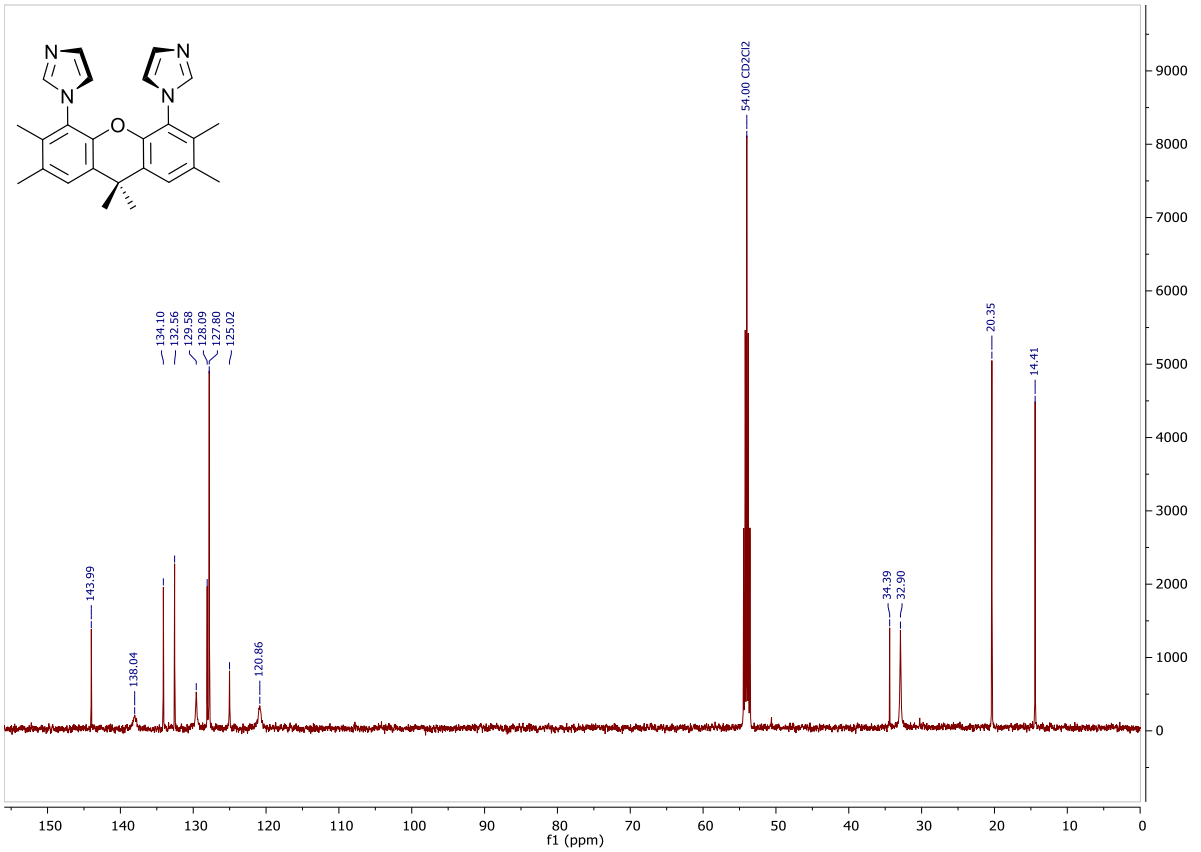


*Figure 57: ^{13}C-NMR of 1,1'-(2,3,6,7,9,9-hexamethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (**15**) in CD_2Cl_2*

Xanthene imidazolium salt (**16** · 2 HBr)

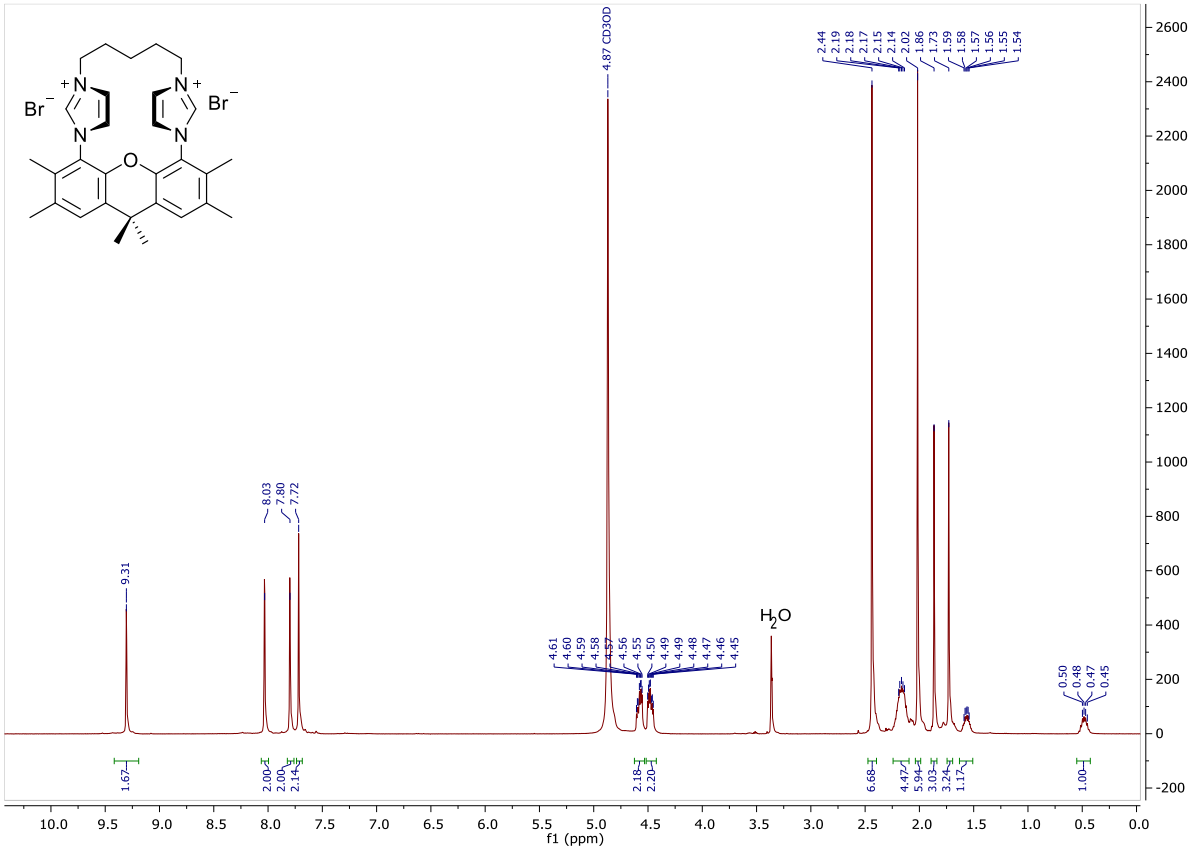


*Figure 58: ^{1}H-NMR of **16** · 2 HBr in CD_2Cl_2.*

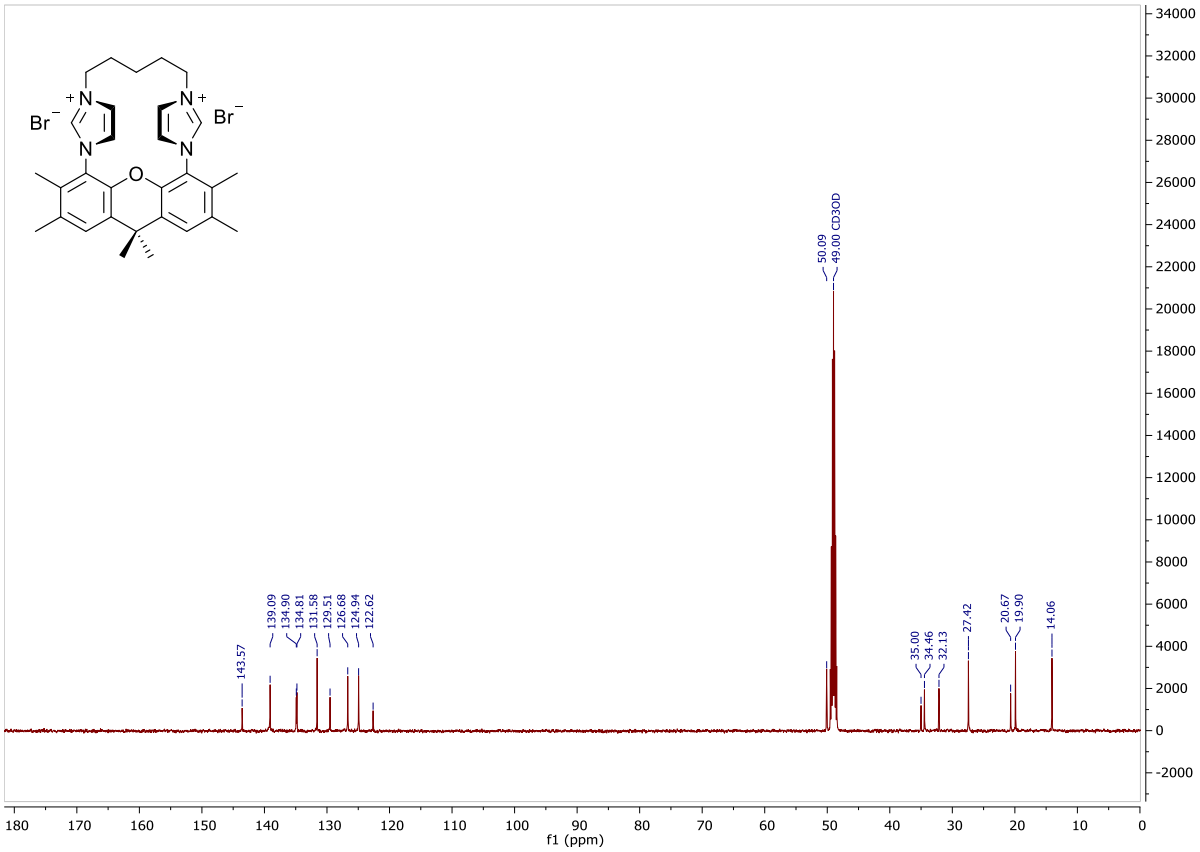


*Figure 59: ^{13}C-NMR of **16** · 2 HBr in CD_2Cl_2.*

Xanthene imidazolium salt (**16** · 2 HBF_4)

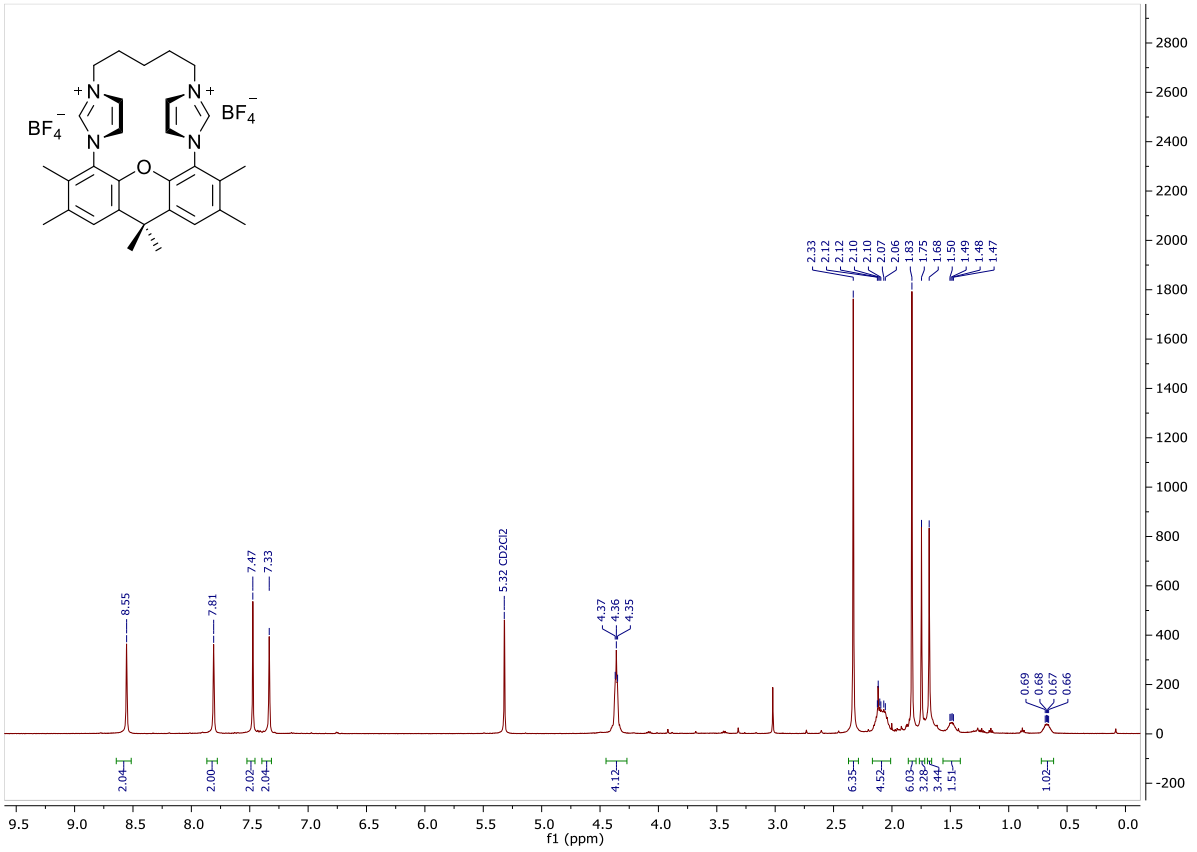


*Figure 60: ^{1}H-NMR of **16** · 2 HBF_4 in CD_2Cl_2.*

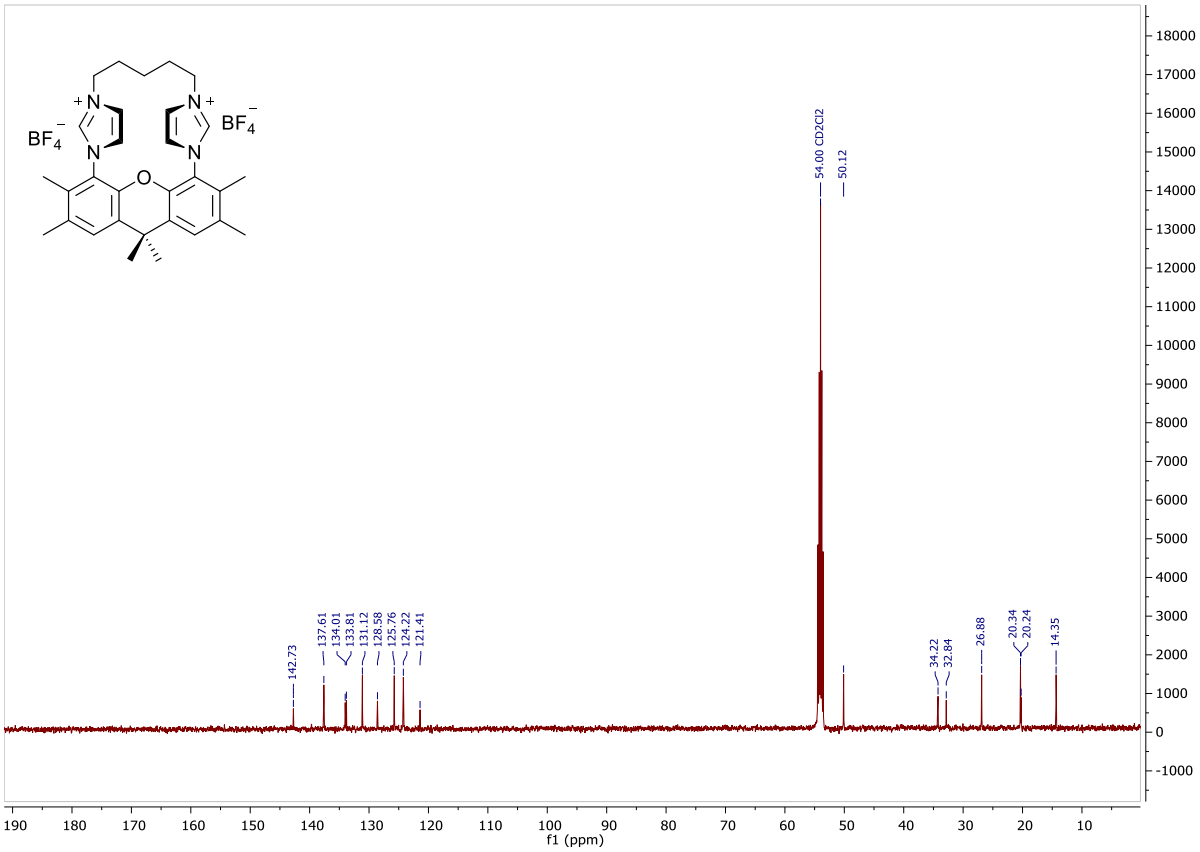


*Figure 61: ^{13}C-NMR of **16** · 2 HBF_4 in CD_2Cl_2.*

[(AgBr)$_2$(**16**)]

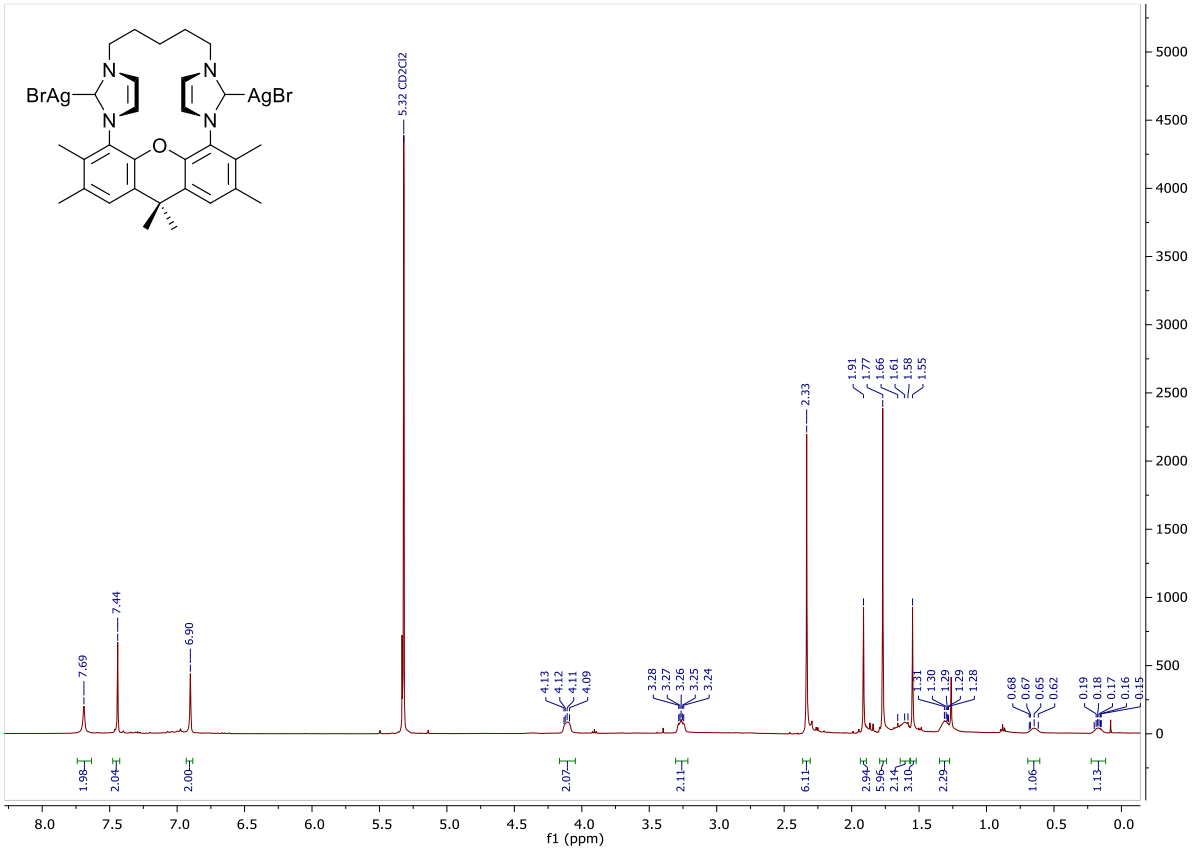


*Figure 62: ^{1}H-NMR of [(AgBr)$_2$(**16**)] in CD_2Cl_2.*

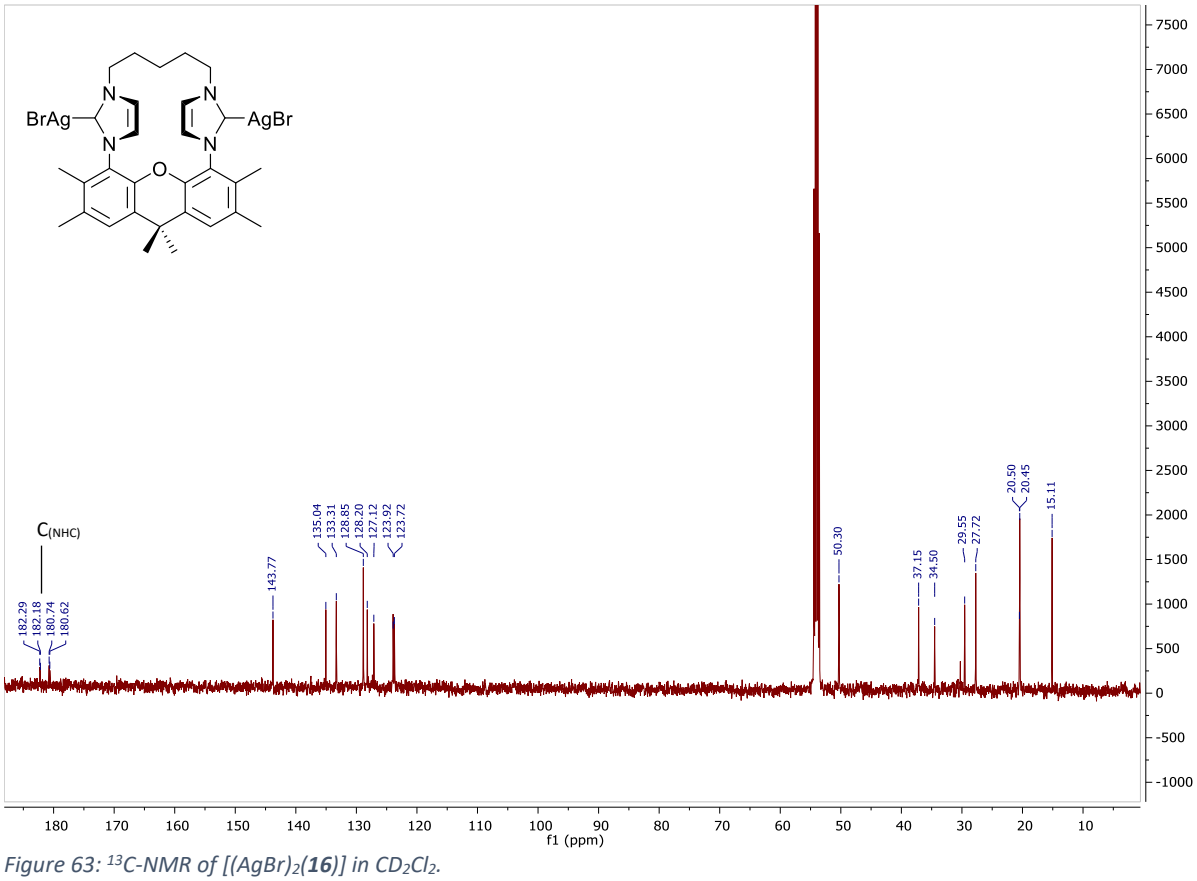


*Figure 63: ^{13}C-NMR of [(AgBr)$_2$(**16**)] in CD_2Cl_2.*

[(AuCl)$_2$(**16**)]

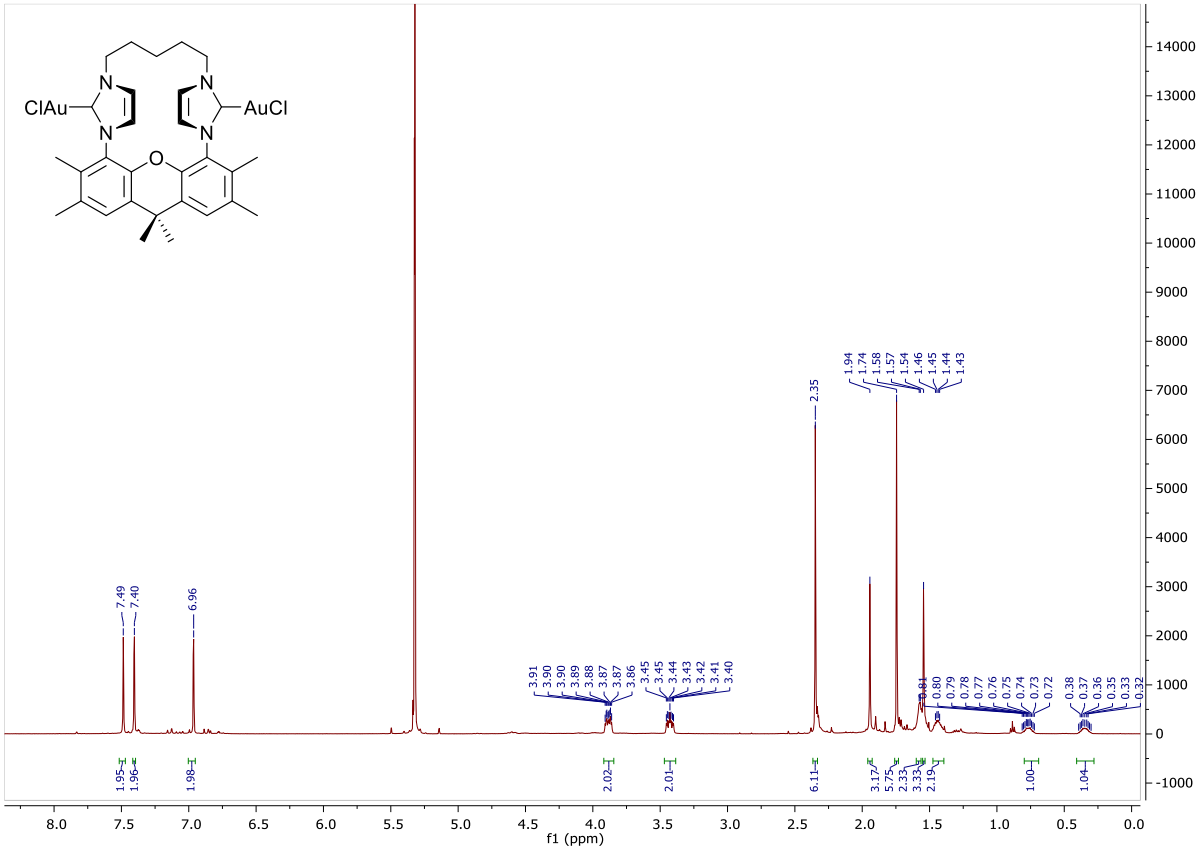


*Figure 64: ^{1}H-NMR of [(AuCl)$_2$(**16**)] in CD_2Cl_2.*

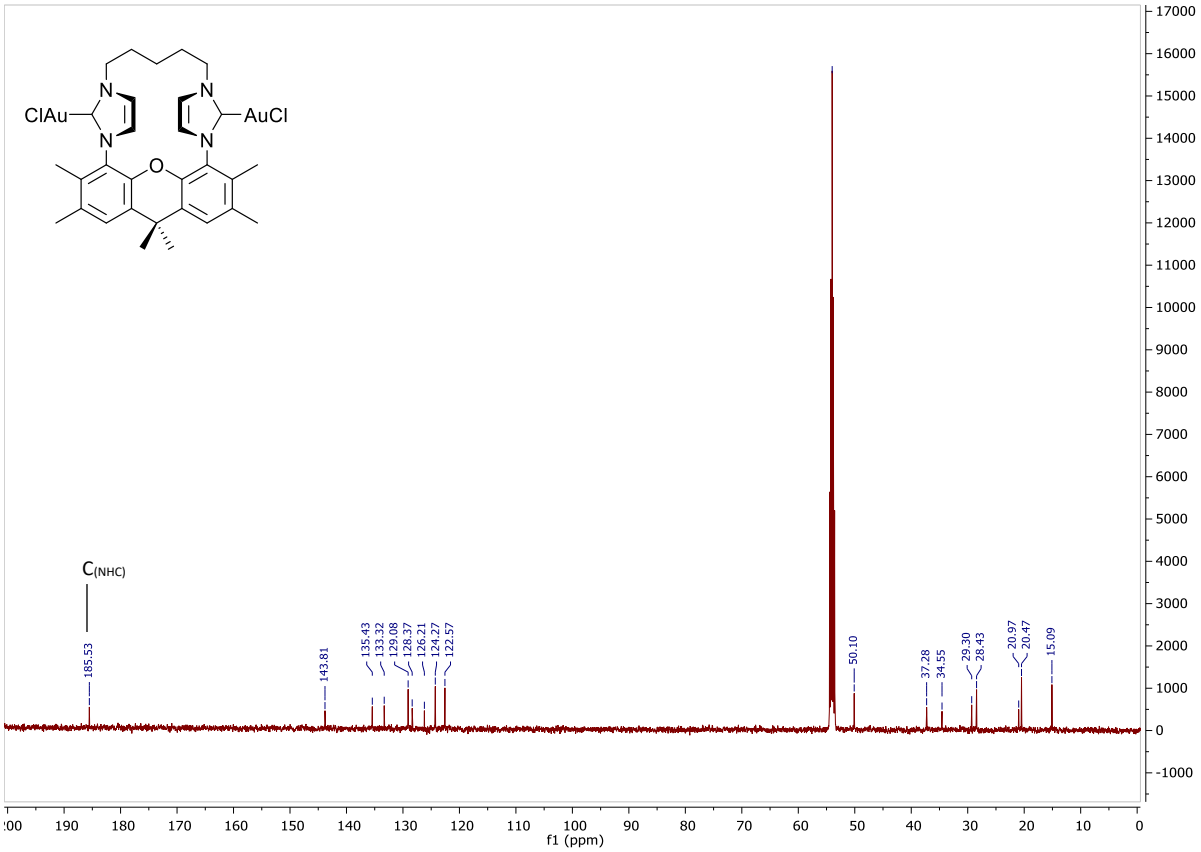


*Figure 65: ^{13}C-NMR of [(AuCl)$_2$(**16**)] in CD_2Cl_2.*

[(Au(AuCl)$_2$)(Cl)(**16**)$_2$]

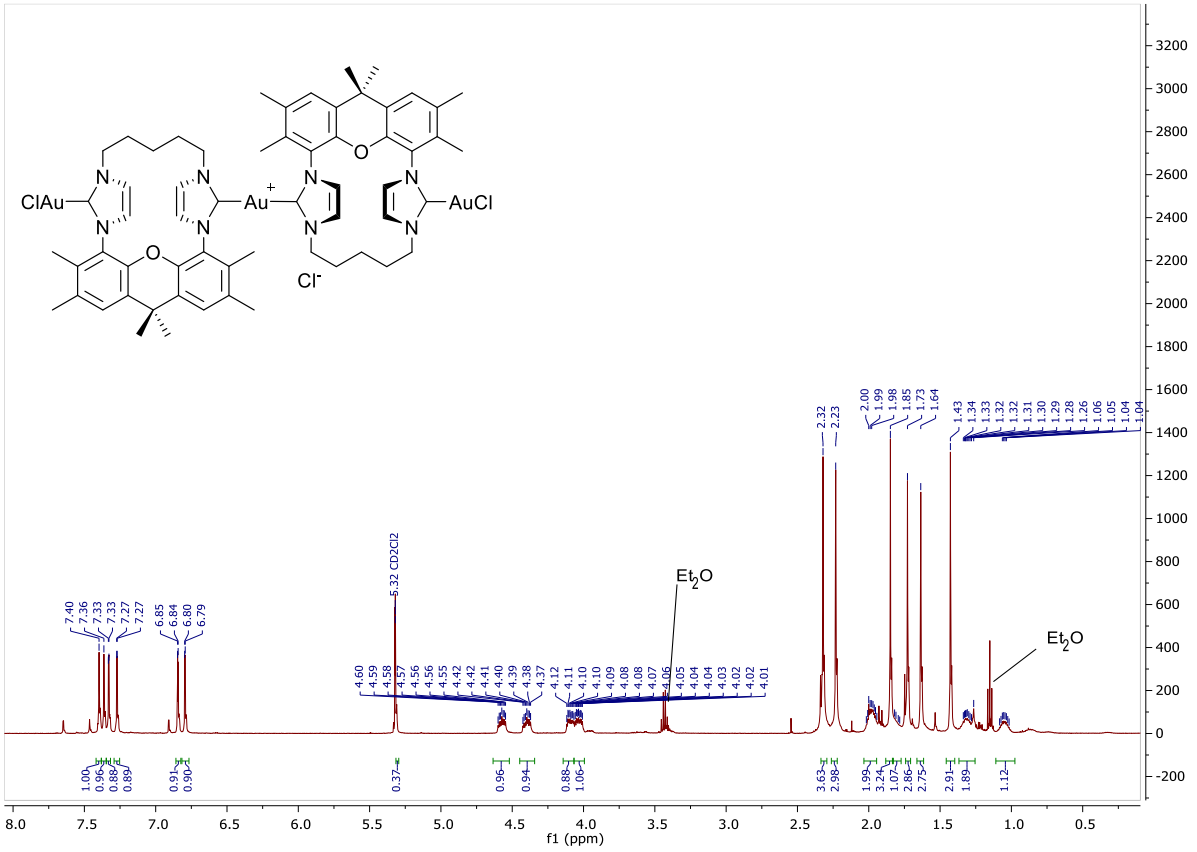


*Figure 66: ^{1}H-NMR of [(Au(AuCl)$_2$)(Cl)(**16**)$_2$] in CD_2Cl_2.*

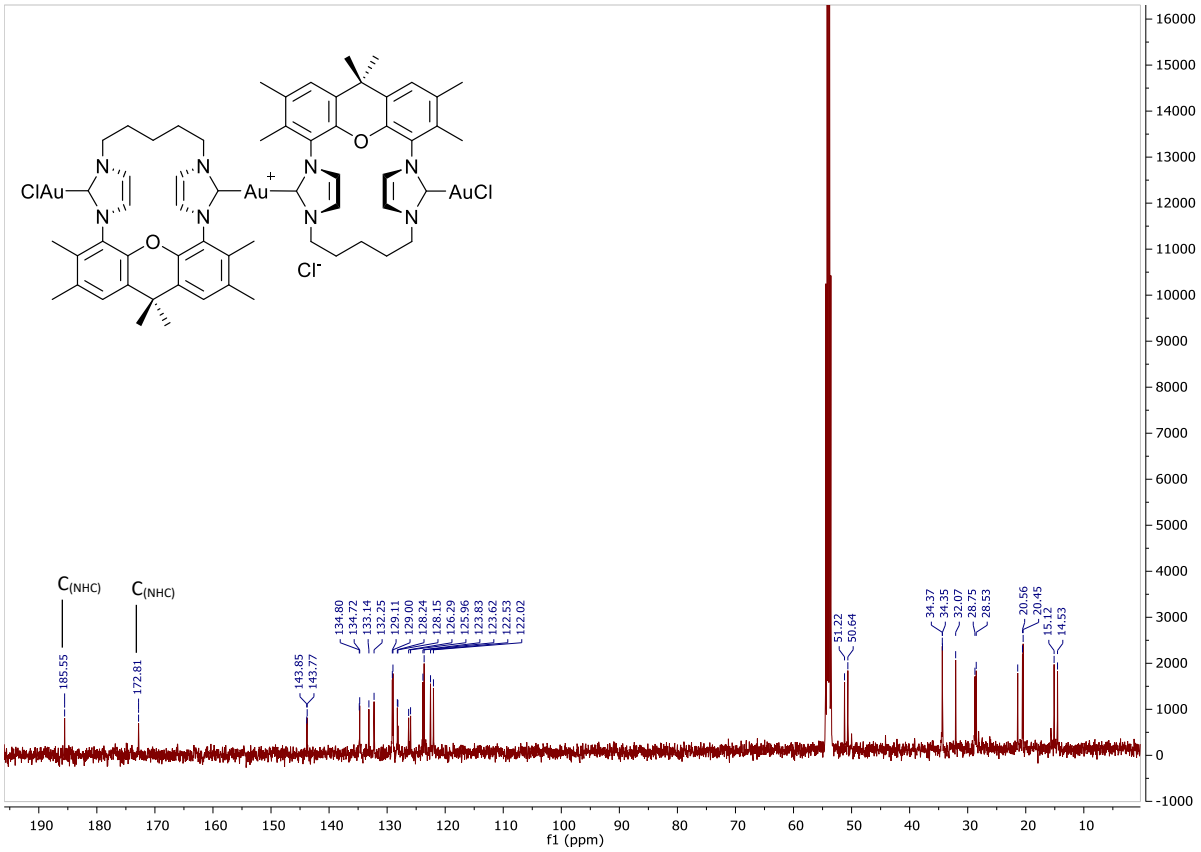


*Figure 67: ^{13}C-NMR of [(Au(AuCl)$_2$)(Cl)(**16**)$_2$] in CD_2Cl_2.*

[(CuI)$_2$(**16**)]

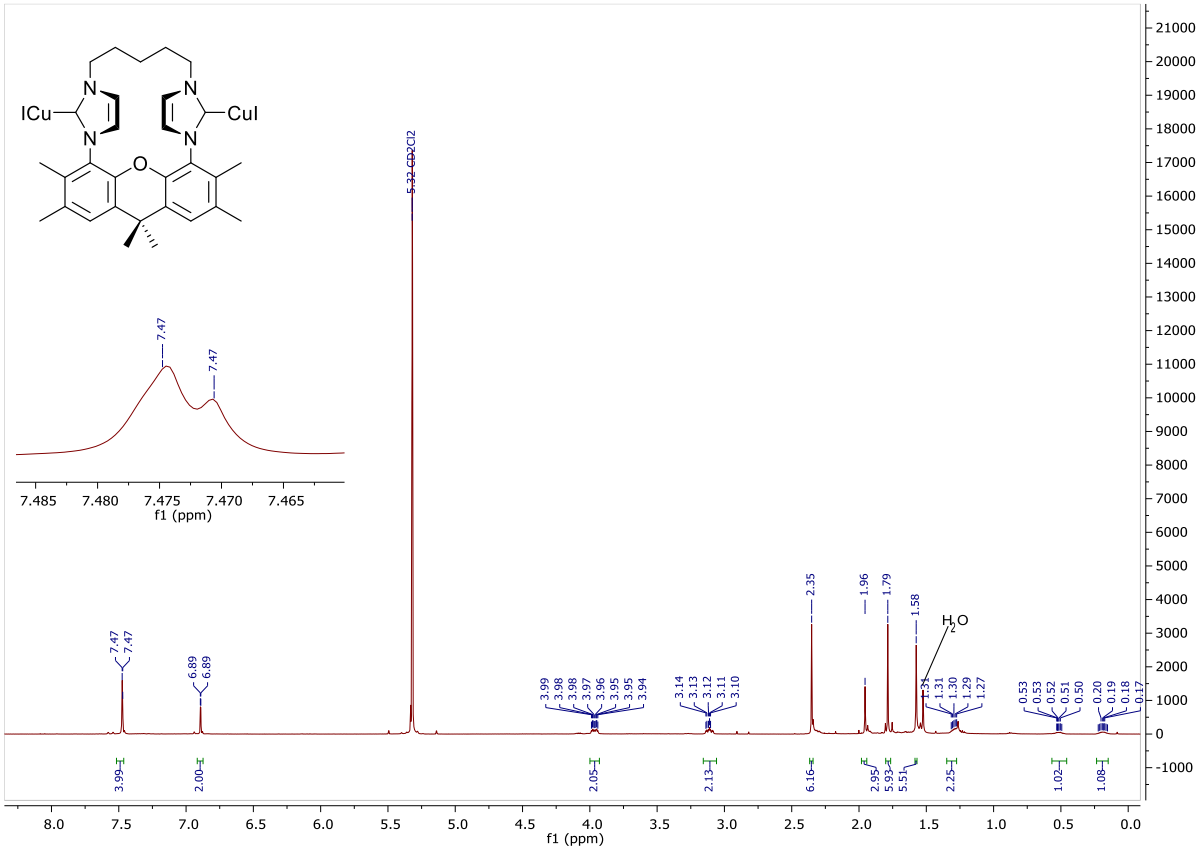


*Figure 68: ^{1}H-NMR of [(CuI)$_2$(**16**)] in CD_2Cl_2.*

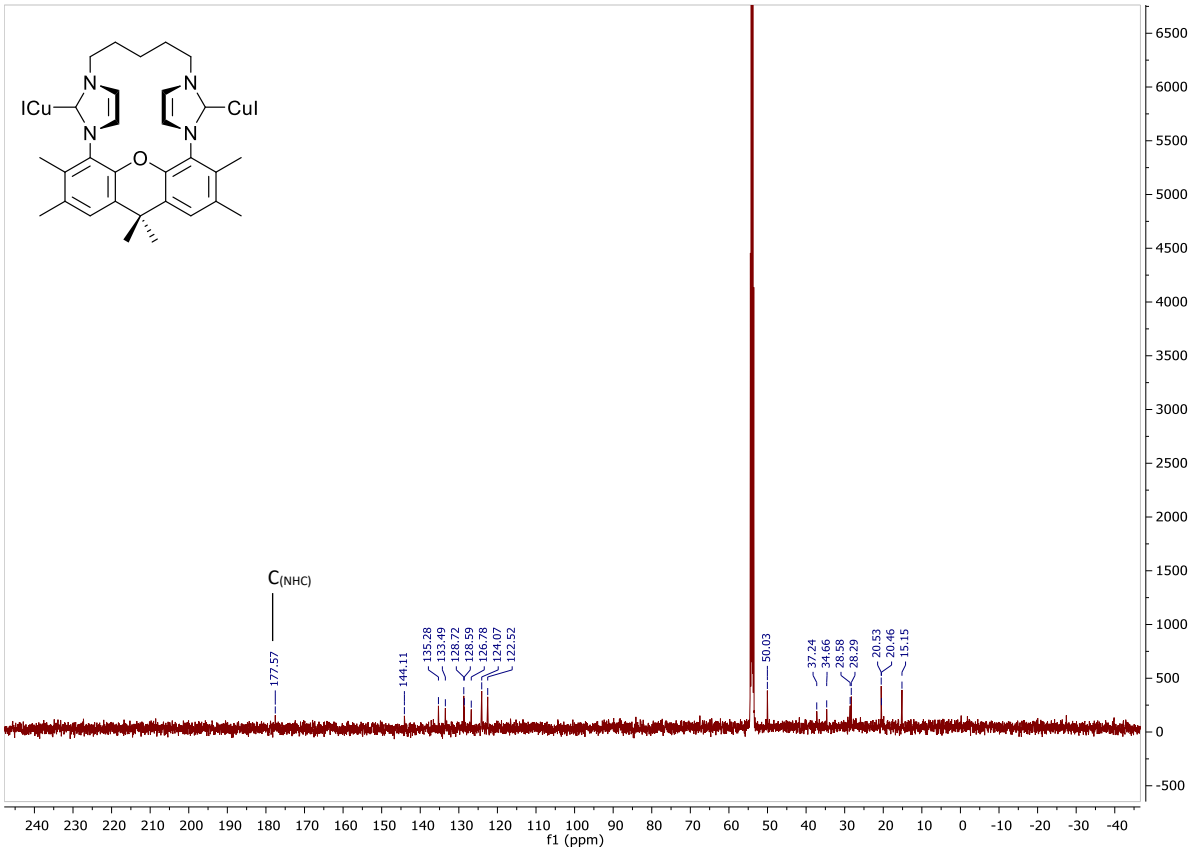


*Figure 69: ^{13}C-NMR of [(CuI)$_2$(**16**)] in CD_2Cl_2.*

[(RhCl(cod))$_2$(**16**)]

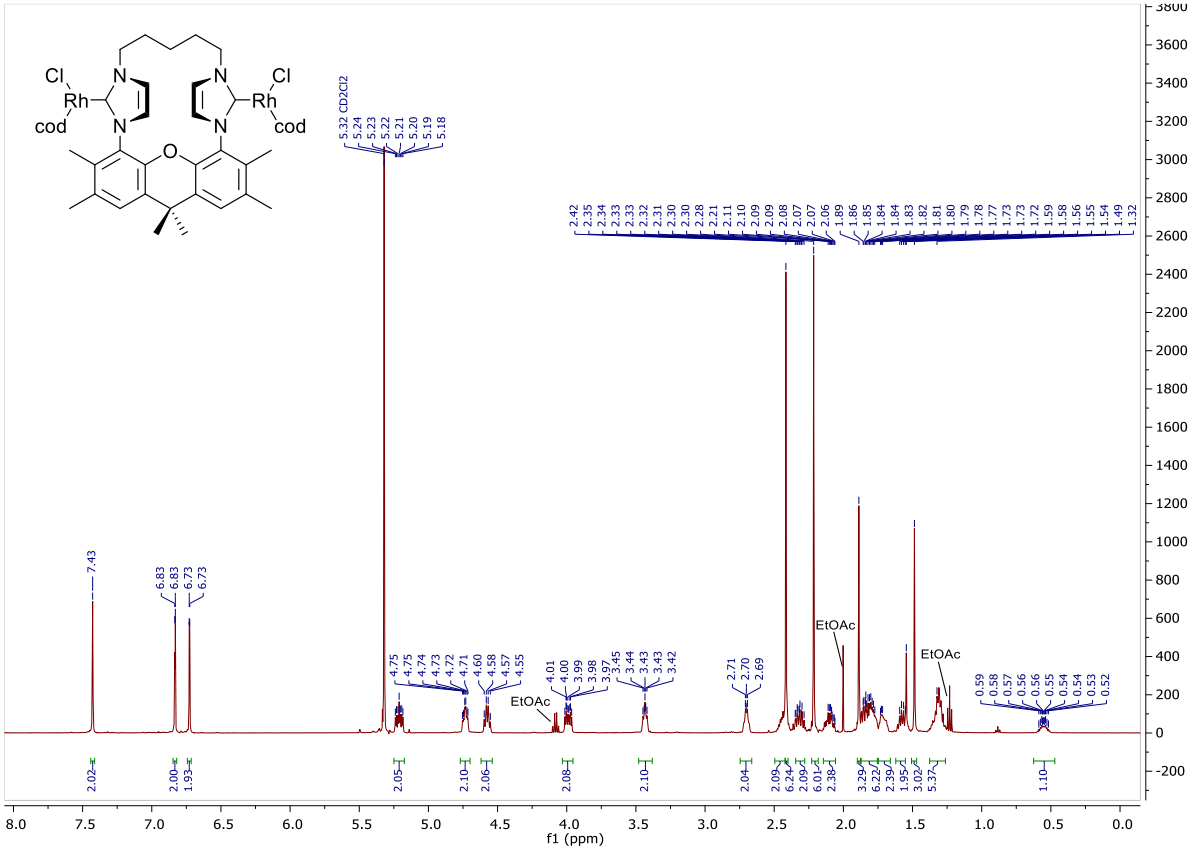


*Figure 70: ^{1}H-NMR of [(RhCl(cod))$_2$(**16**)] in CD_2Cl_2.*

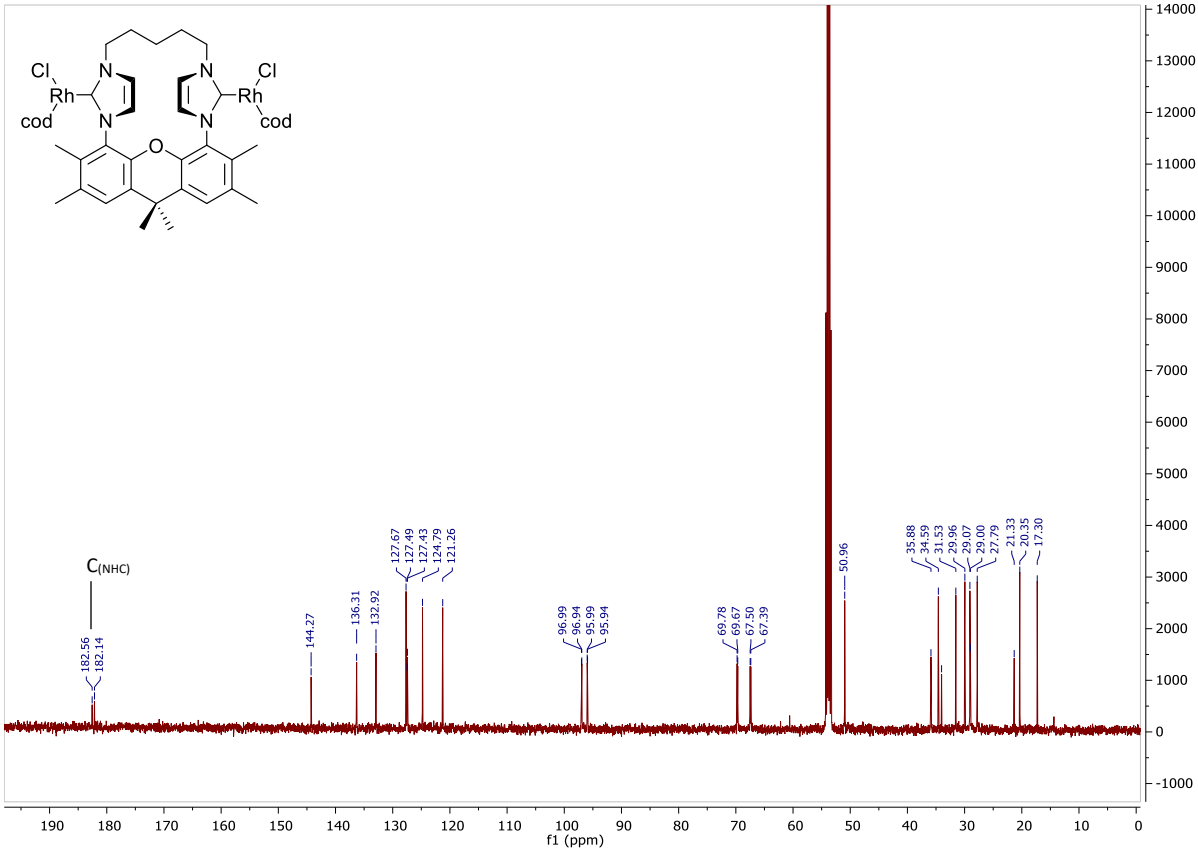


*Figure 71: ^{13}C-NMR of [(RhCl(cod))$_2$(**16**)] in CD_2Cl_2.*

[(RhBr(cod))$_2$(**16**)]

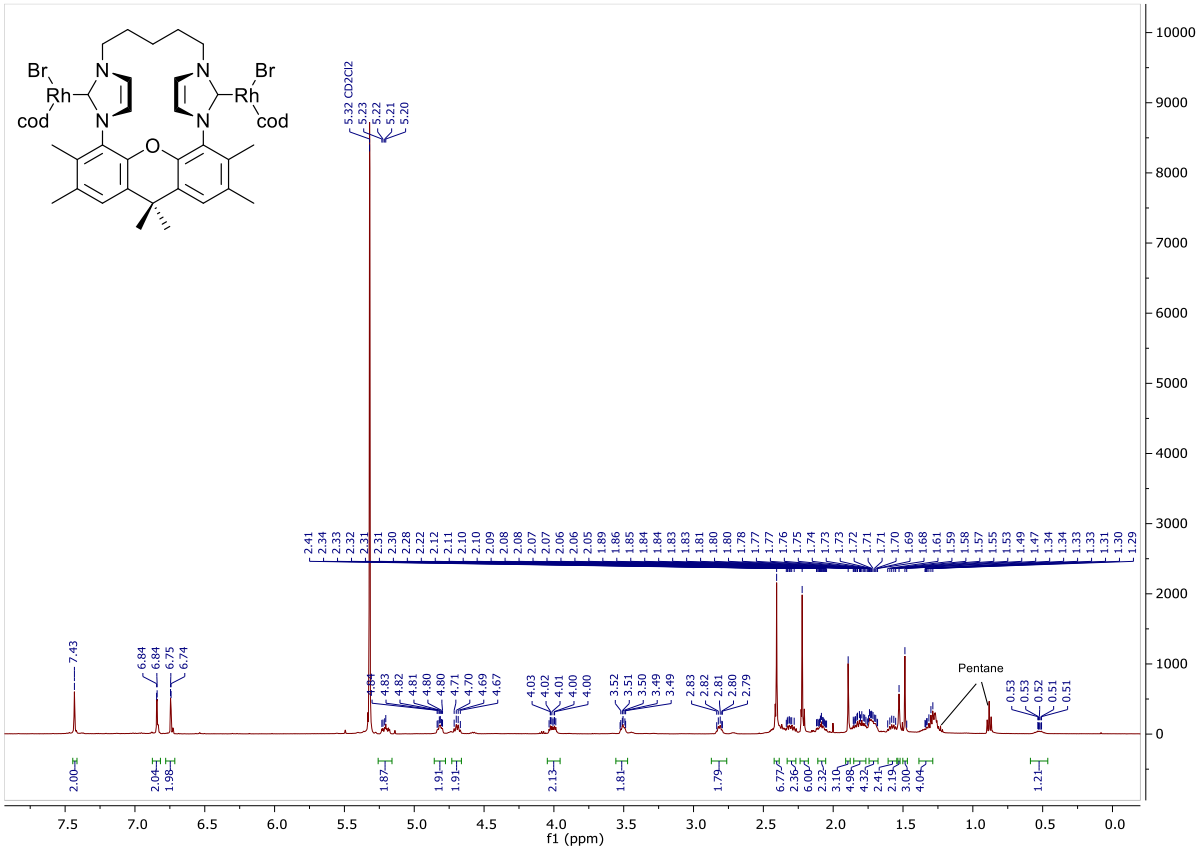


*Figure 72: ^{1}H-NMR of [(RhBr(cod))$_2$(**16**)] in CD_2Cl_2.*

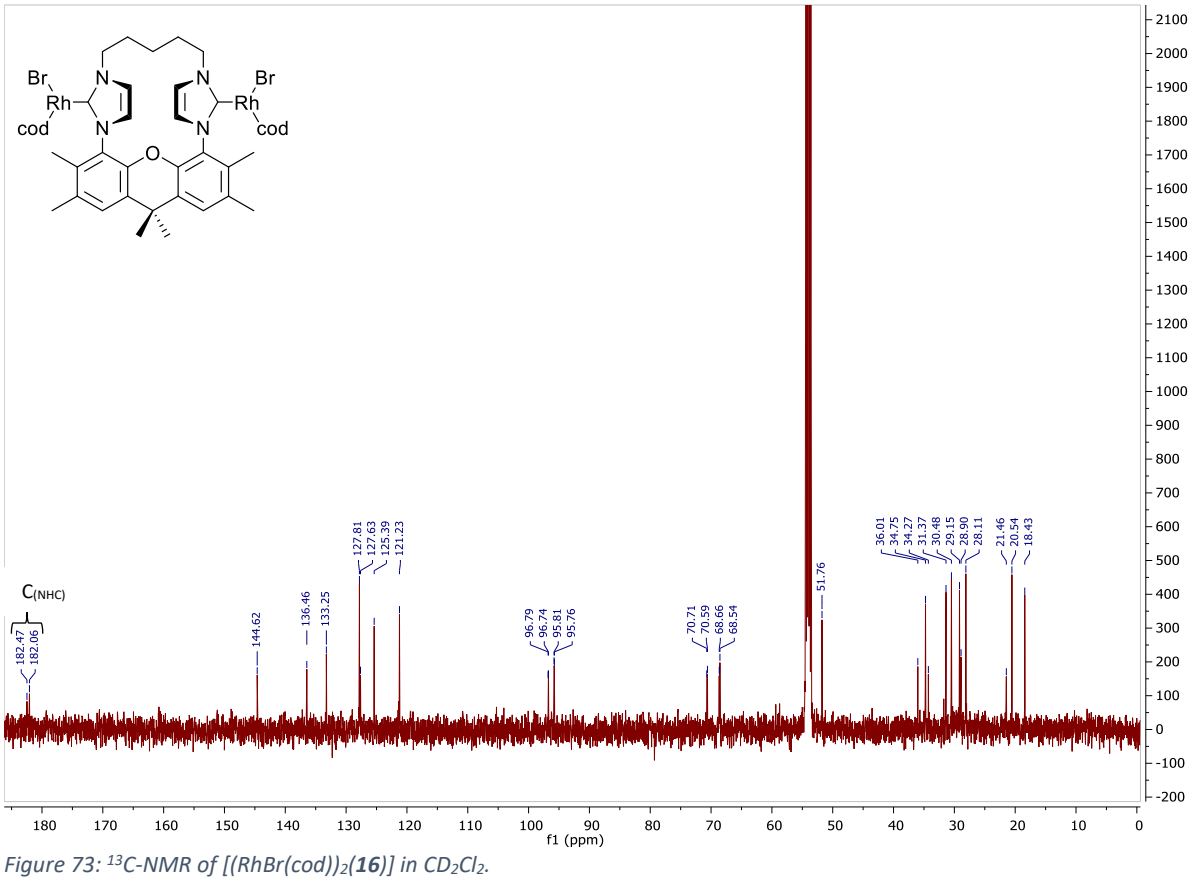


*Figure 73: ^{13}C-NMR of [(RhBr(cod))$_2$(**16**)] in CD_2Cl_2.*

[(IrBr(cod))$_2$(**16**)]

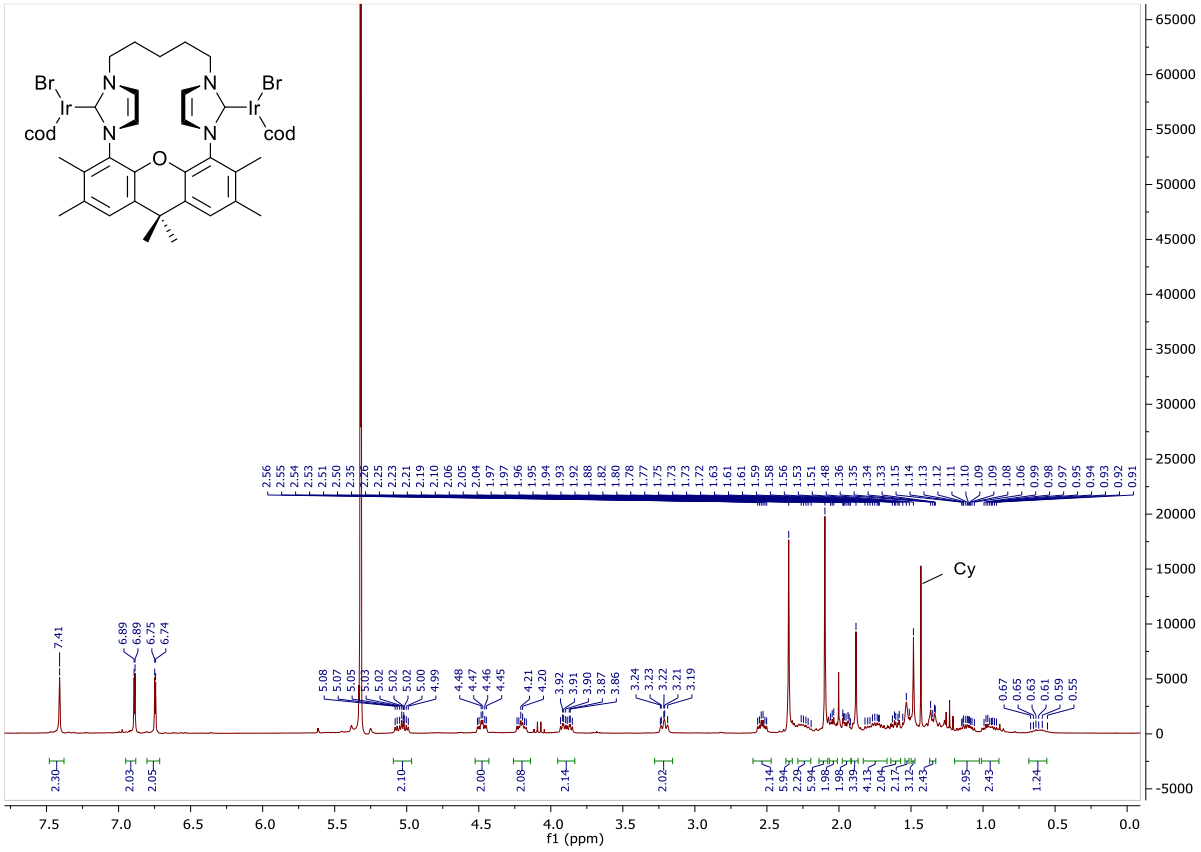


*Figure 74: ^{1}H-NMR of [(IrBr(cod))$_2$(**16**)] in CD_2Cl_2.*

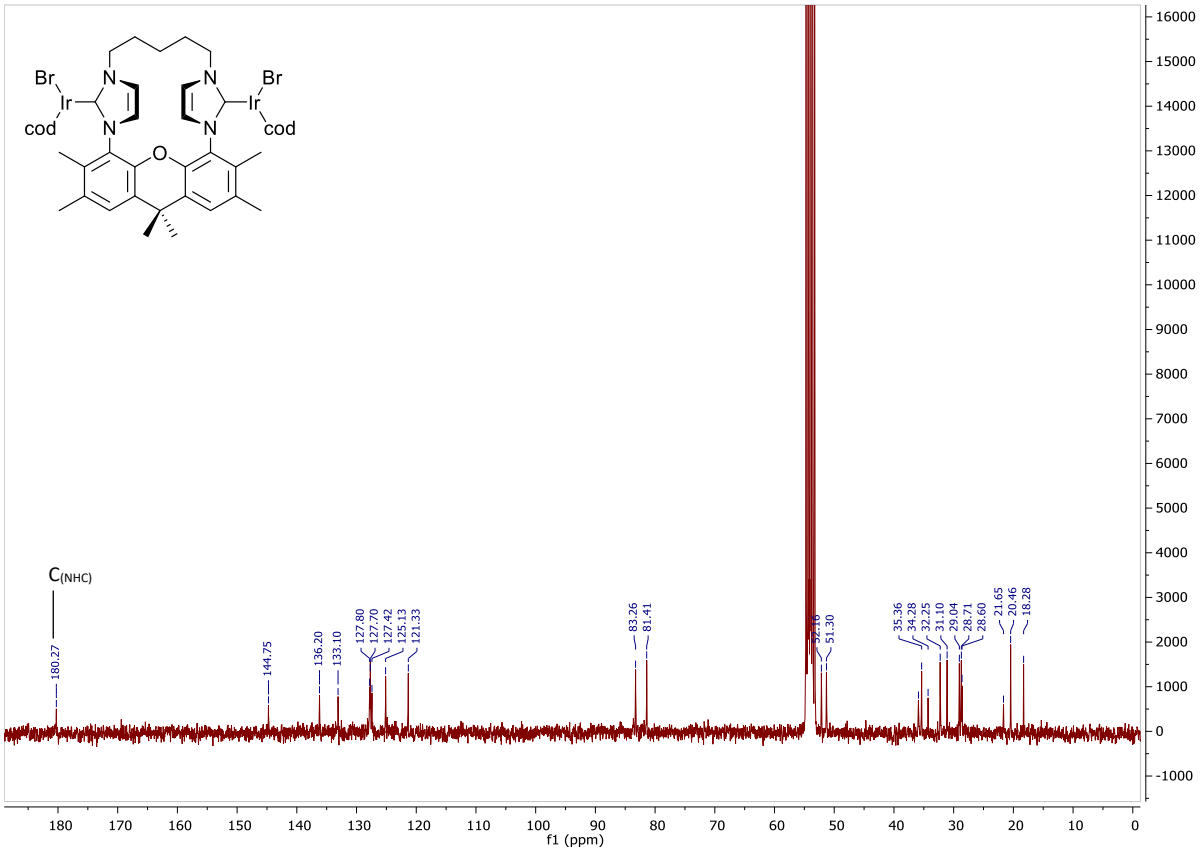


*Figure 75: ^{13}C-NMR of [(IrBr(cod))$_2$(**16**)] in CD_2Cl_2.*

[(RhCl(CO)$_2$)$_2$(**16**)]

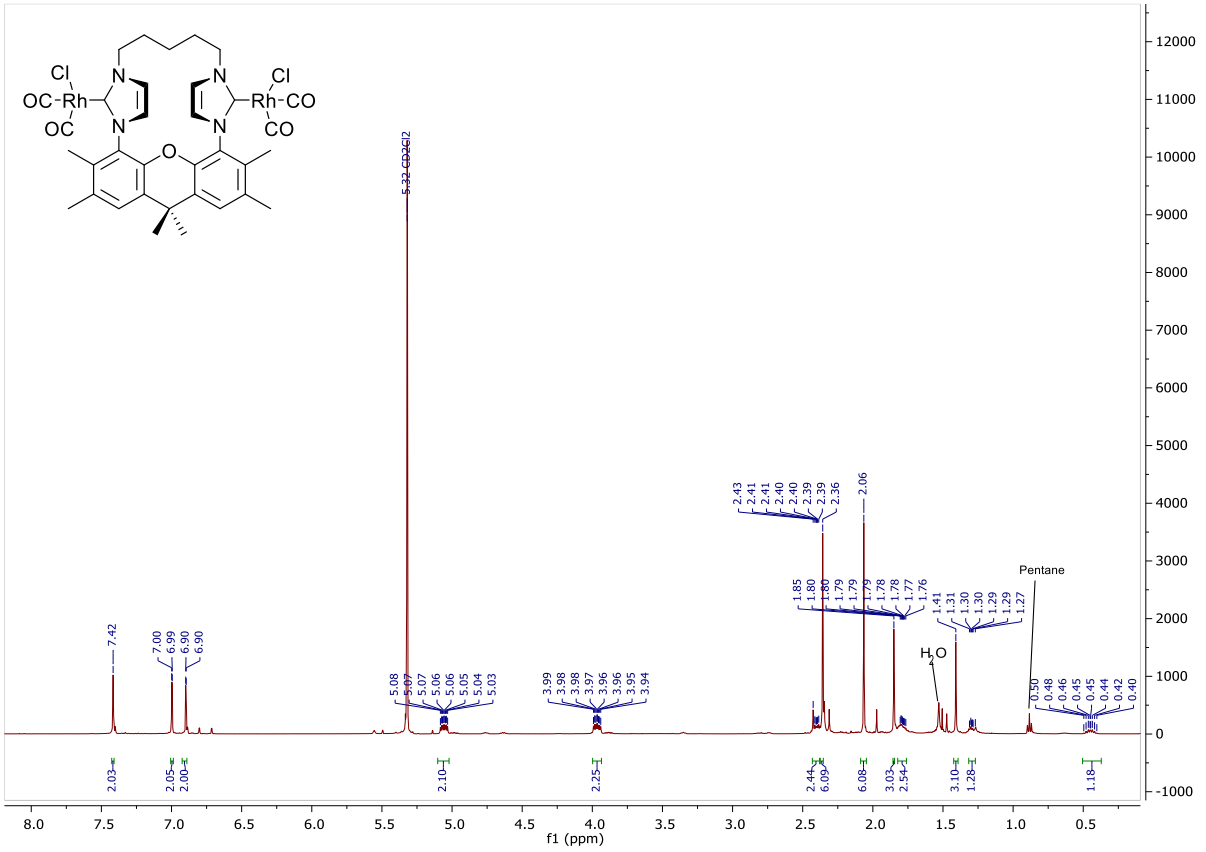


*Figure 76: ^{1}H-NMR of [(RhCl(CO)$_2$)$_2$(**16**)] in CD_2Cl_2.*

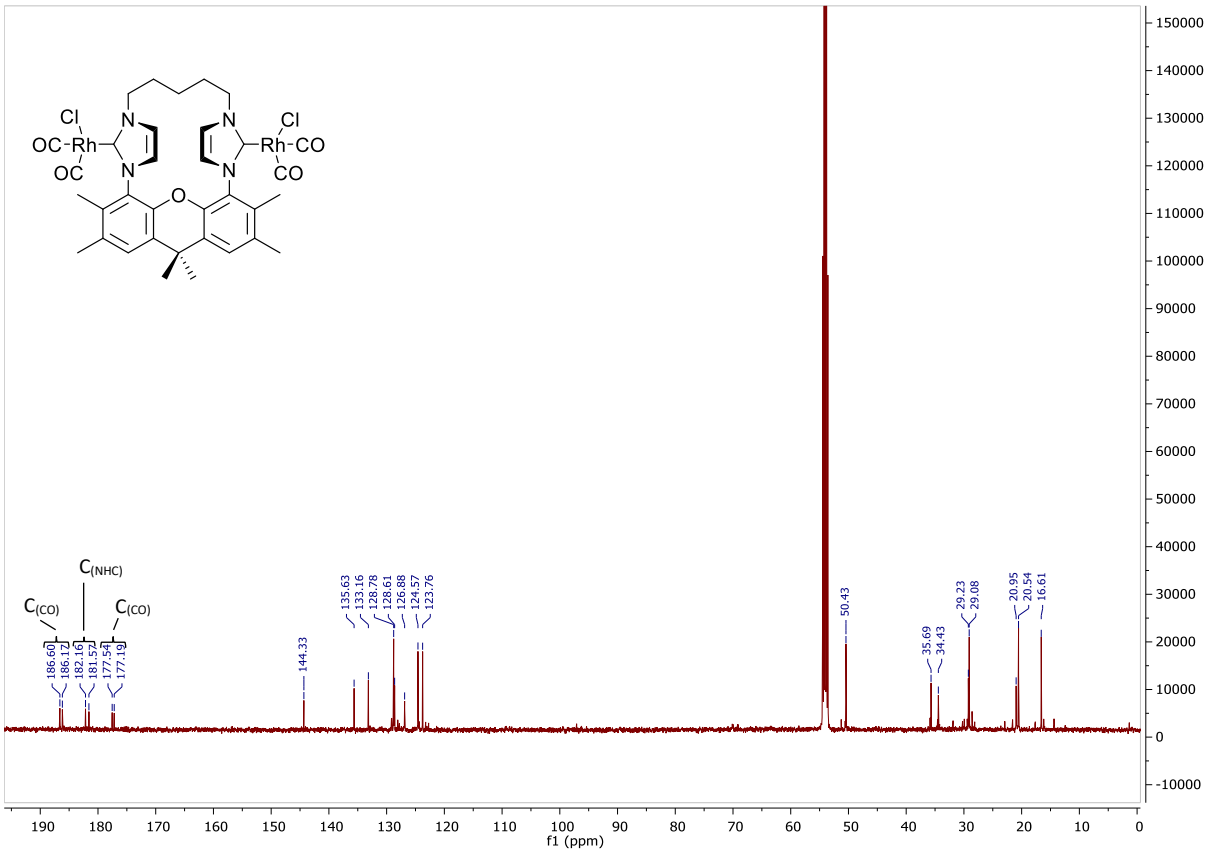


*Figure 77: ^{13}C-NMR of [(RhCl(CO)$_2$)$_2$(**16**)] in CD_2Cl_2.*

[(IrBr(CO)$_2$)$_2$(**16**)]

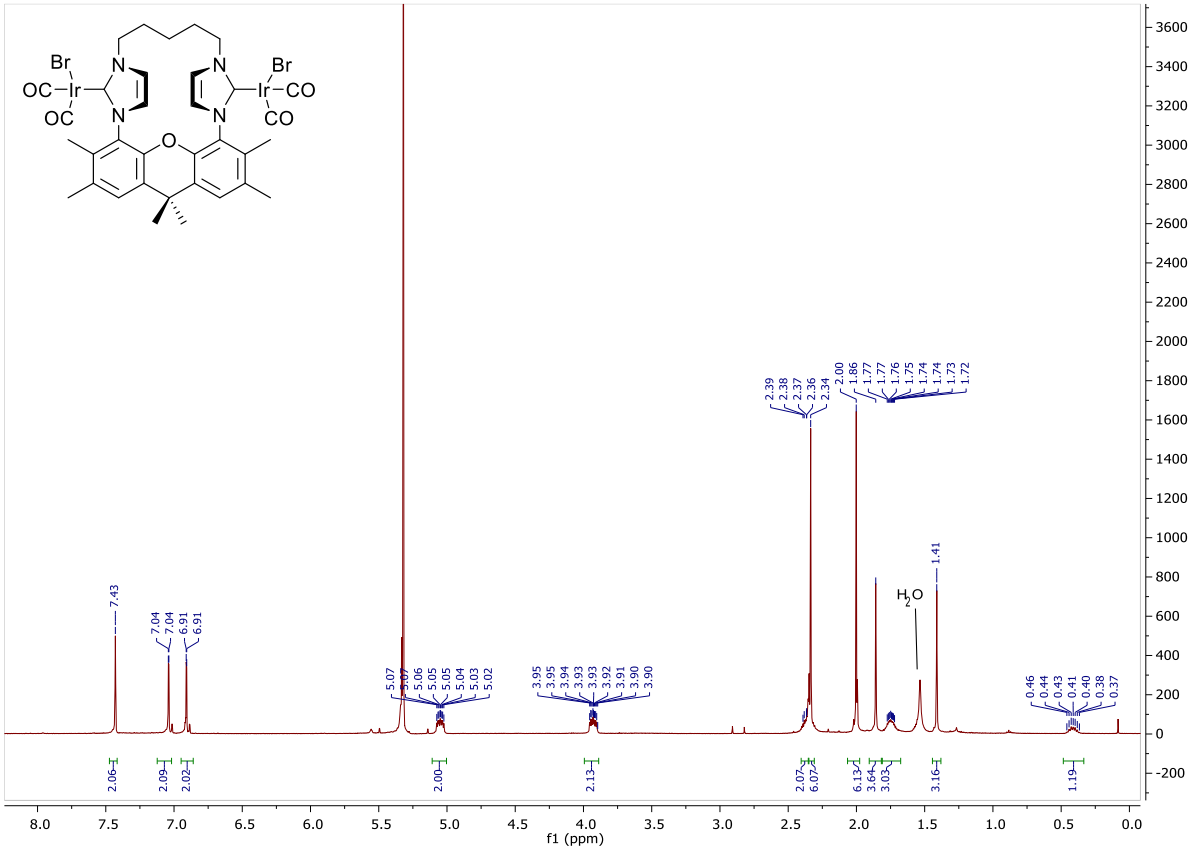


*Figure 78: ^{1}H-NMR of [(IrBr(CO)$_2$)$_2$(**16**)] in CD_2Cl_2.*

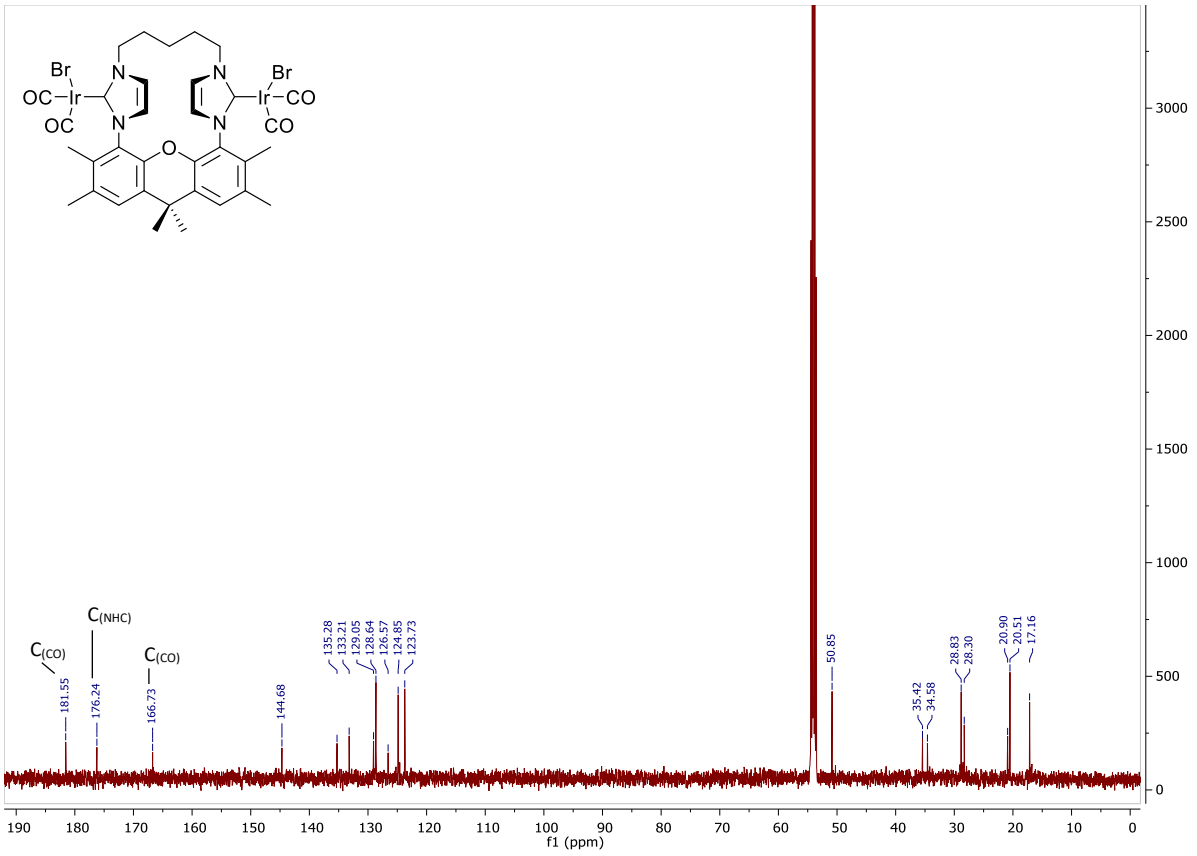


*Figure 79: ^{13}C-NMR of [(IrBr(CO)$_2$)$_2$(**16**)] in CD_2Cl_2.*

[(PdCl(allyl))$_2$(**16**)]

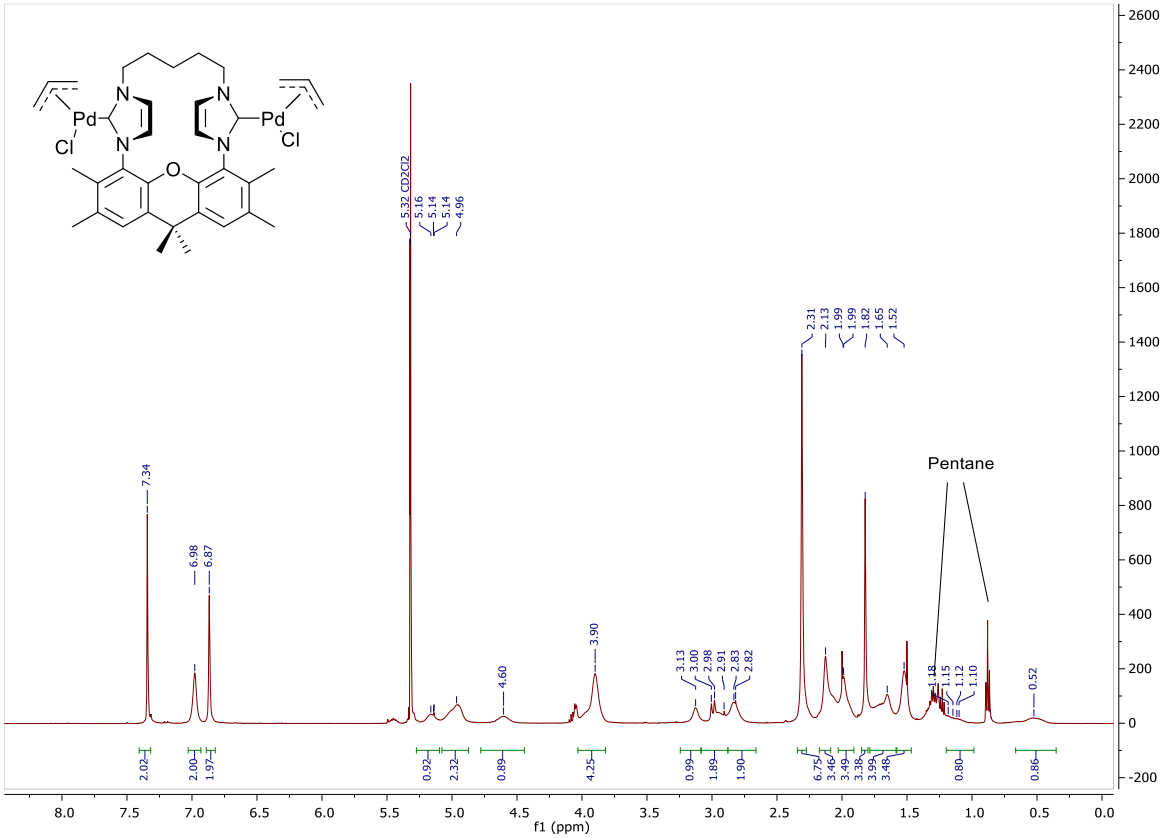


*Figure 80: ^{1}H-NMR of [(PdCl(allyl))$_2$(**16**)] in CD_2Cl_2.*

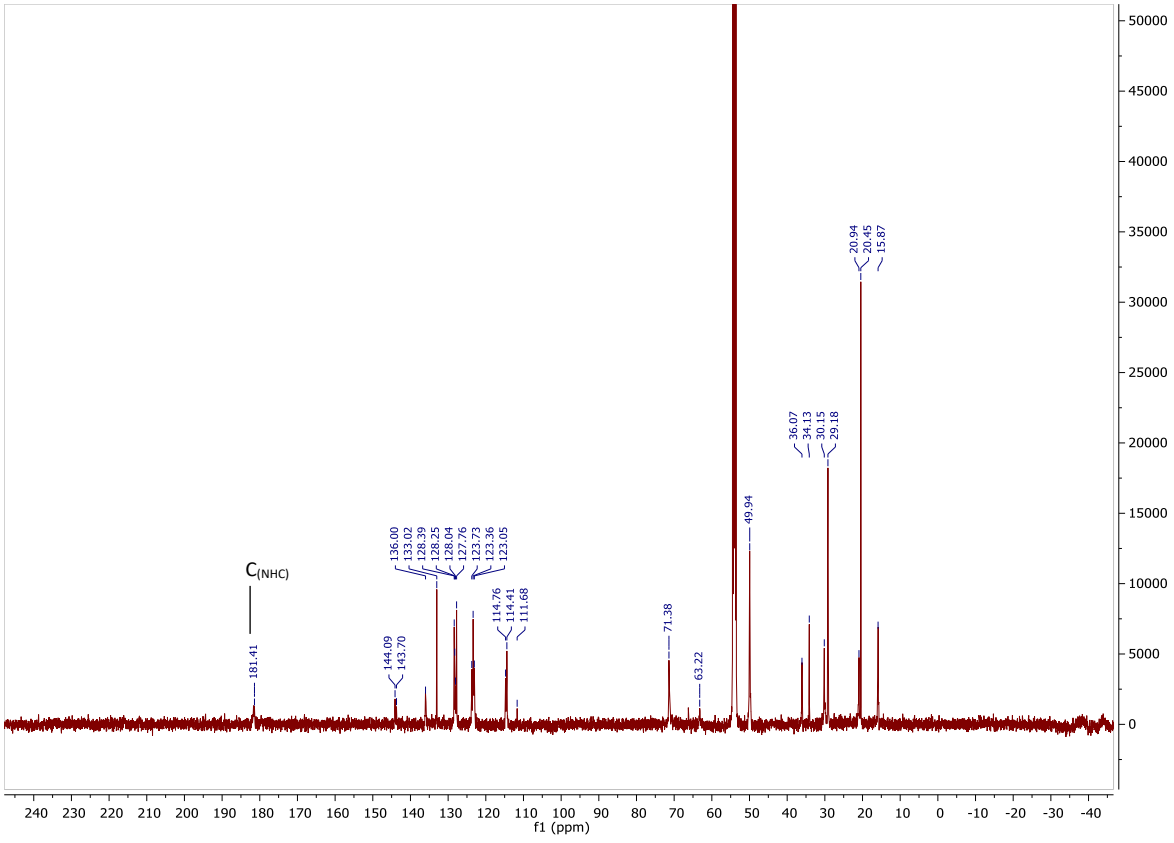
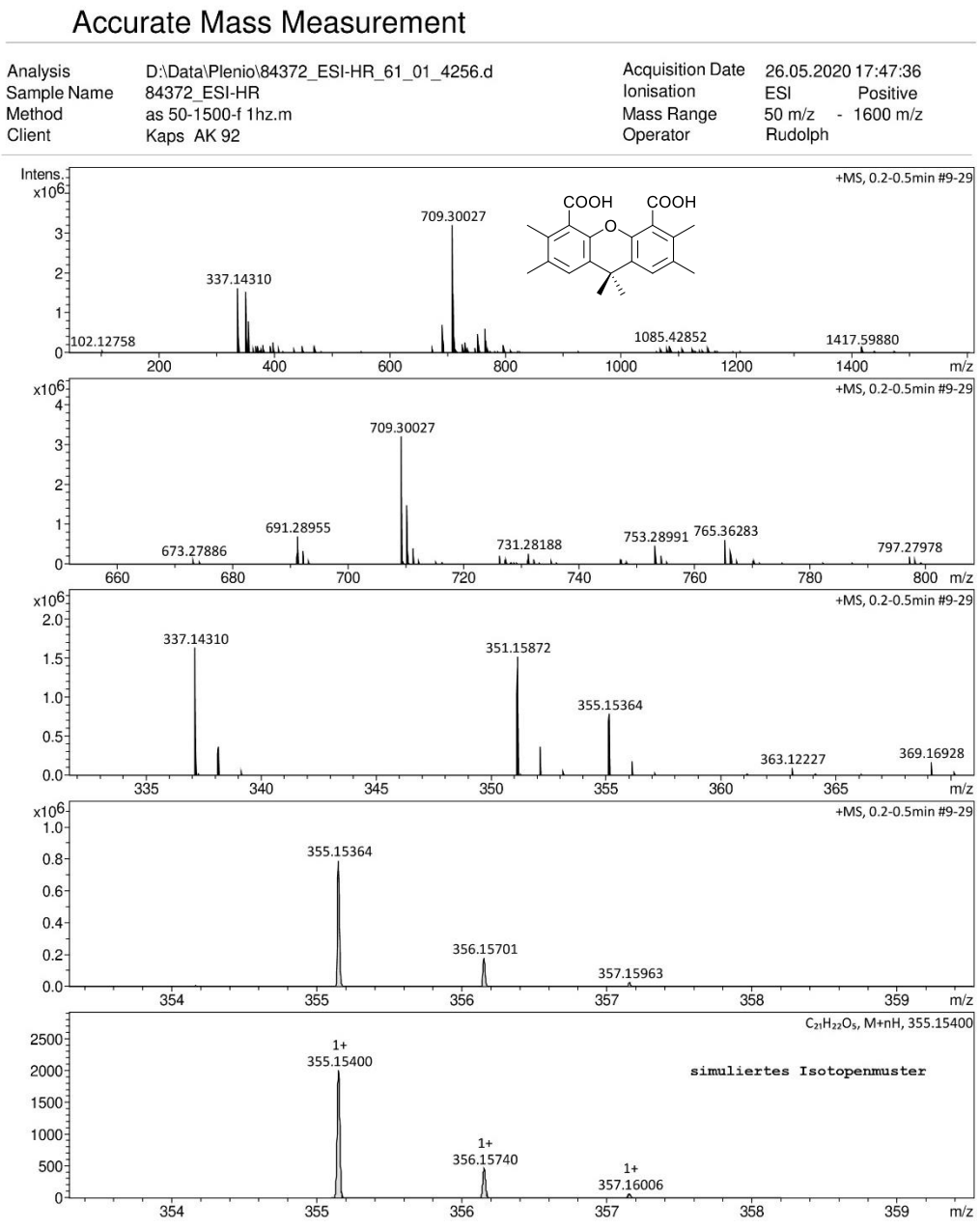


*Figure 81: ^{13}C-NMR of [(PdCl(allyl))$_2$(**16**)] in CD_2Cl_2.*

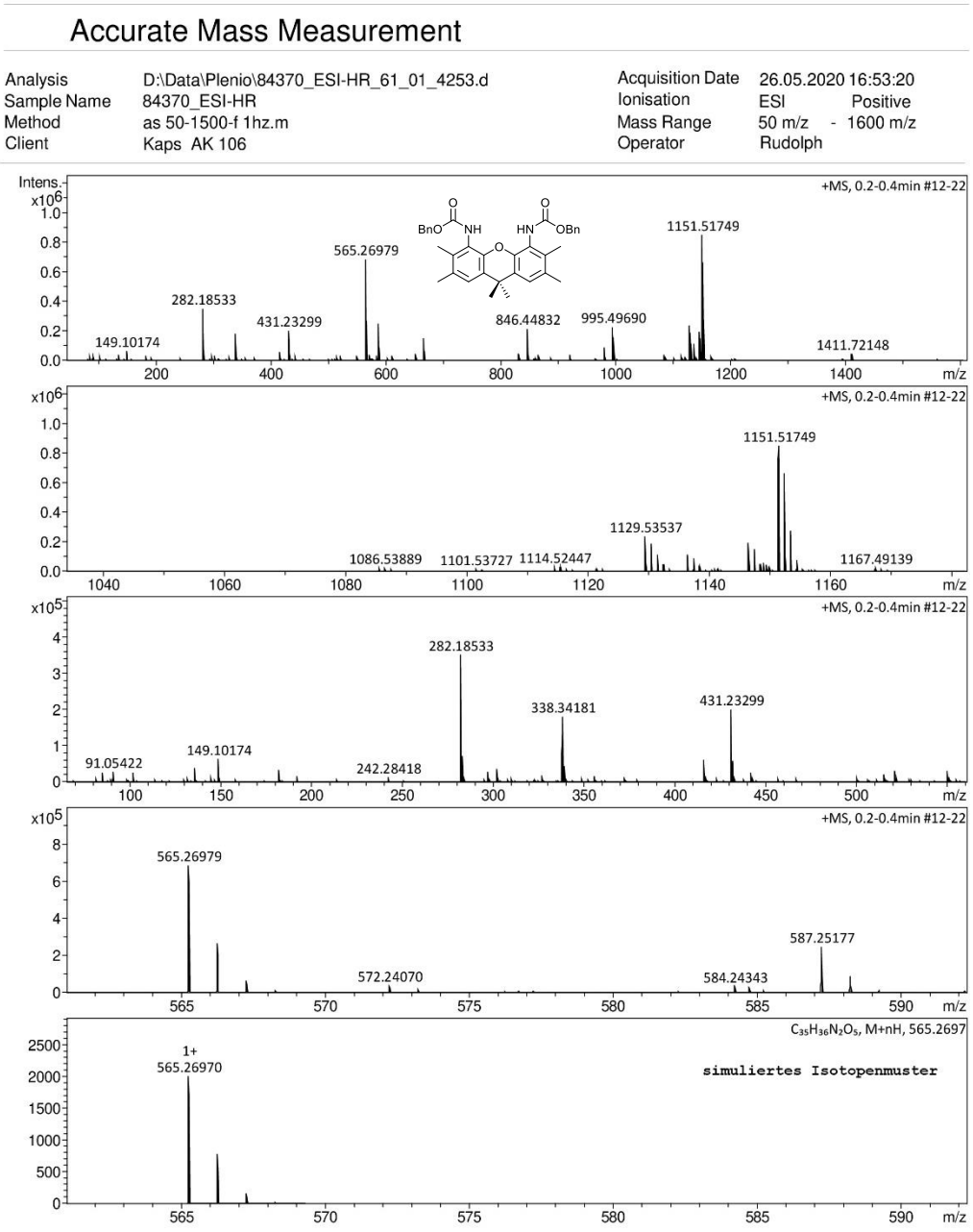
2. Mass spectrometry



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	337.14310	C21H21O4	337.14344	C21H21O4	0.33	0.99	even	M
1	337.14310	C21H21O4	337.14344	C21H20O4	0.33	0.99	even	M+H
1	351.15872	C22H23O4	351.15909	C22H23O4	0.36	1.04	even	M
1	351.15872	C22H23O4	351.15909	C22H22O4	0.36	1.04	even	M+H
1	355.15364	C21H23O5	355.15400	C21H22O5	0.36	1.02	even	M+H
1	709.30027	C42H45O10	709.30072	C21H22O5	0.46	0.65	even	2M+H

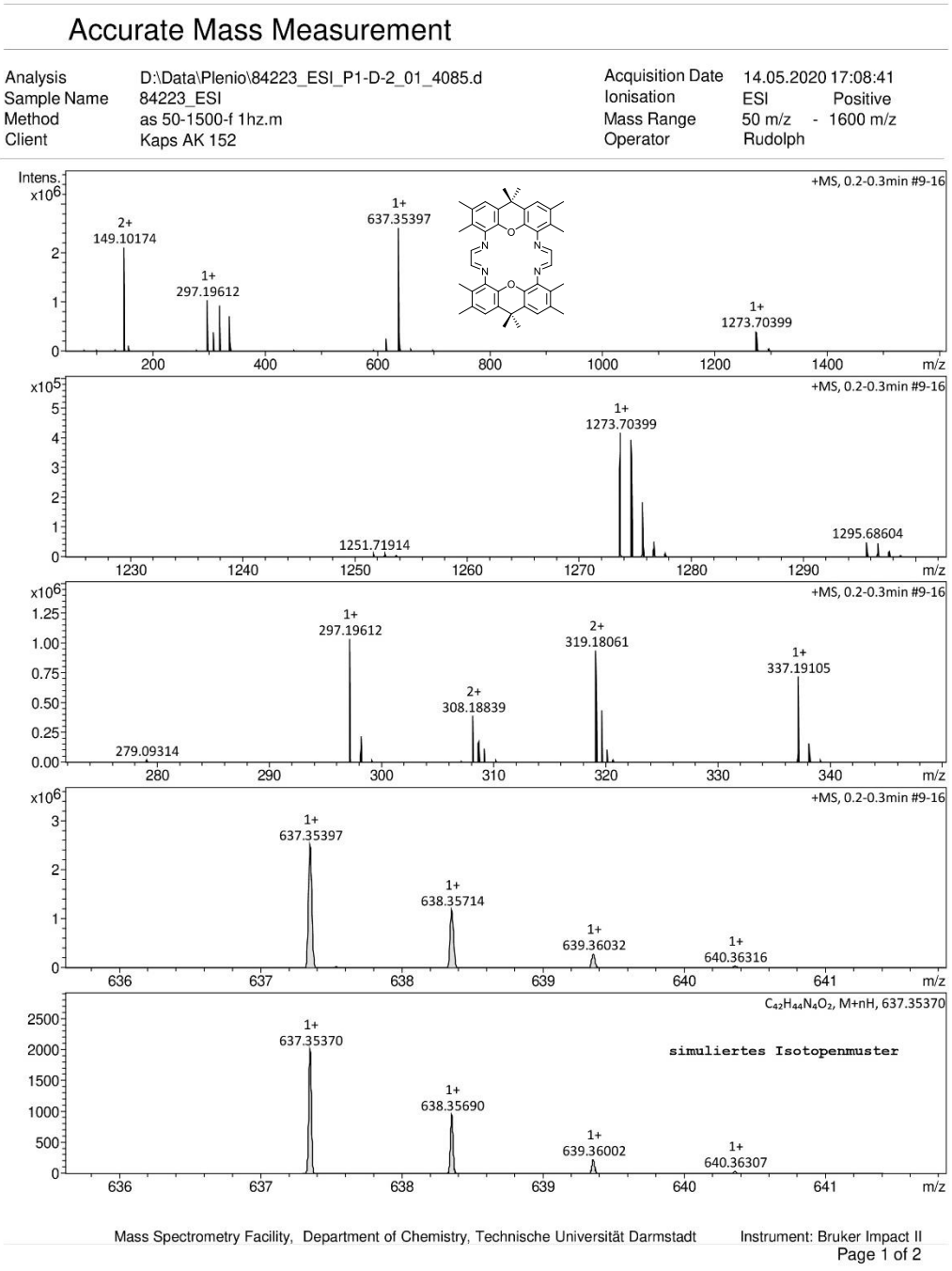
*Figure 82: HRMS (ESI, positive mode) of 2,3,6,7,9,9-hexamethylxanthene-4,5-dicarboxylic acid (**4**).*



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	565.26979	C35H37N2O5	565.26970	C35H36N2O5	0.09	-0.16	even	M+H
1	587.25177	C35H36N2NaO5	587.25164	C35H36N2O5	0.13	-0.21	even	M+Na
1	1151.51749	C70H72N4NaO10	1151.51407	C35H36N2O5	3.42	-2.97	even	2M+Na

Figure 83: HRMS (ESI, positive mode) of dibenzyl (2,3,6,7,9,9-hexamethylxanthene-4,5-diyl)dicarbamate (**5**).



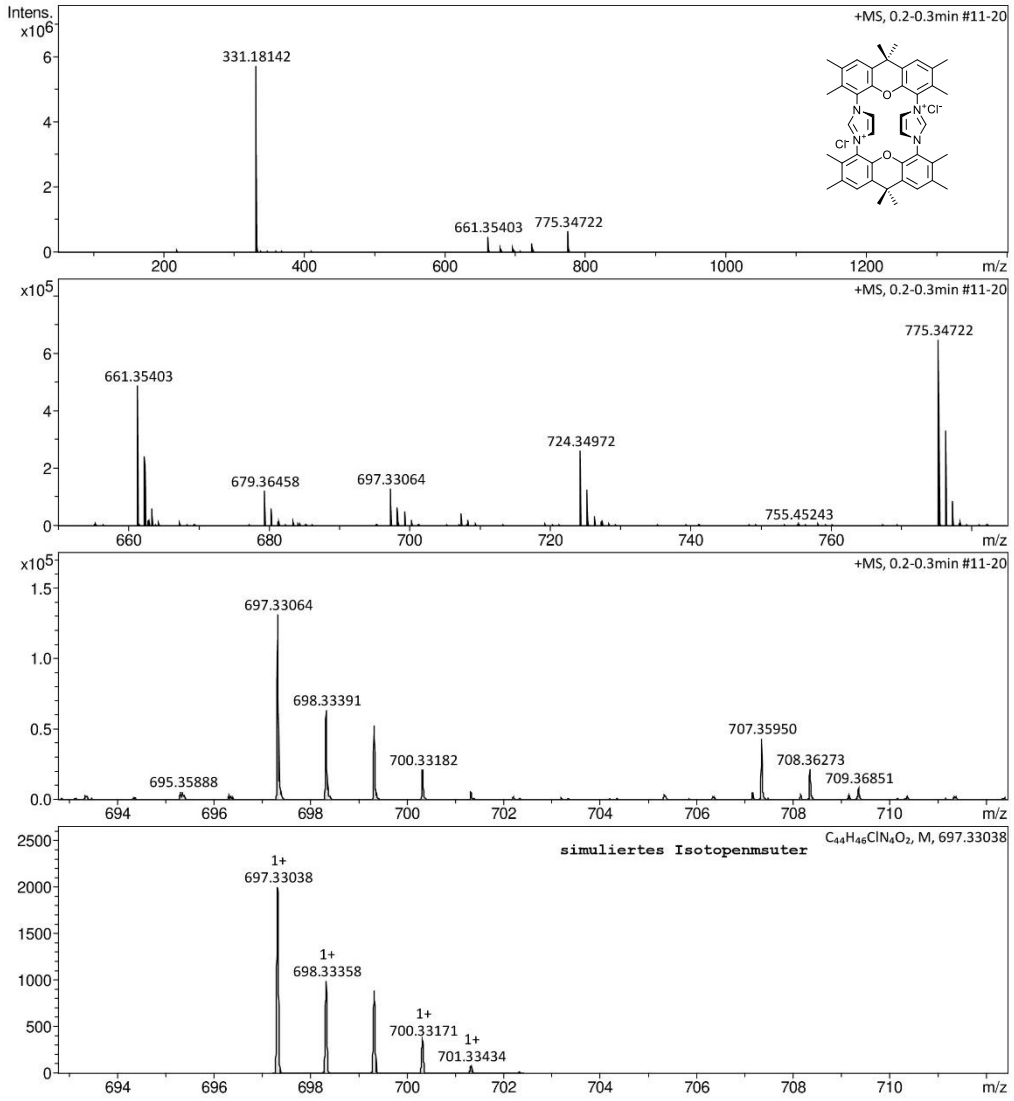
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	637.35397	C42H45N4O2	637.35370	C42H44N4O2	0.27	-0.42	even	M+H
1	1273.70399	C84H89N8O4	1273.70013	C42H44N4O2	3.86	-3.03	even	2M+H

*Figure 84: HRMS (ESI, positive mode) of xanthen diamine (**8**).*

Accurate Mass Measurement

Analysis	D:\Data\Plenio\83506_ESI_HR_61_01_3129.d	Acquisition Date	19.02.2020 11:40:59
Sample Name	83506_ESI_HR	Ionisation	ESI Positive
Method	as 50-2000-f 1hz.m	Mass Range	50 m/z - 2000 m/z
Client	Kaps AK 118	Operator	Rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	661.35403	C44H45N4O2	661.35370	C44H45N4O2	0.33	-0.50	even	M
1	661.35403	C44H45N4O2	661.35370	C44H44N4O2	0.33	-0.50	even	M+H
1	679.36458	C44H47N4O3	679.36427	C44H47N4O3	0.31	-0.46	even	M
1	679.36458	C44H47N4O3	679.36427	C44H46N4O3	0.31	-0.46	even	M+H
1	697.33064	C44H46ClN4O2	697.33038	C44H46ClN4O2	0.26	-0.37	even	M
1	697.33064	C44H46ClN4O2	697.33038	C44H45ClN4O2	0.26	-0.37	even	M+H
1	707.35950	C45H47N4O4	707.35918	C45H47N4O4	0.32	-0.45	even	M
1	707.35950	C45H47N4O4	707.35918	C45H46N4O4	0.32	-0.45	even	M+H
1	724.34972	C44H46N5O5	724.34935	C44H46N5O5	0.37	-0.51	even	M
1	724.34972	C44H46N5O5	724.34935	C44H45N5O5	0.37	-0.51	even	M+H
1	775.34722	C46H45N7O5	775.34767	C46H45N7O5	0.45	0.58	odd	M
1	775.34722	C46H45N7O5	775.34767	C46H44N7O5	0.45	0.58	odd	M+H

*Figure 85: HRMS (ESI, positive mode) of xanthen imidazolium chloride (**9**).*

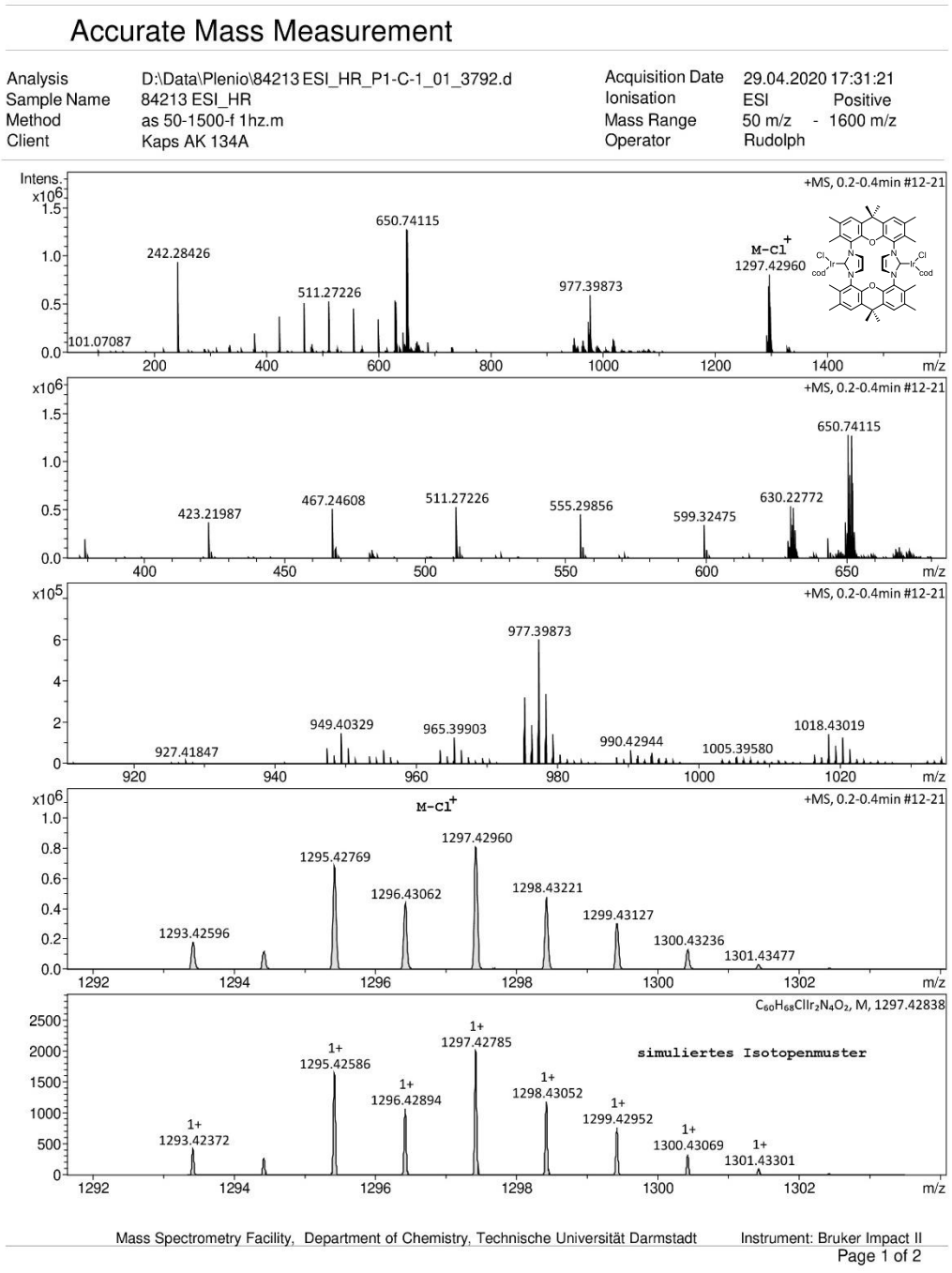
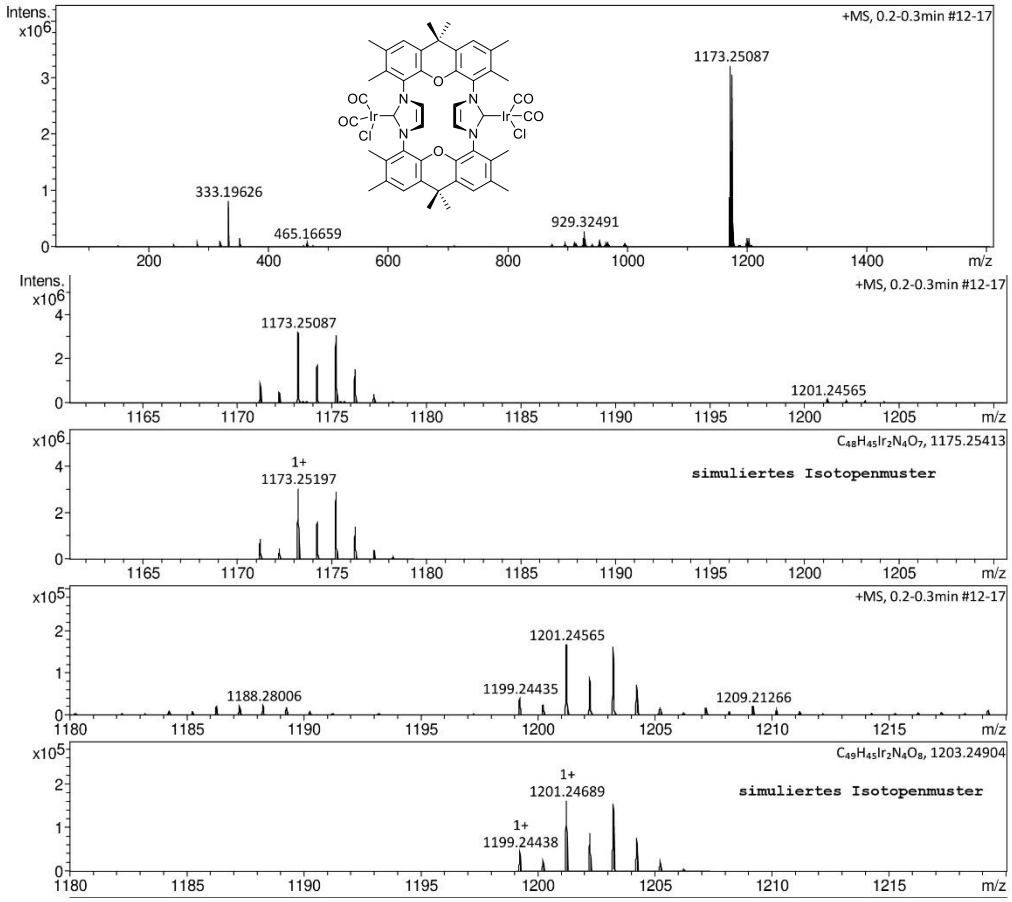


*Figure 86: HRMS (ESI, positive mode) of [(IrCl(cod))$_2$(**9**)].*

Mass spectrum

Analysis	D:\Data\Plenio\84380_ESI-HR_61_01_4322.d	Acquisition Date	29.05.2020 13:52:31
Sample Name	84380_ESI-HR	Ionisation	ESI Positive
Method	as 50-1500-f 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 169	Operator	Rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	1175.25363	C48H45Ir2N4O7	1175.25413	C48H44Ir2N4O7	1.12	0.96	even	M+H
1	1203.24798	C49H45Ir2N4O8	1203.24904	C49H44Ir2N4O8	1.71	1.43	even	M+H

*Figure 87: HRMS (ESI, positive mode) of [(IrCl(CO)$_2$)$_2$(**9**)].*

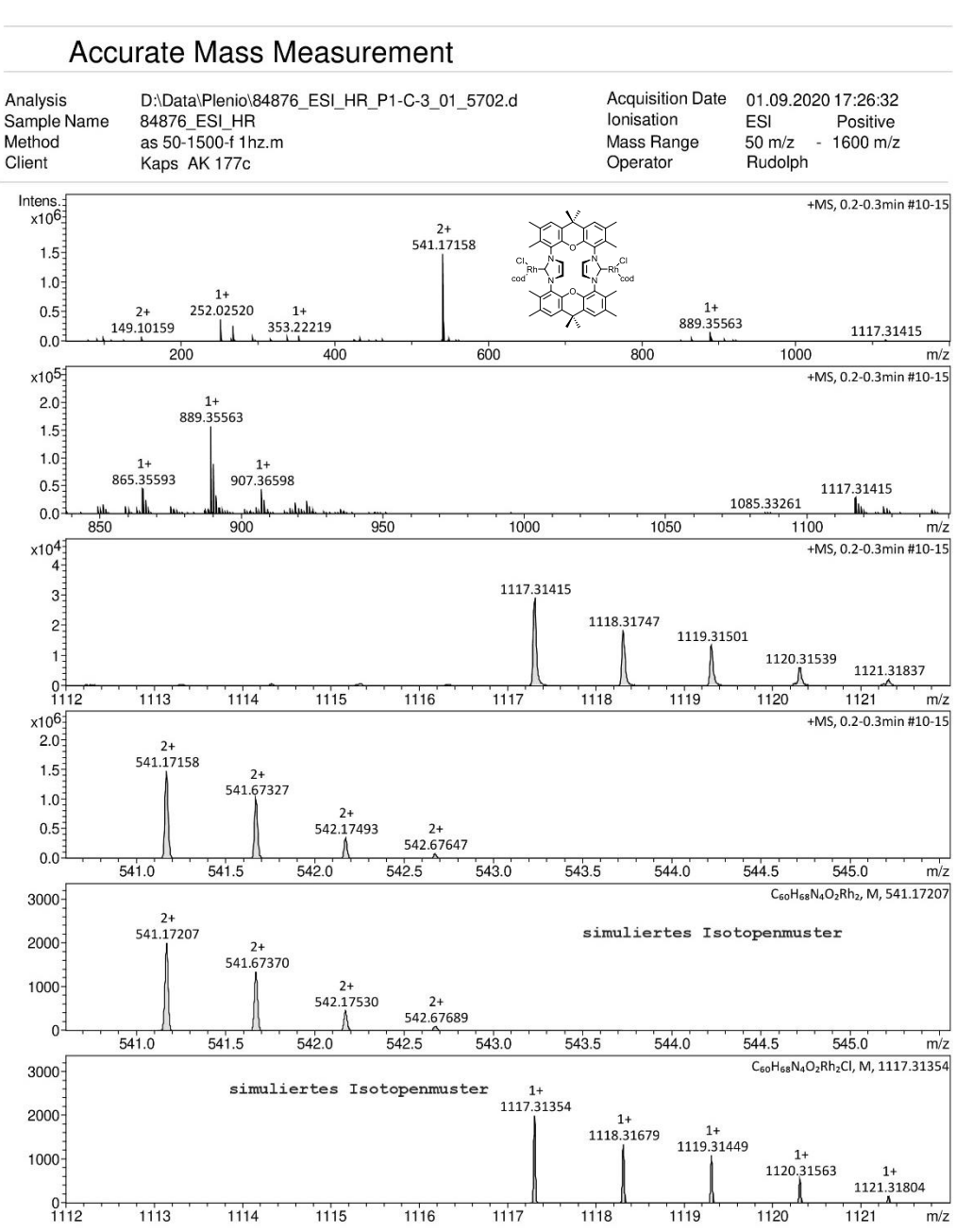


*Figure 88: HRMS (ESI, positive mode) of [(RhCl(cod))$_2$(**9**)].*

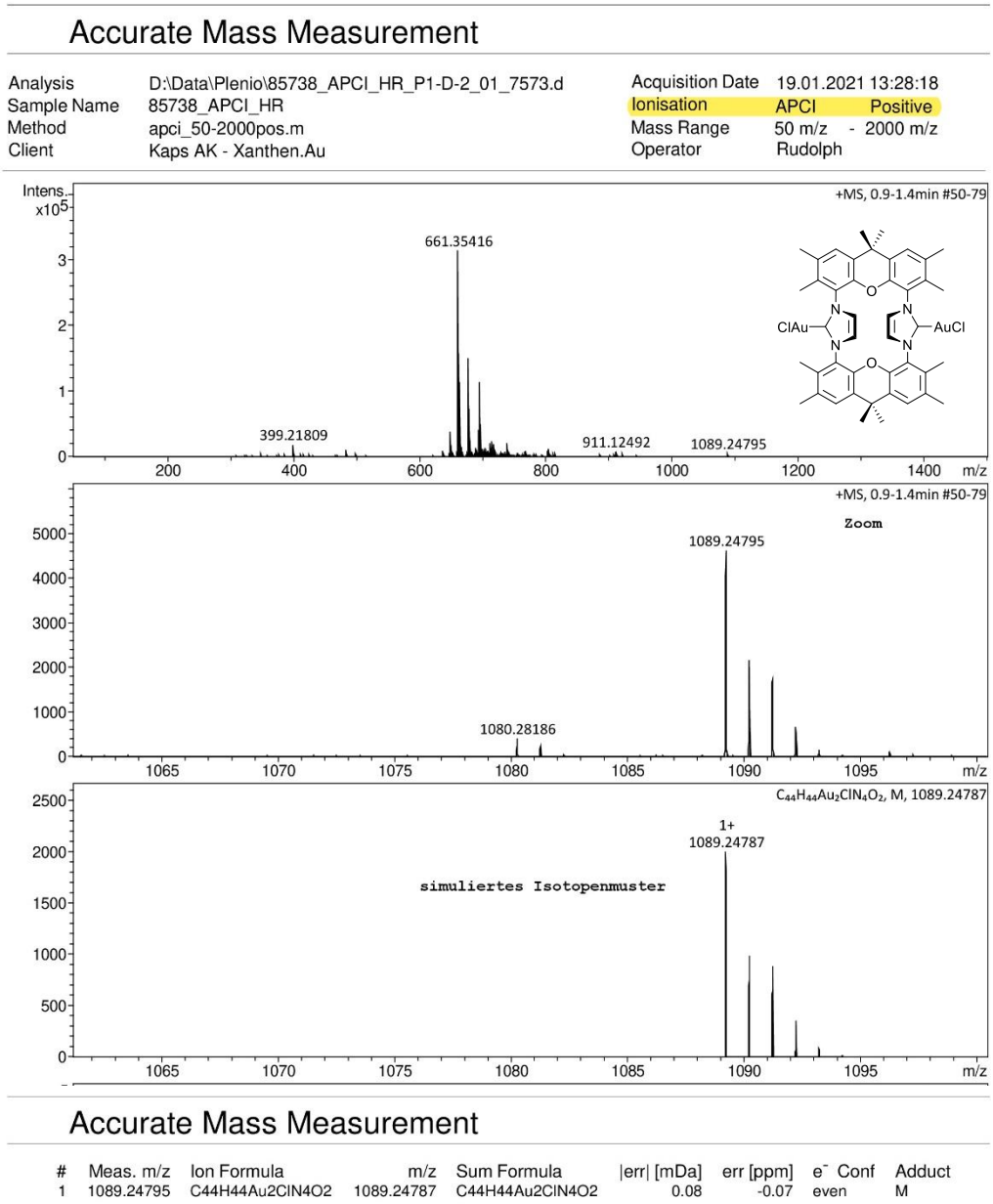
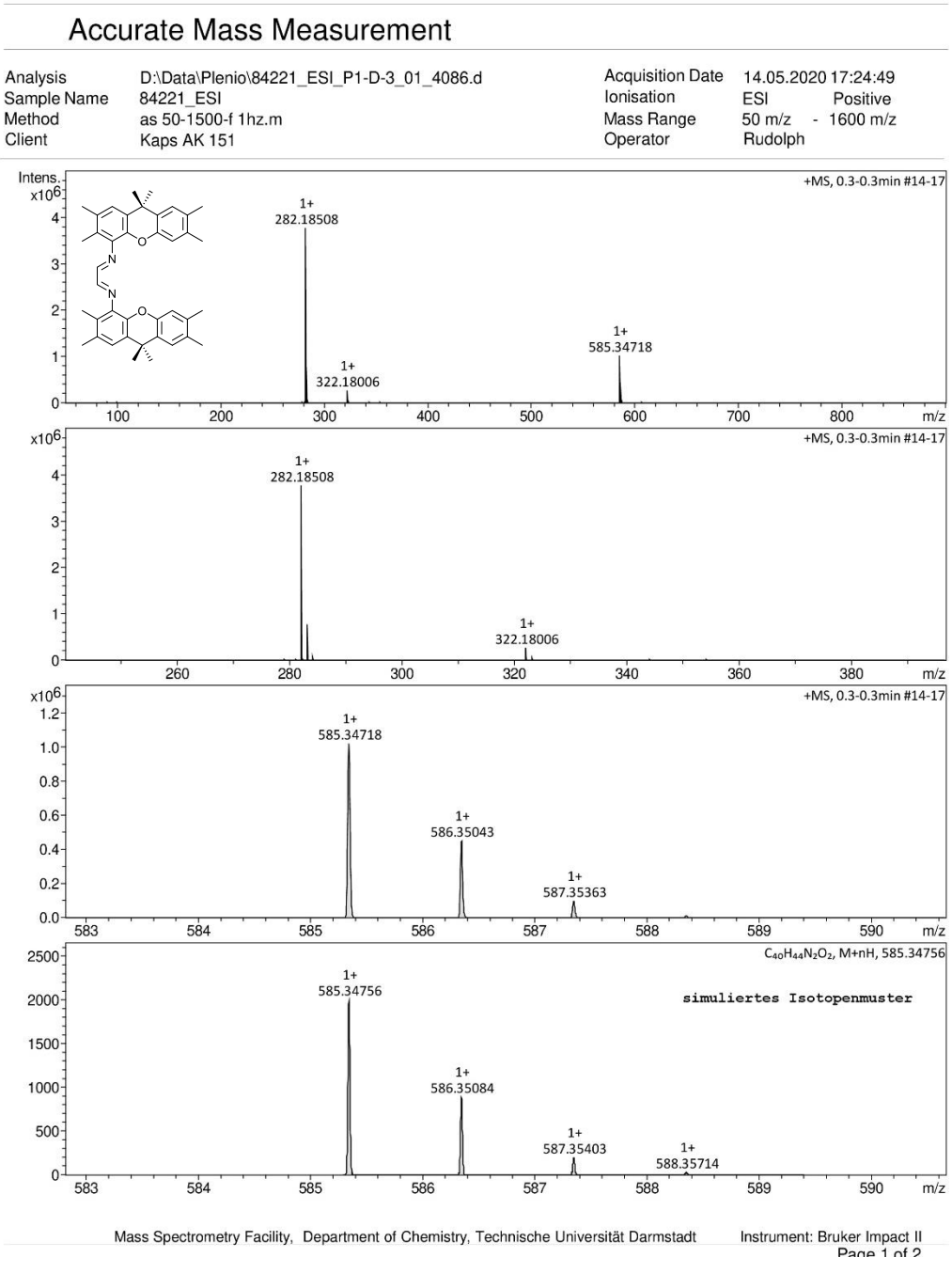


*Figure 89: HRMS (APCI, positive mode) of [(AuCl)$_2$(**9**)].*



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	585.34718	C40H45N2O2	585.34756	C40H44N2O2	0.37	0.64	even	M+H

*Figure 90: HRMS (ESI, positive mode) of xanthene diimine (**10**).*

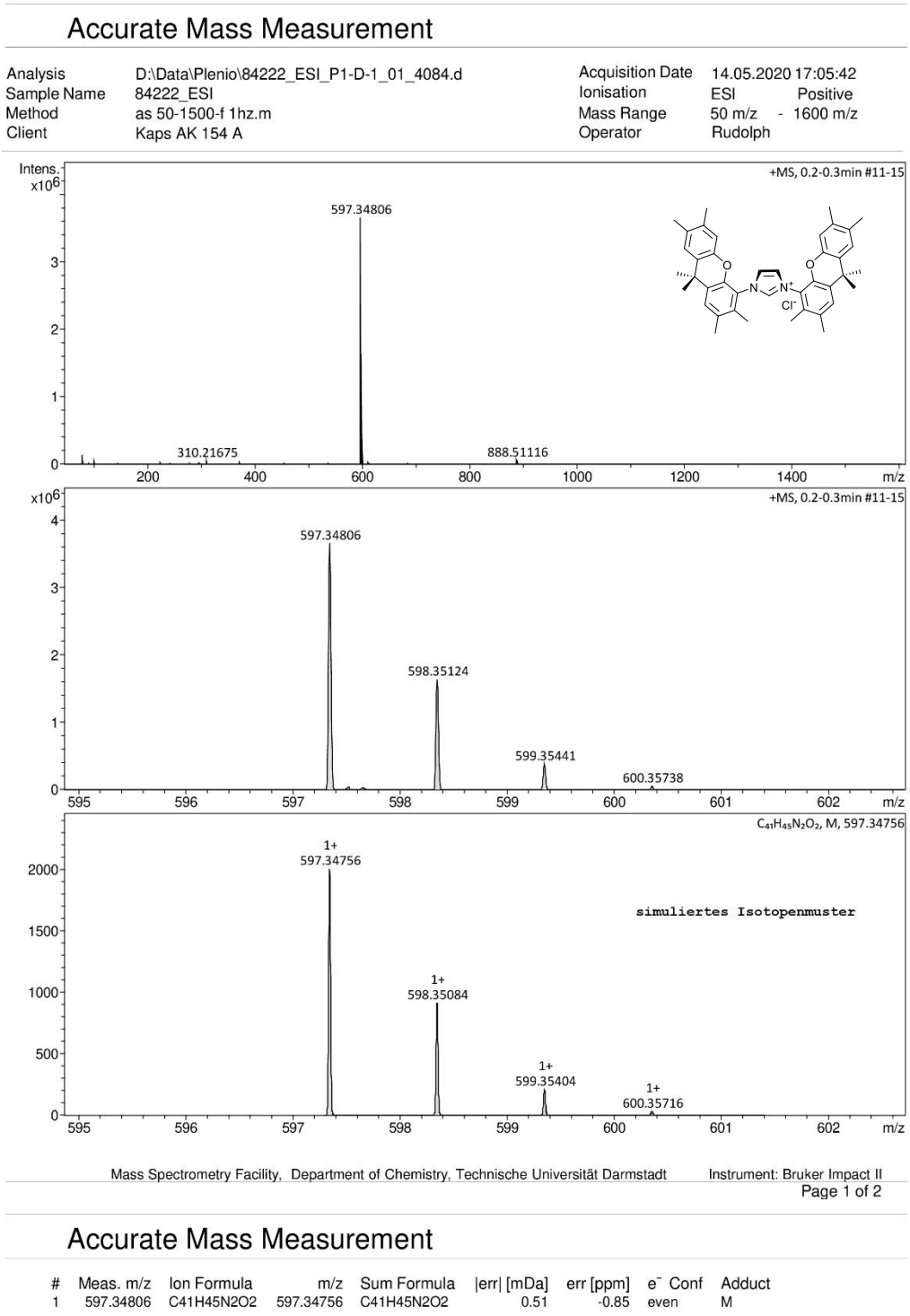
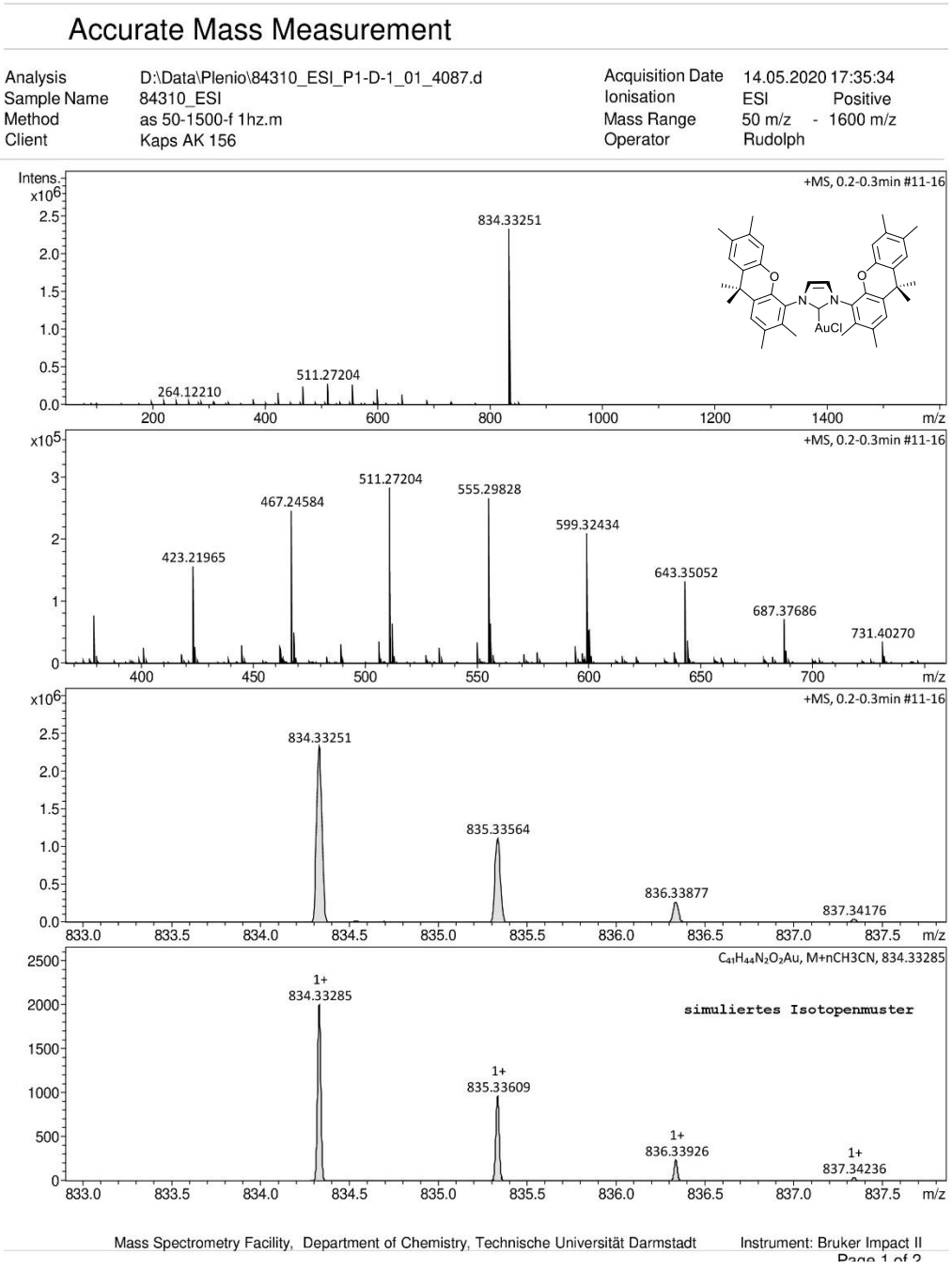


*Figure 91: HRMS (ESI, positive mode) of xanthen imidazolium chloride (**11** · HCl).*

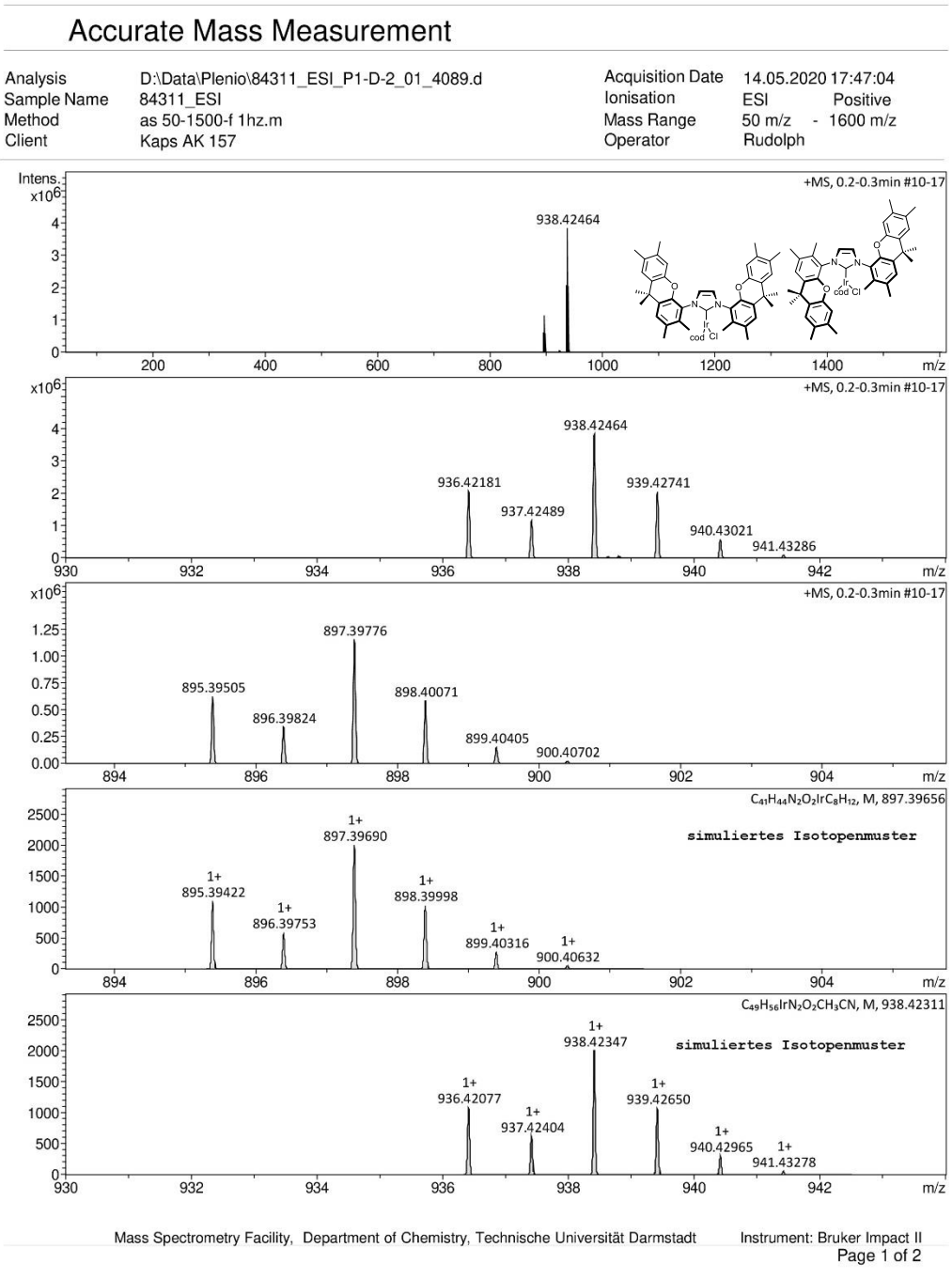


Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	834.33251	C43H47AuN3O2	834.33285	C43H47AuN3O2	0.34	0.40	even	M

gemessen M-Cl+CH3CN+

*Figure 92: HRMS (ESI, positive mode) of [AuCl(**11**)]-complex.*

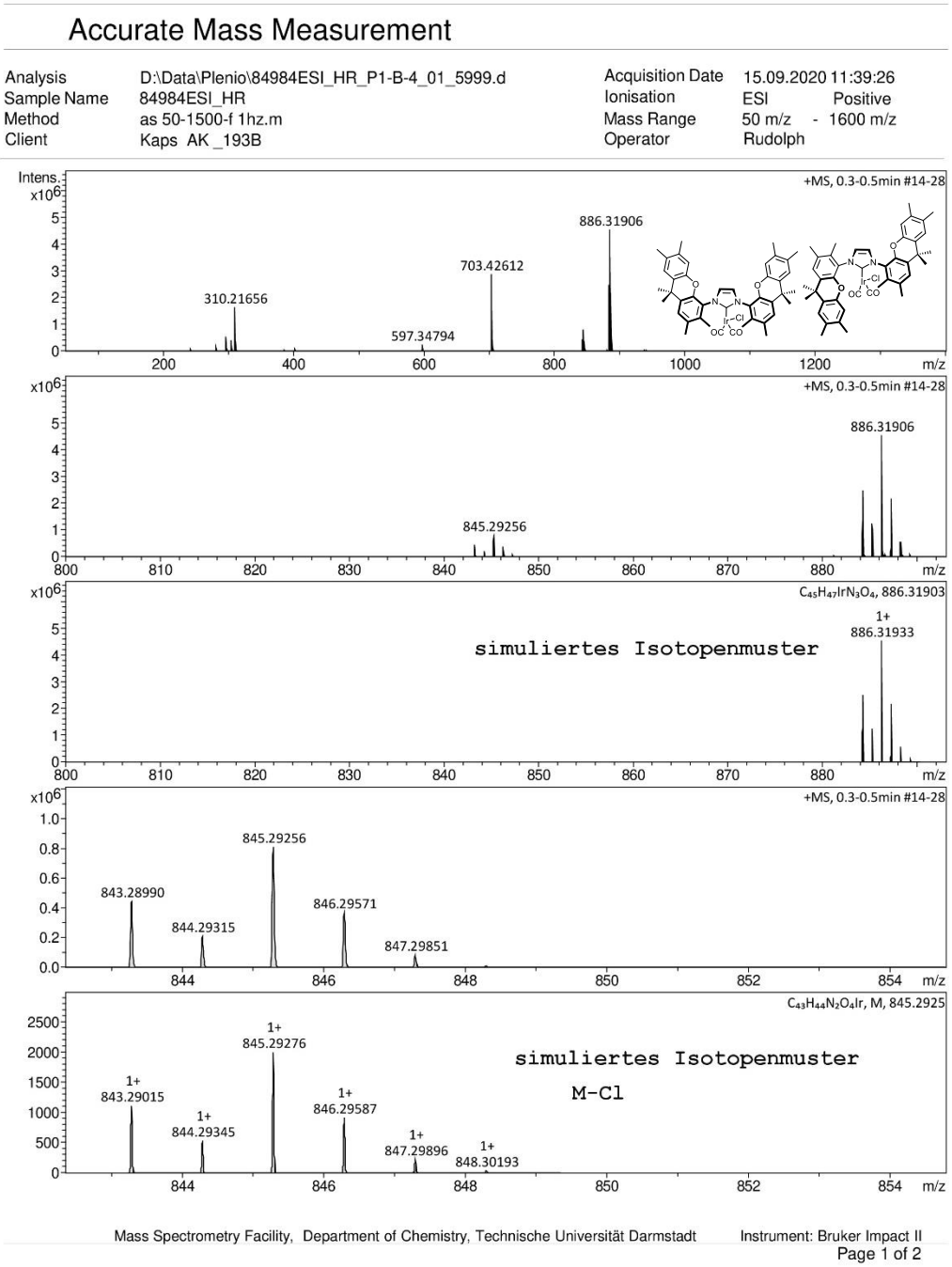


Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	897.39776	C49H56IrN2O2	897.39656	C49H56IrN2O2	0.86	-0.96	even	M
1	938.42464	C51H59IrN3O2	938.42311	C51H59IrN3O2	1.17	-1.25	even	M

gemessen M-Cl+cod$^+$ und M-Cl+cod+CH3CN$^+$

*Figure 93: HRMS(ESI, positive mode) of [IrCl(cod)(**11**)].*



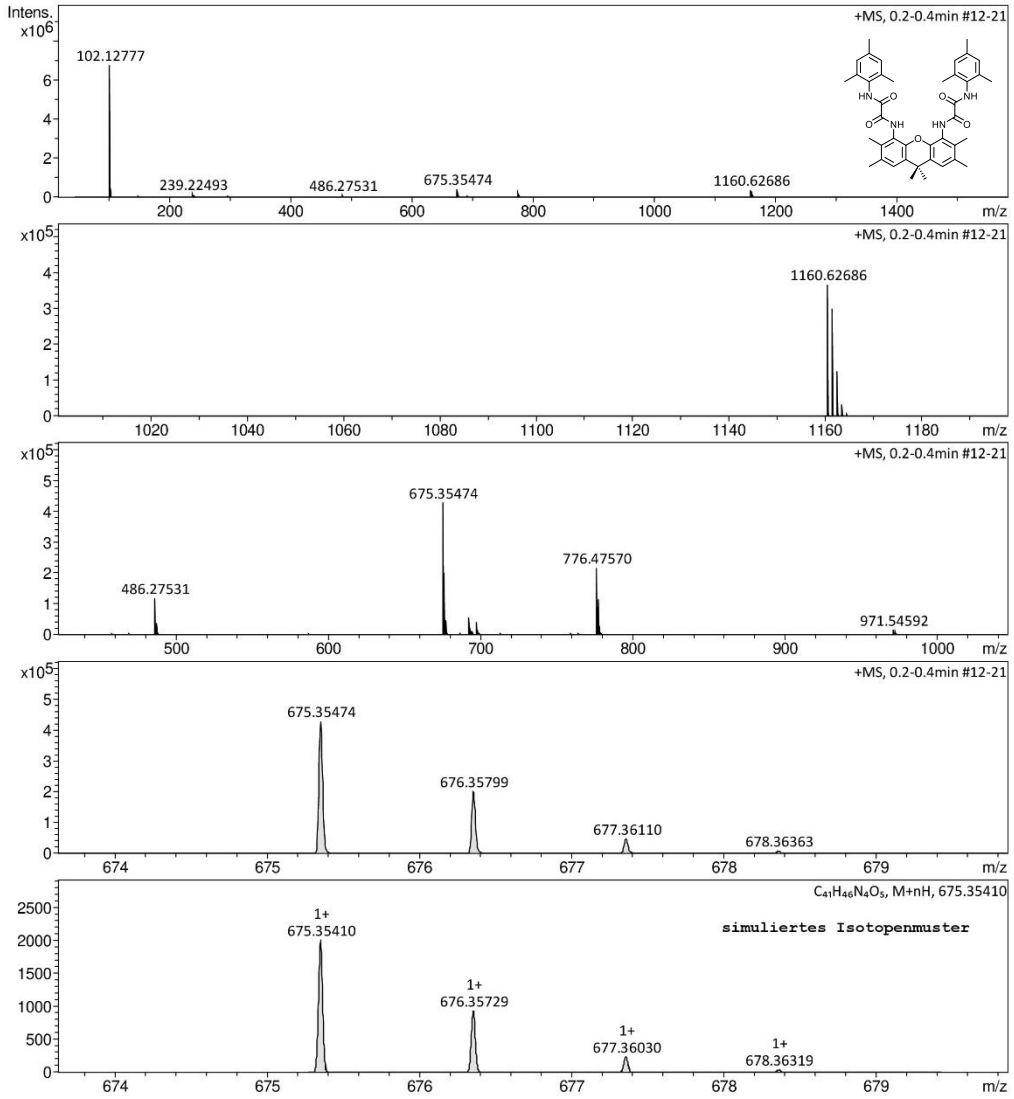
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	845.29256	C43H44IrN2O4	845.29249	C43H44IrN2O4	0.20	0.24	even	M	1+
1	886.31906	C45H47IrN3O4	886.31903	C45H47IrN3O4	0.27	0.31	even	M	1+
1	886.31906	C45H47IrN3O4	886.31903	C45H46IrN3O4	0.27	0.31	even	M+H	1+

*Figure 94: HRMS (ESI, positive mode) of [IrCl(CO)$_2$(**11**)].*

Accurate Mass Measurement

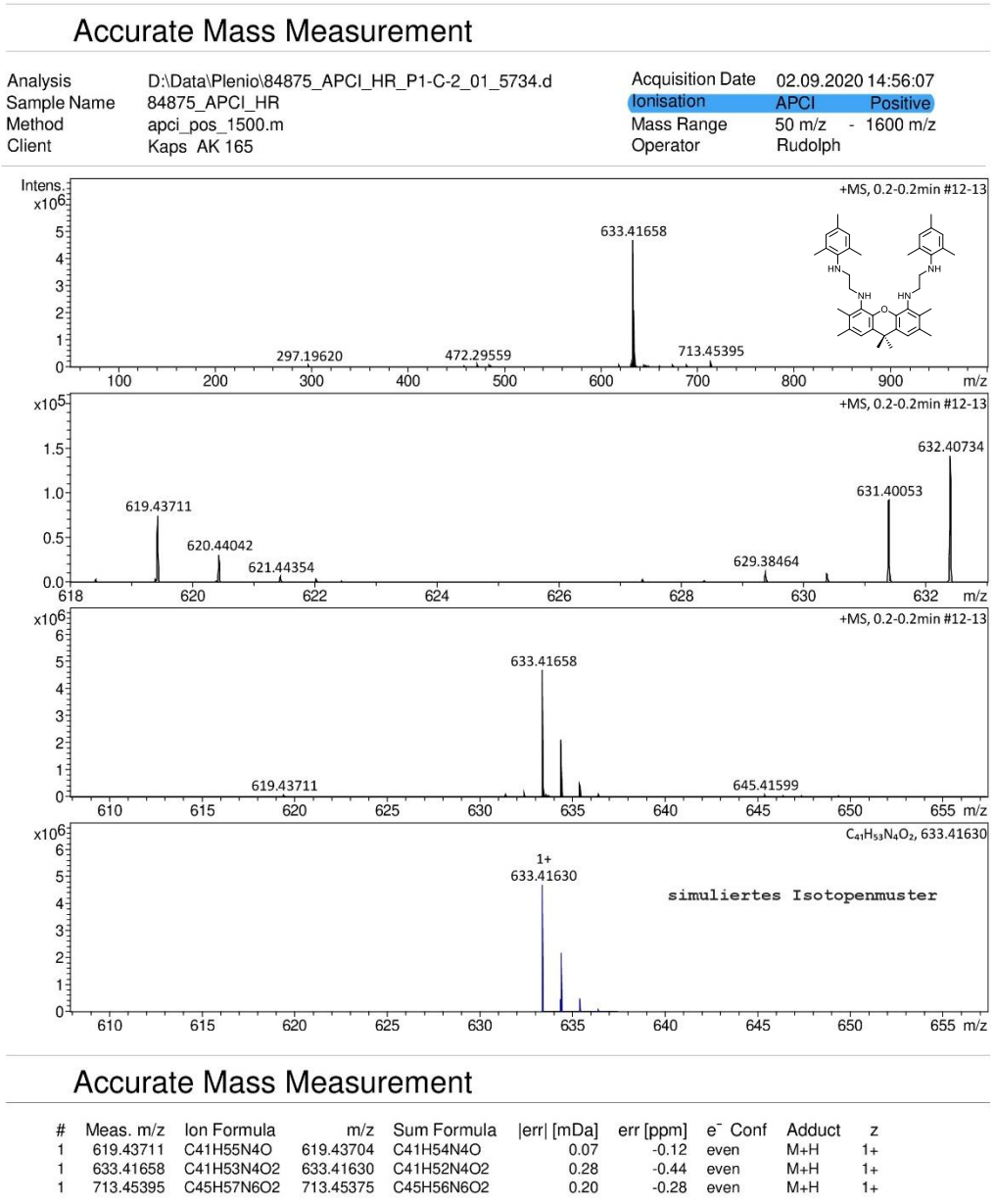
Analysis	D:\Data\Plenio\84373_ESI-HR_63_01_4259.d	Acquisition Date	26.05.2020 18:37:58
Sample Name	84373_ESI-HR	Ionisation	ESI Positive
Method	as 50-1500-f 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 161	Operator	Rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	675.35474	C41H47N4O5	675.35410	C41H46N4O5	0.64	-0.95	even	M+H
1	692.38139	C41H50N5O5	692.38065	C41H46N4O5	0.75	-1.08	even	M+NH4
1	697.33667	C41H46N4NaO5	697.33604	C41H46N4O5	0.63	-0.90	even	M+Na

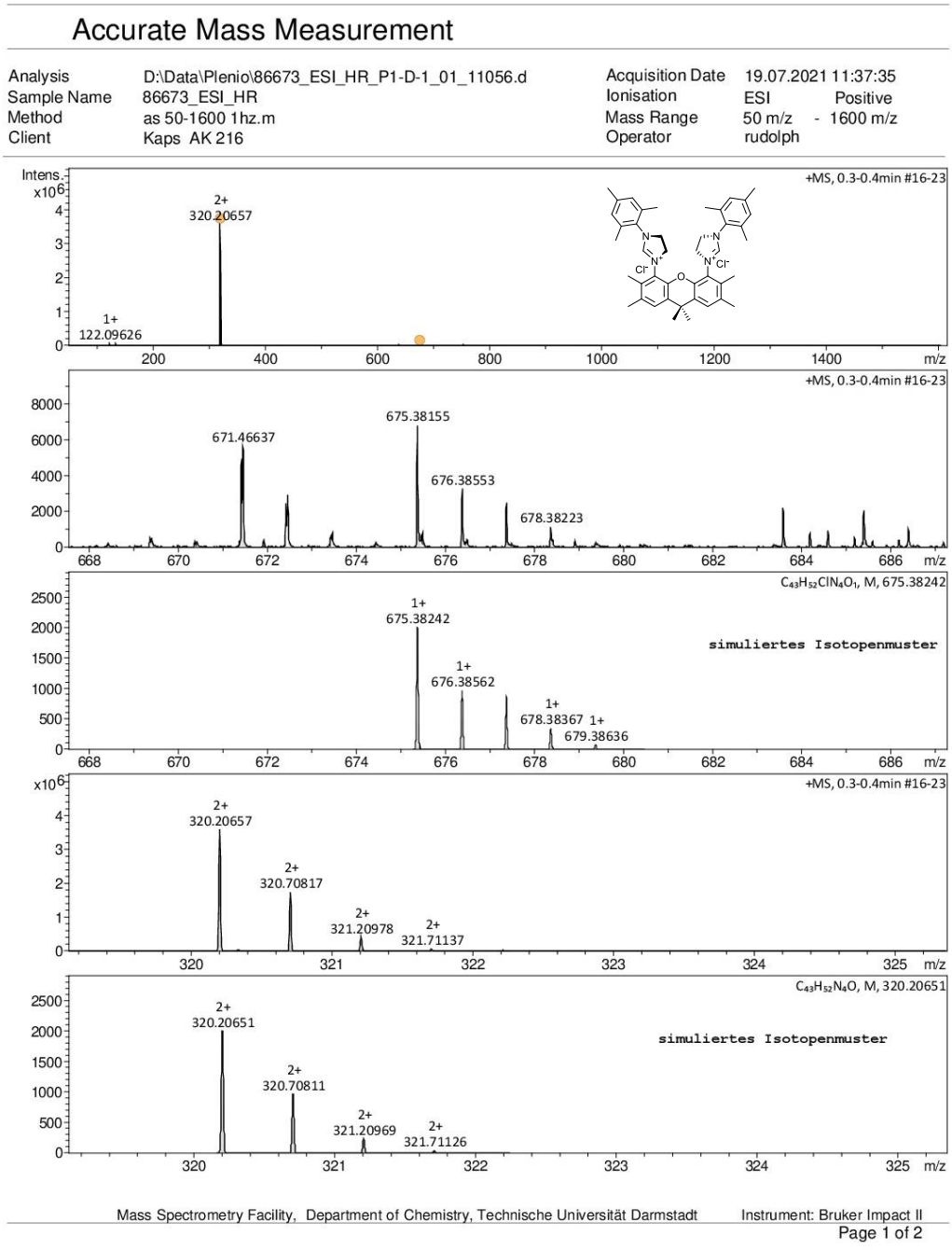
*Figure 95: HRMS (ESI, positive mode) of xanthene tetraamide (**12**).*



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	619.43711	C41H55N4O	619.43704	C41H54N4O	0.07	-0.12	even	M+H	1+
1	633.41658	C41H53N4O2	633.41630	C41H52N4O2	0.28	-0.44	even	M+H	1+
1	713.45395	C45H57N6O2	713.45375	C45H56N6O2	0.20	-0.28	even	M+H	1+

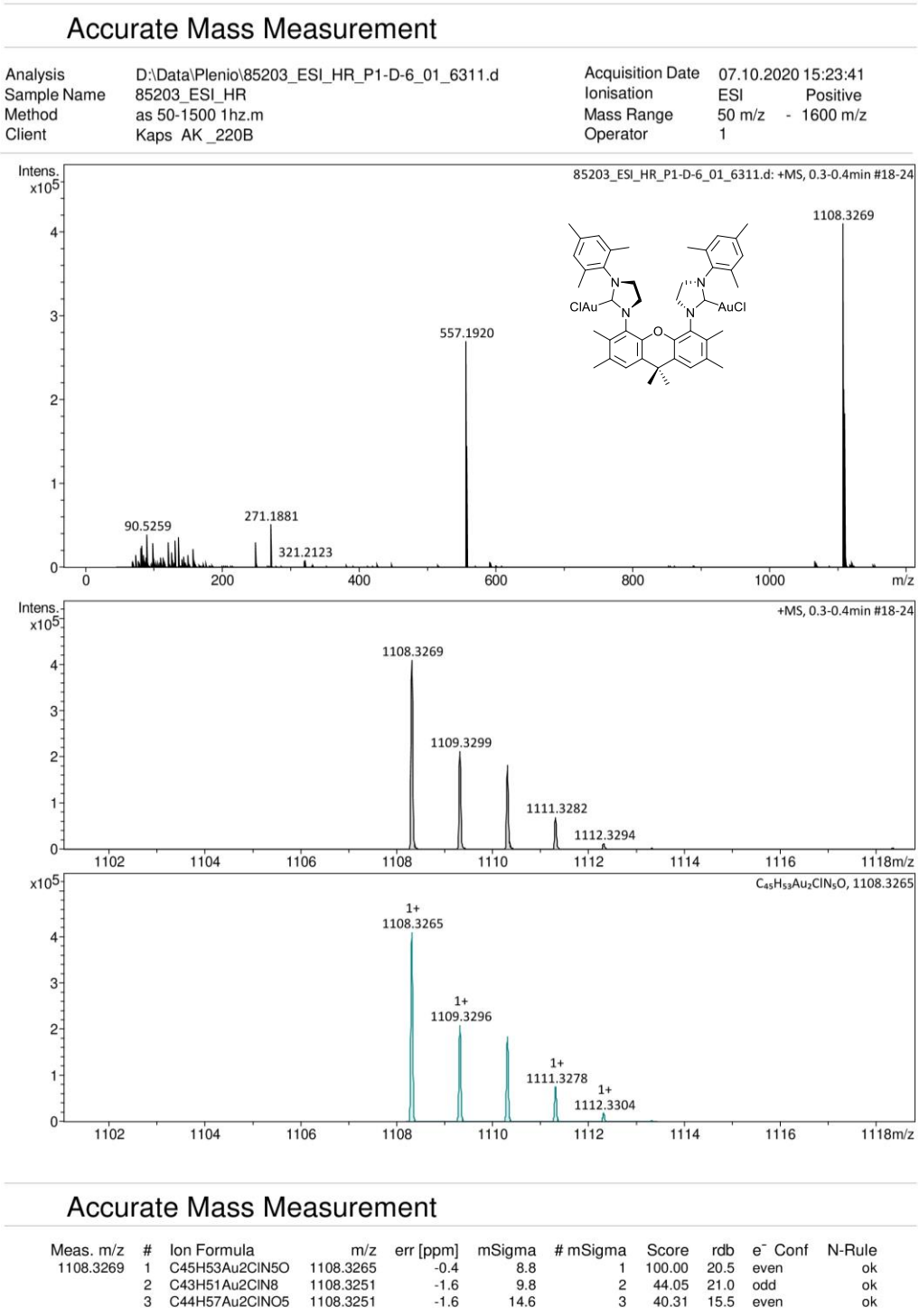
Figure 96: HRMS (APCI, positive mode) of xanthene tetramine (**13**).



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	320.20657	C43H52N4O	320.20651	C43H52N4O	0.06	-0.18	even	M	2+
1	675.38155	C27H52ClN12O6	675.38158	C27H52ClN12O6	0.03	0.04	even	M	1+
2	320.20657	C45H54NO2	320.20718	C45H54NO2	0.61	1.92	odd	M	2+
2	675.38155	C42H56ClO5	675.38108	C42H56ClO5	0.47	-0.70	even	M	1+
3	675.38155	C43H52ClN4O	675.38242	C43H52ClN4O	0.86	1.28	even	M	1+

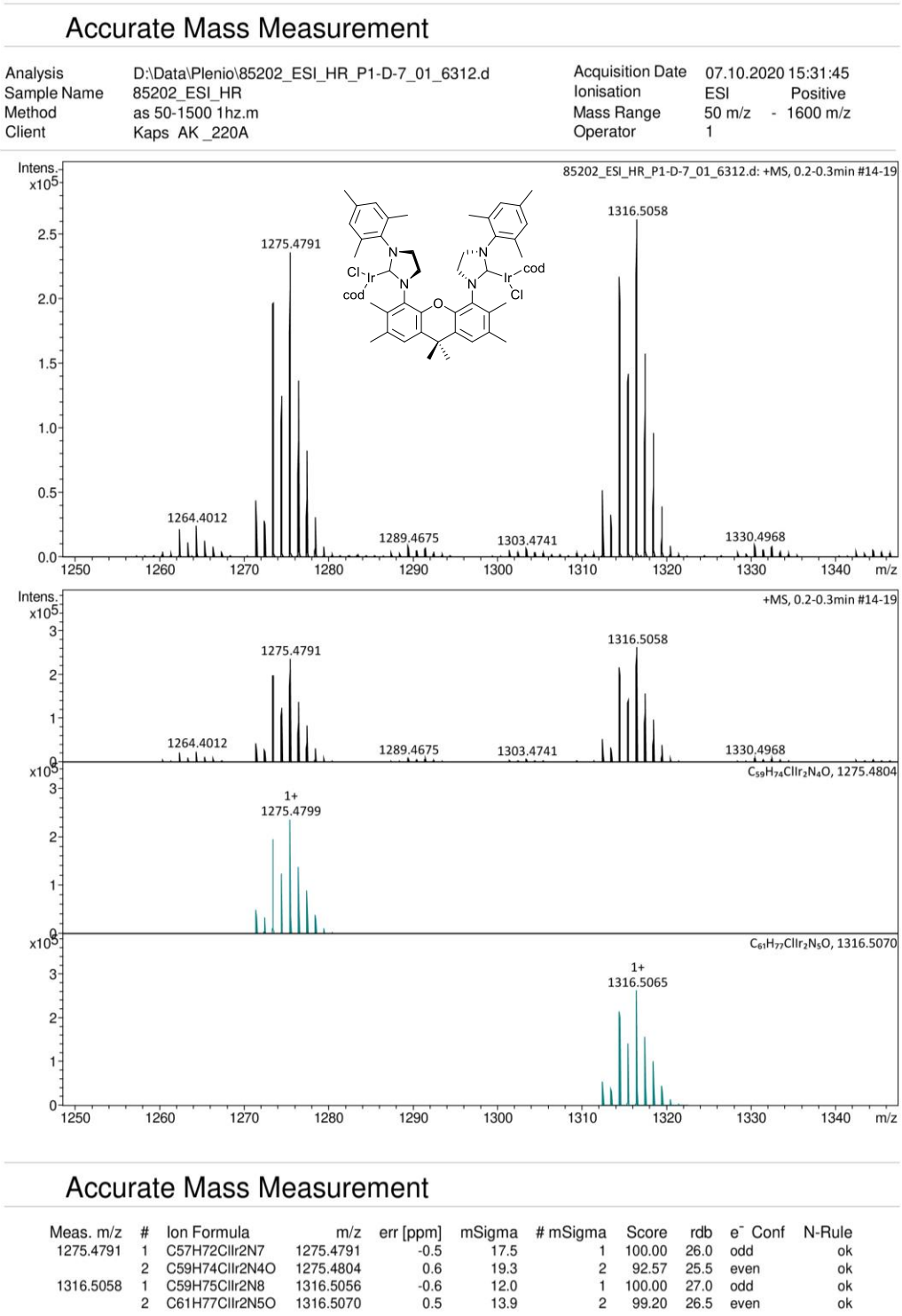
Figure 97: HRMS (ESI, positive mode) of xanthene imidazolinium salt (**14** · 2 HCl).



Accurate Mass Measurement

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
1108.3269	1	C45H53Au2ClN5O	1108.3265	-0.4	8.8	1	100.00	20.5	even	ok
	2	C43H51Au2ClN8	1108.3251	-1.6	9.8	2	44.05	21.0	odd	ok
	3	C44H57Au2ClNO5	1108.3251	-1.6	14.6	3	40.31	15.5	even	ok

Figure 98: HRMS (ESI, positive mode) of $[AuCl)_2$(**14**)].



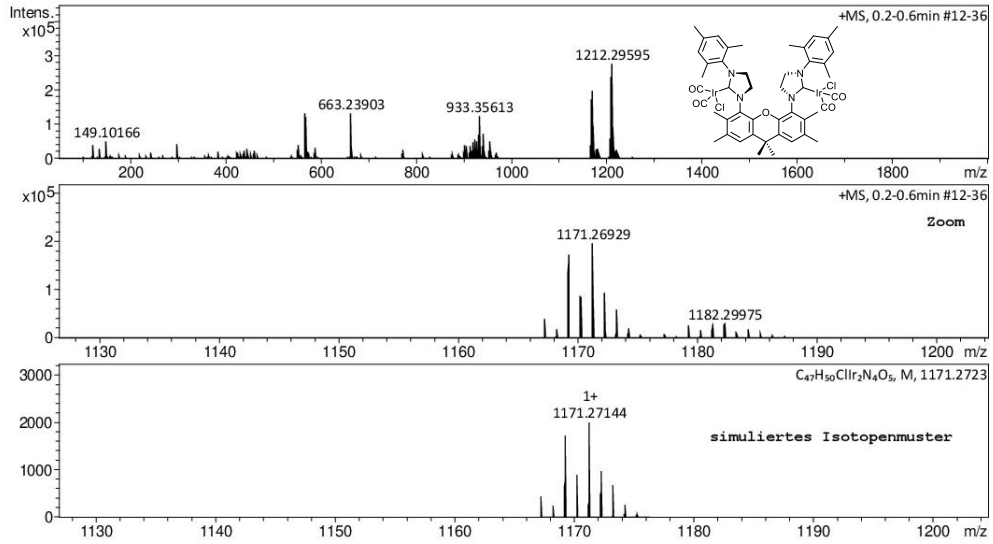
Accurate Mass Measurement

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
1275.4791	1	C57H72ClIr2N7	1275.4791	-0.5	17.5	1	100.00	26.0	odd	ok
	2	C59H74ClIr2N4O	1275.4804	0.6	19.3	2	92.57	25.5	even	ok
1316.5058	1	C59H75ClIr2N8	1316.5056	-0.6	12.0	1	100.00	27.0	odd	ok
	2	C61H77ClIr2N5O	1316.5070	0.5	13.9	2	99.20	26.5	even	ok

Figure 99: HRMS (ESI, positive mode) of [(IrCl(cod))$_2$(**14**)].

Accurate Mass Measurement

Analysis	D:\Data\Plenio\86659_ESI_HR_P1-D-2_01_10969.d	Acquisition Date	14.07.2021 13:12:49
Sample Name	86659_ESI_HR	Ionisation	ESI Positive
Method	as 50-2000 1hz.m	Mass Range	50 m/z - 2000 m/z
Client	Kaps AK 298_IrCO	Operator	rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	1171.26929	C43H175ClIr2N3O	1171.26767	C43H175ClIr2N3O	2.51	-2.14	even	M	1+
1	1212.29595	C47H180ClIr2NO2	1212.29557	C47H180ClIr2NO2	1.18	-0.97	odd	M	1+
2	1171.26929	C45H177ClIr2O2	1171.26902	C45H177ClIr2O2	1.11	-0.95	odd	M	1+
2	1212.29595	C47H51ClIr2N8O4	1212.29748	C47H51ClIr2N8O4	0.68	0.56	odd	M	1+
3	1171.26929	C41H173ClIr2N6	1171.26633	C41H173ClIr2N6	3.91	-3.34	odd	M	1+
3	1212.29595	C45H178ClIr2N4O	1212.29422	C45H178ClIr2N4O	2.58	-2.13	even	M	1+
4	1171.26929	C44H52ClIr2N3O8	1171.26960	C44H52ClIr2N3O8	0.58	-0.49	odd	M	1+
4	1212.29595	C48H57ClIr2NO9	1212.29749	C48H57ClIr2NO9	0.75	0.62	even	M	1+
5	1171.26929	C45H48ClIr2N7O4	1171.27093	C45H48ClIr2N7O4	0.75	0.64	odd	M	1+
5	1212.29595	C49H53ClIr2N5O5	1212.29883	C49H53ClIr2N5O5	2.08	1.72	even	M	1+
6	1171.26929	C42H50ClIr2N6O7	1171.26825	C42H50ClIr2N6O7	1.97	-1.69	even	M	1+
6	1212.29595	C46H55ClIr2N4O8	1212.29615	C46H55ClIr2N4O8	0.65	-0.53	odd	M	1+
7	1171.26929	C46H54ClIr2O9	1171.27094	C46H54ClIr2O9	0.82	0.70	even	M	1+
7	1212.29595	C44H53ClIr2N7O7	1212.29480	C44H53ClIr2N7O7	2.05	-1.69	even	M	1+
8	1171.26929	C47H50ClIr2N4O5	1171.27228	C47H50ClIr2N4O5	2.15	1.84	even	M	1+
8	1212.29595	C56H49ClIr2N5	1212.29295	C56H49ClIr2N5	3.65	-3.01	even	M	1+
9	1171.26929	C39H52ClIr2N5O10	1171.26557	C39H52ClIr2N5O10	4.69	-4.01	odd	M	1+
9	1212.29595	C58H51ClIr2N2O	1212.29430	C58H51ClIr2N2O	2.24	-1.85	odd	M	1+
10	1171.26929	C36H179ClIr2N3O6	1171.27355	C36H179ClIr2N3O6	3.24	2.77	even	M	1+
10	1212.29595	C37H186ClIr2O10	1212.29876	C37H186ClIr2O10	1.84	1.52	even	M	1+

Figure 100: HRMS (ESI, positive mode) of $[(IrCl(CO)_2)_2$(**14**)$]$.

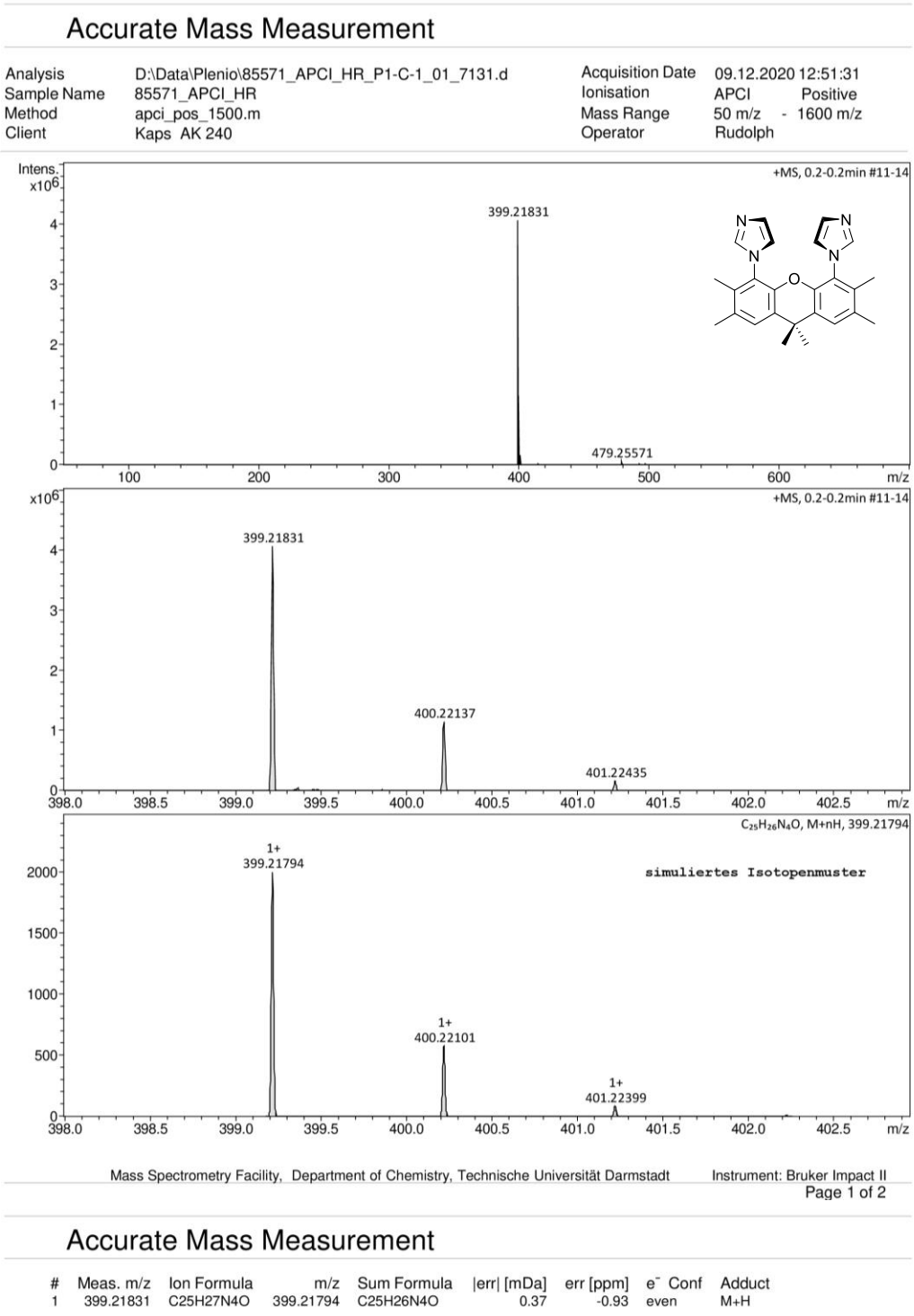


Figure 101: HRMS (APCI, positive mode) of 1,1'-(2,3,6,7,9,9-hexamethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (**15**).

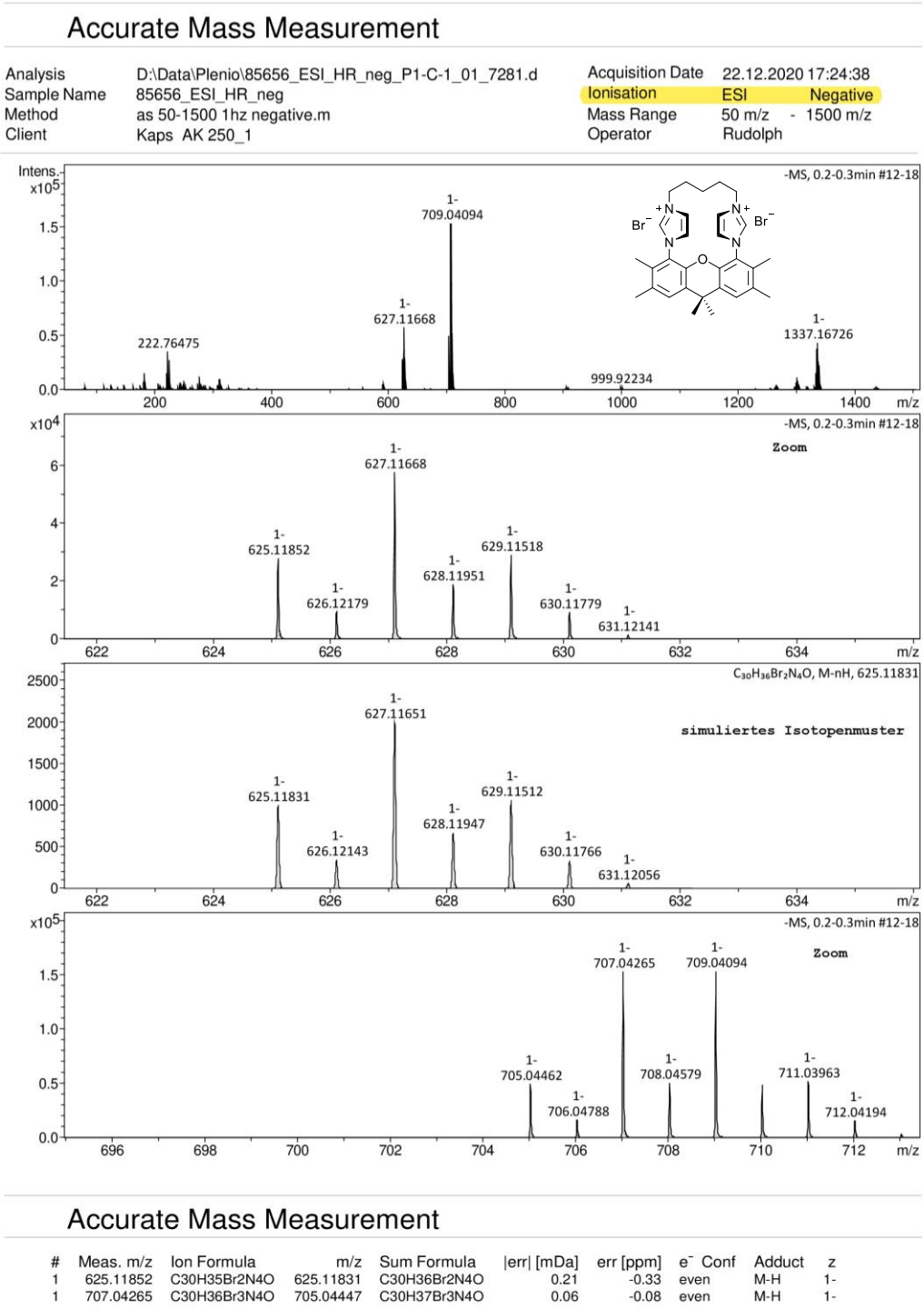
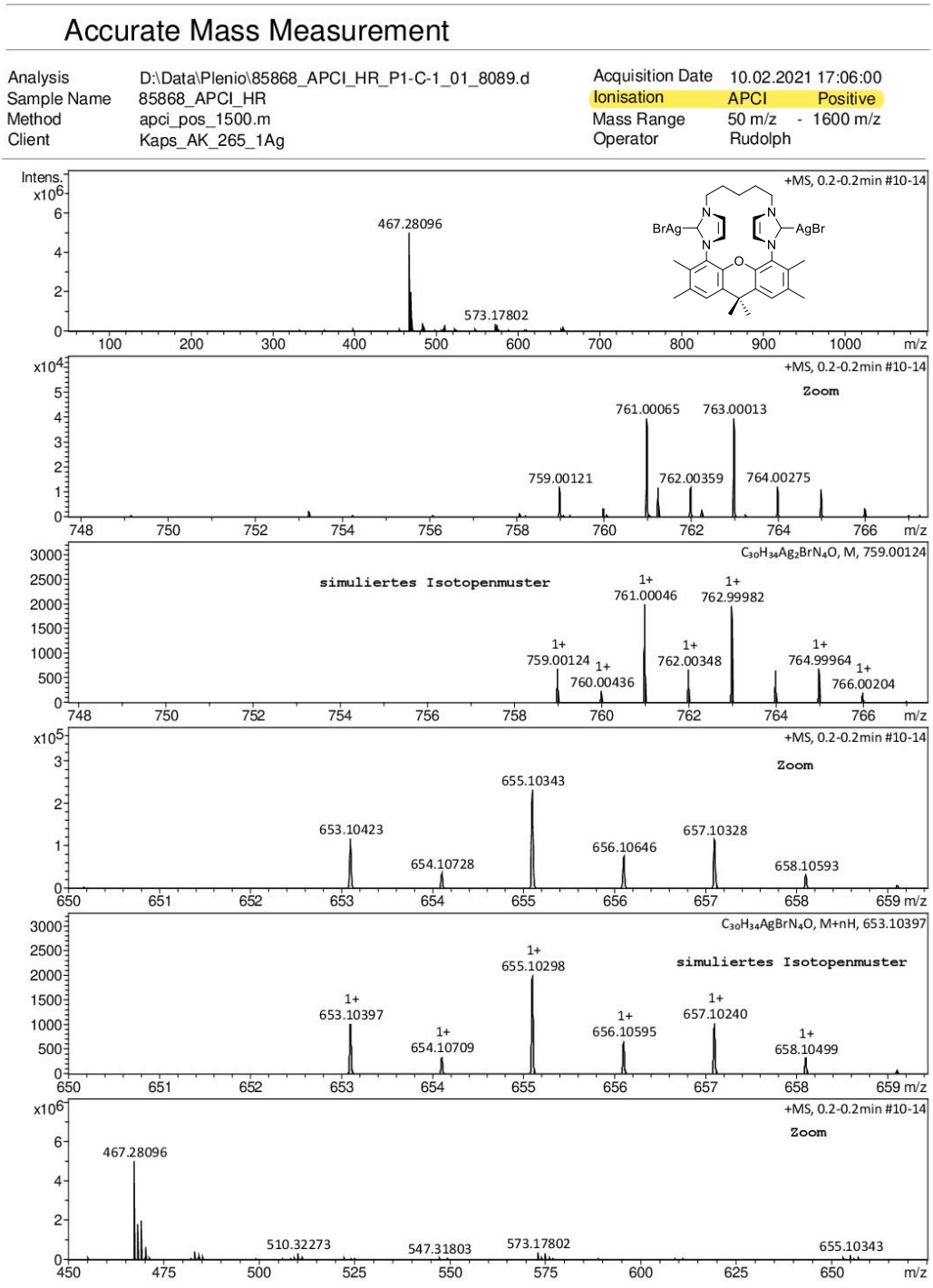


Figure 102: HRMS (ESI, negative mode) of xanthene imidazolium salt (**16** · 2 HBr).



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	573.17802	C30H34AgN4O	573.17781	C30H34AgN4O	0.21	-0.37	even	M
1	653.10423	C30H35AgBrN4O	653.10397	C30H35AgBrN4O	0.26	-0.40	even	M
1	759.00121	C30H34Ag2BrN4O	759.00124	C30H34Ag2BrN4O	0.04	0.05	even	M

Figure 103: HRMS (APCI, positive mode) of [$(AgBr)_2$(**16**)].

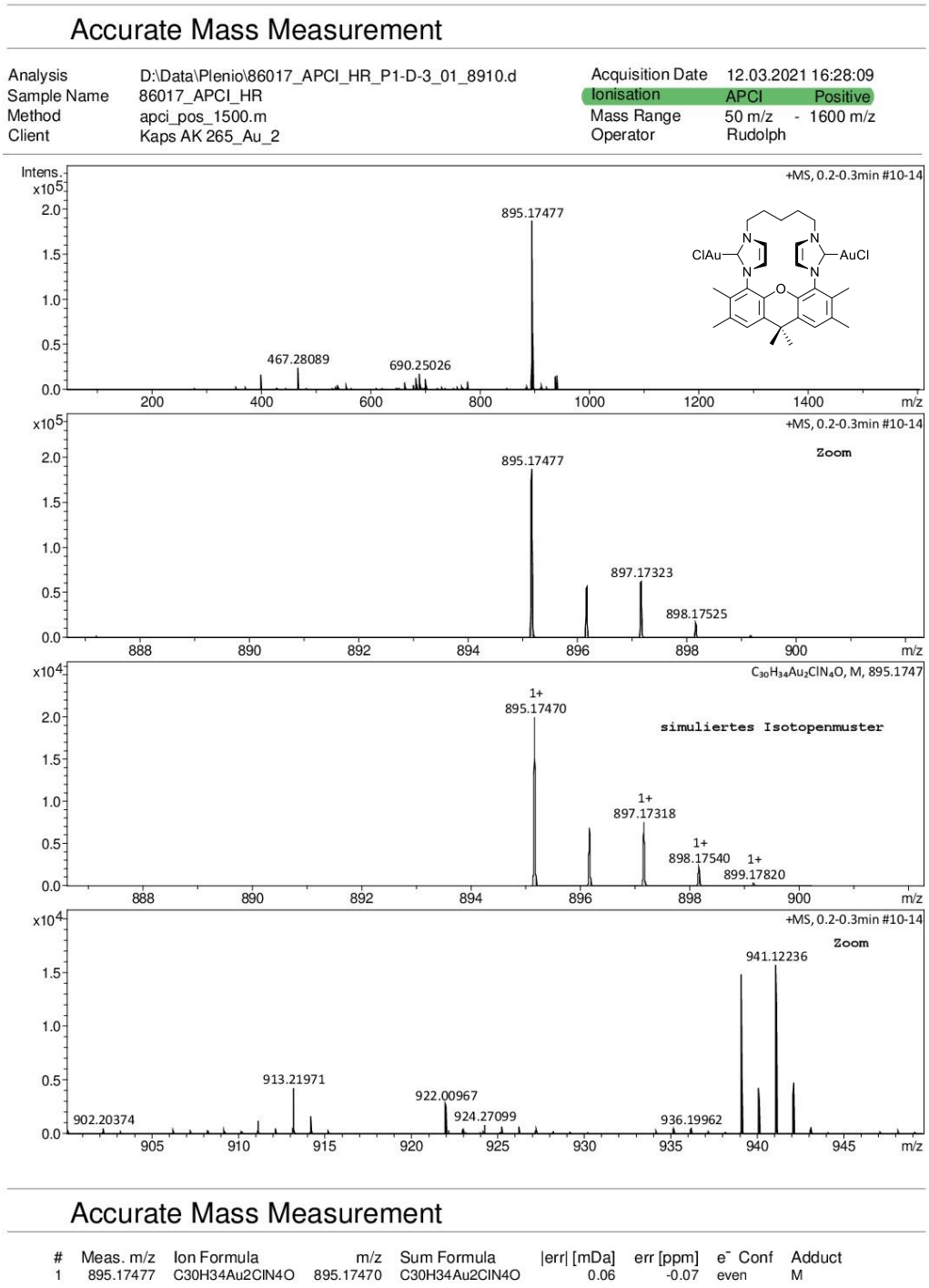


Figure 104: HRMS (APCI, positive mode) of [$(AuCl)_2$(**16**)]

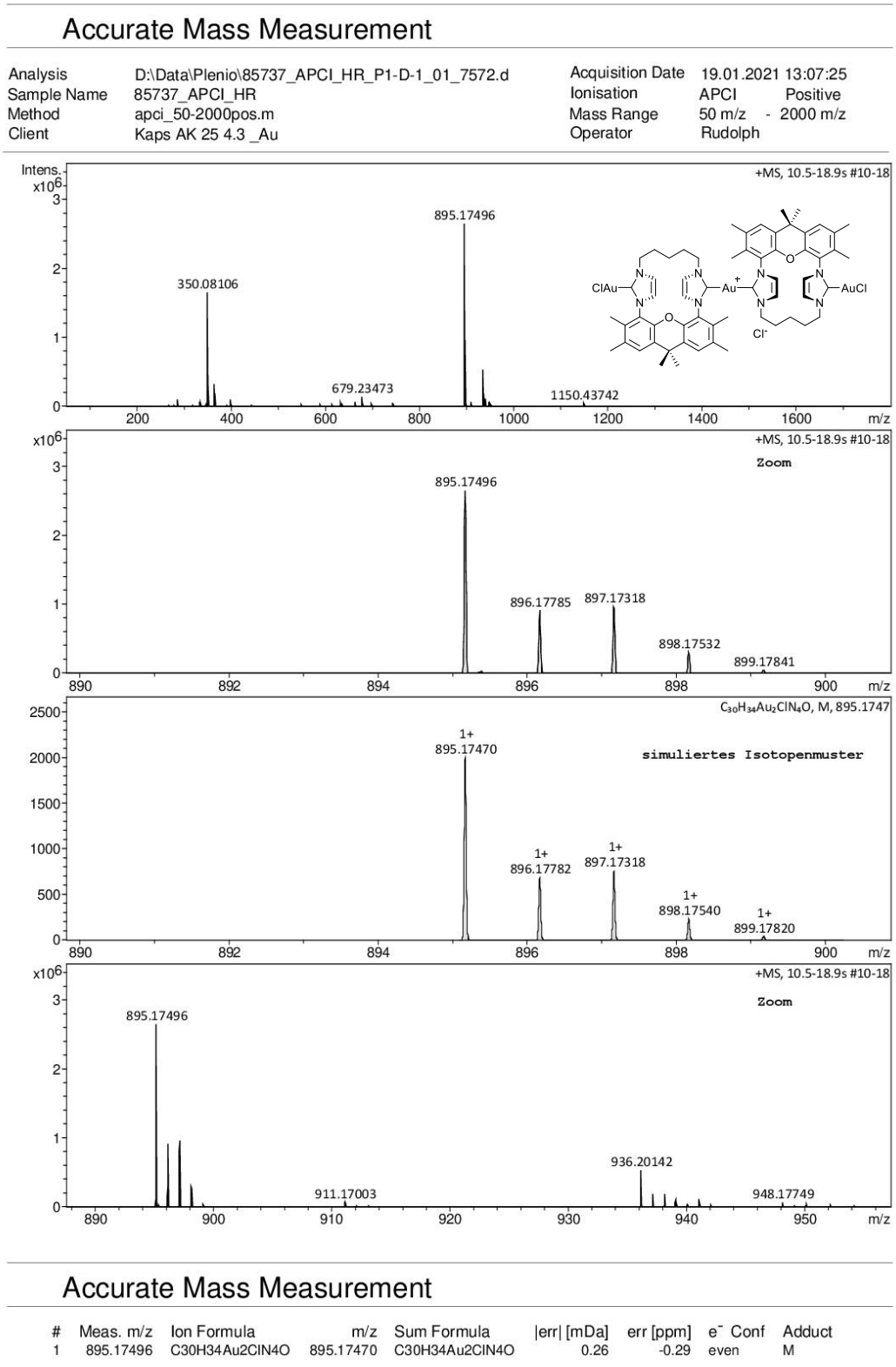
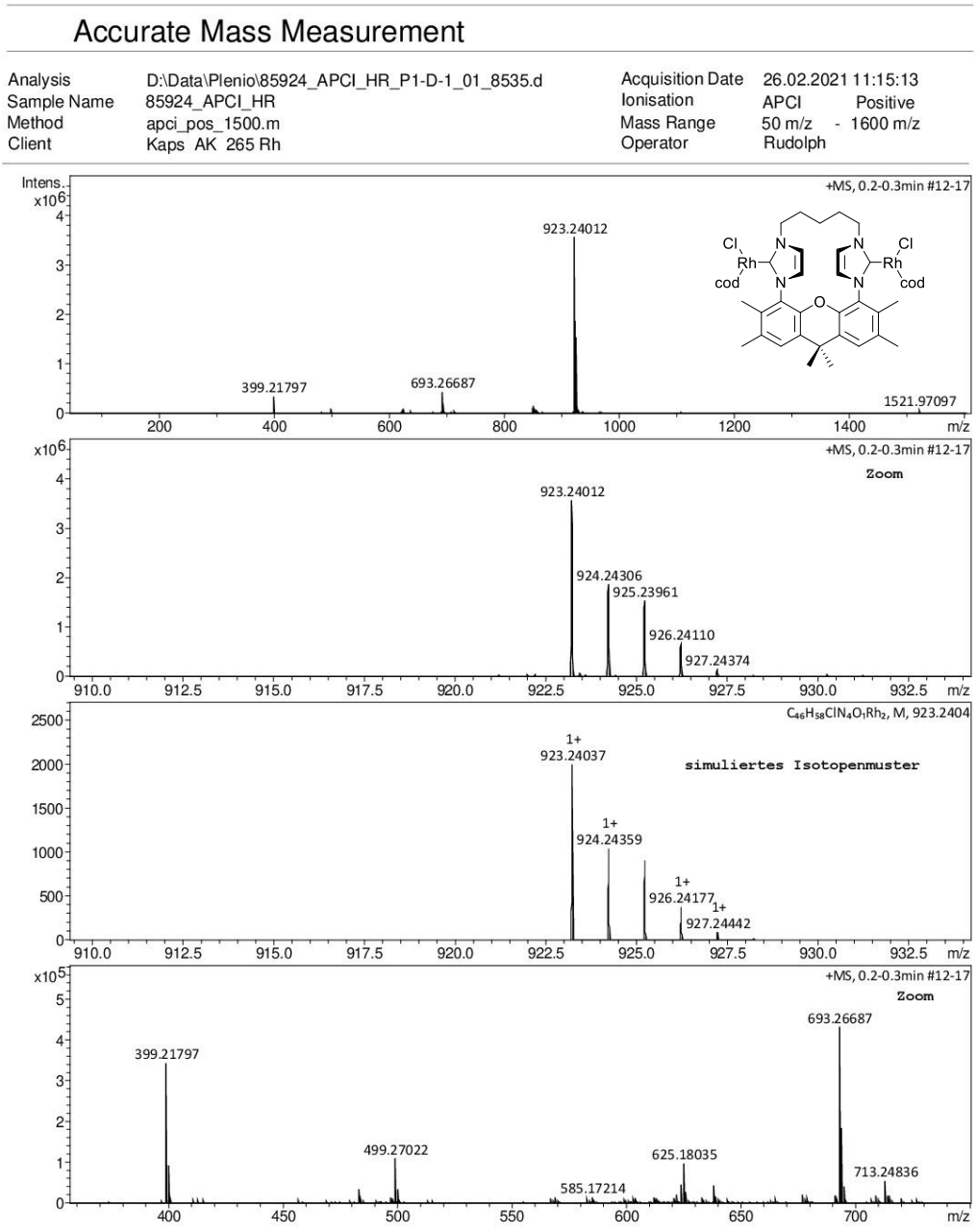


Figure 105: HRMS (APCI, positive mode) of [(Au(AuCl)$_2$)(Cl)(**16**)$_2$].



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	923.24012	C46H58ClN4ORh2	923.24037	C46H58ClN4ORh2	0.26	0.28	even	M

Figure 106: HRMS (APCI, positive mode) of [$(RhCl(CO)_2)_2$(**16**)].

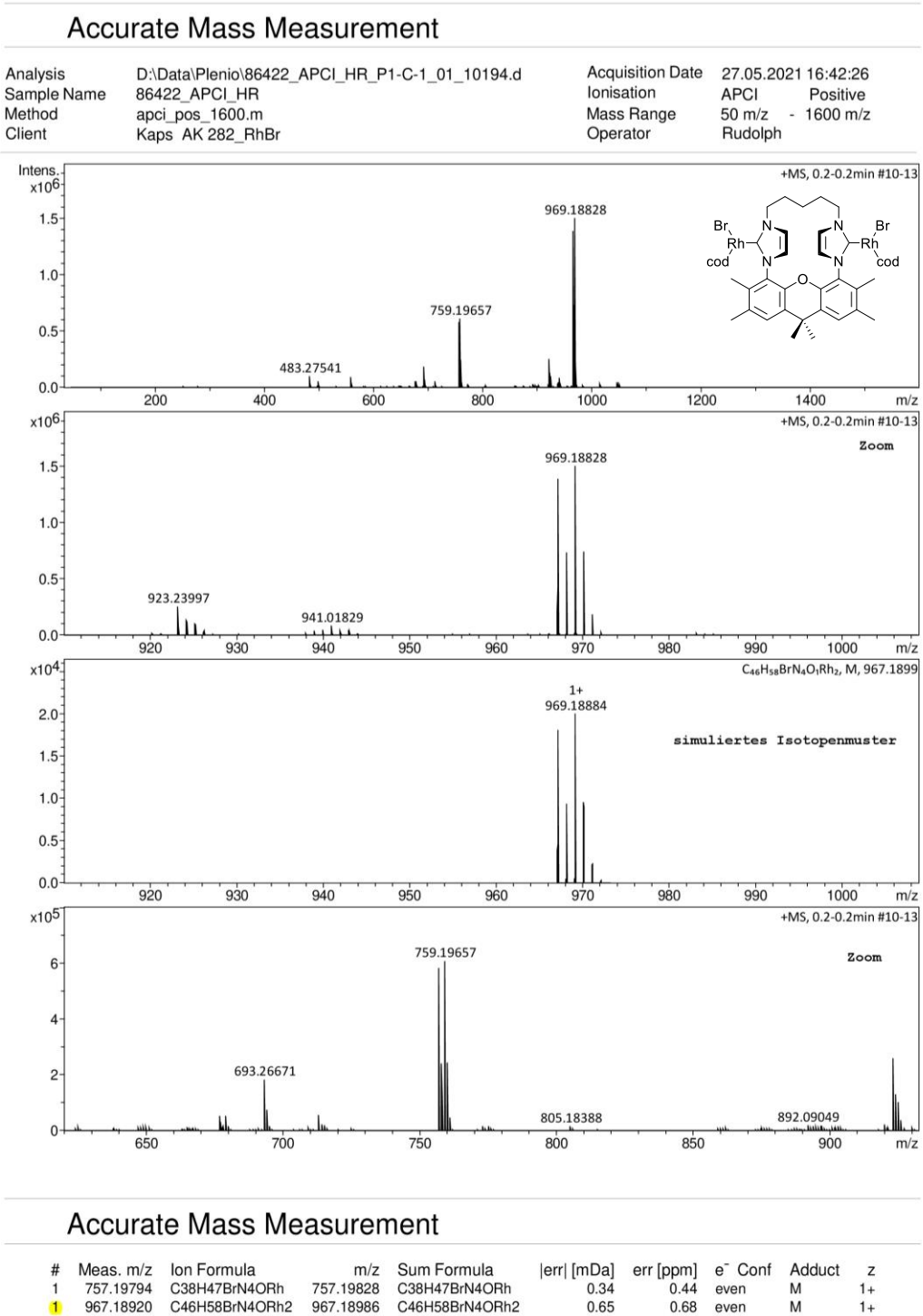
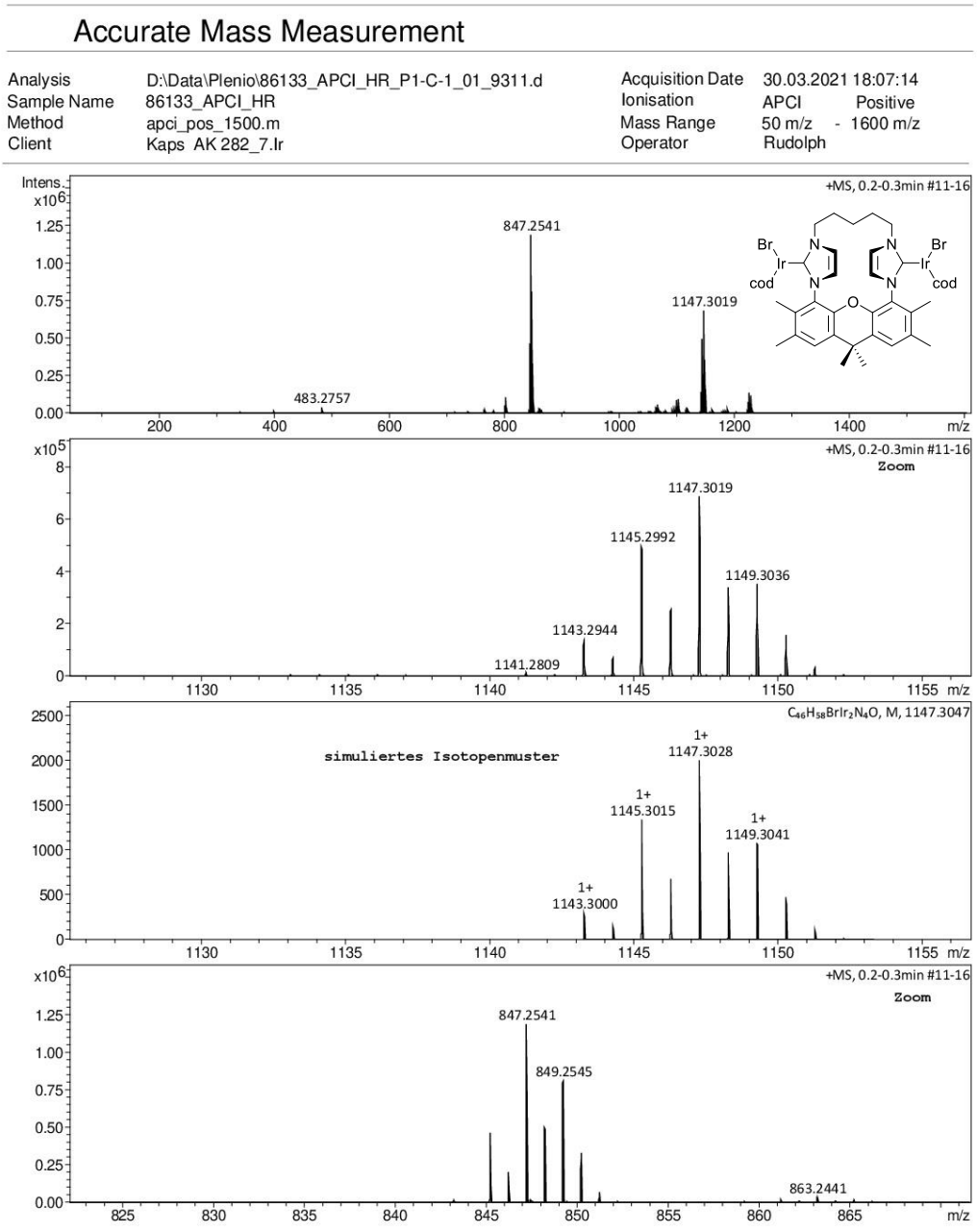


Figure 107: HRMS (APCI, positive mode) of [$(RhBr(CO)_2)_2$(**16**)].



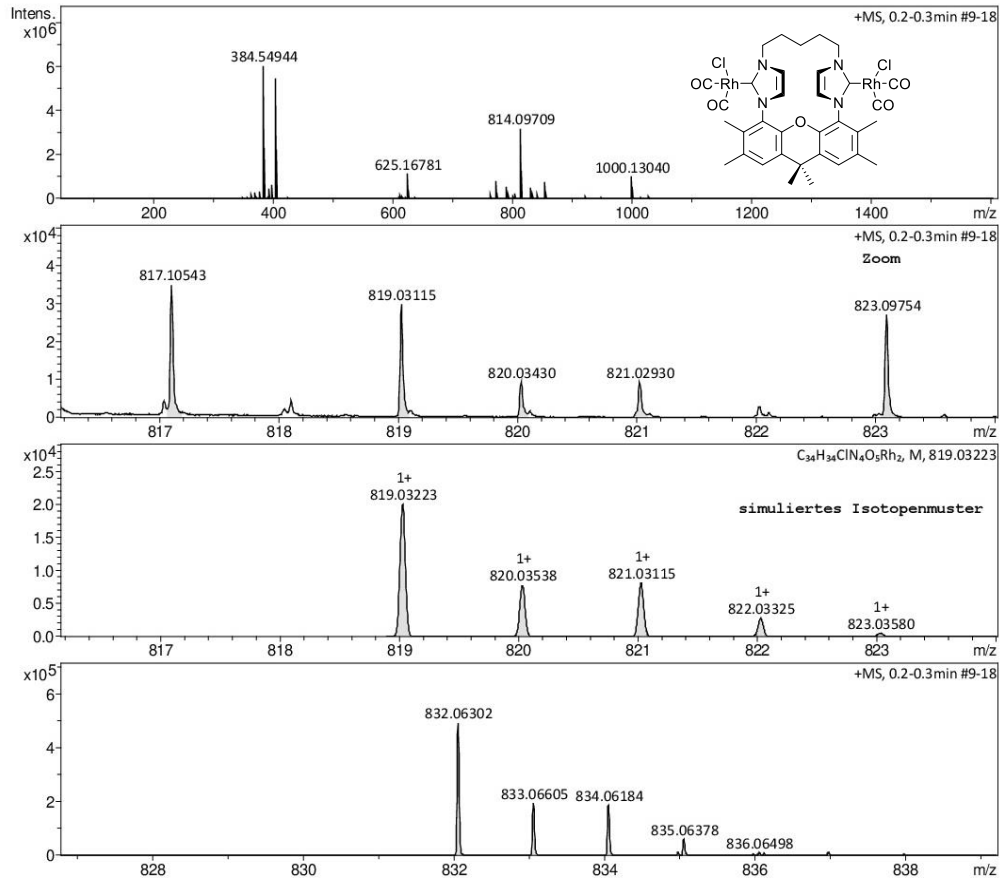
Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	1147.3019	C46H58BrIr2N4O	1147.3047	C46H58BrIr2N4O	1.0	0.9	even	M
1	1227.2254	C46H59Br2Ir2N4O	1227.2309	C46H58Br2Ir2N4O	2.3	1.9	even	M+H

Figure 108: HRMS (APCI, positive mode) of [(IrBr(CO)$_2$)$_2$(**16**)].

Accurate Mass Measurement

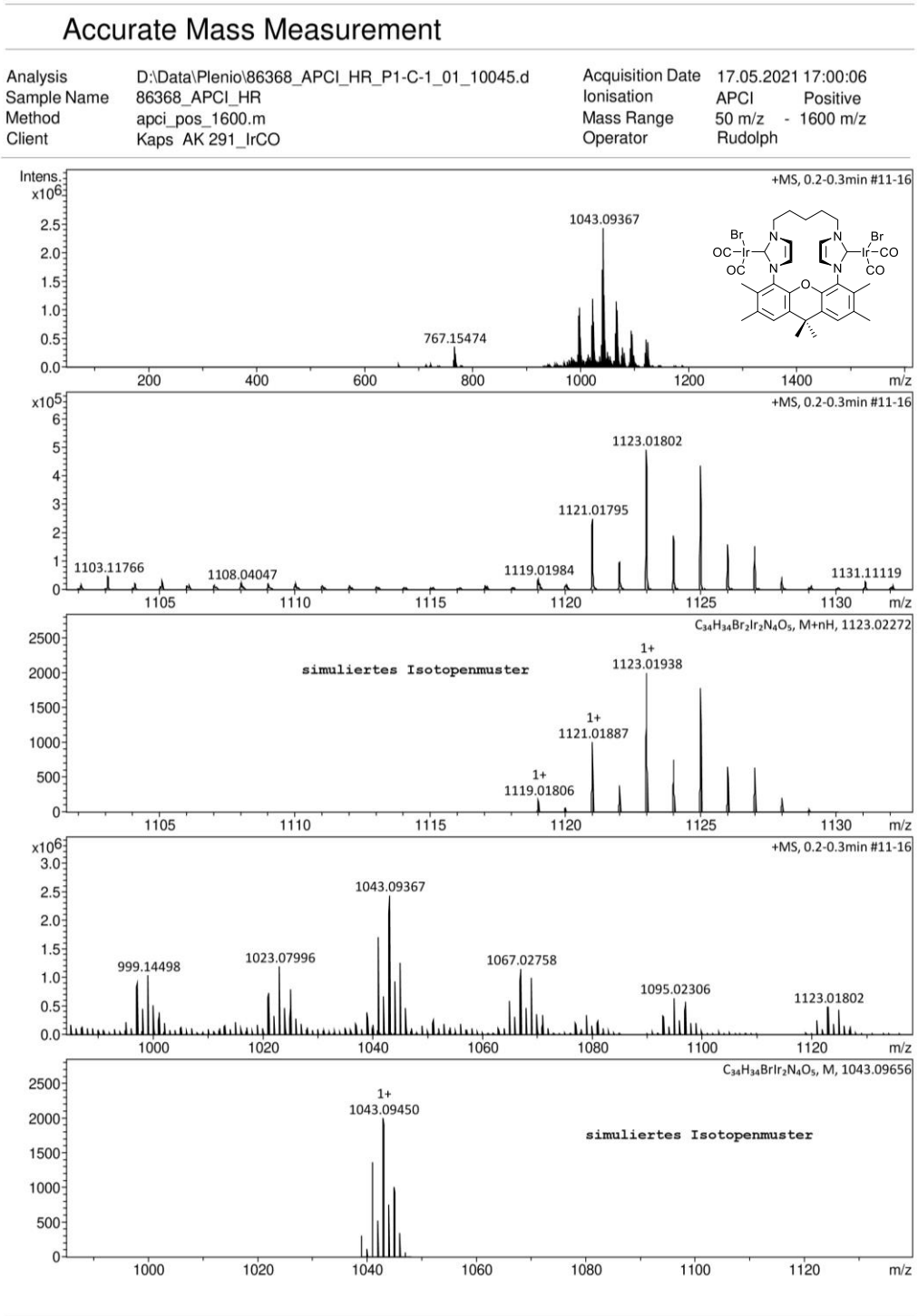
Analysis	D:\Data\Plenio\86016_ESI_HR_P1-D-2_01_8902.d	Acquisition Date	12.03.2021 14:42:35
Sample Name	86016_ESI_HR	Ionisation	ESI Positive
Method	as 50-1500 1hz.m	Mass Range	50 m/z - 1600 m/z
Client	Kaps AK 265_RhCO	Operator	Rudolph



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct
1	763.04174	C31H38ClO7Rh2	763.04107	C31H38ClO7Rh2	0.67	-0.88	even	M
1	791.03658	C32H38ClO8Rh2	791.03598	C32H38ClO8Rh2	0.60	-0.75	even	M
1	804.06842	C32H35ClN8O2Rh2	804.06761	C32H35ClN8O2Rh2	0.81	-1.01	odd	M
1	819.03115	C32H32ClN7O4Rh2	819.03089	C32H32ClN7O4Rh2	0.26	-0.31	odd	M
1	832.06302	C34H41ClNO8Rh2	832.06253	C34H41ClNO8Rh2	0.49	-0.59	even	M
1	855.12372	C37H41N6O5Rh2	855.12430	C37H41N6O5Rh2	0.59	0.69	even	M
2	763.04174	C32H34ClN4O3Rh2	763.04240	C32H34ClN4O3Rh2	0.66	0.87	even	M
2	791.03658	C33H34ClN4O4Rh2	791.03732	C33H34ClN4O4Rh2	0.74	0.94	even	M
2	804.06842	C33H41ClNO7Rh2	804.06761	C33H41ClNO7Rh2	0.81	-1.00	even	M
2	819.03115	C34H34ClN4O5Rh2	819.03223	C34H34ClN4O5Rh2	1.09	1.33	even	M
2	832.06302	C35H37ClN5O4Rh2	832.06387	C35H37ClN5O4Rh2	0.85	1.02	even	M
2	855.12372	C48H28N6O4Rh	855.12216	C48H28N6O4Rh	1.56	-1.82	even	M
3	763.04174	C37H33O5Rh2	763.04326	C37H33O5Rh2	1.52	1.99	even	M
3	791.03658	C38H33O6Rh2	791.03817	C38H33O6Rh2	1.60	2.02	even	M
3	804.06842	C34H37ClN5O3Rh2	804.06895	C34H37ClN5O3Rh2	0.53	0.66	even	M
3	819.03115	C33H28ClN11Rh2	819.03223	C33H28ClN11Rh2	1.08	1.32	odd	M
3	832.06302	C40H36NO6Rh2	832.06472	C40H36NO6Rh2	1.70	2.04	even	M
3	855.12372	C50H30N3O5Rh	855.12350	C50H30N3O5Rh	0.21	-0.25	odd	M
4	763.04174	C33H29N6O3Rh2	763.04057	C33H29N6O3Rh2	1.17	-1.53	even	M
4	791.03658	C34H29N6O4Rh2	791.03549	C34H29N6O4Rh2	1.09	-1.37	even	M
4	832.06302	C36H32N7O4Rh2	832.06204	C36H32N7O4Rh2	0.98	-1.18	even	M
4	855.12372	C52H32O6Rh	855.12484	C52H32O6Rh	1.13	1.32	even	M
5	855.12372	C51H26N7ORh	855.12484	C51H26N7ORh	1.12	1.31	odd	M

Figure 109: HRMS (ESI, positive mode) of [$(RhCl(CO)_2)_2$(**16**)].



Accurate Mass Measurement

#	Meas. m/z	Ion Formula	m/z	Sum Formula	|err| [mDa]	err [ppm]	e⁻ Conf	Adduct	z
1	1043.09367	C34H34BrIr2N4O5	1043.09656	C34H34BrIr2N4O5	0.83	0.80	even	M	1+
1	1067.02758	C32H35Br2Ir2N4O3	1067.03289	C32H35Br2Ir2N4O3	1.94	1.81	even	M	1+
1	1095.02306	C33H35Br2Ir2N4O4	1095.02781	C33H35Br2Ir2N4O4	1.38	1.26	even	M	1+
1	1123.01802	C34H35Br2Ir2N4O5	1123.02272	C34H34Br2Ir2N4O5	1.35	1.21	even	M+H	1+

Figure 110: HRMS (APCI, positive mode) of [$(IrBr(CO)_2)_2$(**16**)].

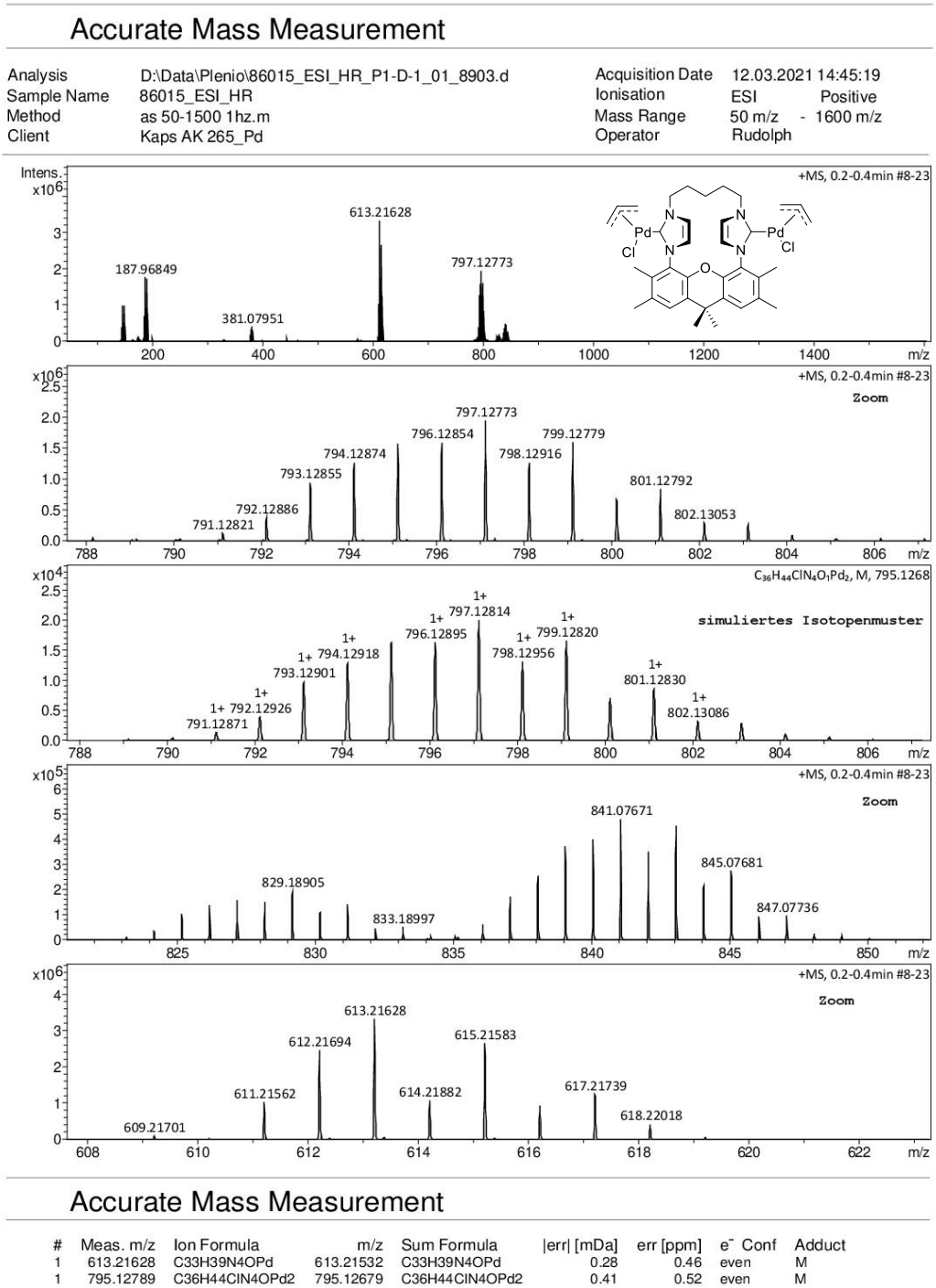


Figure 111: HRMS (ESI, positive mode) of [(PdCl(allyl))$_2$(**16**)].

3. IR spectroscopy

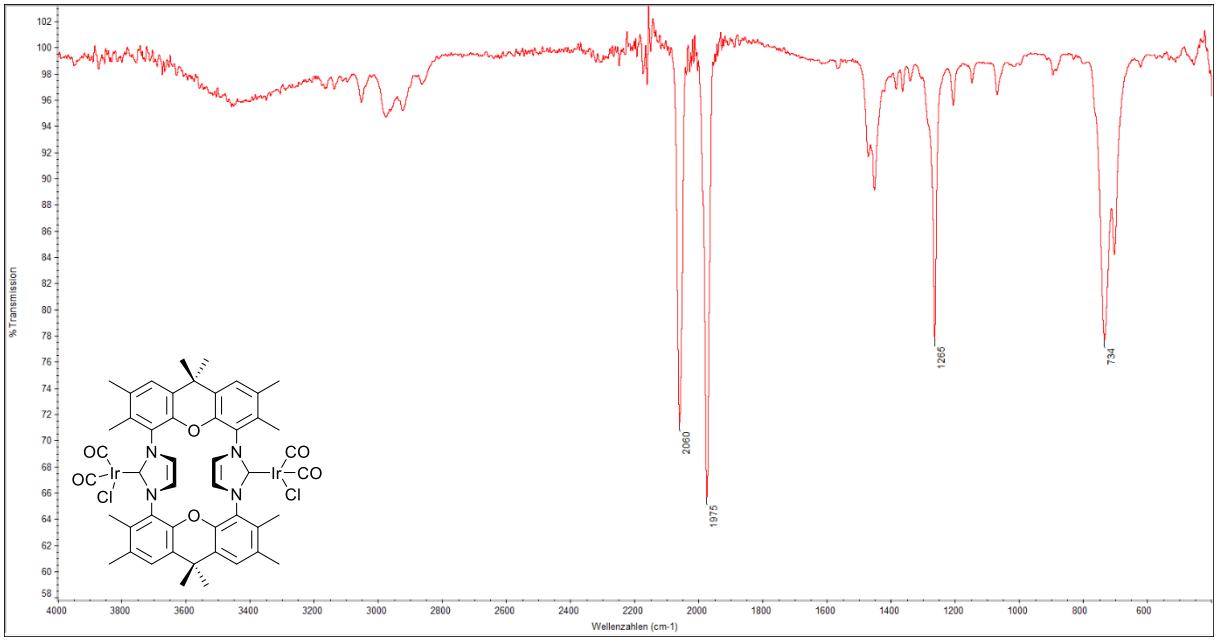


*Figure 112: IR spectrum of [(IrCl(CO)$_2$)$_2$(**9**)]].*

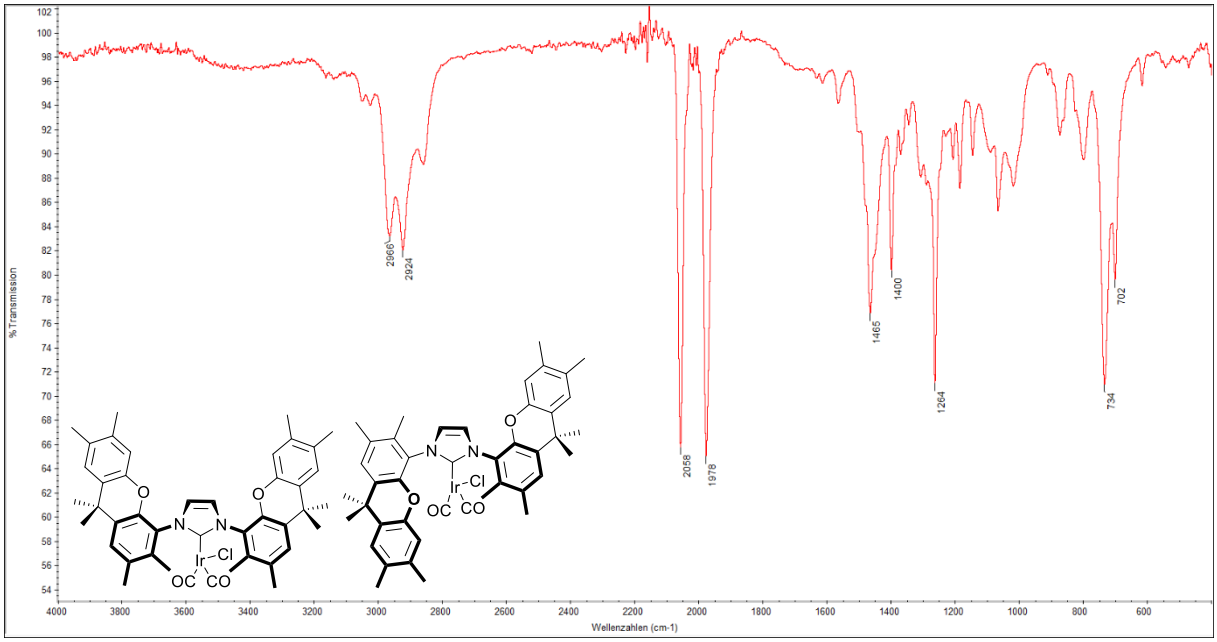


*Figure 113: IR spectrum of [(IrCl(CO)$_2$)(**11**)].*

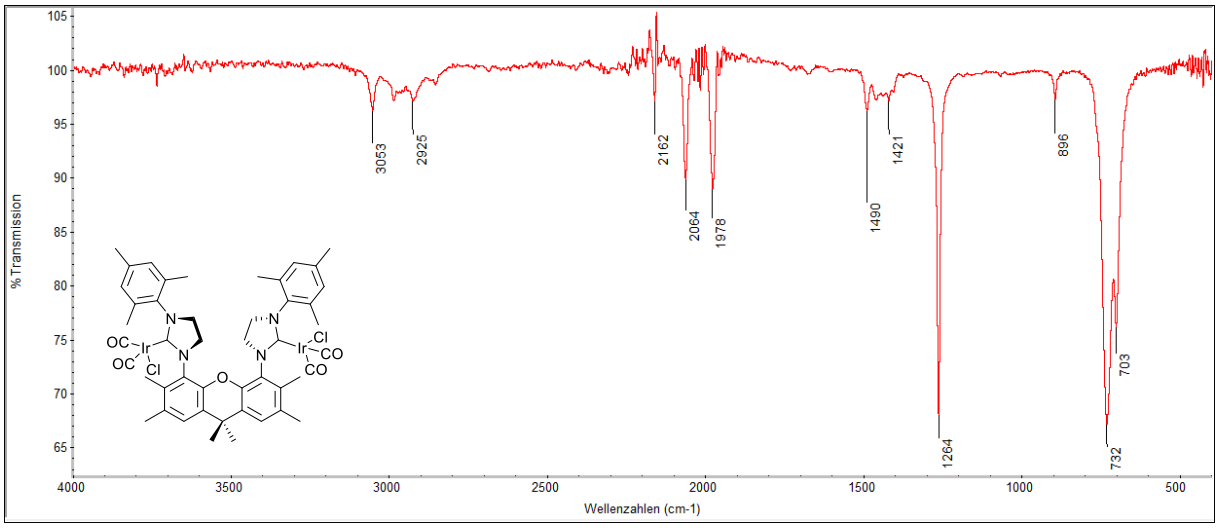


*Figure 114: IR spectrum of [(IrCl(CO)$_2$)(**14**)].*

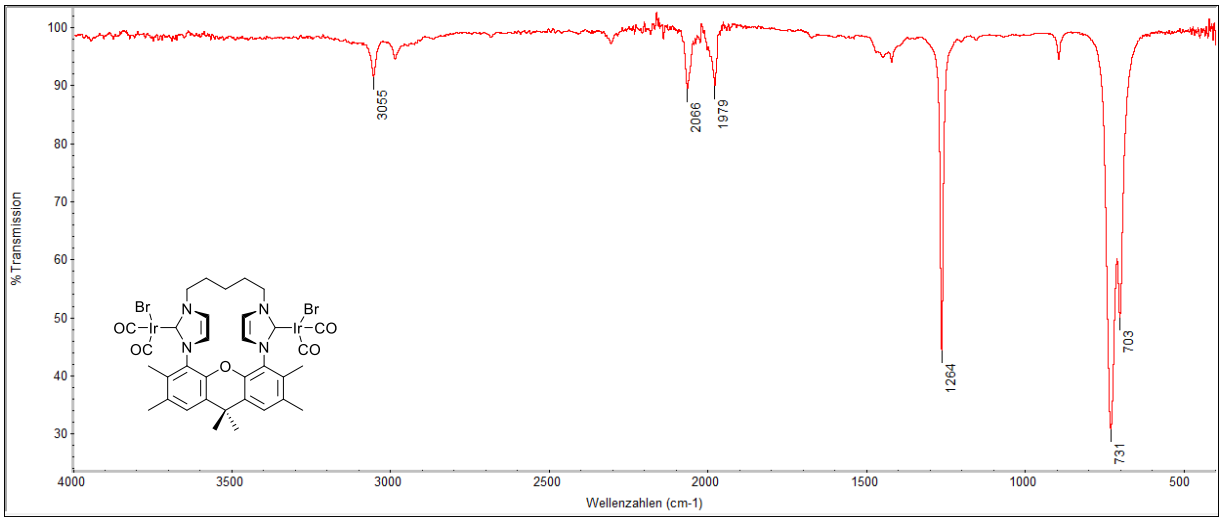


*Figure 115: IR spectrum of [(IrBr(CO)$_2$]$_2$(**16**)].*

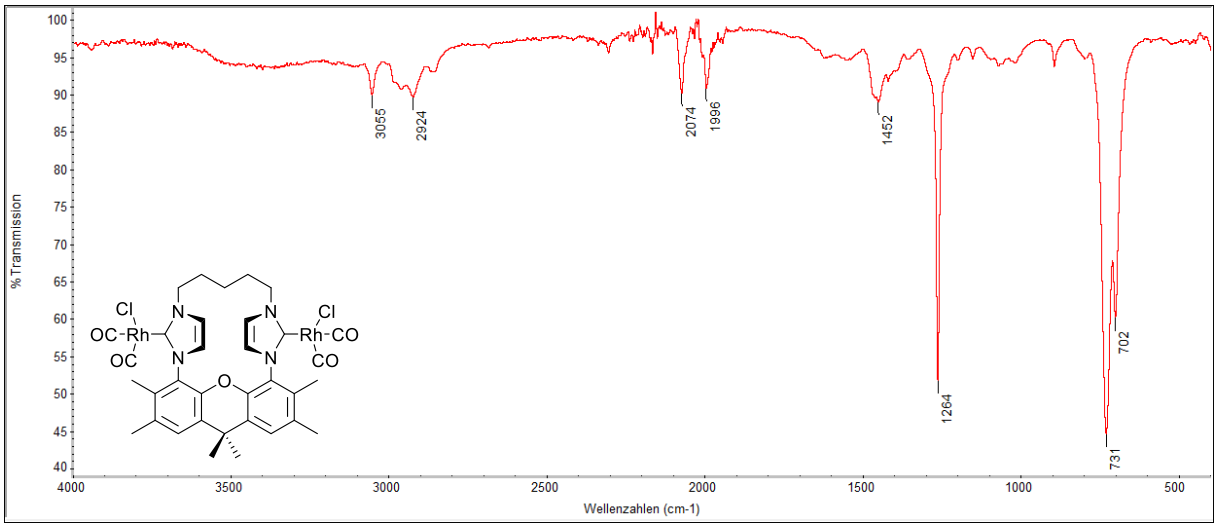


*Figure 116: IR spectrum of [(RhCl(CO)$_2$]$_2$(**16**)]].*

4. Cyclic voltammetry

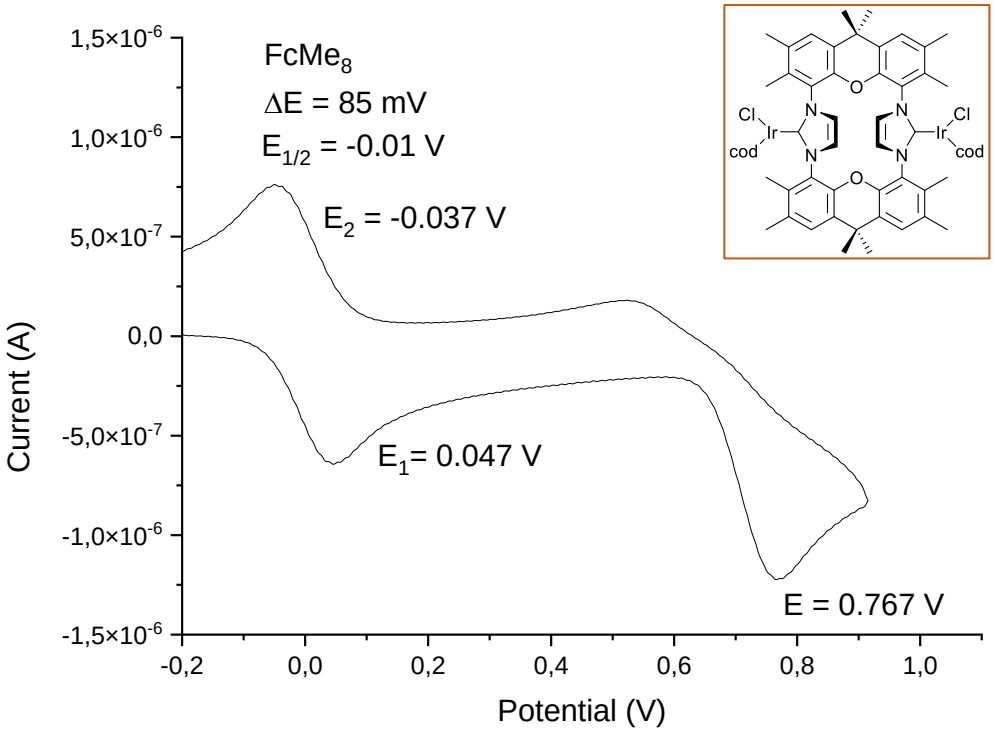


*Figure 117: Cyclic voltammetry diagram of [(IrCl(cod))$_2$(**9**)].*

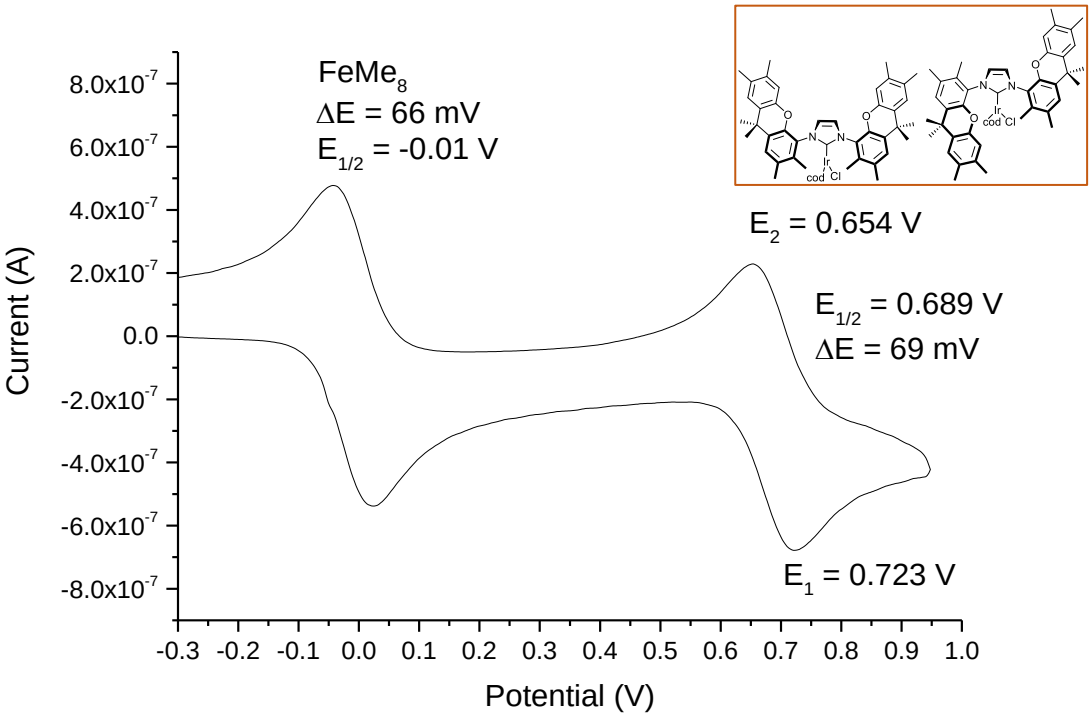


*Figure 118: Cyclic voltammetry diagram of [(IrCl(cod))(**11**)].*

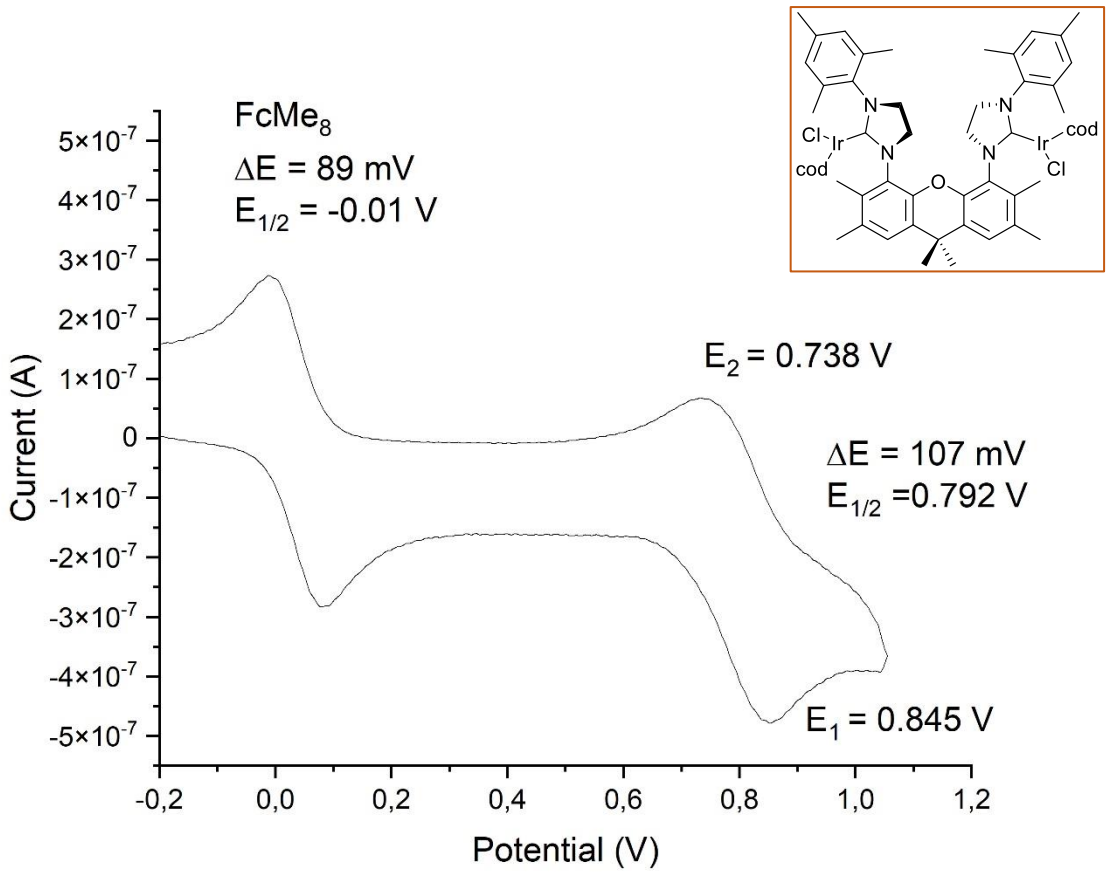


*Figure 119: Cyclic voltammetry diagram of [(IrCl(cod))(**14**)].*

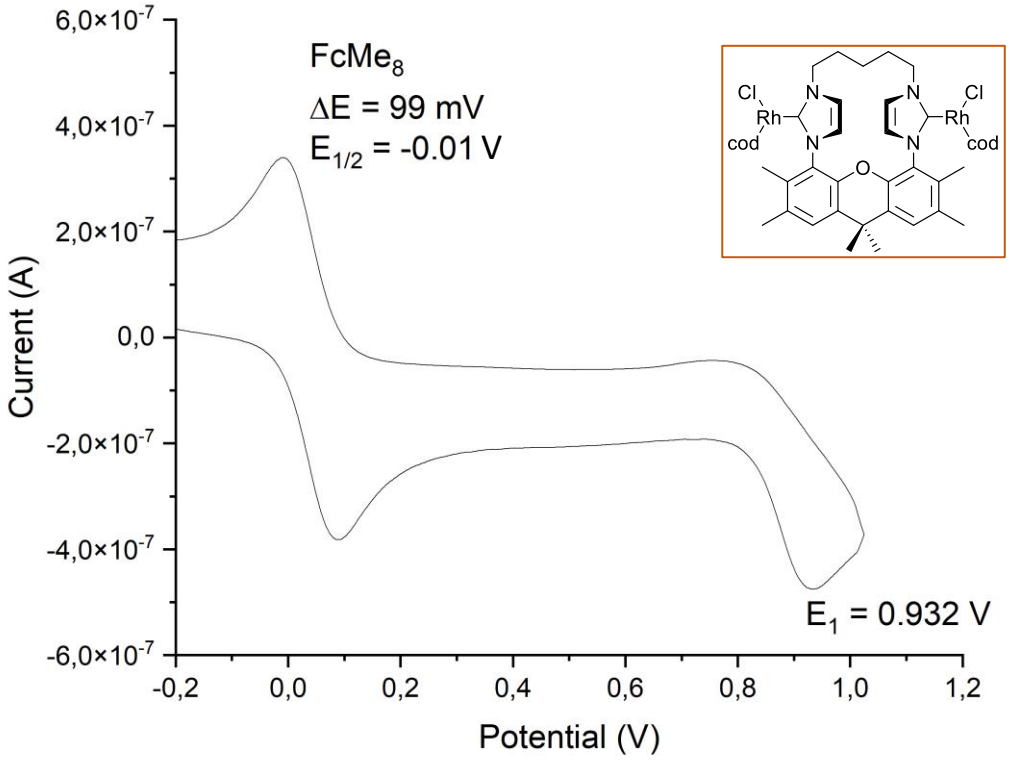


*Figure 120: Cyclic voltammetry diagram of [(IrCl(cod))(**16**)].*

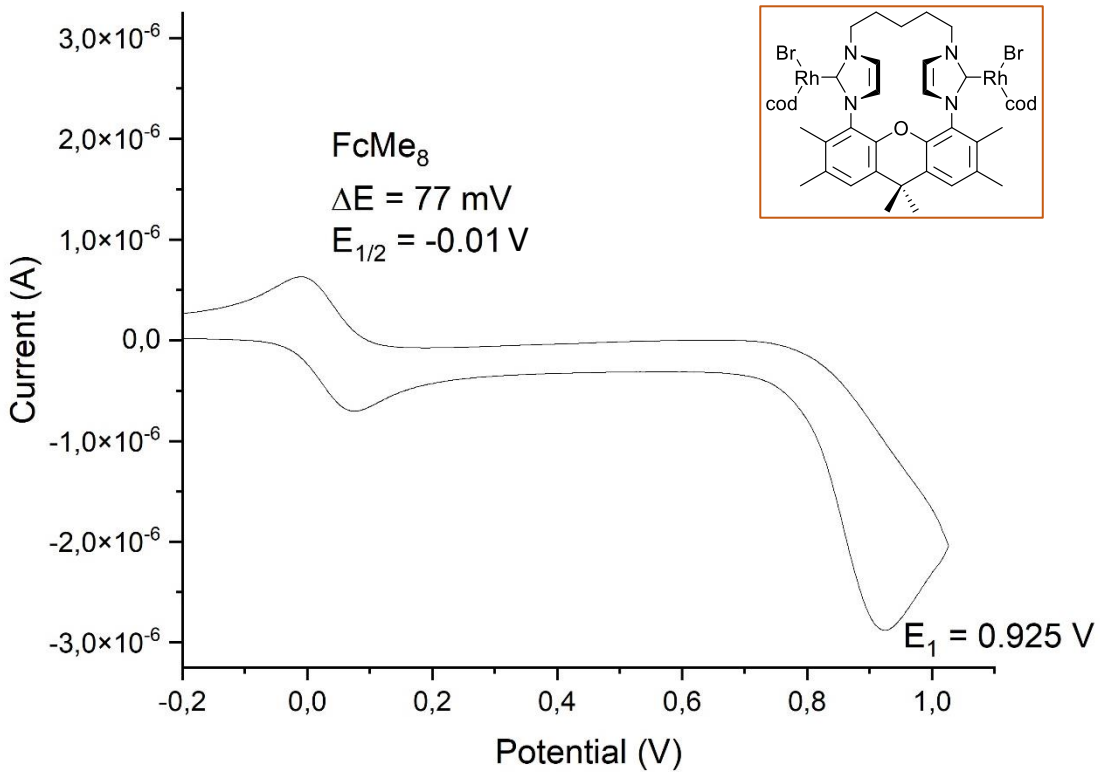


*Figure 121: Cyclic voltammetry diagram of [(IrBr(cod))(**16**)].*

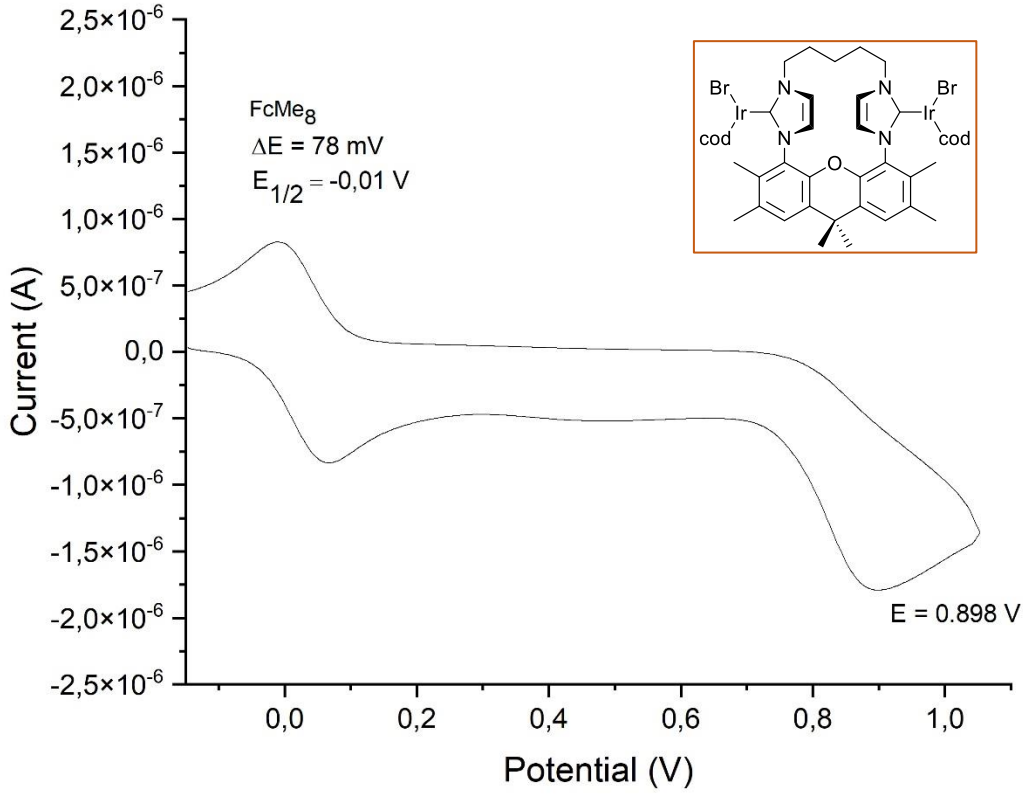


*Figure 122: Cyclic voltammetry diagram of [(IrBr(cod))$_2$(**16**)].*

5. X-ray crystal structure

[(IrCl(cod))$_2$(**9**)]

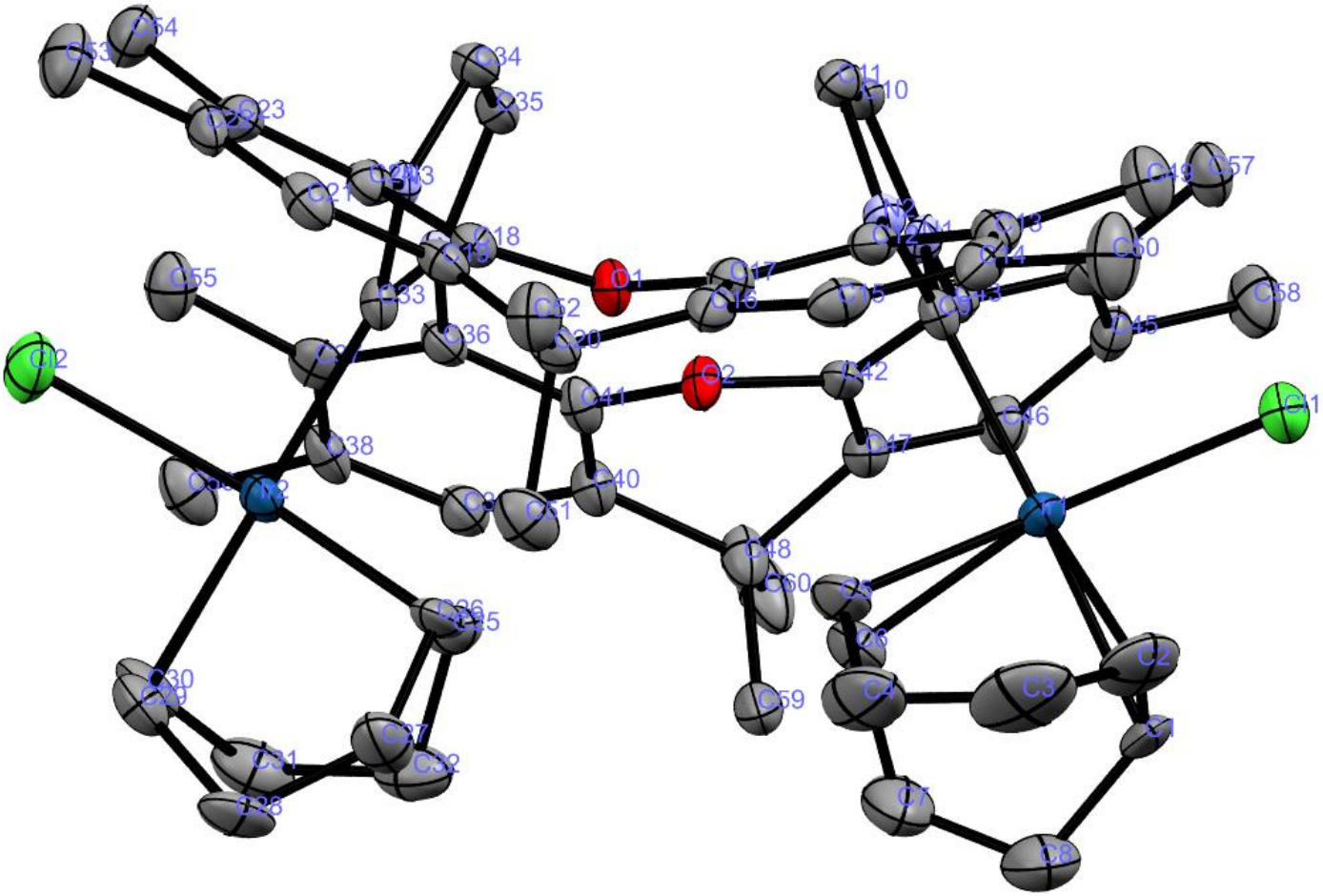
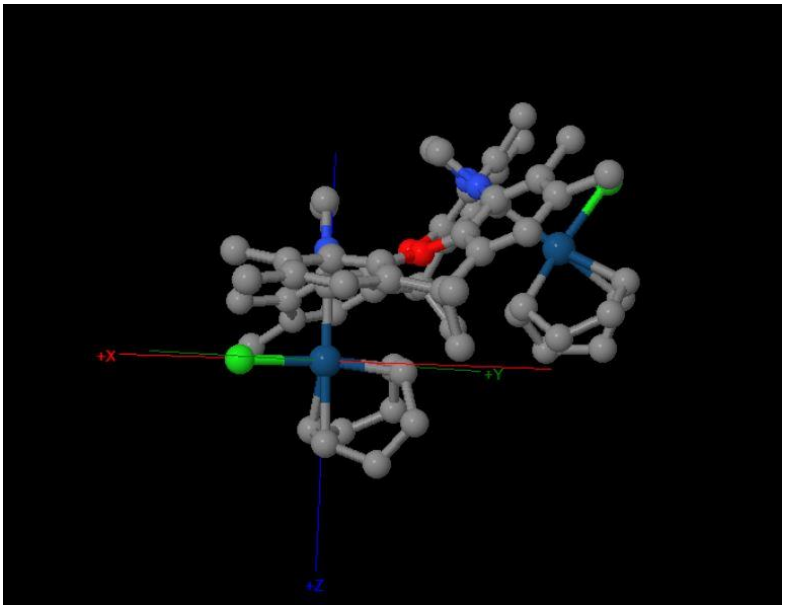


*Figure 123: Crystal structure of [(IrCl(cod))$_2$(**9**)] (thermal ellipsoids are shown at the 50% probability level).*

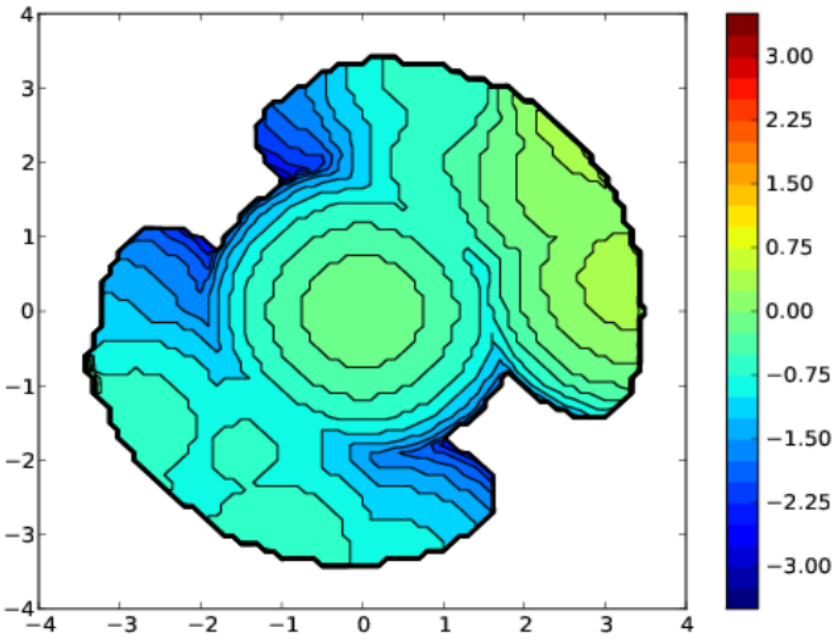
SambVa-buried volume



%V Free	%V Buried	% V Tot/V Ex
67.2	**32.8**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	29.0	15.8	44.9	**64.7**	35.3
NW	35.2	9.7	44.9	**78.5**	21.5
NE	24.6	20.3	44.9	**54.8**	45.2
SE	31.9	13.0	44.9	**71.0**	29.0

Steric Map



[AuCl)$_2$(**14**)]

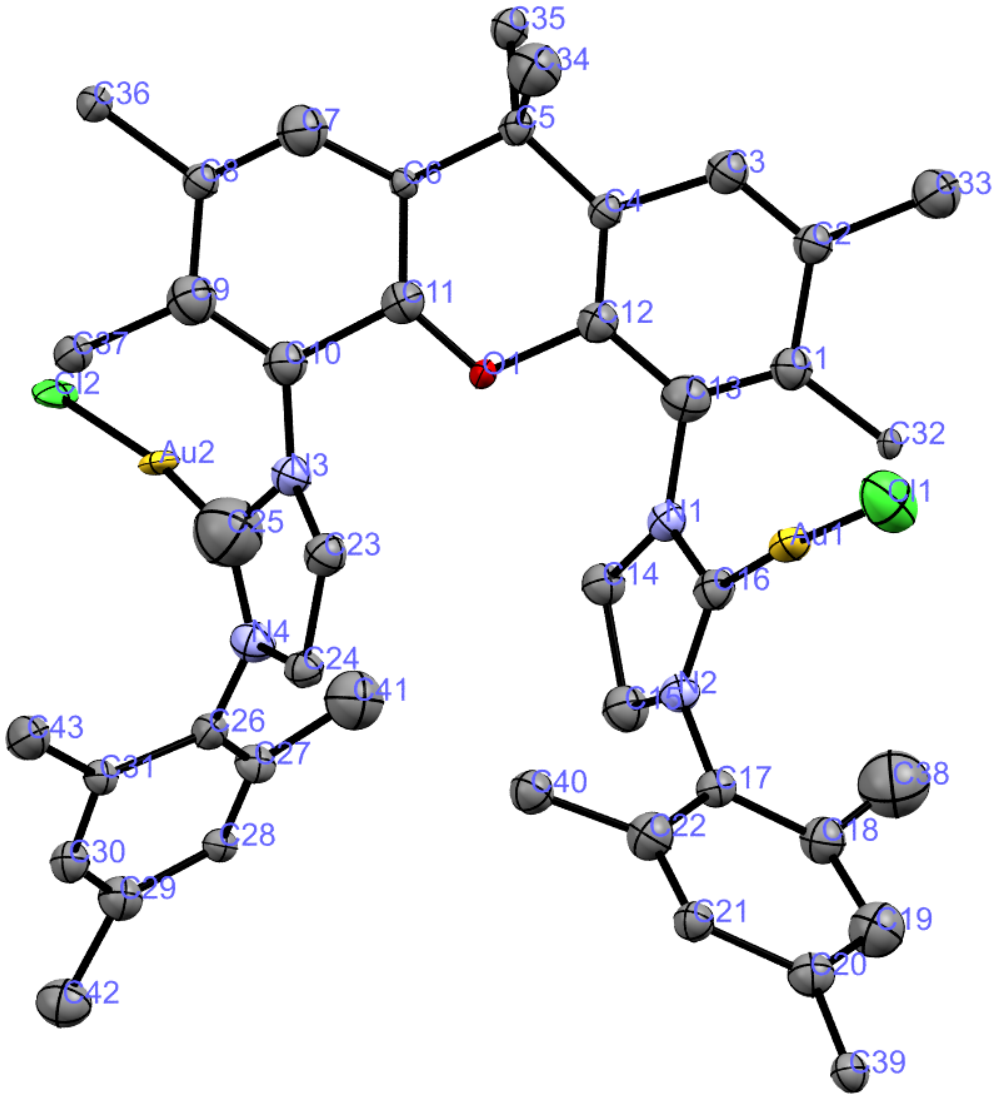
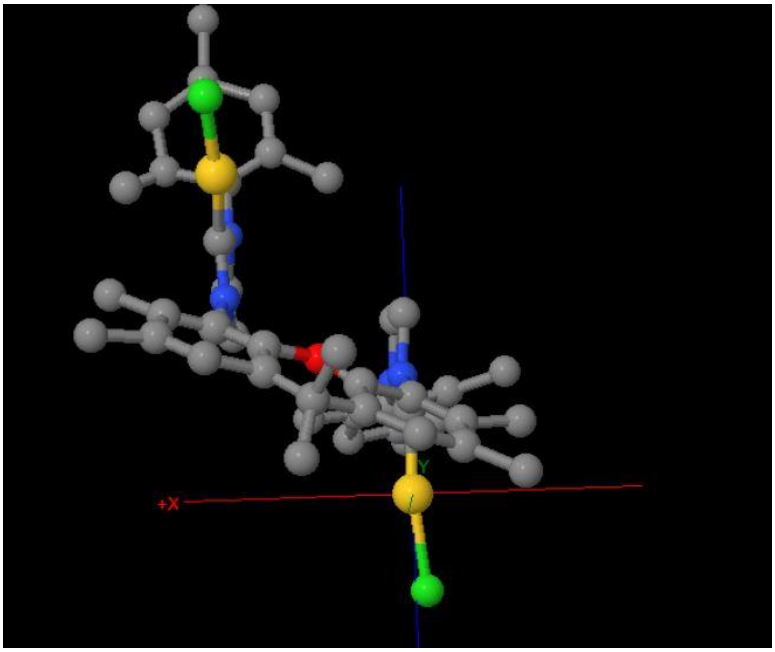


*Figure 124: Crystal structure of [AuCl)$_2$(**14**)] (thermal ellipsoids are shown at the 30% probability level).*

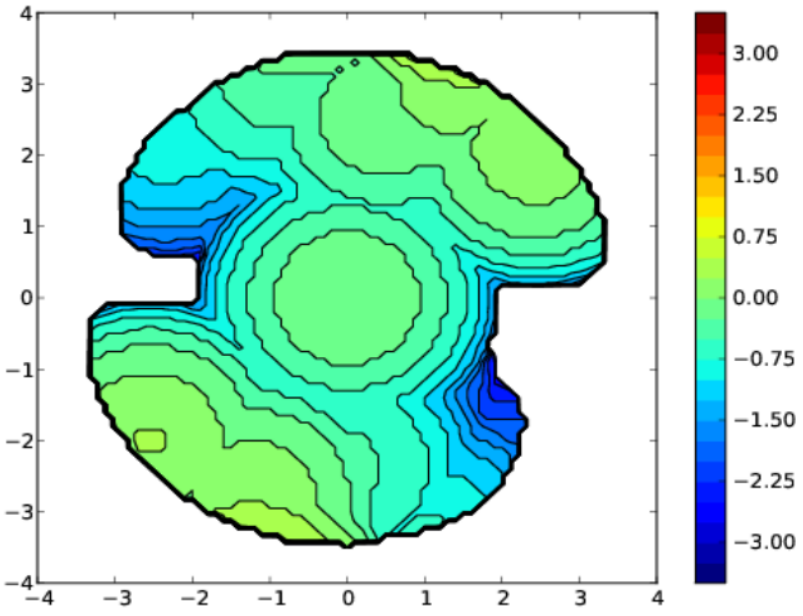
SambVa-buried volume



%V Free	%V Buried	% V Tot/V Ex
61.9	**38.1**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	23.8	21.1	44.9	**53.0**	47.0
NW	30.1	14.7	44.9	**67.2**	32.8
NE	24.6	20.3	44.9	**54.8**	45.2
SE	32.6	12.3	44.9	**72.6**	27.4

Steric Map



[(Au(AuCl)$_2$)(Cl)(**16**)$_2$]

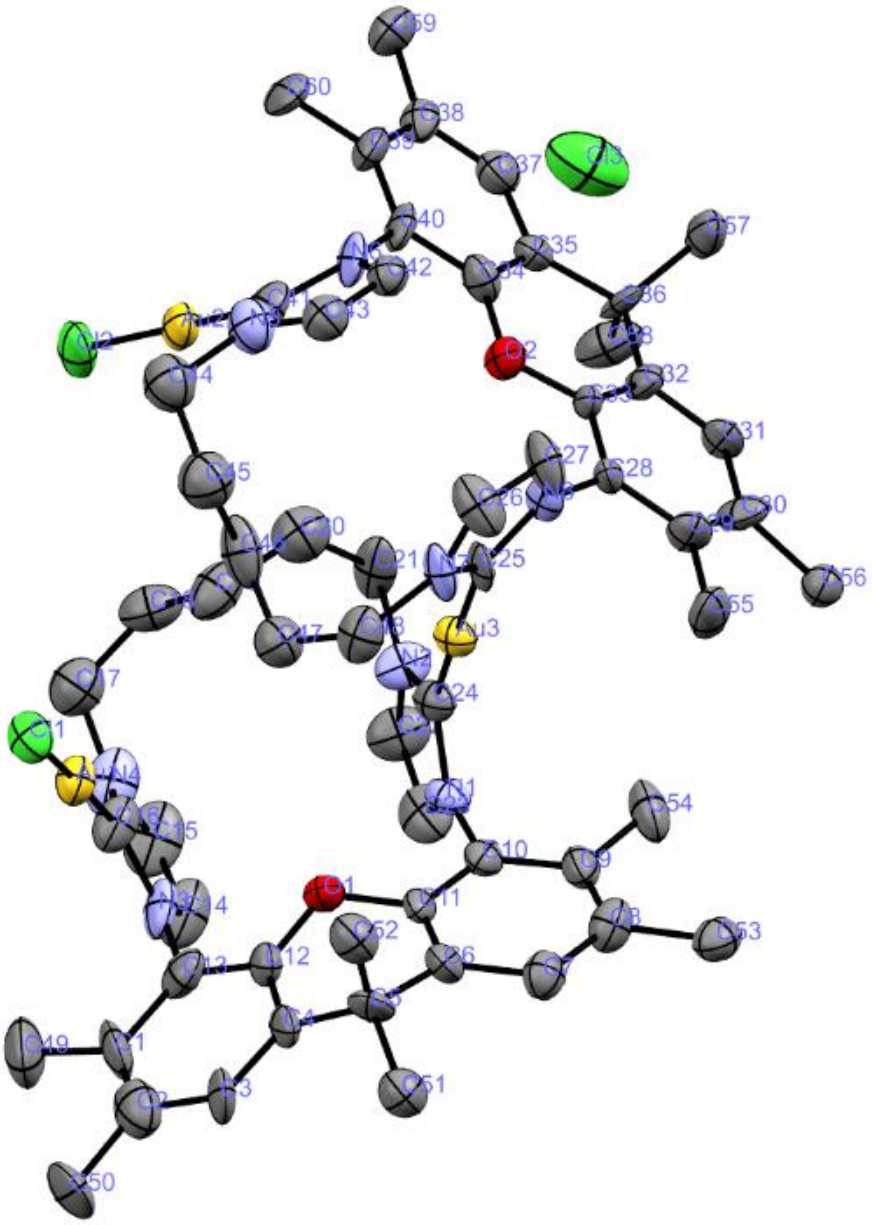
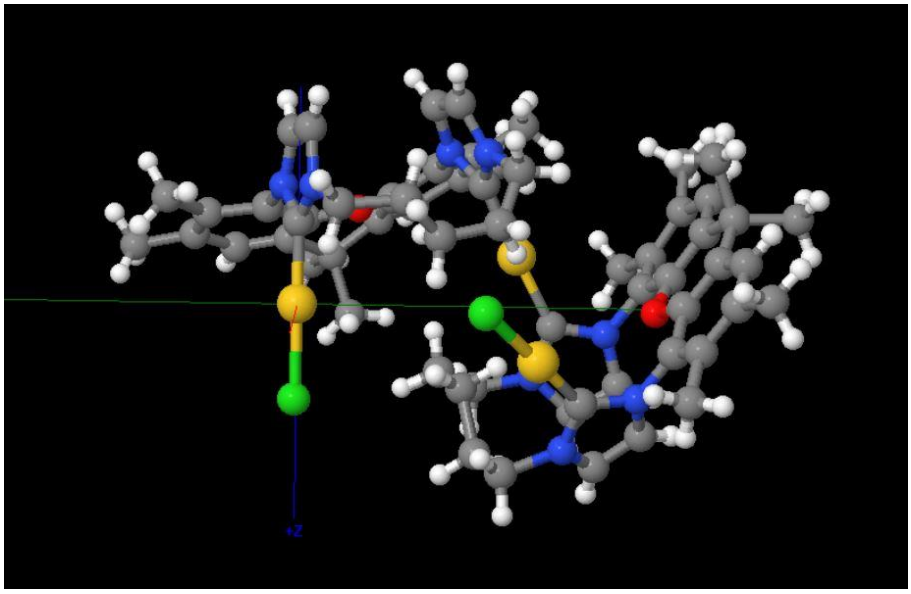


*Figure 125: Crystal structure of [(Au(AuCl)$_2$)(Cl)(**16**)$_2$] (thermal ellipsoids are shown at the 30% probability level).*

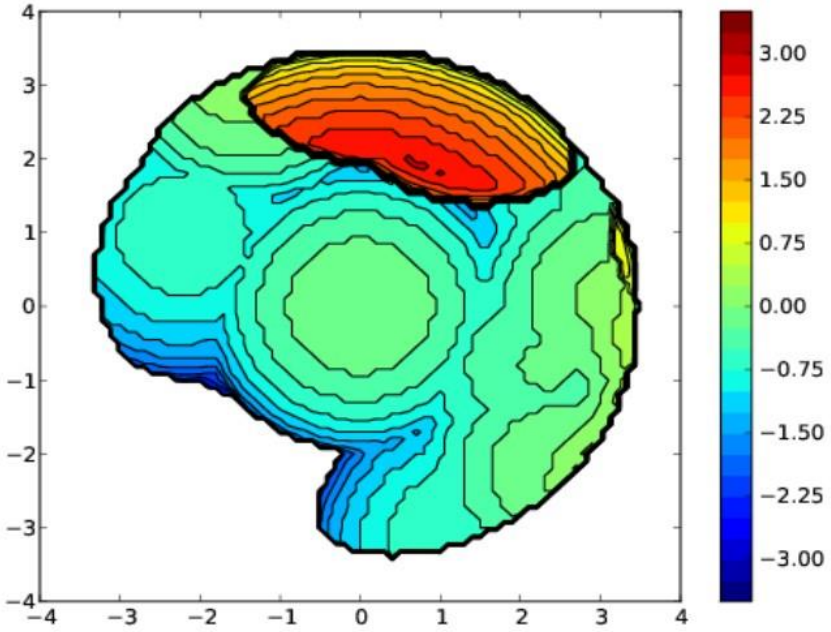
SambVa-buried volume



%V Free	%V Buried	% V Tot/V Ex
60.7	**39.3**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	35.3	9.5	44.9	**78.7**	21.3
NW	24.5	20.3	44.9	**54.7**	45.3
NE	23.4	21.4	44.9	**52.2**	47.8
SE	25.6	19.3	44.9	**57.1**	42.9

Steric Map



[(RhCl(cod))$_2$(**16**)]

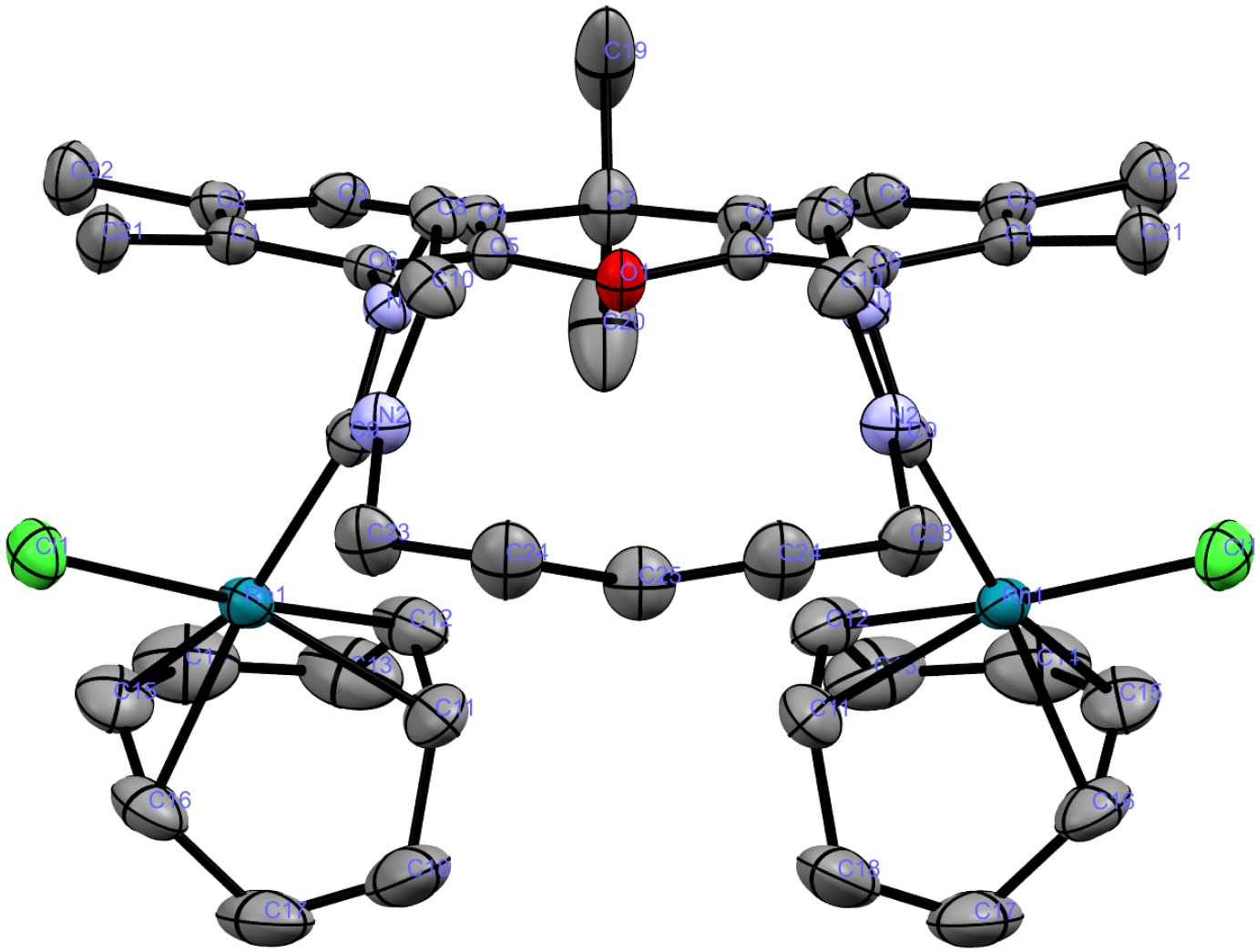
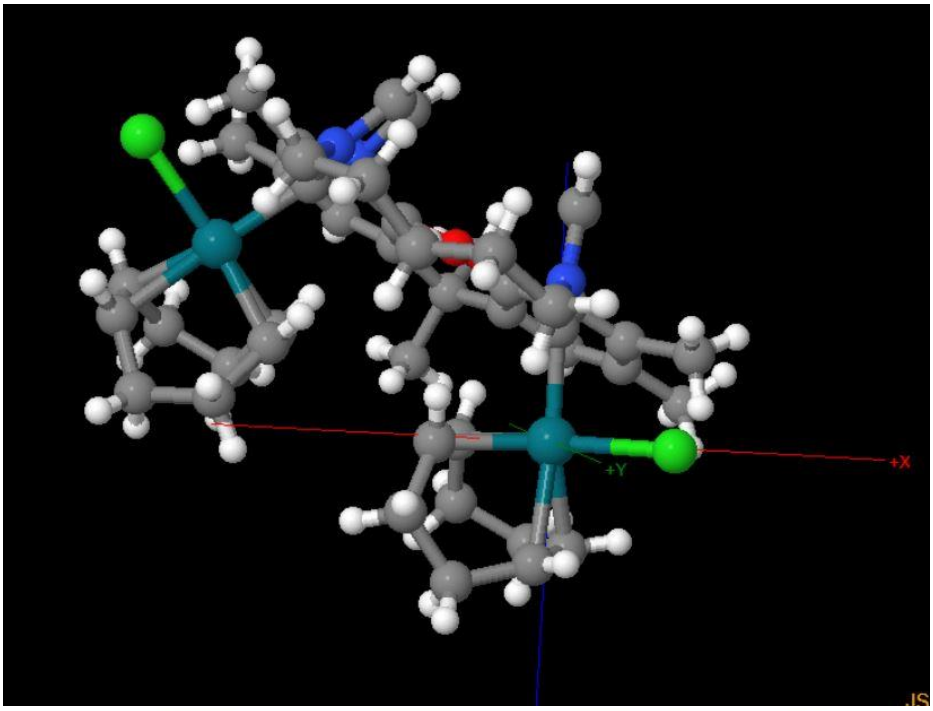


*Figure 126: Crystal structure of [(RhCl(cod))$_2$(**16**)] (thermal ellipsoids are shown at the 50% probability level).*

SambVa-buried volume



%V Free	%V Buried	% V Tot/V Ex
69.1	**30.9**	99.9

Quadrant	V f	V b	V t	%V f	%V b
SW	34.0	10.8	44.9	**75.9**	24.1
NW	31.8	13.1	44.9	**70.9**	29.1
NE	34.3	10.6	44.9	**76.4**	23.6
SE	23.9	21.0	44.9	**53.2**	46.8

Steric Map