Electronic Supplementary Information

for

Chiroptical activity of benzannulated N-heterocyclic carbene rhenium(I) tricarbonyl halide complexes: towards efficient circularly polarized luminescence emitters

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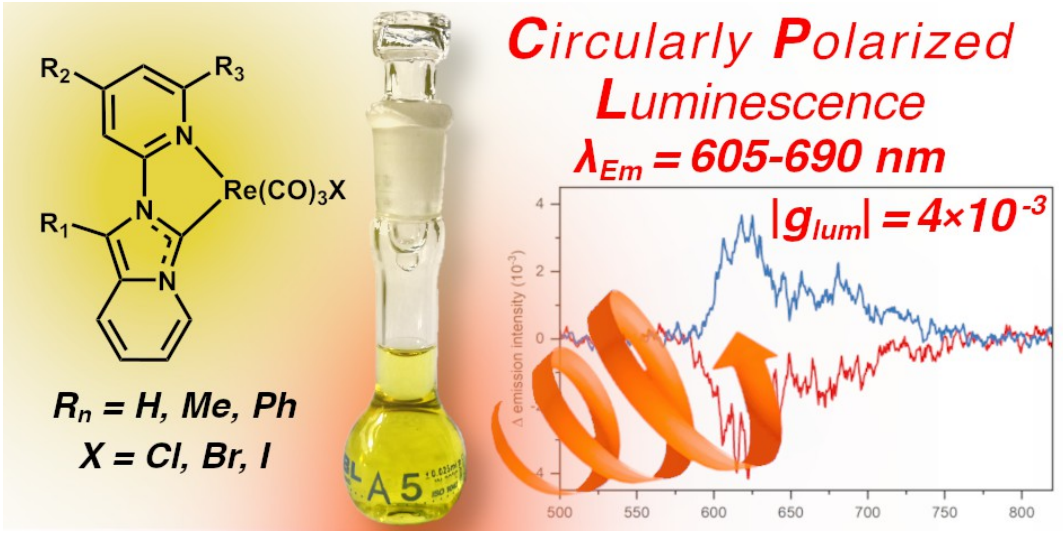
Table of Content: Design of enantiomerically pure circularly polarized luminescent (CPL) Rhenium(I) emitters from an in-depth interpretation of the chiroptical properties by means of jointly (chiroptical) photophysical measurements and state-of-the-art theoretical investigation.

Figure TOC



Supplementary Data: Theory

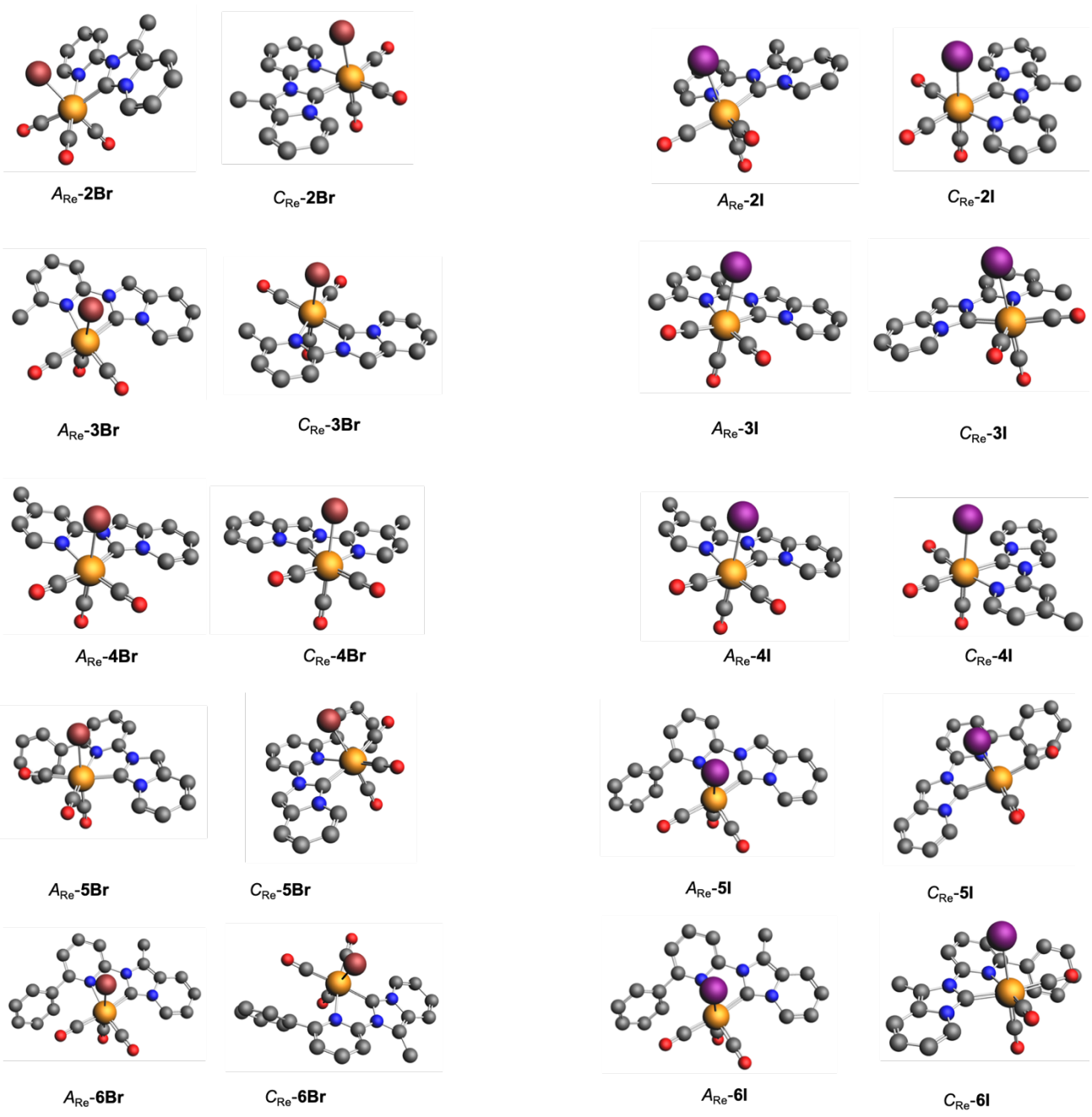


Figure S1. Electronic ground state DFT optimized structures of the A_{Re} and C_{Re} enantiomers of complexes **3–6Br** and **3–6I**.

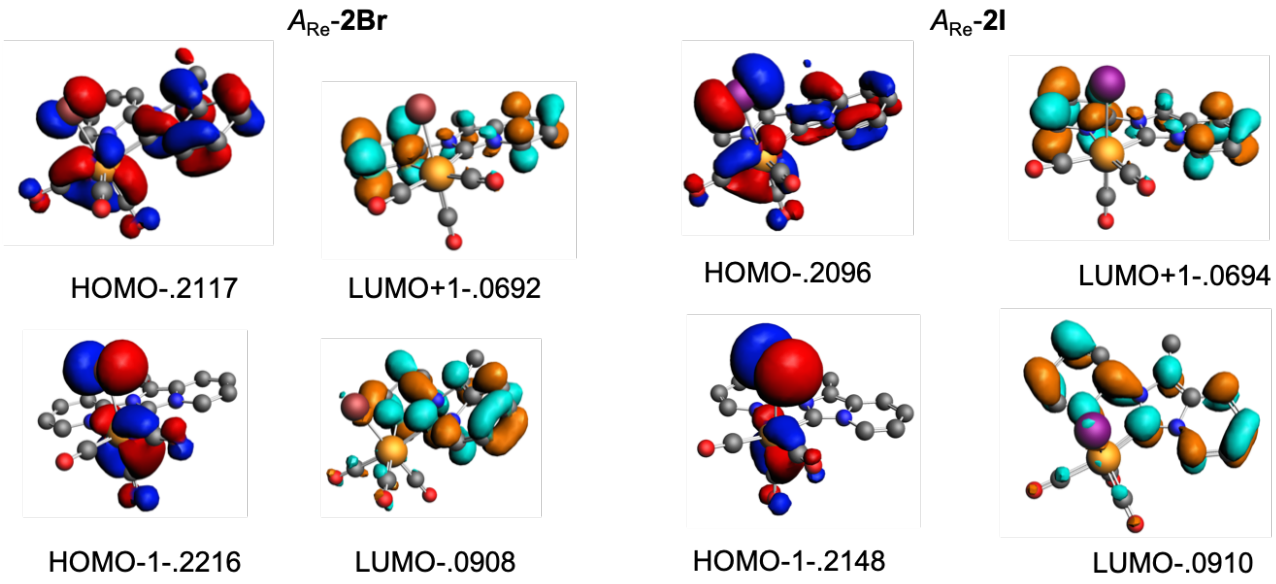


Figure S2. Kohn-Sham FMOs of the investigated complexes **2Br** and **2I** in their A_{Re} stereochemistry, computed at their electronic ground state.

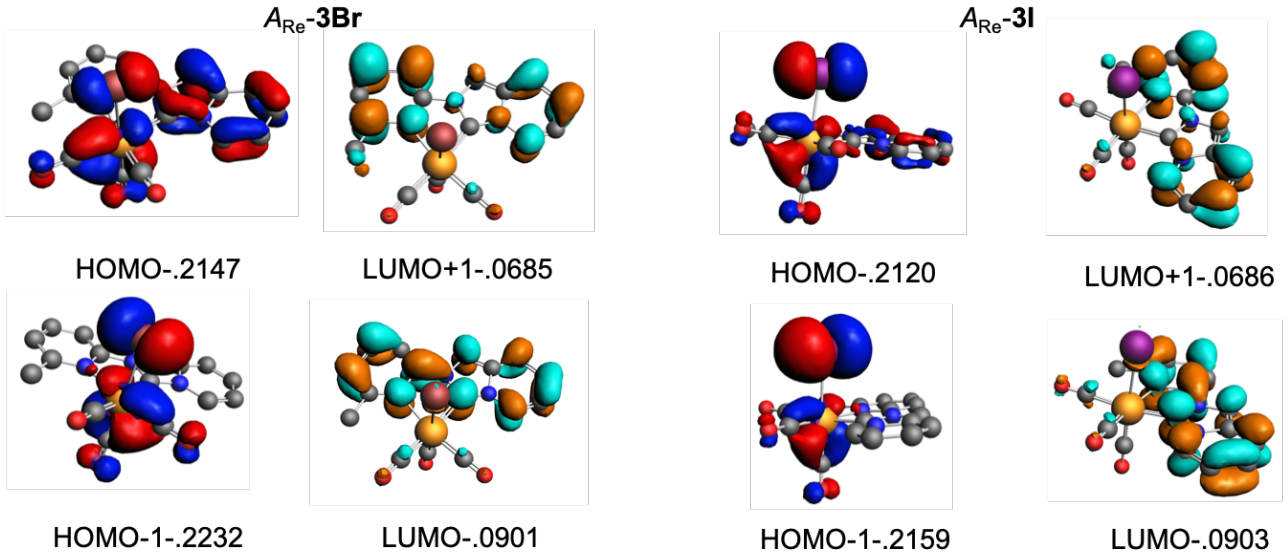


Figure S3. Kohn-Sham FMOs of the investigated complexes **3Br** and **3I** in their A_{Re} stereochemistry, computed at their electronic ground state.

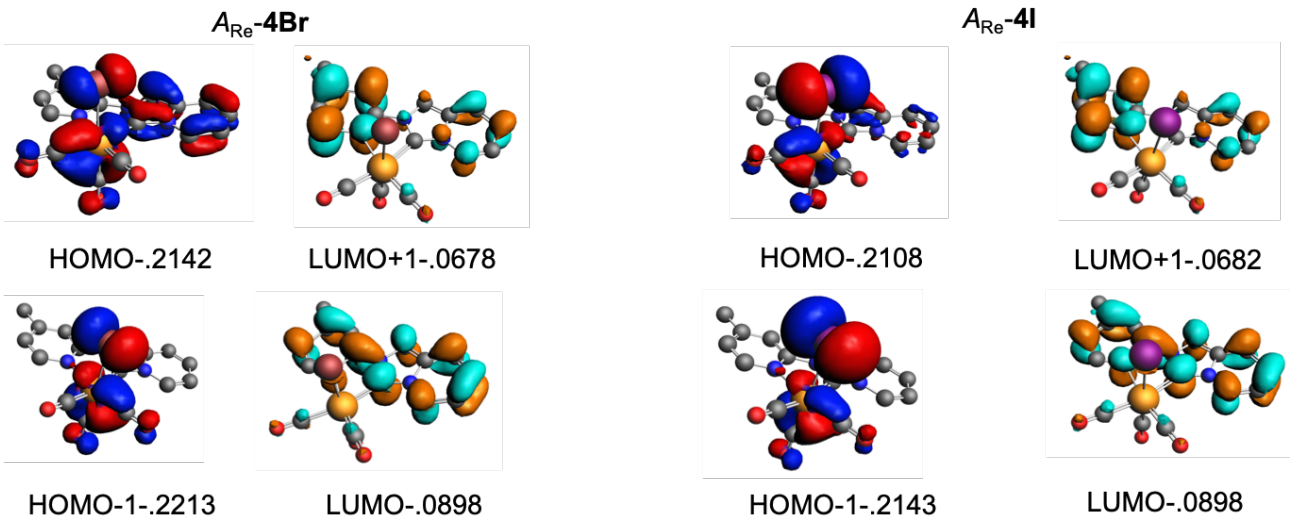


Figure S4. Kohn-Sham FMOs of the investigated complexes **4Br** and **4I** in their A_{Re} stereochemistry, computed at their electronic ground state.

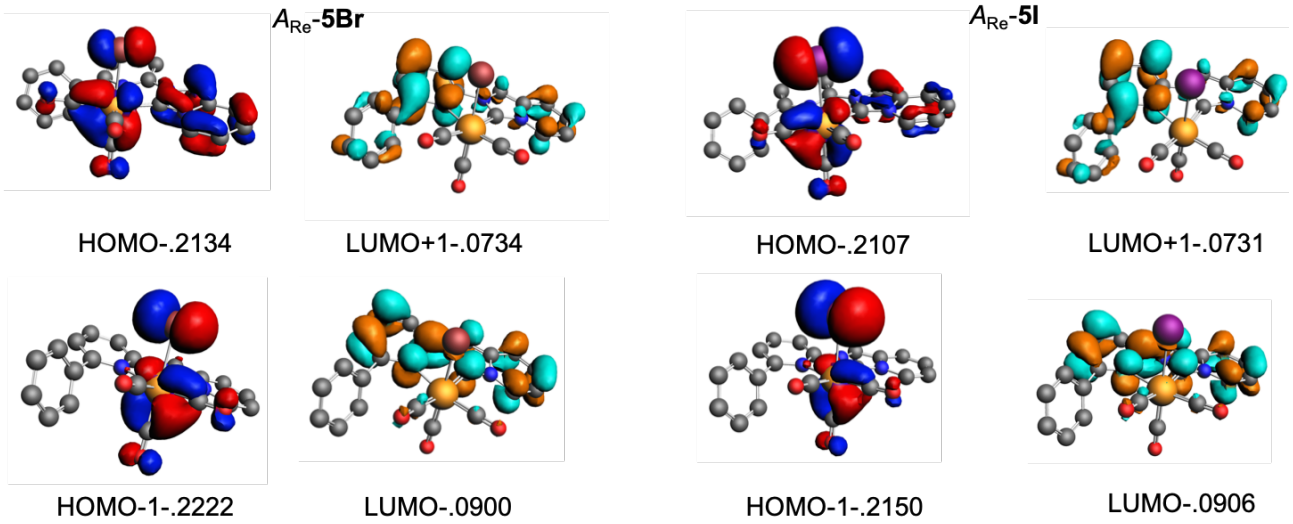


Figure S5. Kohn-Sham FMOs of the investigated complexes **5Br** and **5I** in their A_{Re} stereochemistry, computed at their electronic ground state.

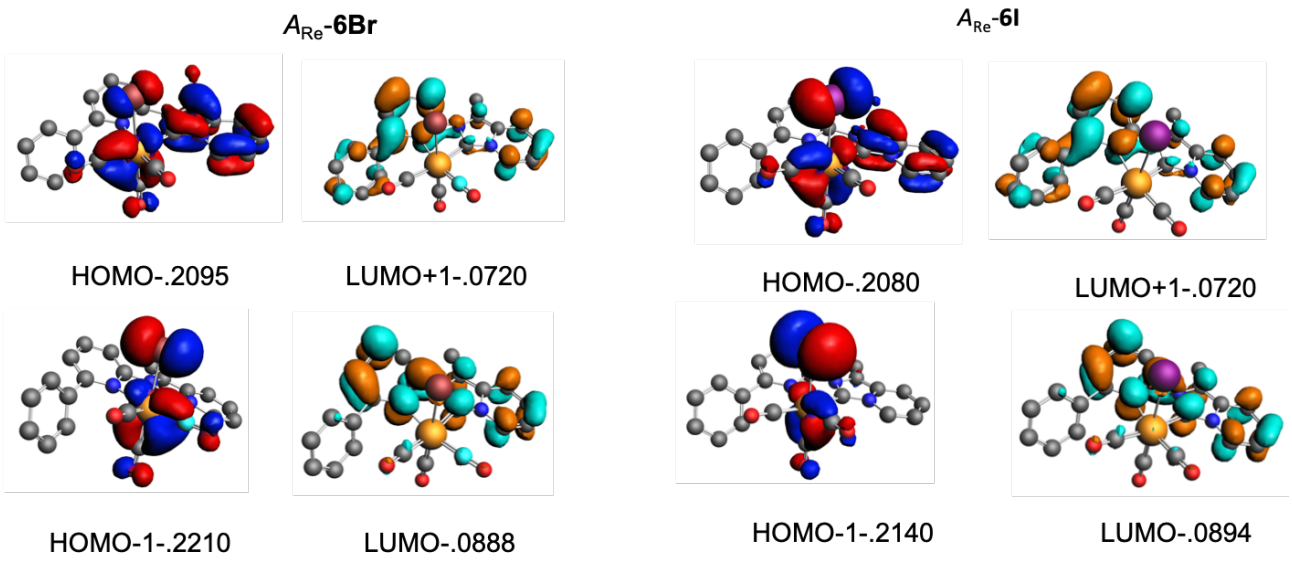


Figure S6. Kohn-Sham FMOs of the investigated complexes **6Br** and **6I** in their A_{Re} stereochemistry, computed at their electronic ground state.

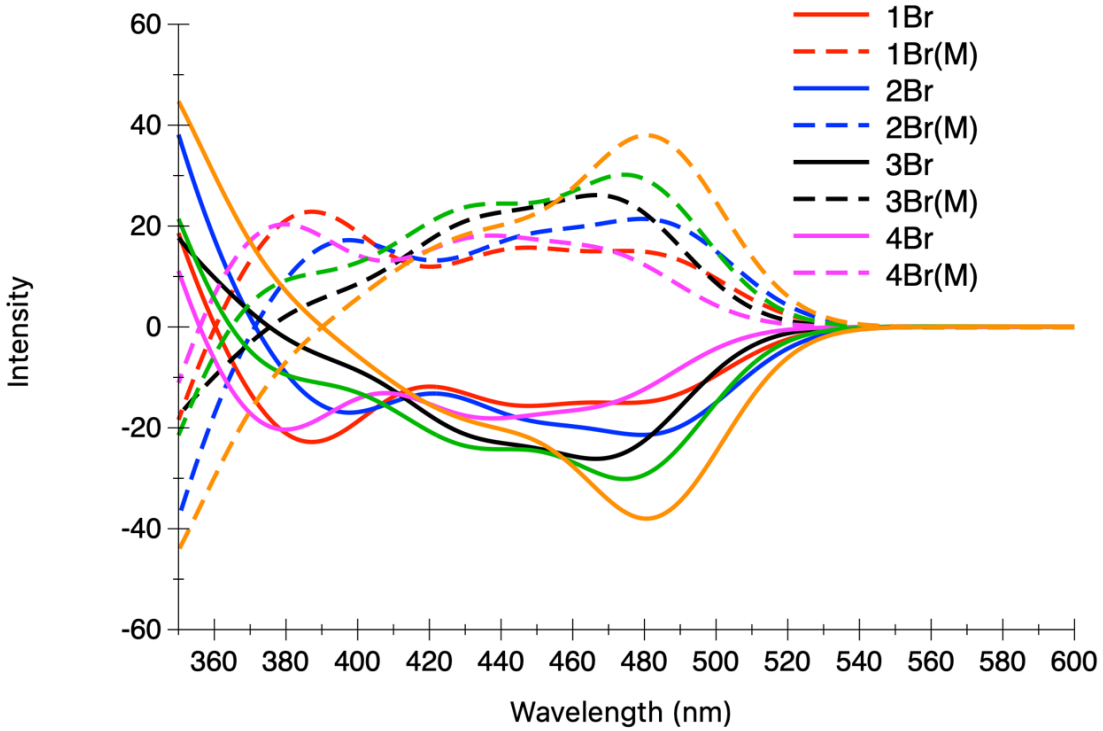


Figure S7. Calculated ECD spectra with SOC of the C_{Re} and A_{Re} enantiomers of complexes **1–4Br**.

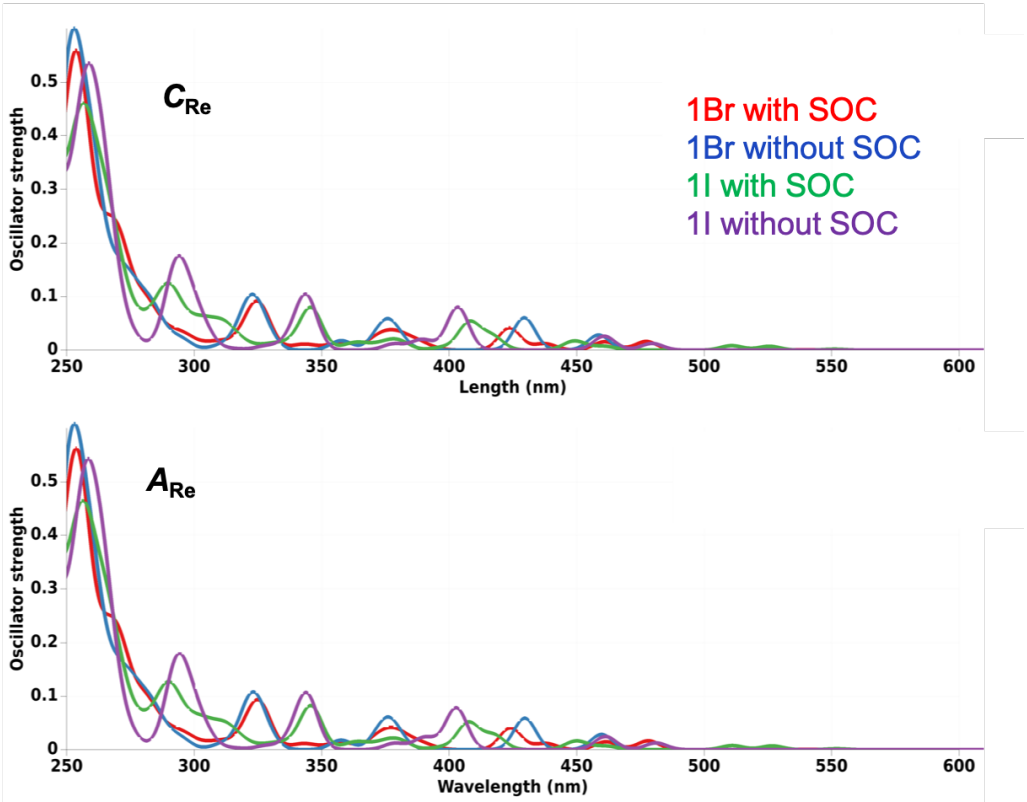


Figure S8. TD-DFT absorption spectra of A_{Re} (bottom) and C_{Re} (top) enantiomers of **1Br** and **1I** with and without SOC perturbation.

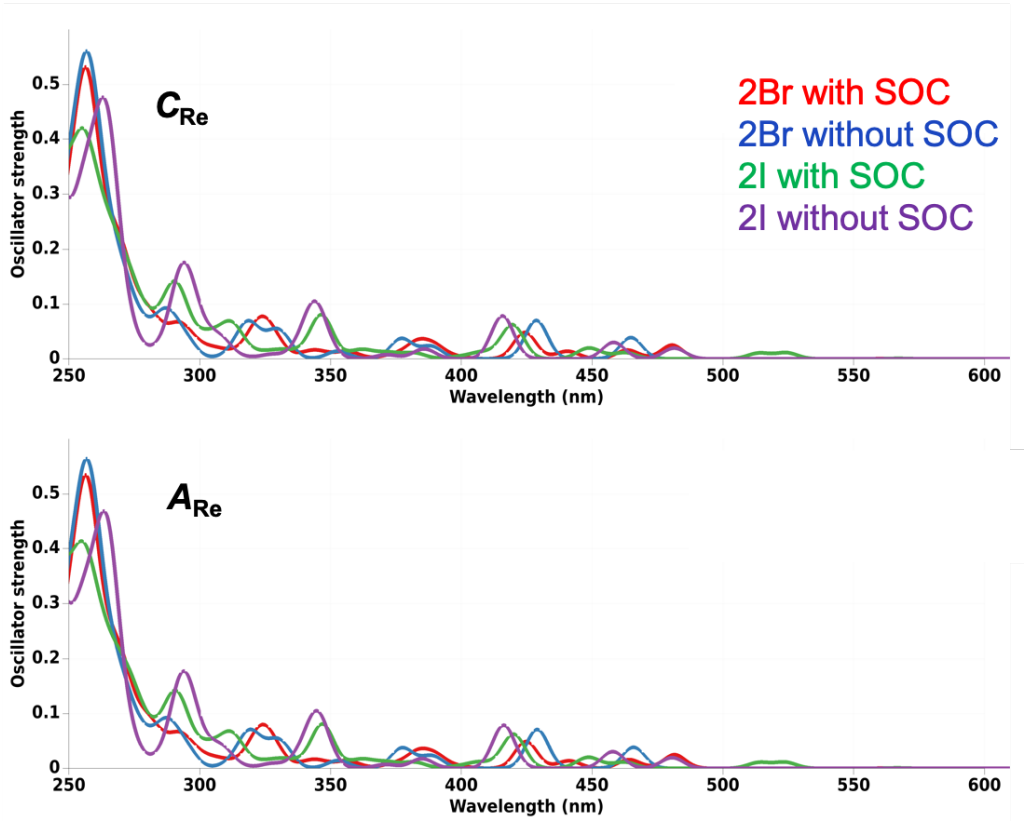


Figure S9. TD-DFT absorption spectra of A_{Re} (bottom) and C_{Re} (top) enantiomers of **2Br** and **2I** with and without SOC perturbation.

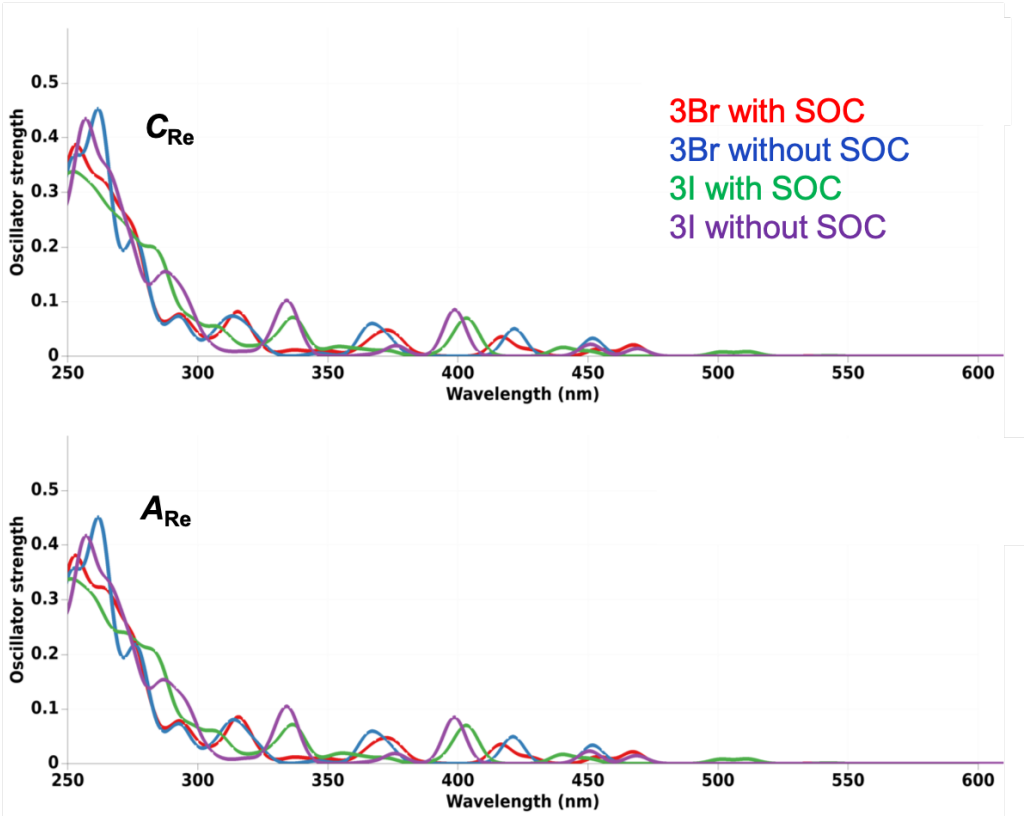


Figure S10. TD-DFT absorption spectra of A_{Re} (bottom) and C_{Re} (top) enantiomers of **3Br** and **3I** with and without SOC perturbation.

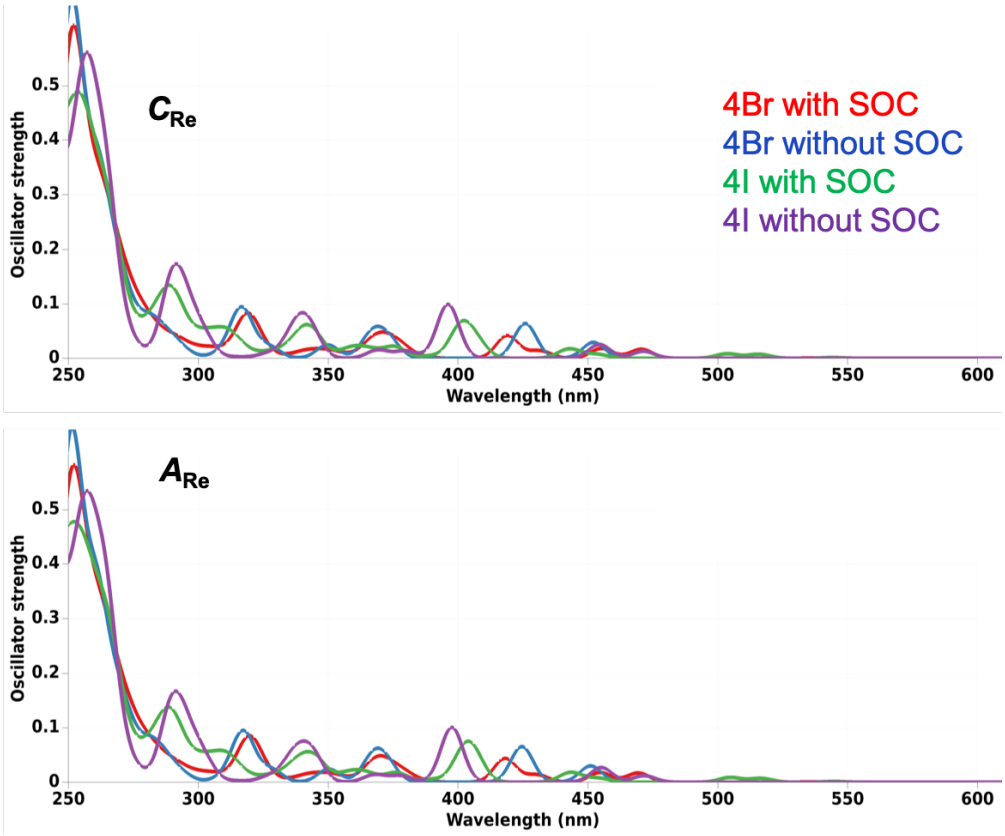


Figure S11. TD-DFT absorption spectra of A_{Re} (bottom) and C_{Re} (top) enantiomers of **4Br** and **4I** with and without SOC perturbation.

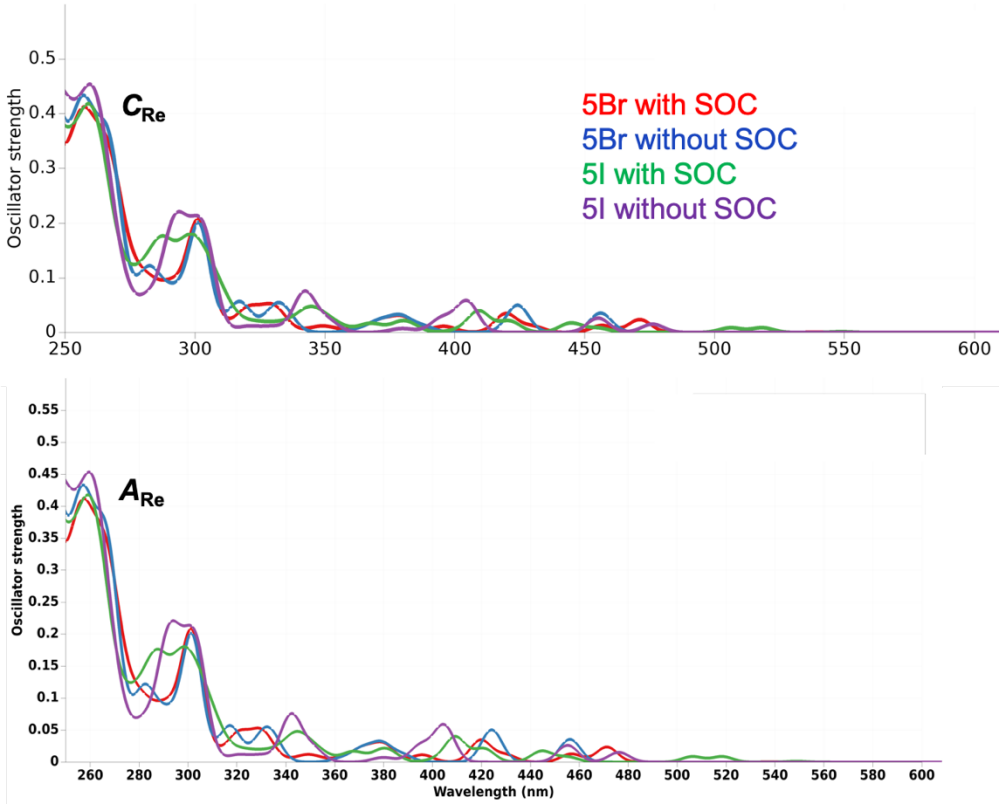


Figure S12. TD-DFT absorption spectra of A_{Re} (bottom) and C_{Re} (top) enantiomers of **5Br** and **5I** with and without SOC perturbation.

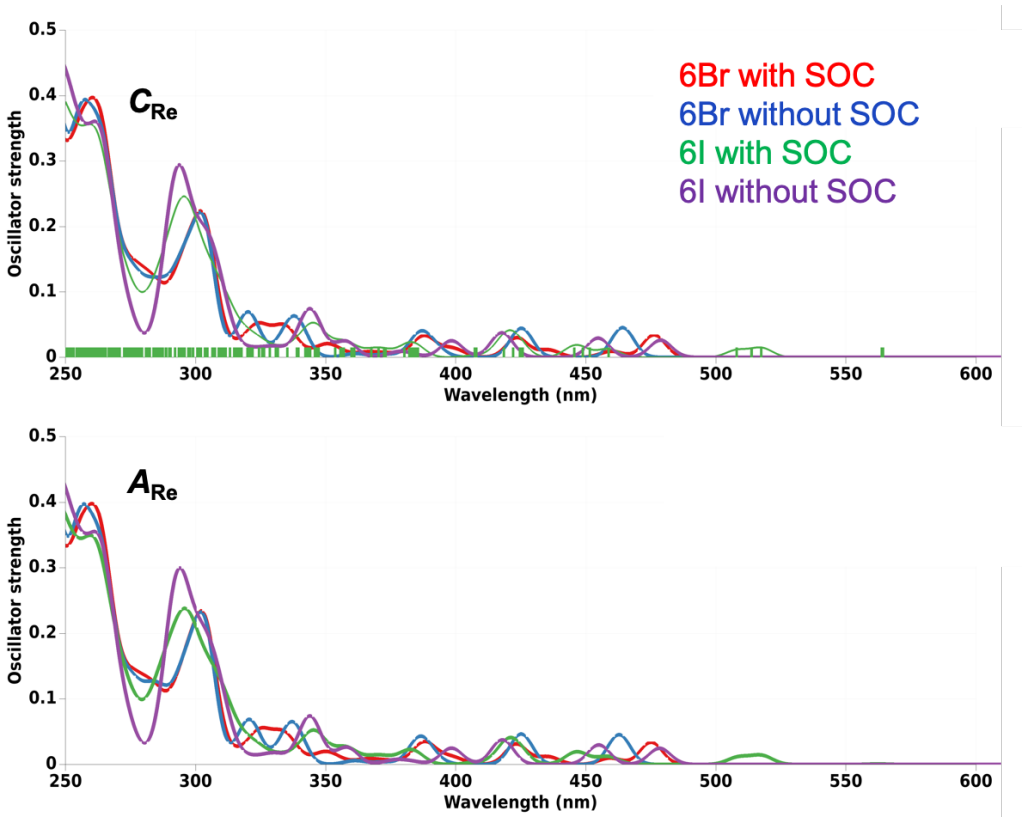


Figure S13. TD-DFT absorption spectra of A_{Re} (bottom) and C_{Re} (top) enantiomers of **6Br** and **6I** with and without SOC perturbation.

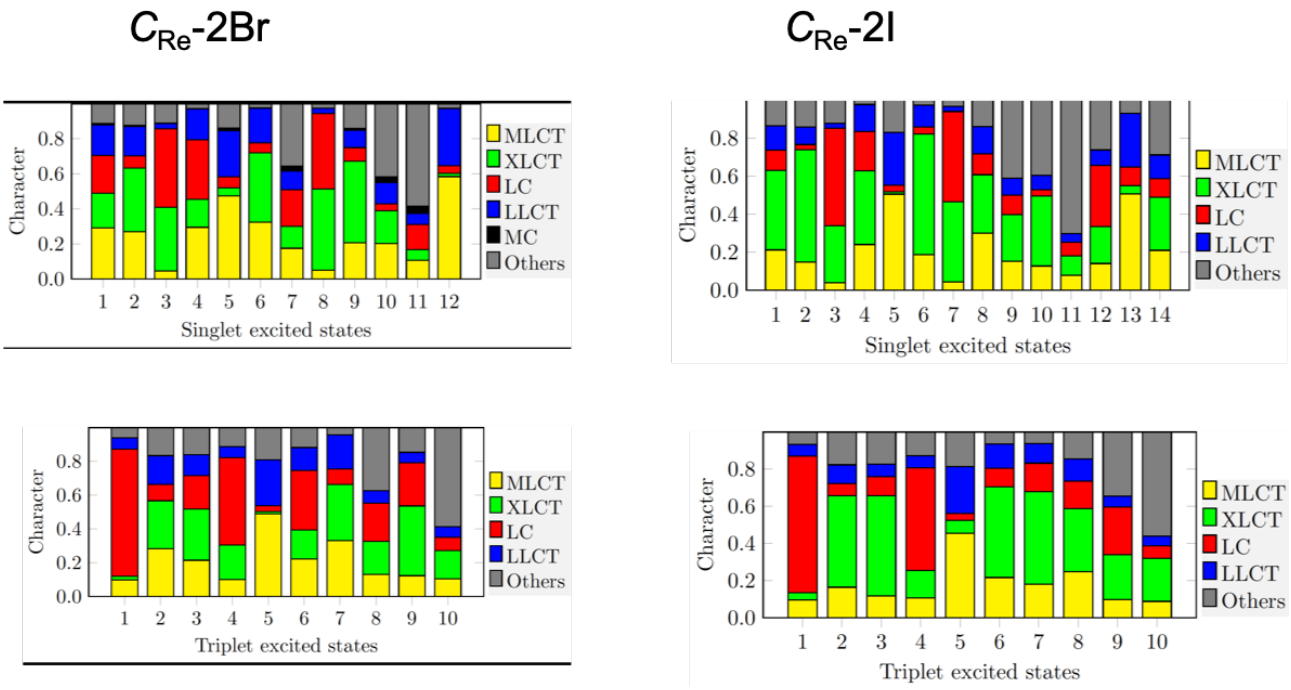


Figure S14. Character of the low-lying electronic transitions (without SOC at FC) obtained by means of TheoDORE analysis for complex **2Br** and **2I**.

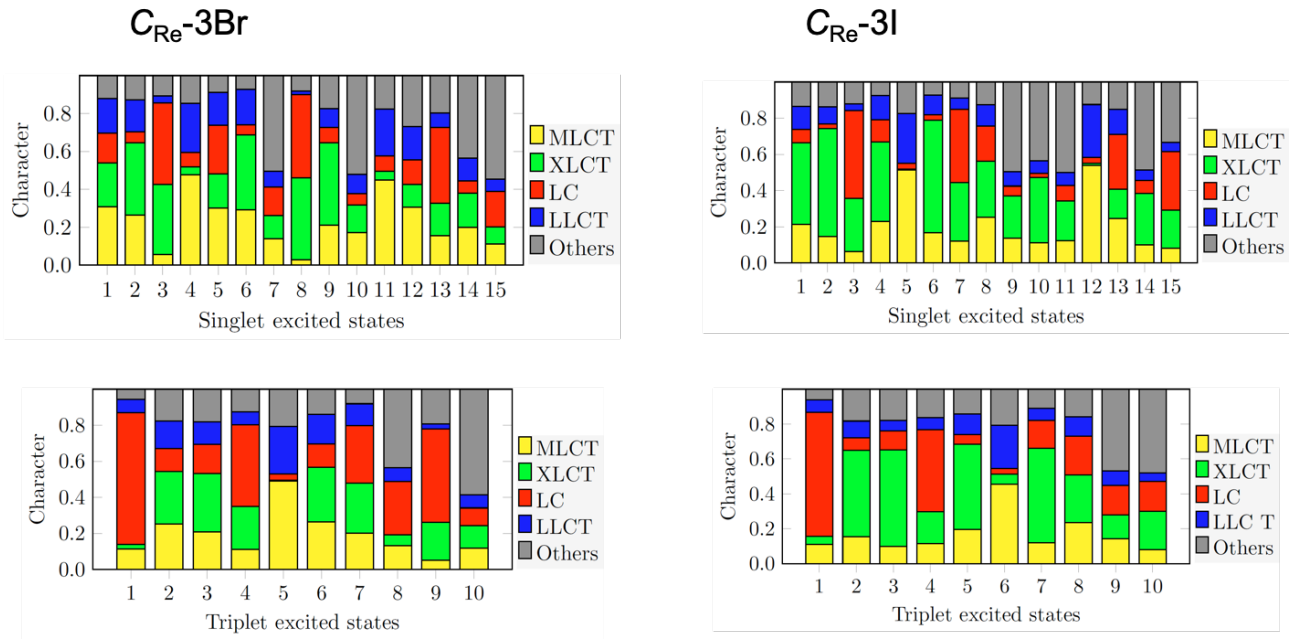


Figure S15. Character of the low-lying electronic transitions (without SOC at FC) obtained by means of TheoDORE analysis for complex **3Br** and **4I**.

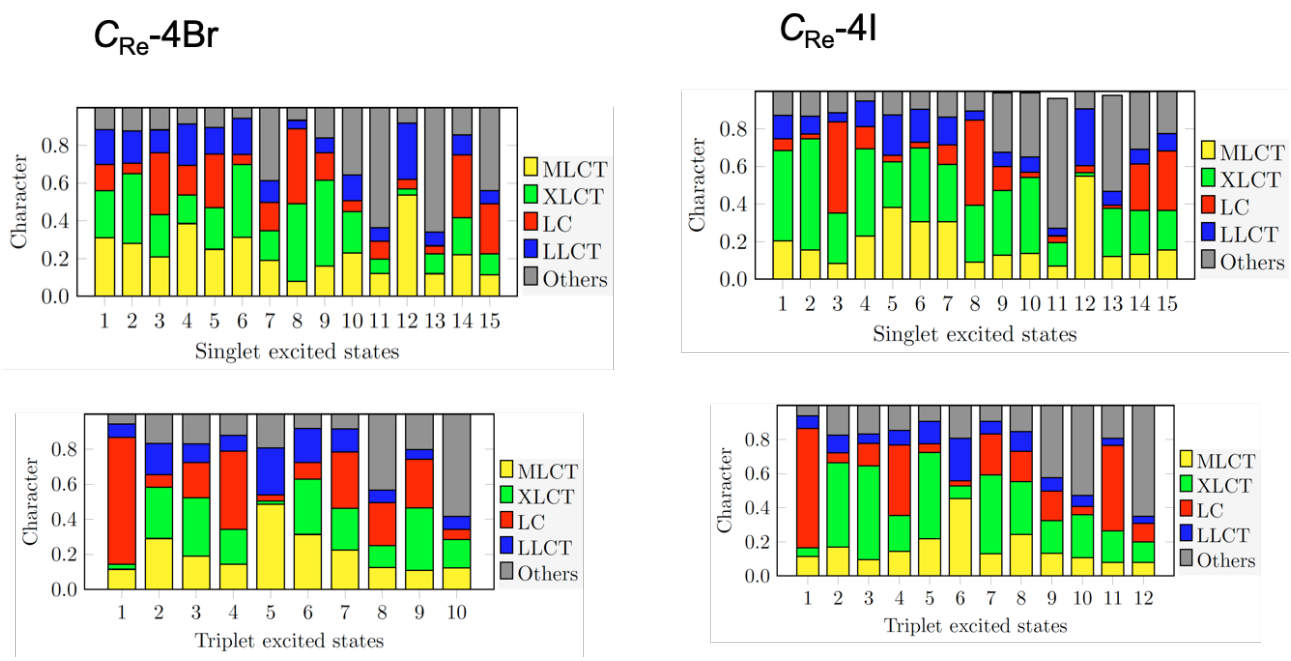


Figure S16. Character of the low-lying electronic transitions (without SOC at FC) obtained by means of TheoDORE analysis for complex **4Br** and **4I**.

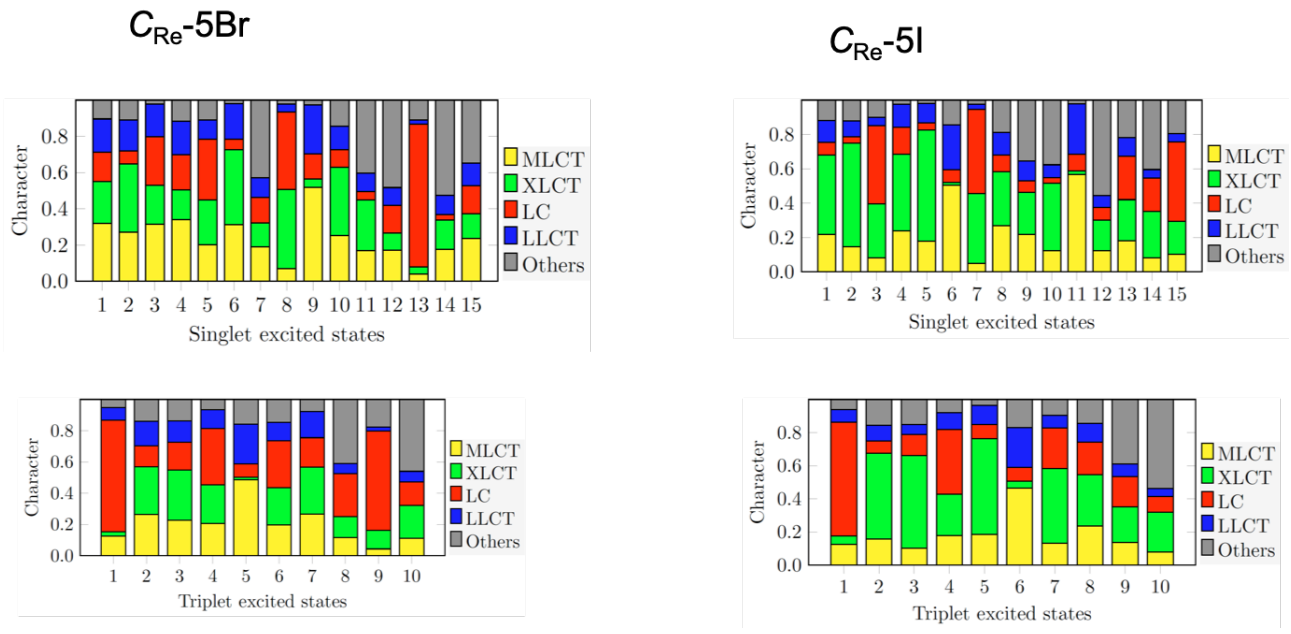


Figure S17. Character of the low-lying electronic transitions (without SOC at FC) obtained by means of TheoDORE analysis for complex **5Br** and **5I**.

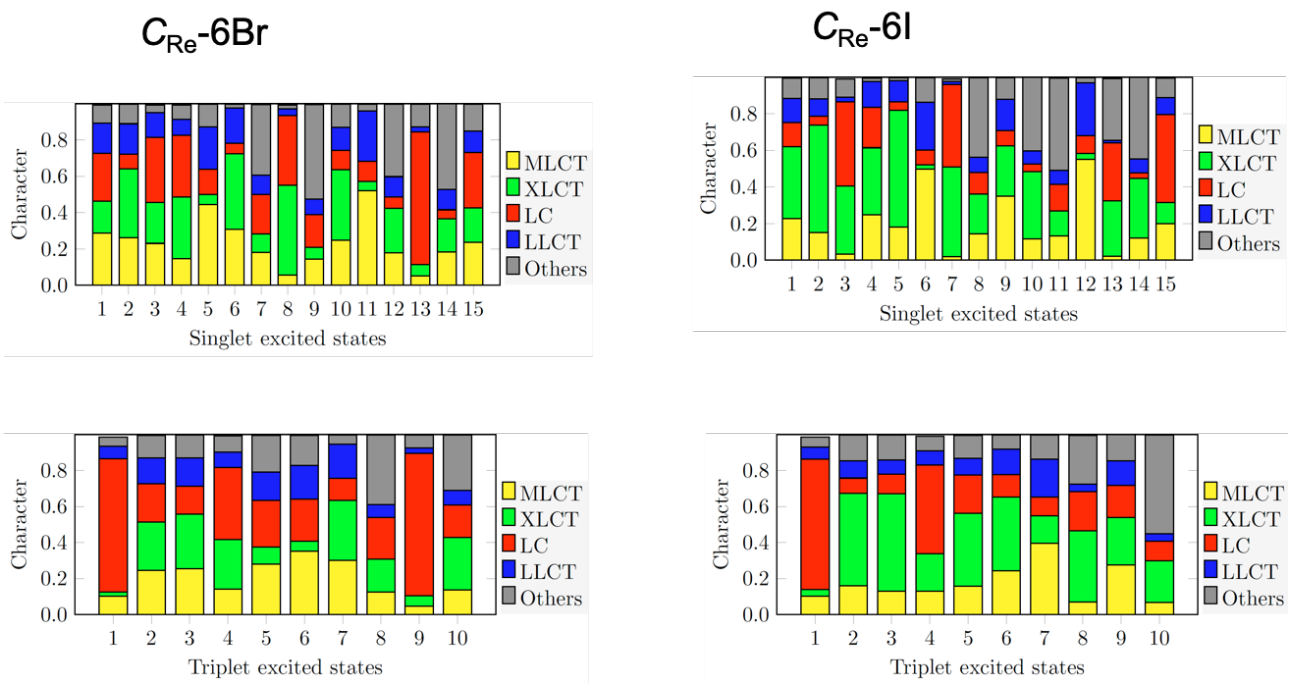


Figure S18. Character of the low-lying electronic transitions (without SOC at FC) obtained by means of TheoDORE analysis for complex **6Br** and **6I**.

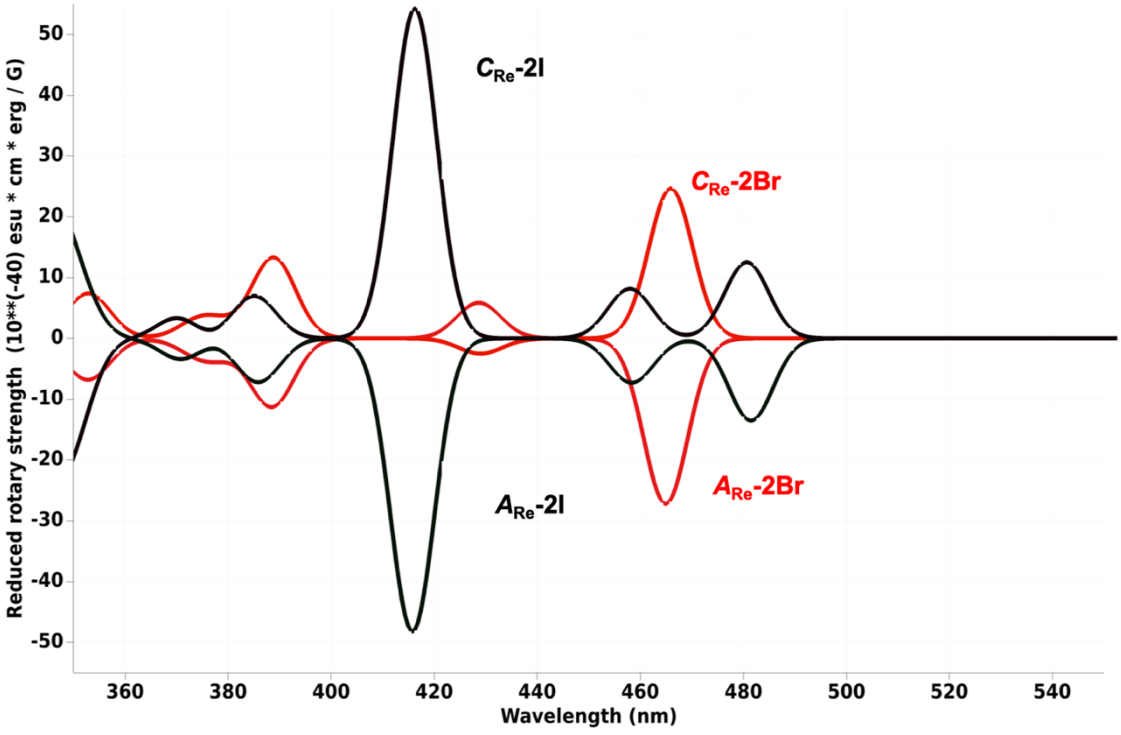


Figure S19. Calculated ECD spectra of the C_{Re} and A_{Re} enantiomers of **2I** and **2Br** without SOC.

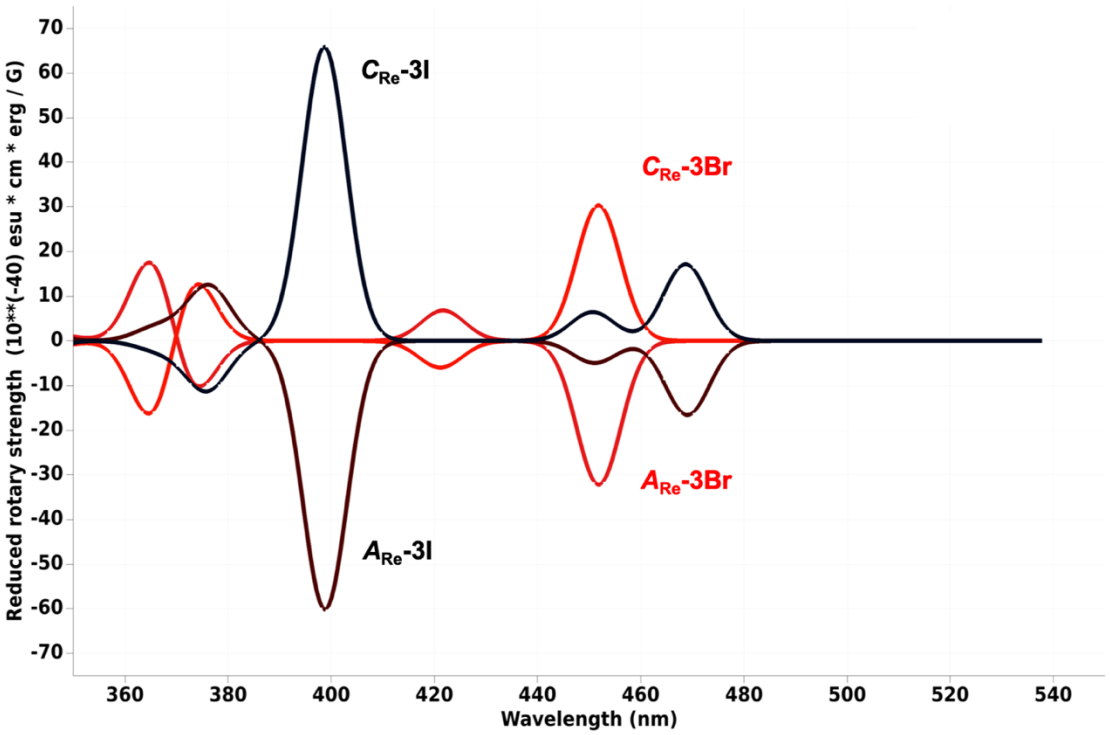


Figure S20. Calculated ECD spectra of the C_{Re} and A_{Re} enantiomers of **3I** and **3Br** without SOC.

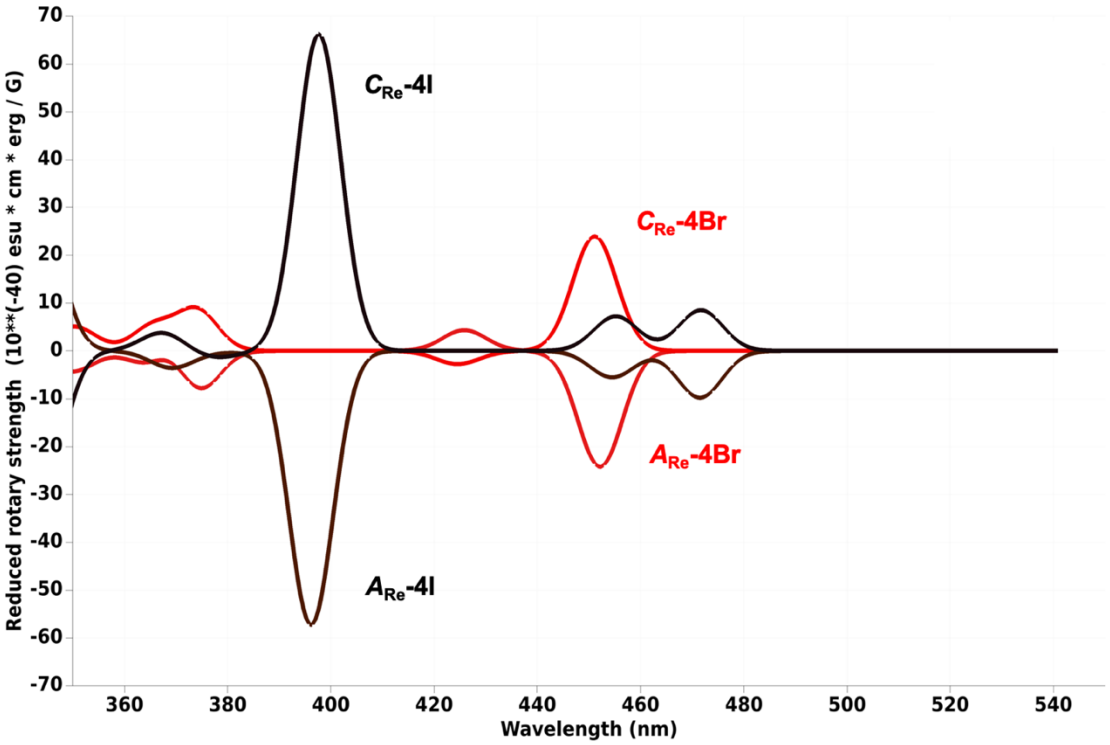


Figure S21. Calculated ECD spectra of the C_{Re} and A_{Re} enantiomers of **4I** and **4Br** without SOC.

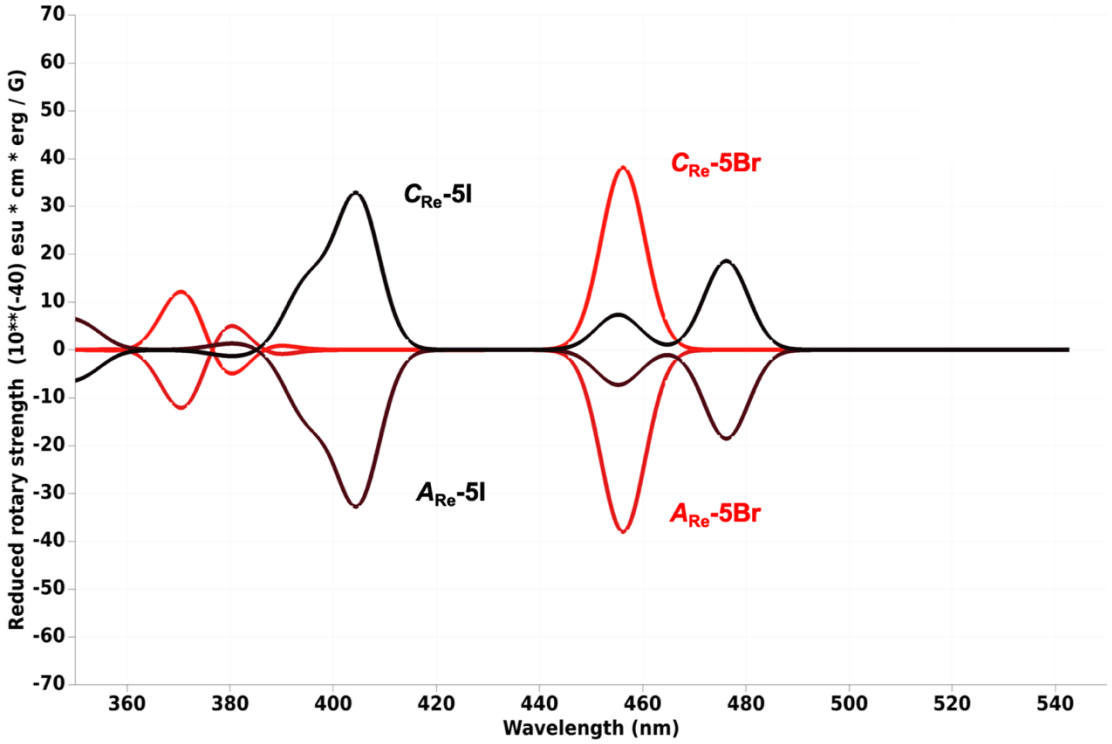


Figure S22. Calculated ECD spectra of the C_{Re} and A_{Re} enantiomers of **5I** and **5Br** without SOC.

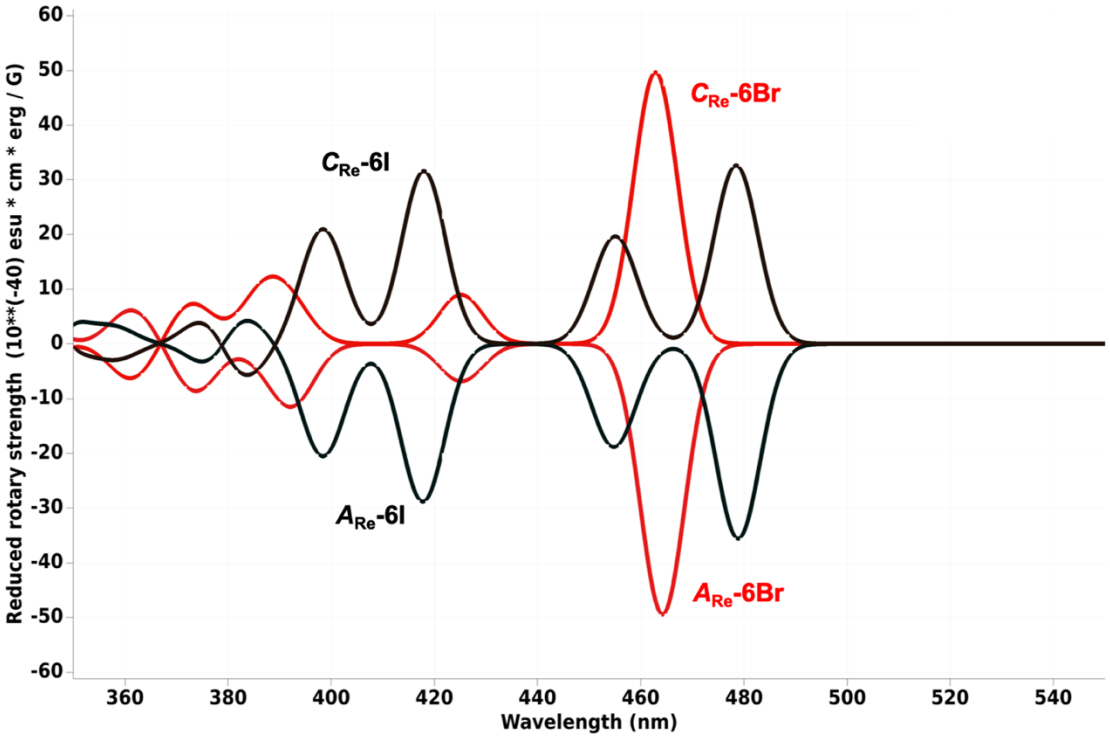


Figure S23. Calculated ECD spectra of the C_{Re} and A_{Re} enantiomers of **6I** and **6Br** without SOC.

Table S1. Transition energies, absorption wavelengths and oscillator strengths associated to the low-lying singlet, triplet and "spin-orbit" states of the bromide complexes

1Br

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.7033**	**0.28174E-01**	**459**	**T1**	**2.3049**	E1	2.2936	0.3179E-04	541	T1
S2	**2.8871**	**0.60724E-01**	**429**	**T2**	**2.7313**	E2	2.2937	0.7362E-04	541	T1 LC_{NHC}
S3	**3.2552**	**0.12080E-01**	**381**	**T3**	**2.8050**	E3	2.2950	0.5900E-03	540	T1
S4	3.2956	0.42054E-01	376	**T4**	**3.1664**	**E4**	**2.5976**	**0.1611E-01**	**477**	**55%S1/27%T2**
S5	3.3330	0.17056E-01	372	T5	3.2772	E5	2.6449	0.1314E-04	469	T2/T3
S6	3.4668	0.17661E-01	358	T6	3.3912	E6	2.6459	0.4803E-03	569	T2/T3
S7	3.7728	0.17337E-01	329	T7	3.4298	**E7**	**2.6899**	**0.1549E-01**	**461**	**26%T2/22%T3/21%S2**
S8	3.8085	0.32137E-01	326	T8	3.6157	**E8**	**2.8328**	**0.1138E-01**	**438**	**35%T3/30%S1/16%T2**
S9	3.8571	0.73499E-01	321	T9	3.6534	E9	2.8609	0.2234E-04	433	T3/T2
S10	3.9387	0.87911E-02	315	T10	3.7277	E10	2.8652	0.1242E-02	433	T3/T2
S11	3.9773	0.20757E-02	312			**E11**	**2.9265**	**0.4150E-01**	**424**	**68%S2/15%T3**
S12	4.0133	0.44298E-02	309							
S13	4.2001	0.12511E-01	295							

2Br

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.6670**	**0.38789E-01**	**465**	**T1**	**2.2193**	E1	2.2117	0.1394E-04	561	T1
S2	**2.8924**	**0.70427E-01**	**429**	**T2**	**2.7233**	E2	2.2117	0.1923E-04	561	T1 **LC_{NHC}**
S3	3.1916	0.22727E-01	389	**T3**	**2.7945**	E3	2.2125	0.3930E-03	560	T1
S4	3.2861	0.34676E-01	377	T4	3.1128	**E4**	**2.5800**	**0.2506E-01**	**481**	**64%S1/ 18%T2**
S5	3.3172	0.28832E-02	374	T5	3.2711	E5	2.6326	0.1478E-04	471	T2/T3
S6	3.5147	0.14111E-01	353	T6	3.3845	E6	2.6337	0.1726E-03	471	T2/T3
S7	3.7405	0.34092E-01	331	T7	3.4549	**E7**	**2.6749**	**0.1593E-01**	**463**	**36%T2/19%S2/15%T3**
S8	3.7858	0.25493E-01	328	T8	3.6110	**E8**	**2.8135**	**0.1364E-01**	**441**	**40%T3/26%S1**
S9	3.8900	0.59801E-01	319	T 9	3.6702	E9	2.8506	0.1500E-04	435	T3/T2
S10	3.9348	0.73228E-02	315	T10	3.7207	E10	2.8539	0.8326E-03	434	T3/T2
S11	3.9713	0.52316E-02	312			**E11**	**2.9225**	**0.4853E-01**	**424**	**69%S2/12%T3**
S12	4.0199	0.13180E-02	308							

3Br

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.7441**	**0.32879E-01**	**452**	**T1**	**2.3239**	E1	2.3145	0.2218E-04	536	T1
S2	**2.9404**	**0.50754E-01**	**422**	**T2**	**2.7851**	E2	2.3145	0.4138E-04	536	T1 LC_{NHC}
S3	3.3250	0.28584E-01	373	**T3**	**2.8695**	E3	2.3153	0.4102E-03	536	T1
S4	3.3802	0.56562E-02	366	T4	3.2090	**E4**	**2.6519**	**0.2080E-01**	**468**	**62%S1/18%T2**
S5	3.3916	0.46323E-01	366	T5	3.3373	E5	2.6996	0.2320E-04	459	T2/T3
S6	3.5808	0.54521E-02	346	T6	3.4841	E6	2.7007	0.2971E-03	459	T2/T3
S7	3.8450	0.24483E-01	322	T7	3.5534	**E7**	**2.7321**	**0.1288E-01**	**454**	**40%T2/20%S2/12%T3**
S8	3.9177	0.40831E-01	316	T8	3.6469	**E8**	**2.8977**	**0.1104E-01**	**428**	**56%T3/25%S1/12%T3**
S9	3.9899	0.45053E-01	311	T9	3.7097	E9	2.9221	0.1305E-04	424	T3/T2
S10	4.0482	0.72426E-02	306	T10	3.7921	E10	2.9257	0.1079E-02	424	T3/T2
S11	4.0709	0.41250E-02	305			**E11**	**2.9757**	**0.3496E-01**	**417**	**69%S2/11%T3**
S12	4.0848	0.94937E-02	304							

4Br

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.7422**	**0.29263E-01**	**452**	**T1**	**2.3194**	E1	2.3091	0.2927E-04	537	T1
S2	**2.9115**	**0.64154E-01**	**426**	**T2**	**2.7654**	E2	2.3092	0.7043E-04	537	T1 LC_{NHC}
S3	3.3203	0.30934E-01	373	**T3**	**2.8488**	E3	2.3102	0.5639E-03	537	T1
S4	3.3579	0.75449E-02	369	T4	3.2259	**E4**	**2.6345**	**0.1648E-01**	**471**	**54%S1 / 30%T2**
S5	3.3816	0.38938E-01	367	T5	3.3133	E5	2.6802	0.1253E-04	463	T2/T3
S6	3.5446	0.24549E-01	350	T6	3.4511	E6	2.6814	0.5271E-03	462	T2/T3
S7	3.7870	0.20605E-01	327	T7	3.4920	**E7**	**2.7238**	**0.1797E-01**	**455**	
S8	3.8918	0.15831E-01	319	T8	3.6374		**25%T2/23%S2/22%T3/11%S1**			
S9	3.9128	0.63133E-01	317	T9	3.6997	**E8**	**2.8729**	**0.1323E-01**	**432**	**35%T3/30%S1/14%T2**
S10	3.9475	0.18609E-01	314	T10	3.7418	E9	2.8729	0.1826E-04	432	T3/T2
S11	4.0120	0.46424E-02	309	T11	3.8499	E10	2.9075	0.1172E-02	426	T3/T2
S12	4.0472	0.27278E-02	306	T12	3.8761	**E11**	**2.9593**	**0.4164E-01**	**419**	**65%S2/19%T3**
				T13	3.9887					

5Br

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.7180**	**0.35515E-01**	**456**	**T1**	**2.3106**	E1	2.3004	0.2423E-04	539	T1
S2	**2.9233**	**0.50285E-01**	**424**	**T2**	**2.7722**	E2	2.3005	0.8995E-04	539	T1 LC_{NHC}
S3	3.1979	0.10942E-01	388	**T3**	**2.8559**	E3	2.3012	0.4611E-03	539	T1
S4	3.2706	0.28103E-01	379	T4	3.1474	**E4**	**2.6310**	**0.2356E-01**	**471**	**65%S1/17%T2**
S5	3.3422	0.19657E-01	371	T5	3.2552	E5	2.6876	0.1080E-04	461	T2/T3
S6	3.4187	0.57769E-02	363	T6	3.3360	E6	2.6888	0.6153E-03	461	T2/T3
S7	3.7065	0.31449E-01	335	T7	3.3767	**E7**	**2.7155**	**0.1244E-01**	**457**	**57%T2/19%S2**
S8	3.7561	0.31326E-01	331	T8	3.5665	**E8**	**2.8832**	**0.1060E-01**	**430**	**60%T3/23%S1**
S9	3.8681	0.65473E-02	321	T9	3.6407	E9	2.9064	0.4203E-04	427	T3/T2
S10	3.9090	0.31678E-01	317	T10	3.6793	E10	2.9092	0.8776E-03	426	T3/T2
S11	3.9145	0.15982E-01	317			**E11**	**2.9551**	**0.3407E-01**	**420**	**68%S2**
S12	3.9478	0.55322E-02	314							
S13	4.1108	0.19364	302							

6Br

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.6710**	**0.45718E-01**	**464**	**T1**	**2.2339**	E1	2.2267	0.1535E-04	557	T1
S2	**2.9158**	**0.44769E-01**	**425**	**T2**	**2.7563**	E2	2.2267	0.3831E-04	557	T1 LC_{NHC}
S3	3.1590	0.10716E-01	392	**T3**	**2.8293**	E3	2.2272	0.2538E-03	557	T1
S4	3.2083	0.36543E-01	386	T4	3.0954	**E4**	**2.6032**	**0.3434E-01**	**476**	**75%S1/17%T3**
S5	3.3185	0.46936E-02	374	T5	3.2442	E5	2.6710	0.2188E-04	464	T2/T3
S6	3.4310	0.58450E-02	361	T6	3.2673	E6	2.6722	0.3516E-03	464	T2/T3
S7	3.6574	0.49906E-01	339	T7	3.3774	**E7**	**2.6967**	**0.9108E-02**	**460**	**72%T2/18%S2**
S8	3.7092	0.22142E-01	334	T8	3.5424	**E8**	**2.8455**	**0.1100E-01**	**436**	**69%T3/20%S1**
S9	3.8575	0.15137E-01	321	T9	3.6103	E9	2.8732	0.9092E-04	432	T3/T2
S10	3.8686	0.39222E-01	320	T10	3.6524	E10	2.8749	0.4311E-03	431	T3/T2
S11	3.8890	0.63000E-02	319			**E11**	**2.9276**	**0.3001E-01**	**424**	**67%S2/10%T2**
S12	3.9017	0.11755E-01	318							
S13	4.0863	0.18399	303							

Table S2. Transition energies (in eV), absorption wavelengths (in nm) and oscillator strengths associated to the low-lying singlet, triplet and "spin-orbit" states of the iodide complexes

1I

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.5853**	**0.12442E-01**	**480**	**T1**	**2.2852**	E1	2.2425	0.1669E-04	553	T1
S2	**2.6900**	**0.25971E-01**	**461**	**T2**	**2.5775**	E2	2.2428	0.1212E-03	553	T1 LC_{NHC}
S3	**3.0735**	**0.80436E-01**	**403**	**T3**	**2.6201**	E3	2.2500	0.1678E-02	551	T1
S4	**3.1831**	**0.19646E-01**	**390**	**T4**	**3.0704**	**E4**	**2.3591**	**0.7133E-02**	**526**	**43%S1/36%T2**
S5	3.2763	0.11341E-01	378	T5	3.2300	E5	2.3974	0.1591E-04	517	T2/T3
S6	3.3174	0.48022E-03	374	T6	3.2717	E6	2.3975	0.8540E-04	517	T2/T3
S7	3.5727	0.33365E-02	347	T7	3.2895	**E7**	**2.4274**	**0.8269E-02**	**511**	**29%T3/28%S2/12%T2**
S8	3.6060	0.97819E-01	344	T8	3.3910	**E8**	**2.6894**	**0.6893E-02**	**461**	**26%S1/19%T3/26%T2**
S9	3.6747	0.13986E-01	337	T9	3.4951	E9	2.7176	0.2219E-04	456	T3/T2
S10	3.7755	0.76985E-02	328	T10	3.6034	E10	2.7420	0.4379E-02	452	T3/T2
S11	3.9253	0.23095E-02	316			**E11**	**2.7647**	**0.1393E-01**	**448**	**53%S2/15%T3**
S12	3.9678	0.51719E-03	312							
S13	4.0523	0.54347E-02	306							

2I

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.5754**	**0.19643E-01**	**481**	**T1**	**2.2057**	E1	2.1838	0.2019E-04	568	T1
S2	**2.7054**	**0.30026E-01**	**458**	**T2**	**2.5805**	E2	2.1842	0.1390E-03	567	T1 **LC_{NHC}**
S3	**2.9823**	**0.78558E-01**	**416**	**T3**	**2.6188**	E3	2.1867	0.7517E-03	567	T1
S4	3.2135	0.18130E-01	386	T4	3.0150	**E4**	**2.3646**	**0.1101E-01**	**524**	**46%S1/27%T2/14%T3**
S5	3.3142	0.15737E-03	374	T5	3.2679	E5	2.3788	0.1795E-04	521	T2/T3
S6	3.3382	0.74748E-02	371	T6	3.2846	E6	2.3791	0.1543E-03	521	T2/T3
S7	3.5475	0.87130E-02	350	T7	3.3105	**E7**	**2.4135**	**0.1043E-01**	**514**	**31%S2/49%T3**
S8	3.6021	0.92587E-01	344	T8	3.3839	**E8**	**2.6793**	**0.1120E-01**	**463**	**30%S1/24%T3**
S9	3.6621	0.20656E-01	339	T9	3.4716	E9	2.7157	0.1848E-04	457	T3/T2
S10	3.7859	0.81705E-02	328	T10	3.6092	E10	2.7395	0.5557E-02	453	T3/T2
S11	3.9087	0.24951E-02	317			**E11**	**2.7678**	**0.1651E-01**	**448**	**55%S2/14%T2/10%T3**
S12	4.0163	0.21037E-01	309			**E12**	**2.9528**	**0.5667E-01**	**420**	**71%S3/T4**
S13	4.0181	0.48344E-02	309							
S14	4.0633	0.12532E-01	305							

3I

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states				
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm	
S1	**2.6436**	**0.14210E-01**	**469**	**T1**	**2.3103**	E1	2.2802	0.1515E-04	544	T1
S2	**2.7489**	**0.21904E-01**	**451**	**T2**	**2.6367**	E2	2.2806	0.1336E-03	544	T1 LC_{NHC}
S3	**3.1091**	**0.85478E-01**	**399**	**T3**	**2.6852**	E3	2.2845	0.9543E-03	543	T1
S4	3.2954	0.19297E-01	376	T4	3.1041	**E4**	**2.4230**	**0.8155E-02**	**512**	**43%S1/30%T2/13%T3**
S5	3.3797	0.51897E-03	367	T5	3.3292	E5	2.4447	0.1552E-04	507	T2/T3
S6	3.3933	0.23720E-02	365	T6	3.3346	E6	2.4449	0.3247E-04	507	T2/T3
S7	3.6721	0.11896E-01	338	T7	3.3868	**E7**	**2.4746**	**0.7621E-02**	**501**	**30%S2/24%T3/22%T2**
S8	3.7072	0.84091E-01	334	T8	3.5014	**E8**	**2.7522**	**0.8803E-02**	**450**	**26%S1/21%T3/20%T2**
S9	3.7687	0.20998E-01	329	T9	3.5910	E9	2.7819	0.1191E-04	446	T3/T2
S10	3.8959	0.74455E-02	318	T10	3.6869	**E10**	**2.8054**	**0.4683E-02**	**442**	**40%T3/16%S1/19%T2**
S11	3.9948	0.56572E-02	310			**E11**	**2.8221**	**0.1176E-01**	**440**	**53%S2/18%T2/11%T3**
S12	4.0711	0.45516E-03	305							

4I

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states			
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm
S1	**2.6299**	**0.12884E-01**	**471**	**T1**	**2.3082**	E1	2.2729 0.4010E-04	546	T1
S2	**2.7281**	**0.25380E-01**	**454**	**T2**	**2.6210**	E2	2.2733 0.1346E-03	545	T1 LC_{NHC}
S 3	3.1298	0.99268E-01	396	**T3**	**2.6613**	E3	2.2784 0.1332E-02	544	T1
S4	3.2629	0.13428E-01	380	T4	3.1354	**E4**	**2.4037 0.7438E-02**	**516**	**44%S1/34T2**
S5	3.3587	0.72330E-02	369	T5	3.2953	E5	2.4327 0.1723E-04	510	T2/T3
S6	3.3594	0.79693E-02	369	T6	3.3144	E6	2.4329 0.8696E-04	510	T3/T2
S7	3.6137	0.47383E-01	343	T7	3.3525	**E7**	**2.4621 0.8376E-02**	**504**	**30%S2/29%T3/17%T2**
S8	3.6653	0.42954E-01	338	T8	3.4183	**E8**	**2.7338 0.7175E-02**	**454**	**25%S1/22%T3/24%T2**
S9	3.6989	0.15080E-01	335	T9	3.5368	E9	2.7598 0.1884E-04	449	T3/T2
S10	3.7926	0.87655E-02	327	T10	3.6302	E10	2.7848 0.4469E-02	445	38%T3/18%S1/15%T2
S11	3.9330	0.25548E-02	315	T11	3.7436	**E11**	**2.8039 0.1368E-01**	**442**	**53%S2/15%T3/12%T2**
S12	4.0362	0.56936E-03	307	T 12	3.7986				
S13	4.0693	0.11581E-02	305	T13	3.8717				
				T14	3.9217				
				T15	3.9279				

5I

Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states			
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm
S1	**2.6039**	**0.15242E-01**	**476**	**T1**	**2.2894**	E1	2.2554 0.4125E-04	550	T1
S2	**2.7237**	**0.26188E-01**	**455**	**T2**	**2.6055**	E2	2.2557 0.1104E-03	550	T1 LC_{NHC}
S3	**3.0638**	**0.57029E-01**	**405**	**T3**	**2.6655**	E3	2.2599 0.1324E-02	550	T1
S4	**3.1392**	**0.25503E-01**	**395**	**T4**	**3.0460**	**E4**	**2.3920 0.8647E-02**	**518**	**43%S1/27%T2/11%T3**
S5	3.2428	0.32871E-02	382	T5	3.2007	E5	2.4230 0.2083E-04	512	T2/T3
S6	3.2775	0.47550E-02	378	T6	3.2326	E6	2.4233 0.3266E-04	512	T2/T3
S7	3.5311	0.20682E-01	351	T7	3.2606	**E7**	**2.4498 0.8623E-02**	**506**	**27%S2/19%T3/19%T2**
S8	3.6213	0.51886E-01	342	T8	3.4375	**E8**	**2.7229 0.7710E-02**	**455**	**25%S1/20%T3/20%T2**
S9	3.6296	0.22081E-01	342	T9	3.4515	E9	2.7537 0.1786E-04	450	T3/T2
S10	3.7594	0.10237E-01	330	T10	3.5614	**E10**	**2.7741 0.4086E-02**	**447**	**42%T3/14%S1/25%T2**
S11	3.8596	0.78062E-02	321			**E11**	**2.7922 0.1386E-01**	**444**	**52%S2/16%T2/12%T3**
S12	3.8972	0.39701E-02	318			E12	2.9322 0.3128E-03	423	T4
S13	4.0454	0.45502E-03	306			E13	2.9325 0.3494E-03	423	T4/T5
S14	4.0539	0.20729E-02	306			E14	2.9407 0.6659E-02	422	T4/S5/S4
						E15	**2.9483 0.1377E-01**	**421**	**S4/T5**
						E16	**3.0299 0.3930E-01**	**409**	**S3/S4**

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Singlet (at FC)				Triplet (at FC)		« Spin-Orbit » states			
no.	E/eV	f	nm	no.	E/eV	no.	Energy (eV)	f	nm
S1	**2.5894**	**0.26224E-01**	**479**	**T1**	**2.2166**	E1	2.1972 0.4195E-04	564	T1
S2	**2.7264**	**0.29413E-01**	**455**	**T2**	**2.6093**	E2	2.1974 0.1202E-03	564	T1 LC_{NHC}
S3	**2.9681**	**0.37766E-01**	**418**	**T3**	**2.6613**	E3	2.1989 0.7175E-03	564	T1
S4	**3.1122**	**0.25374E-01**	**398**	**T4**	**2.9765**	**E4**	**2.3958 0.1407E-01**	**518**	**48%S1/17%T2/15%T3**
S5	3.2456	0.43302E-02	382	T5	3.1802	E5	2.4129 0.3895E-04	514	T2/T3
S6	3.2868	0.64097E-02	377	T6	3.2178	E6	2.4132 0.9752E-04	514	T2/T3
S7	3.4674	0.24554E-01	358	T7	3.2428	**E7**	**2.4404 0.1087E-01**	**508**	**31%S2/29%T2/14%T3**
S8	3.5846	0.26824E-01	346	T8	3.3958	**E8**	**2.7025 0.1264E-01**	**459**	**31%S1/44%T3**
S9	3.6152	0.51525E-01	343	T9	3.4155	E9	2.7453 0.1730E-04	452	T3/T2
S10	3.7397	0.12793E-01	332	T10	3.5260	E10	2.7618 0.5041E-02	449	T3/T2
S11	3.8063	0.72114E-02	326			**E11**	**2.7825 0.1484E-01**	**446**	**50%S2/16%T2**
S12	3.8671	0.86229E-02	321			E12	2.9121 0.4719E-03	426	T4
S13	3.9675	0.21218E-01	313			E13	2.9137 0.8947E-03	426	T4
S14	4.0017	0.14943E-01	310			E14	2.9196 0.5006E-02	425	T4/S5
S15	4.0276	0.62828E-01	308			E15	2.9371 0.2062E-01	422	S3/S4
S16	4.0855	0.10514	304			E16	2.9622 0.2077E-01	419	S4/S3

Table S3. Reduced rotatory strengths R (in 10^{-40} esu·cm·erg/G), magnetic transition dipole *x*, *y*, *z* components (in a.u.) and associated singlet excited states computed for A_{Re} enantiomers of compounds **1Cl**, **1Br**, **1I**, **2-6Br**, **2-6I** in toluene.

Compound		R [10^{-40} esu·cm·erg/G]	m_x	m_y	m_z	State character
	S1	-27.214	0.23909E-03	0.92552E-02	-0.55842	MLCT/XLCT/LC
(A_{Re})-2Br	S2	5.8439	0.14827	0.16157E-01	0.24256E-01	XLCT/MLCT/LC
	S3	-11.214	-0.93033E-01	0.19787	0.39595	LC/XLCT
	S1	-13.508	0.26795E-01	-0.40650E-02	0.38887	XLCT/MLCT
(A_{Re})-2I	S2	-7.2975	-0.71211E-01	0.52285E-01	-0.14500E-01	XLCT
	S3	**-48.235**	**-0.12898E-01**	**0.11697**	**0.5891**	**LC/**XLCT
	S1	-24.246	-0.72515E-01	-0.62280E-01	0.52119	MLCT/XLCT
(A_{Re})-4Br	S2	4.3188	-0.14919	-0.55053E-02	-0.66724E-01	XLC T/MLCT
	S3	-12.062	-0.17127	0.13728	0.33013	LC/MLCT/XLCT
	S1	-9.7919	0.24633E-02	0.40937E-01	-0.34507	XLCT
(A_{Re})-4I	S2	-5.5389	-0.80131E-01	0.48016E-01	-0.26942E-01	XLCT
	S3	**-57.311**	**-0.63313E-01**	**0.10903**	**0.65304**	**LC/**XLCT
	S1	**-32.220**	**0.30033E-01**	**0.28022E-01**	**-0.62238**	**MLCT/XLCT/LC**
(A_{Re})-3Br	S2	6.7995	0.13802	0.67069E-01	0.14979	XLCT/MLCT/LC
	S3	-13.161	0.23341E-01	-0.14938	-0.43144	LC/XLCT
	S1	-16.575	0.14587E-02	-0.63192E-01	0.41348	XLCT/MLCT
(A_{Re})-3I	S2	-4.9473	-0.69111E-01	0.69618E-02	-0.12743	XLCT
	S3	**-60.205**	**-0.40834E-02**	**0.12091**	**0.72458**	**LC/**XLCT
	S1	**-49.504**	**0.72997E-01**	**0.30163E-01**	**0.64075**	**MLCT/LC/XLCT**
(A_{Re})-6Br	S2	-6.8419	0.92757E-02	0.96773E-01	0.28537	XLCT/MLCT
	S3	-10.792	-0.20123E-01	-0.20588E-01	0.30590	LC/MLCT/XLCT
	S1	**-35.592**	**0.75243E-01**	**-0.36832E-01**	**0.46106**	**XLCT/MLCT/LC**
(A_{Re})-6I	S2	-18.856	0.38951E-01	-0.20574E-01	-0.32426	XLC T/MLCT
	S3	-28.858	0.11921	0.13981	0.57613	LC/XLC T
	S1	**-38.070**	**0.41413E-01**	**-0.51204E-01**	**0.53347**	**MLCT/XLCT/LC**
(A_{Re})-5Br	S2	0.0165	0.34158E-01	0.96667E-01	0.21003	XLCT/MLCT/LC
	S3	-1.2786	0.27632E-01	-0.54504E-01	--0.34044	MLCT/LC/XLCT
	S1	-18.556	0.42132E-01	-0.54003E-01	0.34653	XLCT/MLCT
(A_{Re})-5I	S2	-7.3229	-0.14159E-01	0.29005E-01	0.15810	XLCT
	S3	**-31.732**	**0.85297E-01**	**0.16197**	**0.54946**	**LC/**XLCT
	S1	-22.10	0.39572-01	-.83508-04	-.55656	MLCT/LLCT/XLCT
(A_{Re})-1Cl	S2	11.58	-.14537	-.16592-01	.35022-02	MLCT/LLCT/XLCT
	S3	1.7081	-.49069-01	.10619	.37424	MLCT/LC/LLCT
	S1	-23.710	-0.19345E-02	0.31654E-01	-0.49701	MLCT/XLCT
(A_{Re})-1Br	S2	4.9509	-0.16679	0.62757E-02	-0.12887E-01	XLCT/MLCT
	S3	-2.7830	-0.32392E-01	0.82010E-01	0.96020E-01	LC/XLCT/MLCT
	S1	-10.063	-0.28080E-01	0.25982E-01	-0.32881	XLCT/MLCT
(A_{Re})-1I	S2	-6.3573	-0.73000E-01	0.53333E-01	-0.19423E-01	XLCT
	S3	**-48.222**	**0.99895E-02**	**0.11753**	**0.56242**	**LC/**XLCT

Table S4. Transition energies (E in eV), absorption wavelengths (λ in nm) and oscillator strengths (f) associated to the low-lying singlet, triplet and "spin-orbit" states of the Re(I) complexes **1-6Br** in acetone.

1Br											
Scalar Singlet States				Scalar triplet States			Spin-Orbit States				
State	E	λ	f	State	E	λ	State	E	λ	f	Nature
S1	2.938	422	1.27E-01	T1	2.358	526	E1	2.355	527	1.13E-05	99% T1
S2	3.280	378	8.42E-02	T2	3.021	410	E2	2.355	527	2.82E-05	99% T1
S3	3.539	350	2.07E-02	T3	3.136	395	E3	2.355	526	1.54E-04	99% T1
S4	3.559	348	6.46E-02	T4	3.385	366	E4	2.893	429	1.05E-02	83% S1 12% T3
S5	3.612	343	3.60E-03	T5	3.524	352	E5	2.962	419	1.73E-04	71% T2 21% T3
S6	3.827	324	6.68E-02	T6	3.616	343	E6	2.965	418	7.93E-04	71% T2 22% T3
S7	3.975	312	1.72E-02	T7	3.725	333	E7	2.986	415	8.12E-03	83% T2 7% S2
S8	4.025	308	2.31E-02	T8	3.824	324	E8	3.132	396	1.97E-02	79% T3 14% S1
S9	4.175	297	4.37E-02	T9	3.870	320	E9	3.142	395	1.60E-04	66% T3 24% T2 5% T4
S10	4.201	295	3.48E-02	T10	3.912	317	E10	3.142	395	4.53E-04	65% T3 25% T2 6% T4

2Br											
Scalar Singlet States				Scalar triplet States			Spin-Orbit States				
State	E	λ	f	State	E	λ	State	E	λ	f	Nature
S1	2.844	436	1.37E-01	T1	2.258	549	E1	2.255	550	1.17E-05	99% T1
S2	3.281	378	8.04E-02	T2	2.958	419	E2	2.255	550	1.25E-05	99% T1
S3	3.488	355	6.14E-02	T3	3.127	397	E3	2.255	550	9.45E-05	99% T1
S4	3.516	353	1.64E-02	T4	3.344	371	E4	2.818	440	1.26E-01	92% S1 5% T3
S5	3.597	345	1.39E-04	T5	3.517	353	E5	2.922	424	1.25E-04	83% T2 13% T3
S6	3.742	331	9.61E-02	T6	3.533	351	E6	2.924	424	1.98E-04	84% T2 12% T3
S7	3.950	314	2.61E-02	T7	3.727	333	E7	2.935	422	3.40E-03	93% T2
S8	4.026	308	1.01E-02	T8	3.797	327	E8	3.100	400	7.22E-04	71% T3 14% T2 9% T4
S9	4.156	298	3.41E-02	T9	3.882	319	E9	3.102	400	1.90E-03	73% T3 12% T2 10% T4
S10	4.224	294	2.72E-02	T10	3.920	316	E10	3.102	400	8.22E-03	83% T3 5% S1

3Br											
Scalar Singlet States				Scalar triplet States			Spin-Orbit States				
State	E	λ	f	State	E	λ	State	E	λ	f	Nature
S1	2.958	419	1.27E-01	T1	2.373	522	E1	2.370	523	1.35E-05	99% T1
S2	3.326	373	7.07E-02	T2	3.017	411	E2	2.370	523	1.62E-05	99% T1
S3	3.598	345	7.45E-02	T3	3.190	389	E3	2.370	523	1.16E-04	99% T1
S4	3.602	344	4.64E-02	T4	3.421	362	E4	2.918	425	1.10E-01	86% S1 9% T3
S5	3.627	342	3.15E-03	T5	3.550	349	E5	2.973	417	3.82E-04	81% T2 13% T3
S6	3.893	318	4.92E-02	T6	3.631	341	E6	2.975	417	3.27E-04	83% T2 13% T3
S7	4.030	308	3.06E-03	T7	3.749	331	E7	2.987	415	5.29E-03	90% T2 5% S2
S8	4.147	299	4.97E-02	T8	3.827	324	E8	3.176	390	4.89E-04	72% T3 15% T2 8% T4
S9	4.243	292	1.01E-01	T9	3.895	318	E9	3.177	390	1.58E-03	74% T3 13% T2 7% T4
S10	4.281	290	3.30E-01	T10	3.961	313	E10	3.178	390	1.41E-02	81% T3 9% S1

4Br		
Scalar Singlet States	Scalar triplet States	Spin-Orbit States

State	E	λ	f	State	E	λ	State	E	λ	f	Nature
S1	2.994	414	1.43E-01	T1	2.379	521	E1	2.375	522	1.26E-05	99% T1
S2	3.321	373	8.66E-02	T2	3.058	405	E2	2.375	522	2.74E-05	99% T1
S3	3.595	345	2.75E-02	T3	3.172	391	E3	2.376	522	1.43E-04	99% T1
S4	3.603	344	5.99E-02	T4	3.426	362	E4	2.946	421	1.15E-01	80% S1 14% T3
S5	3.656	339	3.04E-03	T5	3.561	348	E5	2.999	413	3.18E-04	72% T2 22% T3
S6	3.846	322	5.48E-02	T6	3.681	337	E6	3.002	413	9.79E-04	73% T2 22% T3
S7	4.004	310	1.87E-02	T7	3.740	331	E7	3.022	410	8.66E-03	85% T2 8% S2
S8	4.045	307	2.46E-02	T8	3.845	322	E8	3.173	391	2.42E-02	78% T3 16% S1
S9	4.199	295	4.64E-02	T9	3.868	321	E9	3.179	390	3.40E-04	66% T3 25% T2 6% T4
S10	4.243	292	3.51E-02	T10	3.932	315	E10	3.179	390	9.67E-04	66% T3 24% T2 6% T4

5Br											
Scalar Singlet States				Scalar triplet States			Spin-Orbit States				
State	E	λ	f	State	E	λ	State	E	λ	f	Nature
S1	2.922	424	1.24E-01	T1	2.359	526	E1	2.356	526	1.56E-05	99% T1
S2	3.299	376	5.61E-02	T2	3.015	411	E2	2.356	526	2.59E-05	99% T1
S3	3.425	362	6.69E-02	T3	3.183	390	E3	2.356	526	9.99E-05	99% T1
S4	3.525	352	1.72E-02	T4	3.391	366	E4	2.886	430	1.09E-01	88% S1 7% T3
S5	3.594	345	2.36E-03	T5	3.447	360	E5	2.969	418	1.15E-04	80% T2 13% T3
S6	3.739	332	1.12E-01	T6	3.454	359	E6	2.972	417	5.43E-04	81% T2 13% T3
S7	3.878	320	1.18E-02	T7	3.623	342	E7	2.983	416	4.04E-03	90% T2 6% S2
S8	4.003	310	7.14E-03	T8	3.687	336	E8	3.168	391	1.23E-02	81% T3 10% S1
S9	4.097	303	2.78E-01	T9	3.772	329	E9	3.169	391	5.06E-05	68% T3 17% T2 6% T4
S10	4.117	301	8.22E-02	T10	3.839	323	E10	3.170	391	5.53E-04	71% T3 16% T2 6% T4

6Br											
Scalar Singlet States				Scalar triplet States			Spin-Orbit States				
State	E	λ	f	State	E	λ	State	E	λ	f	Nature
S1	2.813	441	1.10E-01	T1	2.813	441	E1	2.272	546	2.51E-05	99% T1
S2	3.290	377	1.53E-02	T2	3.290	377	E2	2.272	546	1.17E-05	99% T1
S3	3.317	374	1.16E-01	T3	3.317	374	E3	2.272	546	6.69E-05	99% T1
S4	3.521	352	1.53E-02	T4	3.521	352	E4	2.792	444	1.04E-01	95% S1
S5	3.578	347	1.95E-02	T5	3.578	347	E5	2.913	426	4.95E-05	91% T2 6% T3
S6	3.622	342	1.31E-01	T6	3.622	342	E6	2.914	425	2.62E-04	91% T2 5% T3
S7	3.842	323	1.81E-02	T7	3.842	323	E7	2.918	425	1.74E-03	95% T2
S8	3.862	321	1.89E-02	T8	3.862	321	E8	3.138	395	5.65E-05	74% T3 11% T5 6% T2
S9	4.063	305	2.48E-02	T9	4.063	305	E9	3.141	395	1.00E-03	75% T3 11% T5 7% T2
S10	4.070	305	3.53E-01	T10	4.070	305	E10	3.146	394	5.63E-03	84% T3

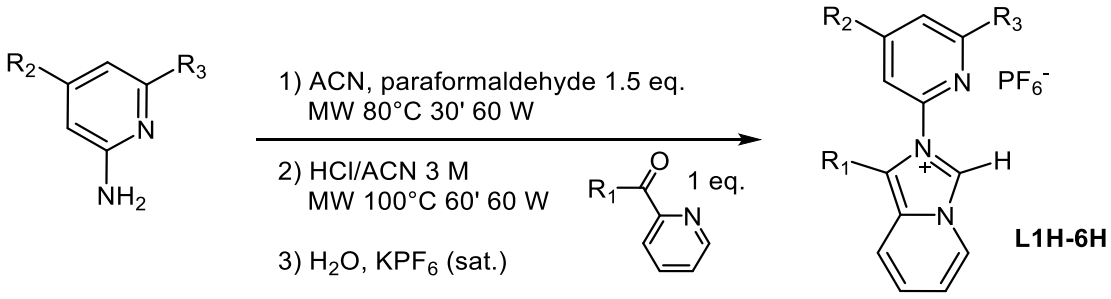
Table S5. Reduced rotatory strengths R (in 10^{-40} esu·cm·erg/G), magnetic transition dipole *x*, *y*, *z* components (in a.u.) and associated singlet excited states computed for A_{Re} enantiomers of compounds **1-6Br** in acetone.

Compound		R [10^{-40} esu·cm·erg/G]	m_x	m_y	m_z	State character
	S1	-29.9	4.45E-02	-2.44E-01	6.45E-01	LC/MLCT
(A_{Re})-1Br	S2	23.5	-2.59E-01	-5.79E-02	1.47E-01	MLCT/XLCT/LLCT
	S3	-8.4	1.20E-01	-1.16E-01	2.46E-01	LC/MLCT/XLCT
	S1	-57.6	9.91E-03	2.19E-01	-7.08E-01	LC/MLCT
(A_{Re})-2Br	S2	31.5	2.57E-01	1.74E-02	-1.49E-01	MLCT/XLCT/LLCT
	S3	5.2	-1.75E-02	6.29E-02	-5.73E-01	LC
	S1	-73.6	-4.98E-02	2.76E-01	-7.52E-01	LC/MLCT/LLCT
(A_{Re})-3Br	S2	36.1	2.42E-01	1.17E-01	-5.56E-02	MLCT/XLCT/LLCT
	S3	14.8	1.69E-02	-2.26E-02	4.79E-01	LC/XLCT/MLCT
	S1	-63.1	1.42E-01	-2.67E-01	6.91E-01	LC/MLCT/LLCT
(A_{Re})-4Br	S2	33.3	-2.27E-01	-1.97E-01	8.53E-02	MLCT/XLCT/LLCT
	S3	-2.9	9.49E-02	-3.61E-02	3.15E-01	LC/MLCT/LLCT
	S1	-72.1	1.34E-01	-2.18E-01	7.01E-01	LC/MLCT/LLCT
(A_{Re})-5Br	S2	22.3	-1.32E-01	-1.48E-01	-9.22E-02	MLCT/XLCT/LLCT
	S3	-16.7	9.68E-02	-6.06E-02	8.01E-01	LC/MLCT/LLCT
	S1	-63.8	-1.57E-01	1.76E-01	-7.20E-01	LC/LLCT/MLCT
(A_{Re})-6Br	S2	4.6	-1.55E-02	1.71E-01	-2.75E-01	LC/MLCT/LLCT
	S3	-22.0	1.49E-01	-2.46E-02	6.77E-01	LC/MLCT/LLCT

Table S6. Transition energies (E_{abs} in [eV]) and character at Franck-Condon (FC), emission wavelengths (E_{em} in [eV] and λ_{em} [nm]), character at the triplet optimized structure of the lowest triplet states of complexes **1Cl**, **1Br**, **1I**, **2Br**, **3Br**, **4Br**, **5Br**, **6Br** as A_{Re} enantiomers computed in acetone.

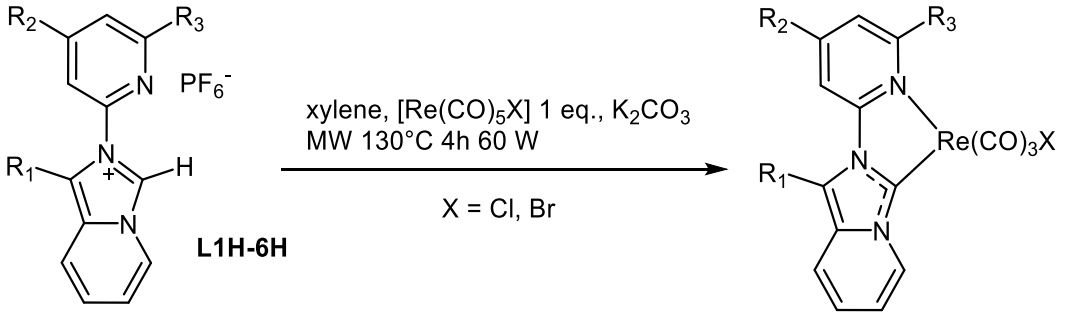
	1Cl	**1Br**	**1I**	**2Br**	**3Br**	**4Br**	**5Br**	**6Br**
E_{abs}	2.365	2.358	2.348	2.258	2.373	2.379	2.359	2.274
Character	LC	LC	LC	LC	LC	LC	LC	LC
E_{em}	1.731	1.730	1.724	1.640	1.743	1.746	1.725	1.642
λ_{em}	716	716	719	756	711	710	719	755
Character	LC	LC	LC	LC	LC	LC	LC	LC

Supplementary Data: synthetic protocols



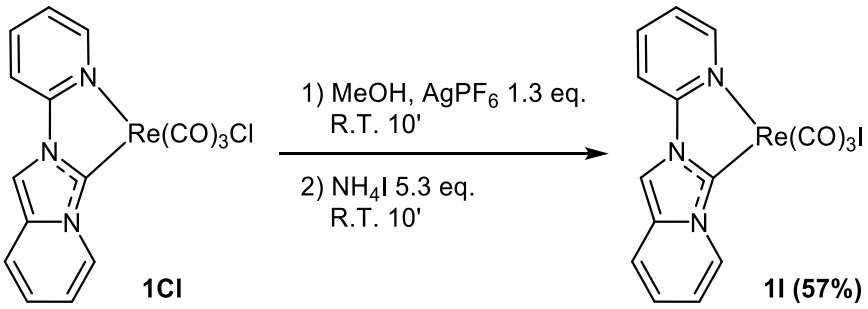
L1H	**(91%)**	R_1 = H	R_2 = H	R_3 = H
L2H	**(68%)**	R_1 = CH_3	R_2 = H	R_3 = H
L3H	**(75%)**	R_1 = H	R_2 = H	R_3 = CH_3
L4H	**(81%)**	R_1 = H	R_2 = CH_3	R_3 = H
L5H	**(81%)**	R_1 = H	R_2 = H	R_3 = C_6H_5
L6H	**(65%)**	R_1 = CH_3	R_2 = H	R_3 = C_6H_5

Scheme S1. Schematic synthetic pathway employed for the preparation of pro-carbenic ligands **L1H**–**L6H**.



1Cl	**(74%)**	**3Br**	**(71%)**
1Br	**(68%)**	**4Br**	**(97%)**
2Br	**(82%)**	**5Br**	**(30%)**
		6Br	**(37%)**

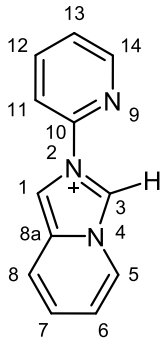
Scheme S2. Schematic synthetic pathway employed for the preparation of *fac*-[Re(**L1**–**L6**)$(CO)_3$X] complexes.



Scheme S3. Schematic synthetic pathway employed for the preparation of *fac*-[Re(**L1**)$(CO)_3$I] complex (**1I**).

Synthesis of ligands L1H-L6H

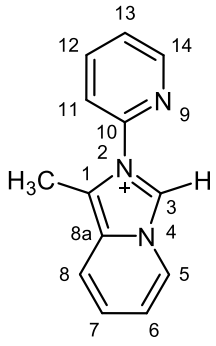
2-(pyridin-2-yl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate (L1H)



To a 30 mm glass microwave vial were added 2-aminopyridine (1.00 g, 10.68 mmol, 1.0 eq.), paraformaldehyde (478.1 mg, 15.92 mmol, 1.5 eq.) and acetonitrile 8 mL. The suspension was kept under stirring and heated at 80˚C under microwave irradiation (60 W) for 30 minutes. To the resulting yellow solution were added picolinaldehyde (1025 µL, 10.62 mmol, 1.0 eq.) and 5 mL of a 3M HCl solution in acetonitrile (2.5 mL HCl 37% in 10 mL acetonitrile). The mixture was kept under stirring and heated at 100˚C microwave irradiation (60 W) for 60 minutes. The resulting biphasic system was transferred in a round bottom flask with the aid of MeOH and evaporated to dryness under reduced pressure. The residue was dissolved in 20 mL of water and a 5 mL of a saturated aqueous solution of KPF_6 were added dropwise under heavy stirring. The ligand precipitated as KPF_6^- salt and was collected on a G4 glass frit and washed with acetone (5 mL), Et_2O:acetone 2:3 (20 mL) and E_2O (5 mL). Pure ligand **L1H** was obtained as an off-white crystalline powder (3.30 g, 9.68 mmol, yield 91%).

^{1}H NMR (500 MHz, 298 K, DMSO-d_6) δ: 10.53 (1H, d, $J^4_{H3\text{-}H1}$ 1.1, H^3), 8.94 (1H, s, H^1), 8.72 (1H, dd, J_o 4.8, J_m 1.4, H^{14}), 8.58 (1H, dd, J_o 7.0, J_m 1.0, H^8), 8.26 (1H, ddd, J_o 8.7, J_o 7.5, J_m 1.4, H^{12}), 8.17 (1H, d, J_o 8.7, H^{11}), 7.90 (1H, dd, J_o 9.3, J_m 1.1, H^5), 7.70 (1H, ddd, J_o 7.5, J_o 4.8, J_m 0.9, H^{13}), 7.33 (1H, ddd, J_o 9.3, J_o 6.7, J_m 1.0, H^6), 7.26 (1H, td, J_o 7.0, J_o 6.7, J_m 1.1, H^7). **^{1}H NMR** (500 MHz, 298 K, acetone-d_6) δ: 10.39 (1H, d, $J^4_{H3\text{-}H1}$ 1.1, H^3), 8.91 (1H, s, H^1), 8.74 (1H, ddd, J_o 4.8, J_m 1.8, J_p 0.9, H^{14}), 8.70 (1H, dd, J_o 7.0, J_m 1.0, H^8), 8.29 (1H, ddd, J_o 8.2, J_o 7.5, J_m 1.8, H^{12}), 8.17 (1H, dt, J_o 8.2, J_m 0.9, H^{11}), 7.99 (1H, dd, J_o 9.3, J_m 1.2, H^5), 7.75 (1H, ddd, J_o 7.5, J_o 4.8, J_m 0.9, H^{13}), 7.44 (1H, ddd, J_o 9.3, J_o 6.8, J_m 1.0, H^6), 7.36 (1H, td, J_o 7.0, J_o 6.8, J_m 1.2, H^7). **^{13}C NMR** APT (125.7 MHz, 298 K, DMSO-d_6) δ: 149.98 (C^{14}), 146.97 (C^{10}), 141.25 (C^{12}), 130.57 (C^{8a}), 126.42 (C^{13}), 125.87 (C^6), 125.40 (C^3), 124.83 (C^8), 119.06, 119.03 ($C^{5,7}$), 115.52 (C^{11}), 110.43 (C^1). **^{13}C NMR** APT (125.7 MHz, 298 K, acetone-d_6) δ: 150.59 (C^{14}), 147.67 (C^{10}), 141.62 (C^{12}), 131.89 (C^{8a}), 126.97 (C^{13}), 126.56 (C^6), 125.20 ($C^{3,8}$), 119.90, 119.54 ($C^{5,7}$), 115.78 (C^{11}), 111.02 (C^1).

1-methyl-2-(pyridin-2-yl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate (L2H)

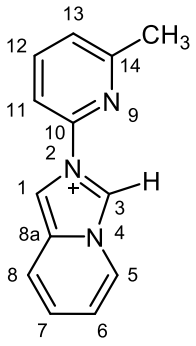


To a 30 mm glass microwave vial were added 2-aminopyridine (1.20 g, 12.76 mmol, 1.0 eq.), paraformaldehyde (553.4 mg, 18.42 mmol, 1.4 eq.) and acetonitrile 3 mL. The suspension was kept under stirring and heated at 80˚C under microwave irradiation (60 W) for 30 minutes. To the resulting yellow solution were added acetylpyridine (1440 µL, 12.75 mmol, 1.0 eq.) and 5 mL of a 3M HCl solution in acetonitrile (2.5 mL HCl 37% in 10 mL acetonitrile). The mixture was kept under stirring and heated at 100˚C microwave irradiation (60 W) for 60 minutes. The resulting red solution was transferred in a round bottom flask with the aid of MeOH and evaporated to dryness under reduced pressure. The residue was dissolved in 20 mL of water and 5 mL of a saturated aqueous solution of KPF_6 were added dropwise under heavy stirring. The ligand precipitated as KPF_6^- salt and was collected on a G4 glass frit and washed with water (3x5 mL) and E_2O (2x10 mL). Pure ligand **L2H** was obtained as an off-white crystalline powder (3.09 g, 8.70 mmol, yield 68%).

^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ: 10.16 (1H, s, H^3), 8.79 (1H, ddd, J_o 4.9, J_m 1.9, J_p 0.8, H^{14}), 8.52 (1H, d, J_o 6.7, H^8), 8.26 (1H, td, J_o 7.9, J_o 7.8, J_m 1.9, H^{12}), 8.03 (1H, d, J_o 8.5, H^{11}), 7.96 (1H, dt, J_o 8.1, J_m 0.9, J_p 0.9, H^5), 7.79 (1H, ddd, J_o 7.6, J_o 4.9, J_m 1.0, H^{13}), 7.31-7.19 (2H, m, $H^{6,7}$), 2.71 (3H, s, $CH_3{}^1$). **^{13}C NMR** APT (101 MHz, 298 K, DMSO-d_6) δ: 149.88 (C^{14}), 146.83 (C^{10}), 140.53 (C^{12}), 126.92 (C^{8a}), 126.20 (C^{13}), 125.95 (C^3), 123.86, 123.57 ($C^{6,8}$), 121.43 (C^1),

120.33 (C^5), 118.61 (C^7), 118.29 (C^{11}), 9.28 ($CH_3{}^1$). ESI-MS calcd for $C_{13}H_{12}N_3$: 210.1026. Found: 210.1035.

2-(6-methylpyridin-2-yl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate (L3H)



To a 30 mm glass microwave vial were added 6-methyl-2-aminopyridine (2.01 g, 18.58 mmol, 1.0 eq.), paraformaldehyde (1.001 g, 33.36 mmol, 1.8 eq.) and acetonitrile 7 mL. The suspension was kept under stirring and heated at 80˚C under microwave irradiation (60 W) for 30 minutes. To the resulting yellow solution were added picolinaldehyde (1933 µL, 18.57 mmol, 1.0 eq.) and 7 mL of a 3M HCl solution in acetonitrile (2.5 mL HCl 37% in 10 mL acetonitrile). The mixture was kept under stirring and heated at 100˚C microwave irradiation (60 W) for 60 minutes. The resulting brown solution was transferred in a round bottom flask with the aid of MeOH and evaporated to dryness under reduced pressure. The residue was dissolved in 20 mL of water and 5 mL of a saturated aqueous solution of KPF_6 were added dropwise under heavy stirring. The ligand precipitated as KPF_6^- salt and was collected on a G4 glass frit and washed with water (2x10 mL) and E_2O (15 mL). Pure ligand **L3H** was obtained as a white crystalline powder (4.92 g, 13.8 mmol, yield 75%).

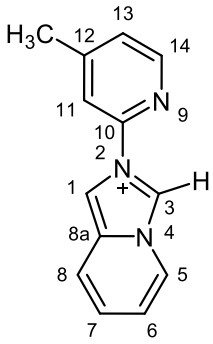
^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ: 10.53 (1H, d, $J^4_{H3\text{-}H1}$ 1.1, H^3), 8.97 (1H, s, H^1), 8.60 (1H, dd, J_o 7.0, J_m 1.0, H^8), 8.16 (1H, t, J_o 8.0, J_o 7.8, H^{12}), 8.01 (1H, d, J_o 8.0, H^{11}), 7.92 (1H, d, J_o 9.3, H^5), 7.59 (1H, d, J_o 7.8, H^{13}), 7.34 (1H, ddd, J_o 9.3, J_o 6.8, J_m 1.0, H^6), 7.27 (1H, td, J_o 7.0, J_o 6.8, J_m 1.2, H^7), 2.63 (1H, s, $CH_3{}^{14}$).

^{13}C NMR APT (101 MHz, 298 K, DMSO-d_6) δ: 158.89 (C^{14}), 145.86 (C^{10}), 140.89 (C^{12}), 130.06 (C^{8a}), 125.39, 125.37 ($C^{6,13}$), 124.92 (C^3), 124.46 (C^8), 118.59, 118.52 ($C^{5,7}$), 111.92 (C^{11}), 109.96 (C^1), 23.71 ($CH_3{}^{14}$).

ESI-MS calcd for $C_{13}H_{12}N_3$: 210.1026. Found: 210.1032.

Found: N, 12.04; C, 43.60; H, 3.40. Calc. for $C_{13}H_{12}N_3PF_6$: N, 11.83; C, 43.96; H, 3.41%.

2-(4-methylpyridin-2-yl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate (L4H)



To a 30 mm glass microwave vial were added 4-methyl-2-aminopyridine (2.02 g, 18.68 mmol, 1.0 eq.), paraformaldehyde (1.009 g, 33.59 mmol, 1.8 eq.) and acetonitrile 5 mL. The suspension was kept under stirring and heated at 80˚C under microwave irradiation (60 W) for 30 minutes. To the resulting yellow solution were added picolinaldehyde (1945 µL, 18.68 mmol, 1.0 eq.) and 7 mL of a 3M HCl solution in acetonitrile (2.5 mL HCl 37% in 10 mL acetonitrile). The mixture was kept under stirring and heated at 100˚C under microwave irradiation (60 W) for 60 minutes. The resulting brown solution was transferred in a round bottom flask with the aid of MeOH and evaporated to dryness under reduced pressure. The residue was dissolved in 20 mL of water and 5 mL of a saturated aqueous solution of KPF_6 were added dropwise under heavy stirring. The ligand precipitated as KPF_6^- salt and was collected on a G4 glass frit and washed with water (3x5 mL) and E_2O (2x10 mL). Pure ligand **L4H** was obtained as an off-white crystalline powder (5.36 g, 15.0 mmol, yield 81%).

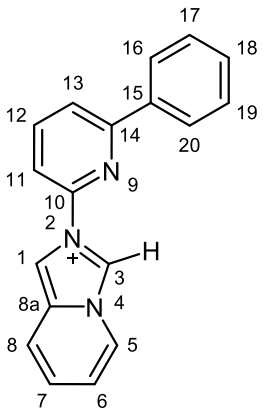
^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ: 10.55 (1H, d, $J^4_{H3\text{-}H1}$ 1.1, H^3), 8.97 (1H, s, H^1), 8.63-8.54 (2H, m, $H^{8,14}$), 8.11 (1H, s, H^{11}), 7.93 (1H, dd, J_o 9.3, J_m 1.1, H^5), 7.57 (1H, d, J_o 5.3, H^{13}), 7.34 (1H, ddd, J_o 9.3, J_o 6.8, J_m 1.1, H^6), 7.27 (1H, td, J_o 6.9, J_o 6.8, J_m 1.1, H^7), 2.53 (1H, s, $CH_3{}^{12}$).

^{13}C NMR APT (101 MHz, 298 K, DMSO-d_6) δ: 152.29 (C^{12}), 149.08 (C^{14}), 146.68 (C^{10}), 130.07 (C^{8a}), 126.65 (C^{13}), 125.41 (C^6), 125.03 (C^3), 124.46 (C^8), 118.61, 118.57 ($C^{5,7}$), 115.49 (C^{11}), 109.93 (C^1), 20.77 ($CH_3{}^{12}$).

ESI-MS calcd for $C_{13}H_{12}N_3$: 210.1026. Found: 210.1035.

Found: N, 12.08; C, 43.51; H, 3.41. Calc. for $C_{13}H_{12}N_3PF_6$: N, 11.83; C, 43.96; H, 3.41%.

2-(6-phenylpyridin-2-yl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate (L5H)



To a 30 mm glass microwave vial were added 6-phenyl-2-aminopyridine (304.5 mg, 1.79 mmol, 1.0 eq.), paraformaldehyde (82.8 mg, 2.76 mmol, 1.5 eq.) and acetonitrile 2 mL. The suspension was kept under stirring and heated at 80˚C under microwave irradiation (60 W) for 30 minutes. To the resulting yellow solution were added picolinaldehyde (172 µL, 1.79 mmol, 1.0 eq.) and 1.5 mL of a 3M HCl solution in acetonitrile (2.5 mL HCl 37% in 10 mL acetonitrile). The mixture was kept under stirring and heated at 100˚C under microwave irradiation (60 W) for 60 minutes. The resulting brown solution was transferred in a round bottom flask with the aid of MeOH and evaporated to dryness under reduced pressure. The residue was dissolved in 10 mL of water and 3 mL of a saturated aqueous solution of KPF_6 were added dropwise under heavy stirring. The ligand precipitated as KPF_6^- salt and was collected on a G4 glass frit and washed with MeOH (2 mL) and E_2O:MeOH 9:1 (10 mL). Three crops were recovered, and pure ligand **L5H** was obtained as an ochra crystalline powder (603.5 mg, 1.45 mmol, yield 81%).

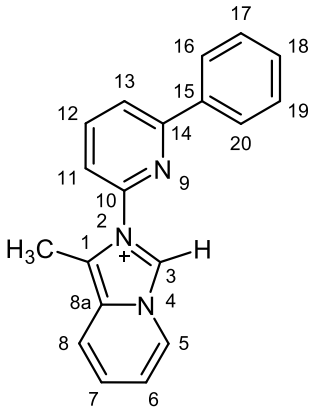
^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ: 10.74 (1H, d, $J^4_{H3\text{-}H1}$ 1.1, H^3), 9.13 (1H, s, H^1), 8.63 (1H, dd, J_o 7.0, J_m 1.1, H^8), 8.40-8.28 (4H, m, $H^{12,13,Ph}$), 8.17 (1H, dd, J_o 7.7, J_m 0.9, H^{11}), 7.95 (1H, dd, J_o 9.2, J_m 1.2, H^5), 7.65-7.52 (3H, m, H^{Ph}), 7.36 (1H, ddd, J_o 9.2, J_o 6.8, J_m 1.1, H^6), 7.30 (1H, td, J_o 7.0, J_o 6.8, J_m 1.2, H^7).

^{13}C NMR APT (101 MHz, 298 K, DMSO-d_6) δ: 155.99 (C^{14}), 146.34 (C^{10}), 141.92 (C^{12}), 136.41 (C^{15}), 130.43 (C^{Ph}), 130.14 (C^{8a}), 129.06 (C^{Ph}), 126.98 (C^{Ph}), 125.44 (C^6), 125.16 (C^3), 124.47 (C^8), 121.82 (C^{13}), 118.68 (C^5), 118.66 (C^7), 113.27 (C^{11}), 110.12 (C^1).

ESI-MS calcd for $C_{18}H_{14}N_3$: 272.1182. Found: 272.1185.

Found: N, 10.28; C, 51.57; H, 3.40. Calc. for $C_{18}H_{14}N_3PF_6$: N, 10.07; C, 51.81; H, 3.38%.

1-methyl-2-(6-phenylpyridin-2-yl)imidazo[1,5-a]pyridin-2-ium hexafluorophosphate (L6H)



To a 30 mm glass microwave vial were added 6-phenyl-2-aminopyridine (723.7 mg, 4.25 mmol, 1.0 eq.), paraformaldehyde (193.9 mg, 6.46 mmol, 1.5 eq.) and acetonitrile 4 mL. The suspension was kept under stirring and heated at 80˚C under microwave irradiation (60 W) for 30 minutes. To the resulting yellow solution were added acetylpyridine (480 µL, 4.25 mmol, 1.0 eq.) and 2 mL of a 3M HCl solution in acetonitrile (2.5 mL HCl 37% in 10 mL acetonitrile). The mixture was kept under stirring and heated at 100˚C under microwave irradiation (60 W) for 60 minutes. The resulting brown solution was transferred in a round bottom flask with the aid of MeOH and evaporated to dryness under reduced pressure. The residue was dissolved in 10 mL of water and 3 mL of a saturated aqueous solution of $NaPF_6$ were added dropwise under heavy stirring. The ligand precipitated as KPF_6^- salt and was collected on a G4 glass frit and washed with E_2O:acetonitrile 6:1 (10 mL). Two crops were recovered, and **L6H** was obtained as colourless needles (1.19 g, 2.75 mmol, yield 65%).

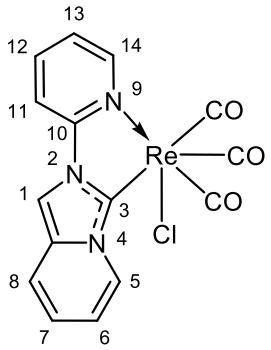
^{1}H NMR (500 MHz, 298 K, DMSO-d_6) δ: 10.29 (1H, s, H^3), 8.55 (1H, d, J_o 6.7, H^8), 8.37-8.34 (2H, m, $H^{12,11}$), 8.23-8.18 (2H, m, $H^{16,20}$), 8.06 (1H, d, J_o 8.0, H^5), 7.96-7.89 (1H, m, H^{13}), 7.60-7.52 (3H, m, $H^{17,18,19}$), 7.32-7.22 (2H, m, $H^{6,7}$), 2.82 (3H, s, $CH_3{}^1$).

^{13}C NMR APT (101 MHz, 298 K, DMSO-d_6) δ: 156.57 (C^{14}), 146.71 (C^{10}), 141.59 (C^{12}), 136.64 (C^{15}), 130.31, 129.11 ($C^{17,18,19}$), 127.03 (C^3), 126.94 ($C^{16,20}$), 126.03 (C^{8a}), 123.89 (C^6), 123.59 (C^8), 122.14 (C^{11}), 121.37 (C^1), 118.65(C^7), 118.36(C^{13}), 118.32 (C^5), 9.58 ($CH_3{}^1$).

ESI-MS calcd for $C_{19}H_{16}N_3$: 286.1339. Found: 286.1343.
Found: N, 9.94; C, 51.73; H, 3.65. Calc. for $C_{19}H_{16}N_3PF_6$: N, 9.74; C, 52.91; H, 3.74%.

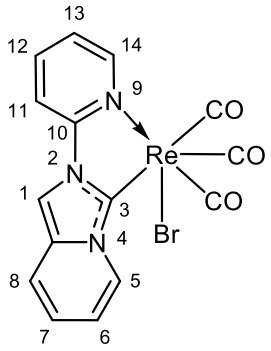
Synthesis of [*fac*-Re(L1–L6)(CO)$_3$X] complexes

Complex [Re^{I}(CO)$_3$(L1)Cl] (1Cl)



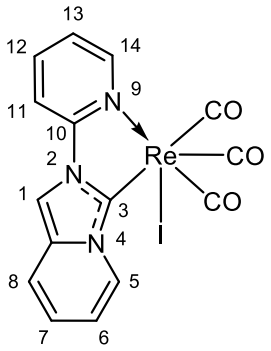
To a 30 mm glass microwave vial were added **L1H** (101.3 mg, 0.29 mmol, 1.0 eq.), $Re(CO)_5Cl$ (129.6 mg, 0.36 mmol, 1.2 eq.), K_2CO_3 (115 mg) and xylene 7 mL. The suspension was bubbled with Ar for 10 minutes, kept under stirring and heated at 130˚C under microwave irradiation (60 W) for 4 hours. The resulting brown xylene solution was decanted and discarded and the yellow precipitate washed with xylene (7 mL), Et_2O (2x7 mL) and pentane (4x7 mL). The yellow powder was dissolved in acetone (200 mL) and flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.1 g Al_2O_3 / 1 mg of complex). The resulting solution was quickly evaporated under reduced pressure and dried *in vacuo* overnight. Pure complex **1Cl** was obtained as a lemon-yellow powder (110.5 mg, 0.221 mmol, yield 74%).
^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 9.05 (1H, dt, J_o 5.5, J_m 1.2, H^{14}), 8.65 (1H, s, H^1), 8.42-8.39 (2H, m, H^{8,12}), 8.38 (1H, dd, J_o 7.3, J_m 1.2, H^{11}), 7.70-7.61 (1H, m, H^{13}), 7.63 (1H, d, J_o 9.6, H^5), 7.12 (1H, ddd, J_o 9.6, J_o 6.5, J_m 1.0, H^6), 7.02 (1H, ddd, J_o 7.5, J_o 6.5, J_m 1.2, H^7).
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 154.86 (C^{14}), 143.16 (C^{12}), 128.78 (C^{13}), 125.93 (C^6), 125.44 (C^8), 119.47 (C^5), 117.00 (C^7), 115.06 (C^{11}), 108.82 (C^1).
ESI-MS calcd for $C_{15}H_9ClN_3NaO_3Re$: 523.9773. Found for ([M+Na]$^+$): 523.9769.
FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2013s, 1889br (C≡O).

Complex [Re^{I}(CO)$_3$(L1)Br] (1Br)



To a 30 mm glass microwave vial were added **L1H** (106.9 mg, 0.31 mmol, 1.0 eq.), $Re(CO)_5Br$ (106.2 mg, 0.26 mmol, 1.2 eq.), K_2CO_3 (119 mg) and xylene 7 mL. The suspension was bubbled with Ar for 10 minutes, kept under stirring and heated at 130˚C under microwave irradiation (60 W) for 4 hours. The resulting brown xylene solution was decanted and discarded and the yellow precipitate washed with xylene (7 mL), Et_2O (2x5 mL) and pentane (4x7 mL). The yellow powder was dissolved in acetone (200 mL) and flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.1 g Al_2O_3 / 1 mg of complex). The resulting solution was quickly evaporated under reduced pressure and dried *in vacuo* overnight. Traces of ligand can be removed by washing the powder with Et_2O:*i*PrOH 9:1 (4x5 mL). Pure complex **1Br** was obtained as a yellow powder (97.5 mg, 0.179 mmol, yield 68%).
^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 9.06 (1H, ddd, J_o 5.6, J_m 1.6, J_p 1.0, H^{14}), 8.67 (1H, s, H^1), 8.44-8.37 (2H, m, H^{8,12}), 8.36 (1H, dq, J_o 7.3, J_m 1.1, J_p 1.0, H^{11}), 7.67-7.62 (2H, m, H^{13,5}), 7.12 (1H, ddd, J_o 9.3, J_o 6.5, J_m 1.0, H^6), 7.02 (1H, ddd, J_o 7.5, J_o 6.5, J_m 1.2, H^7).
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 154.90 (C^{14}), 142.95 (C^{12}), 133.26, 128.63 (C^{13}), 125.68 (C^6), 125.32 (C^8), 119.34 (C^5), 116.81 (C^7), 114.97 (C^{11}), 108.73 (C^1).
FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2013s, 1889br (C≡O).

Complex [Re^{I}(CO)$_3$(L1)I] (1I)



The ligand exchange was carried out on a fresh batch of complex **1Cl** prepared on a scale of 112.4 mg of $Re(CO)_5Cl$ (0.31 mmol, 1.0 eq.) and purified up until the flash filtration step. The crude yellow powder was transferred to a 2-neck 100 mL round bottom flask under inert atmosphere with the aid of MeOH (50 mL), and to the yellow suspension was added solid $AgPF_6$ (100.3 mg, 0.39 mmol, 1.3 eq.) and left to stir for 10 minutes in the dark. Next, a fresh solution of NH_4I (238.6 mg, 1.64 mmol, 5.3 eq.) in MeOH (3 mL) was added dropwise and left to stir for 10 minutes. The pale-yellow suspension was evaporated under reduced pressure, washed with water (100 mL), and the precipitate recovered by filtration on a Kieselguhr plug. The filter cake was washed with acetone (5x10 mL) and the cloudy yellow solution flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.01 g Al_2O_3 / 1 mg of complex). A total of 20 mL of acetone were necessary to fully discharge the complex from the plug. The yellow solution was evaporated under reduced pressure. Pure complex **1I** was obtained as a yellow powder (104.3 mg, 0.176 mmol, yield 57%).

^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 9.11 (1H, ddd, J_o 5.6, J_m 1.6, J_p 0.8, H^{14}), 8.69 (1H, s, H^1), 8.43 (1H, dt, J_o 7.3, J_m 1.1 H^8), 8.40-8.35 (1H, m, H^{12}), 8.32 (1H, dq, J_o 7.4, J_m 1.1, H^{11}), 7.67-7.60 (2H, m, H^{13,5}), 7.13 (1H, ddd, J_o 9.4, J_o 6.5, J_m 1.1, H^6), 7.03 (1H, ddd, J_o 7.3, J_o 6.5, J_m 1.2, H^7).

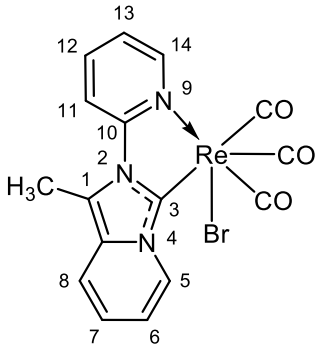
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 155.32 (C^{14}), 142.95 (C^{12}), 128.79 (C^{13}), 125.65 (C^6), 125.51 (C^8), 119.51 (C^5), 116.86 (C^7), 115.23 (C^{11}), 108.96 (C^1).

ESI-MS calcd for $C_{15}H_9N_3O_3Re$: 466.0196. Found for ([M-I]$^+$): 466.0216.

FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2012s, 1896br (C≡O).

Found: N, 6.68; C, 31.02; H, 1.63. Calc. for $ReIN_3C_{15}O_3H_9$: N, 7.09; C, 30.41; H, 1.53.

Complex [Re^{I}(CO)$_3$(L2)Br] (2Br)



To a 30 mm glass microwave vial were added **L2H** (97.0 mg, 0.27 mmol, 1.0 eq.), $Re(CO)_5Br$ (112.5 mg, 0.28 mmol, 1.2 eq.), K_2CO_3 (96 mg) and xylene 7 mL. The suspension was bubbled with Ar for 10 minutes, kept under stirring and heated at 130˚C under microwave irradiation (60 W) for 4 hours. The resulting orange xylene solution was decanted and discarded and the yellow precipitate washed with xylene (7 mL), Et_2O (2x5 mL) and pentane (7 mL). The yellow powder was dissolved in acetone (450 mL) and flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.1 g Al_2O_3 / 1 mg of complex). The resulting solution was quickly evaporated under reduced pressure and dried *in vacuo* overnight. Traces of ligand can be removed by washing the powder with Et_2O:acetone 7:3 (4x4 mL). Pure complex **2Br** was obtained as a yellow powder (125 mg, 0.223 mmol, yield 82%).

^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 9.12 (1H, ddd, J_o 5.5, J_m 1.8, J_p 0.7, H^{14}), 8.52 (1H, d, J_o 8.0, H^8), 8.37 (1H, ddd, J_o 8.6, J_o 7.4, J_m 1.8, H^{12}), 8.28 (1H, dt, J_o 7.4, J_m 1.1, H^{11}), 7.67-7.61 (2H, m, H^{13,5}), 7.01 (1H, dd, J_o 9.4, J_o 6.2, H^6), 6.95 (1H, ddd, J_o 8.0, J_o 6.2, J_m 1.2, H^7), 3.08 (1H, s, CH$_3$^{1}).

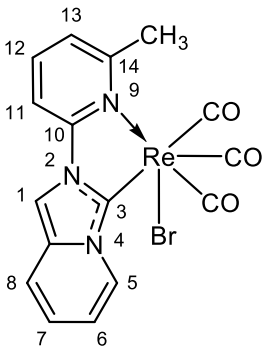
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 155.75 (C^{14}), 142.84 (C^{12}), 128.55 (C^{13}), 125.53 (C^6), 123.50 (C^8), 118.94 (C^5), 116.95 (C^7), 116.93 (C^{11}), 12.17 (CH$_3$^{1}).

ESI-MS calcd for $C_{16}H_{11}BrN_3NaO_3Re$: 581.9416. Found for ([M+Na]$^+$): 581.9424.

FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2012s, 1888br, 1845br (C≡O).

Found: N, 7.31; C, 34.62; H, 2.02. Calc. for $ReBrN_3C_{16}O_3H_{11}$: N, 7.51; C, 34.35; H, 1.98.

Complex [Re^{I}(CO)$_3$(L3)Br] (3Br)



To a 30 mm glass microwave vial were added **L3H** (104.1 mg, 0.293 mmol, 1.0 eq.), $Re(CO)_5Br$ (110.5 mg, 0.27 mmol, 1.2 eq.), K_2CO_3 (97 mg) and xylene 7 mL. The suspension was bubbled with Ar for 10 minutes, kept under stirring and heated at 130˚C under microwave irradiation (60 W) for 4 hours. The resulting orange xylene solution was decanted and discarded and the yellow precipitate washed with xylene (7 mL), Et_2O (2x5 mL) and pentane (4x7 mL). The yellow powder was dissolved in acetone (250 mL) and flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.1 g Al_2O_3 / 5 mg of complex). The resulting solution was quickly evaporated under reduced pressure and dried *in vacuo* overnight. Traces of ligand were removed by washing the powder with Et_2O:acetone 7:3 (4x4 mL). Pure complex **3Br** was obtained as a yellow powder (107.3 mg, 0.192 mmol, yield 71%).

^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 8.62 (1H, d, J_o 7.8, H^8), 8.48 (1H, dq, J_o 7.4, J_m 1.0, H^{11}), 8.22-8.20 (2H, m, H^{1,12}), 7.78-7.71 (1H, m, H^{13}), 7.64 (1H, dt, J_o 9.4, J_m 1.2, H^5), 7.12 (1H ddd, J_o 9.4, J_o 6.5, J_m 0.9, H^6), 7.02 (1H, ddd, J_o 7.8, J_o 6.5, J_m 1.2, H^7), 3.05 (1H, s, CH_3^{14}).

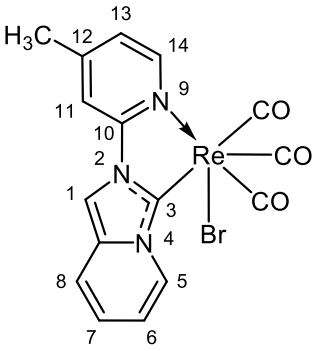
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 142.63 (C^{12}), 128.54 (C^{13}), 125.28 (C^6), 124.93 (C^8), 119.35 (C^5), 116.73 (C^7), 112.11 (C^{11}), 109.01 (C^1), 31.15 (CH_3^{14}).

ESI-MS calcd for $C_{16}H_{11}BrKN_3O_3Re$: 597.9155. Found for ([M+K]$^+$): 597.9165.

FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2013s, 1877br (C≡O).

Found: N, 7.37; C, 34.32; H, 1.95. Calc. for $ReBrN_3C_{16}O_3H_{11}$: N, 7.51; C, 34.35; H, 1.98.

Complex [Re^{I}(CO)$_3$(L4)Br] (4Br)



To a 30 mm glass microwave vial were added **L4H** (104.5 mg, 0.29 mmol, 1.0 eq.), $Re(CO)_5Br$ (108.0 mg, 0.27 mmol, 1.2 eq.), K_2CO_3 (97 mg) and xylene 7 mL. The suspension was bubbled with Ar for 10 minutes, kept under stirring and heated at 130˚C under microwave irradiation (60 W) for 4 hours. The resulting orange xylene solution was decanted and discarded and the yellow precipitate washed with xylene (7 mL), Et_2O (2x5 mL) and pentane (2x7 mL). The yellow powder was dissolved in acetone (75 mL) and flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.1 g Al_2O_3 / 1 mg of complex). The resulting solution was quickly evaporated under reduced pressure and dried *in vacuo* overnight. Traces of ligand were removed by washing the powder with Et_2O:acetone 7:3 (4x4 mL). Pure complex **4Br** was obtained as a yellow powder (144.2 mg, 0.258 mmol, yield 97%).

^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 8.87 (1H, d, J_o 5.7, H^{14}), 8.61 (1H, s, H^1), 8.35 (1H, dd, J_o 7.4, J_m 1.0, H^8), 8.26 (1H, s, H^{11}), 7.61 (1H, dt, J_o 9.3, J_m 1.2, H^5), 7.47 (1H ddd, J_o 5.7, J_m 1.6, $J^4_{H13\text{-}CH3}$ 0.8, H^{13}), 7.11 (1H ddd, J_o 9.3, J_o 6.5, J_m 1.0, H^6), 7.01 (1H, ddd, J_o 7.4, J_o 6.5, J_m 1.2, H^7), 2.64 (1H, s, CH_3^{12}).

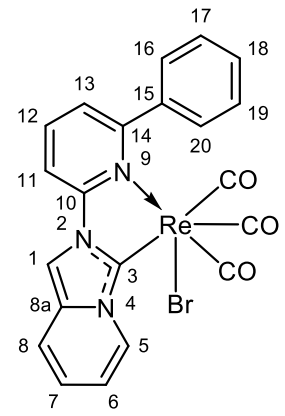
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 154.21 (C^{14}), 128.80 (C^{13}), 126.71 (C^6), 125.44 (C^8), 119.48 (C^5), 116.91 (C^7), 115.58 (C^{11}), 108.66 (C^1), 21.73 (CH_3^{12}).

ESI-MS calcd for $C_{16}H_{11}BrN_3NaO_3Re$: 581.9416. Found for ([M+Na]$^+$): 581.9426.

FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2013s, 1869br (C≡O).

Found: N, 7.37; C, 34.32; H, 1.95. Calc. for $ReBrN_3C_{16}O_3H_{11}$: N, 7.51; C, 34.35; H, 1.98.

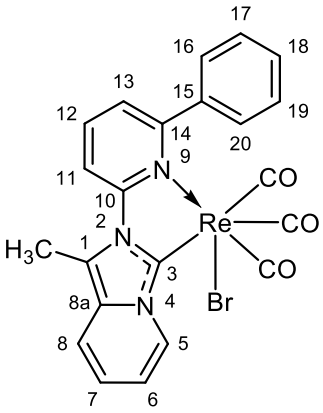
Complex [Re^{I}(CO)$_3$(L5)Br] (5Br)



To a 30 mm glass microwave vial were added **L5H** (151.8 mg, 0.36 mmol, 1.0 eq.), $Re(CO)_5Br$ (167.3 mg, 0.41 mmol, 1.2 eq.), Li_2CO_3 (101 mg) and xylene 6 mL. The suspension was bubbled with Ar for 10 minutes, kept under stirring and heated at 130˚C under microwave irradiation (60 W) for 4 hours. The resulting orange xylene solution was decanted and discarded and the yellow precipitate washed with benzene (10 mL) and pentane (2x10 mL). The yellow powder was suspended in chloroform (150 mL), filtered on a G4 glass frit to remove the unreacted ligand and flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.1 g Al_2O_3 / 10 mg of complex). The resulting solution was quickly evaporated under reduced pressure and dried *in vacuo* overnight. Pure complex **5Br** was obtained as a yellow powder (67.8 mg, 0.109 mmol, yield 30%).

^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 8.70 (1H, s, H^1), 8.42 (1H, dq, J_o 7.5, J_m 1.0, H^8), 8.41-8.37 (2H, m, H^{12,13}), 7.68 (1H, dd, J_o 6.2, J_m 2.6, H^{11}), 7.65 (1H, dt, J_o 9.5, J_m 1.2, H^5), 7.67-7.55 (5H, m, H^{Ph}), 7.12 (1H ddd, J_o 9.5, J_o 6.4, J_m 1.0, H^6), 6.99 (1H, ddd, J_o 7.5, J_o 6.4, J_m 1.2, H^7).
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 142.16 (C^{12}), 130.65 (C^{Ph}), 128.40, 125.31 (C^{Ph}), 125.05 (C^{Ph}), 119.06, 116.30, 113.48 (C^{11}), 108.90 (C^1).
ESI-MS calcd for $C_{21}H_{13}BrN_3NaO_3Re$: 643.9573. Found for ([M+Na]$^+$): 643.9612.
FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2018s, 1926s, 1882br, 1866br (C≡O).

Complex [Re^{I}(CO)$_3$(L6)Br] (6Br)



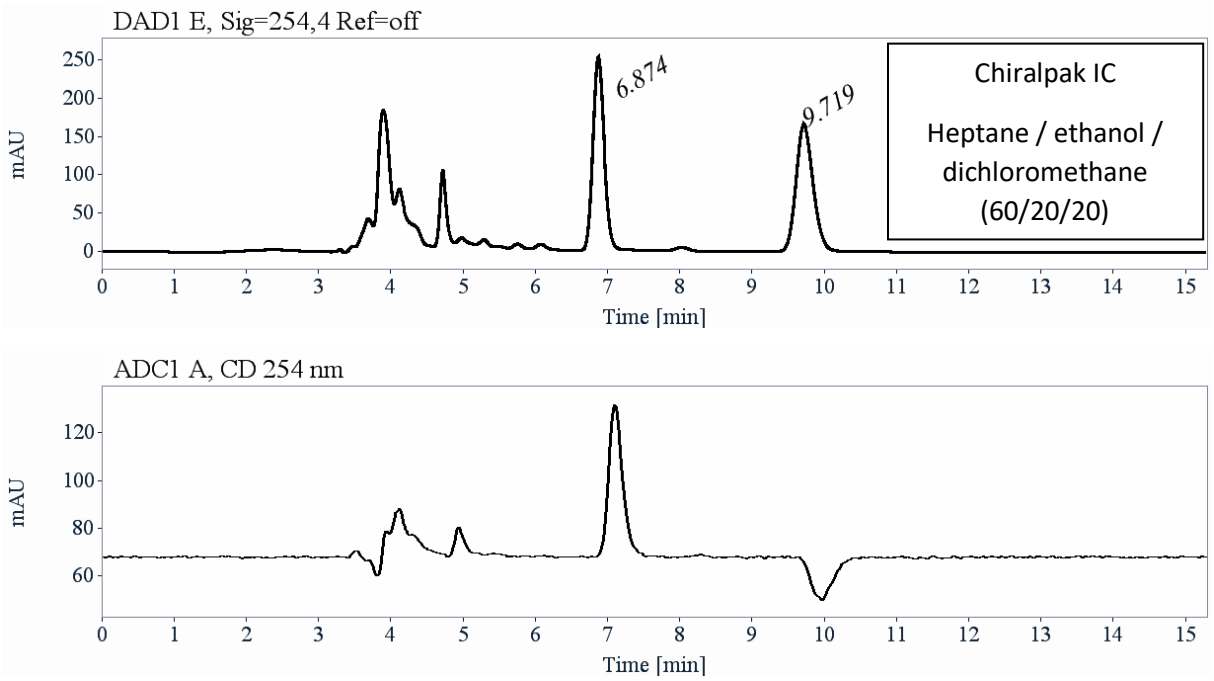
To a 30 mm glass microwave vial were added **L6H** (116.7 mg, 0.27 mmol, 1.0 eq.), $Re(CO)_5Br$ (116.4 mg, 0.29 mmol, 1.2 eq.), Cs_2CO_3 (263 mg) and xylene 7 mL. The suspension was bubbled with Ar for 10 minutes, kept under stirring and heated at 130˚C under microwave irradiation (60 W) for 4 hours. The resulting orange xylene solution was decanted and discarded and the yellow precipitate washed with xylene (5 mL) and Et_2O (4x5 mL). The yellow powder was suspended in chloroform (20 mL), filtered on a G4 glass frit to remove the unreacted ligand and flash filtered on a burette packed with neutral Al_2O_3 (ca. 0.1 g Al_2O_3 / 10 mg of complex). The resulting solution was quickly evaporated under reduced pressure and dried *in vacuo* overnight. Pure complex **6Br** was obtained as a yellow powder (63.0 mg, 0.099 mmol, yield 37%).

^{1}H NMR (500 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 8.44 (1H, dd, J_o 8.0, J_m 1.0, H^8), 8.38 (1H, dd, J_o 8.9, J_o 7.4, H^{12}), 8.35 (1H, dt, J_o 7.4, J_m 1.1, H^{11}), 7.72 (1H, dd, J_o 7.9, J_m 1.1, H^{13}), 7.66-7.59 (6H, m, H^{5,Ph}), 7.02 (1H, ddd, J_o 9.2, J_o 6.4, J_m 1.0, H^6), 6.93 (1H, ddd, J_o 8.0, J_o 6.4, J_m 1.2, H^7), 3.07 (1H, s, CH$_3$^{1}).
^{13}C NMR DEPT135 (125.7 MHz, 298 K, acetone-d_6, inert atmosphere) δ: 142.36 (C^{12}), 131.14 (C^{Ph}), 128.47, 125.37 (C^{Ph}), 123.48 (C^{Ph}), 118.95, 116.68, 116.02 (C^{11}), 12.21 (CH$_3$^{1}).
ESI-MS calcd for $C_{22}H_{15}BrN_3NaO_3Re$: 657.9729. Found for ([M+Na]$^+$): 657.9767.
FT-ATR-IR (neat powder) ν_{max}/cm^{-1}: 2010s, 1911s, 1873br (C≡O).
Found: N, 6.35; C, 41.54; H, 2.50. Calc. for $ReBrN_3C_{22}O_3H_{15}$: N, 6.61; C, 41.58; H, 2.38.

Chiral chromatographic separation

Analytical chiral HPLC separation for compound 1Cl

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.87	2766	50.14	1.33		
9.72	2751	49.86	2.29	1.73	7.94
Sum	5517	100.00			

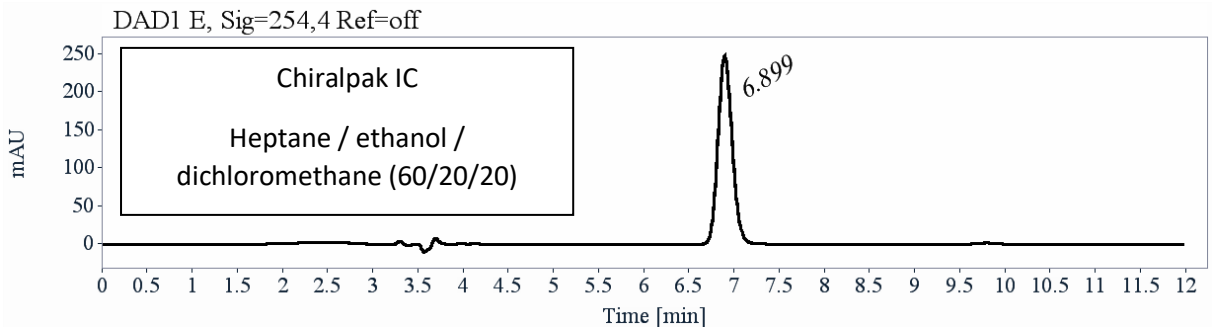
Preparative separation for compound 1Cl:

• Sample preparation: About 82 mg of purified compound **1Cl** are dissolved in 45 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IC (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 320 nm.

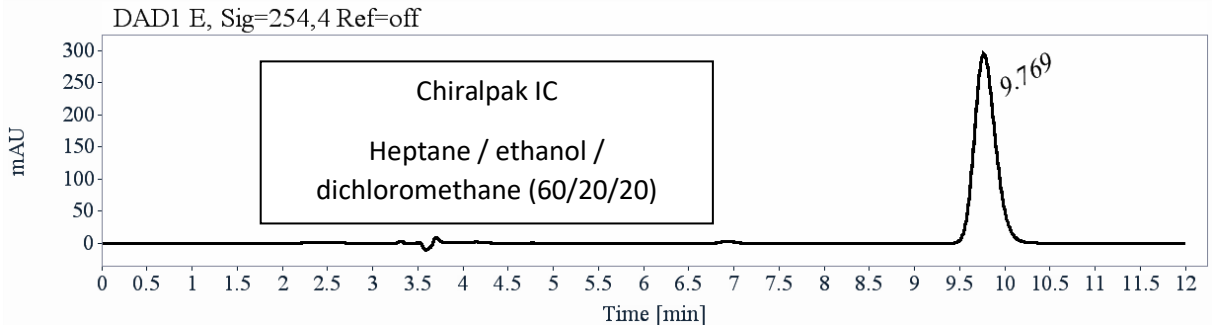
• Injections (stacked): 33 times 1400 □L, every 5.5 minutes.

• Fraction1: 40 mg of the first eluted enantiomer with *ee* >99.5%



RT [min]	Area	Area%
6.90	4247	100.00
Sum	4247	100.00

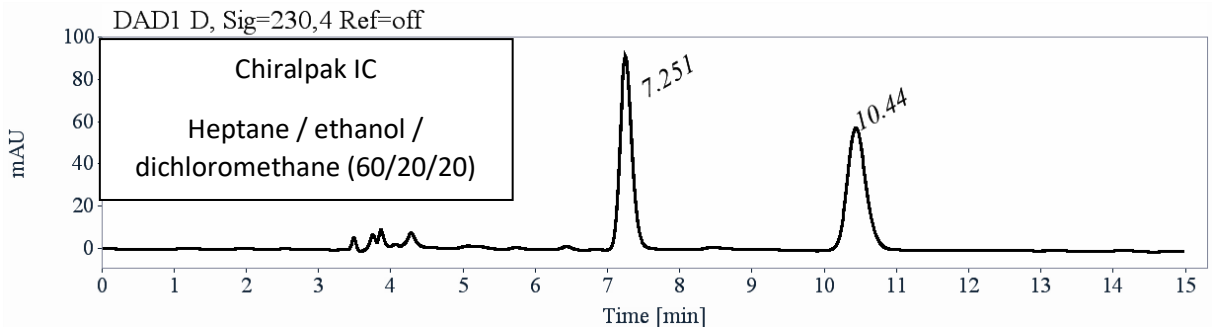
• Fraction-2: 37 mg of the second eluted enantiomer with *ee* >99.5%

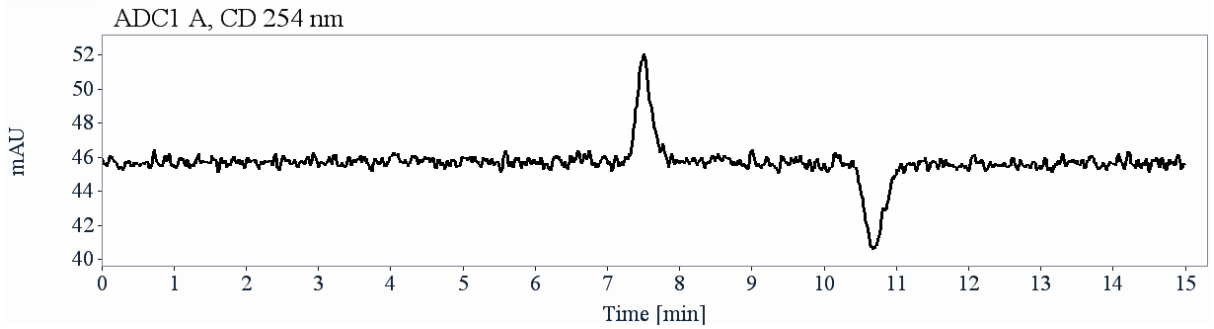


RT [min]	Area	Area%
9.77	4878	100.00
Sum	4878	100.00

Analytical chiral HPLC separation for compound 1Br

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.25	1056	49.77	1.46		
10.44	1066	50.23	2.54	1.74	8.18
Sum	2121	100.00			

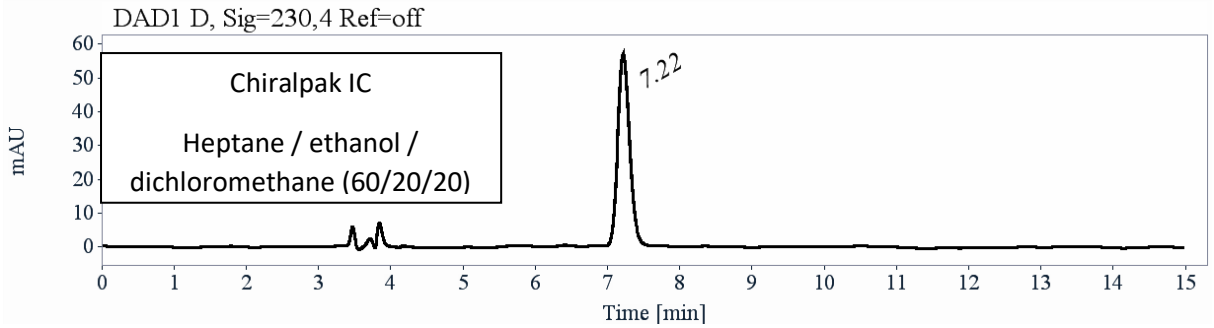
Preparative separation for purified compound 1Br:

•Sample preparation: About 68 mg of purified compound **1Br** are dissolved in 36 mL of a mixture of dichloromethane and ethanol (85/15).

• Chromatographic conditions: Chiralpak IC (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

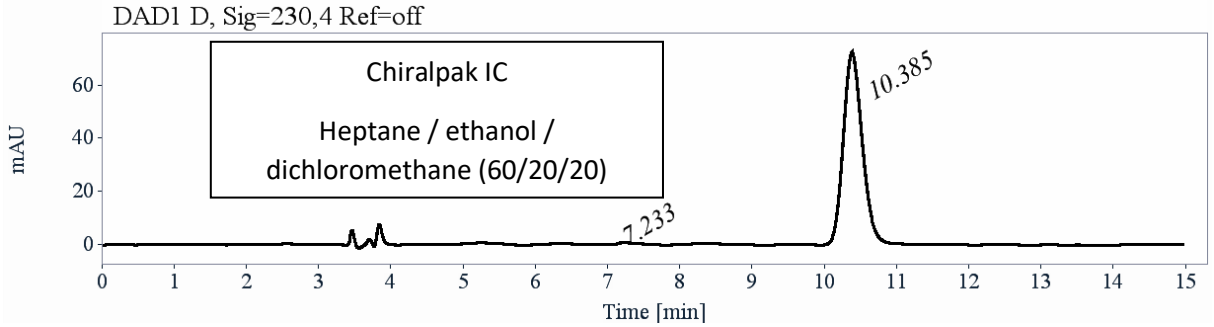
• Injections (stacked): 90 times 400 □L, every 7.3 minutes.

• First fraction: 31 mg of the first eluted enantiomer with *ee* >99.5%



RT [min]	Area	Area%
7.22	648	100.00
Sum	648	100.00

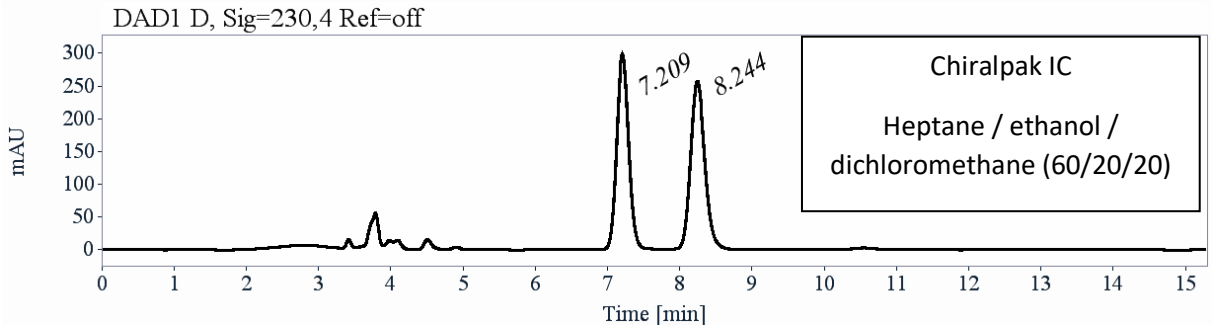
• Second fraction: 31 mg of the second eluted enantiomer with *ee* >98%

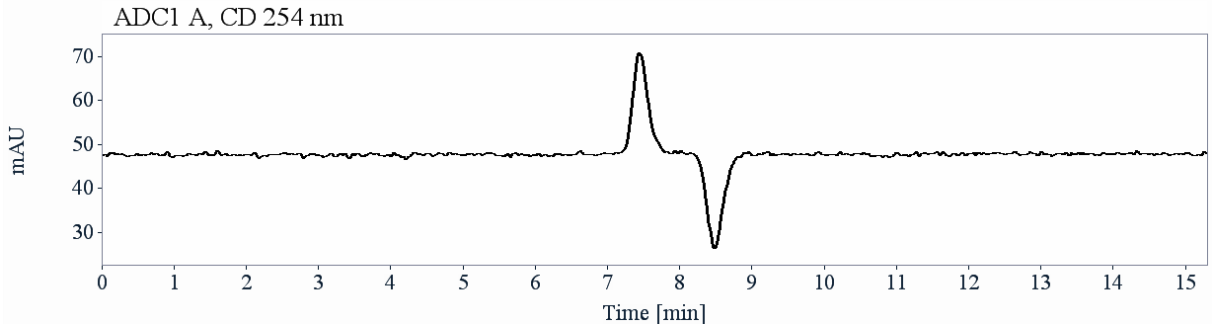


RT [min]	Area	Area%
7.23	10	0.74
10.39	1323	99.26
Sum	1333	100.00

Analytical chiral HPLC separation for compound 2Br

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.21	3446	49.33	1.44		
8.24	3540	50.67	1.79	1.24	3.14
Sum	6986	100.00			

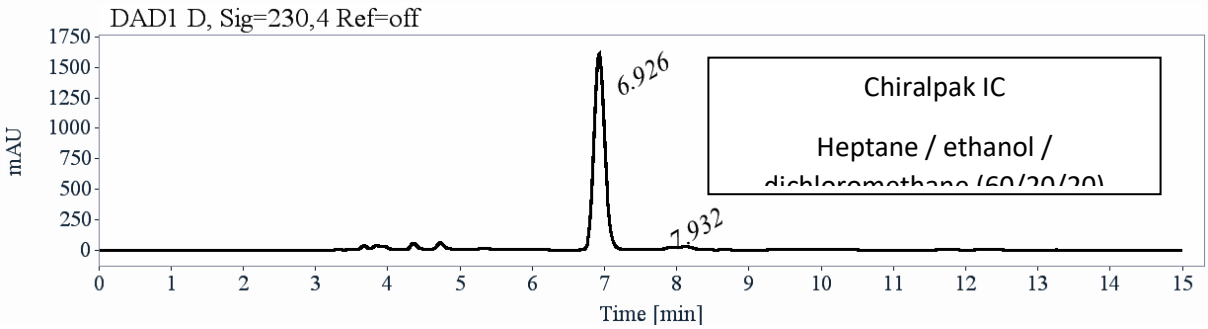
Preparative separation for compound 2Br:

• Sample preparation: About 130 mg of purified compound **2Br** are dissolved in 205 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IC (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 320 nm.

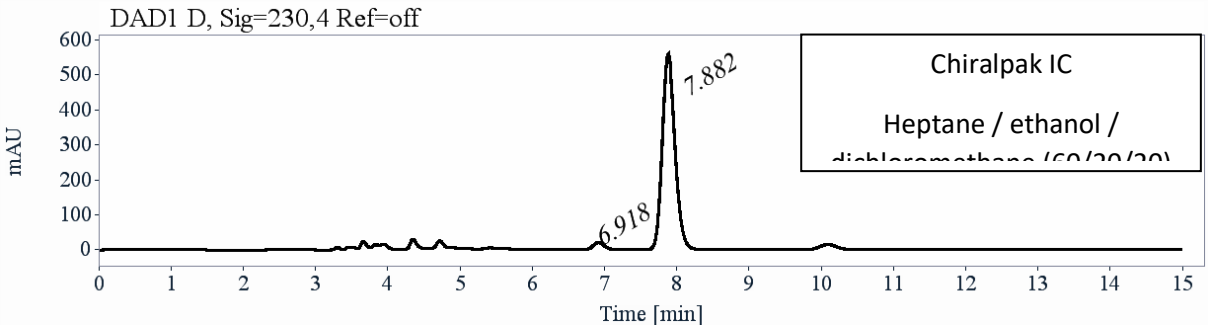
• Injections (stacked): 215 times 250 □L, every 4 minutes.

• Fraction 1: 11 mg of the first eluted enantiomer with *ee* >97%



RT [min]	Area	Area%
6.93	16735	98.69
7.93	222	1.31
Sum	16957	100.00

• Fraction 2: 12 mg of the second eluted enantiomer with *ee* >94%

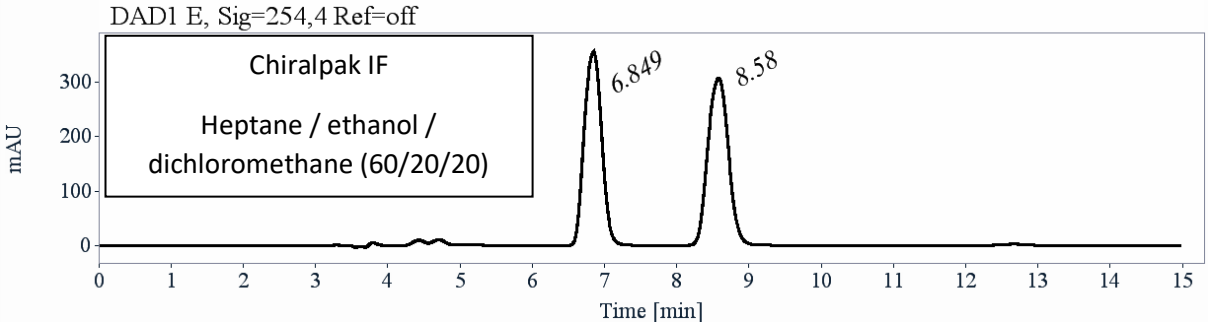


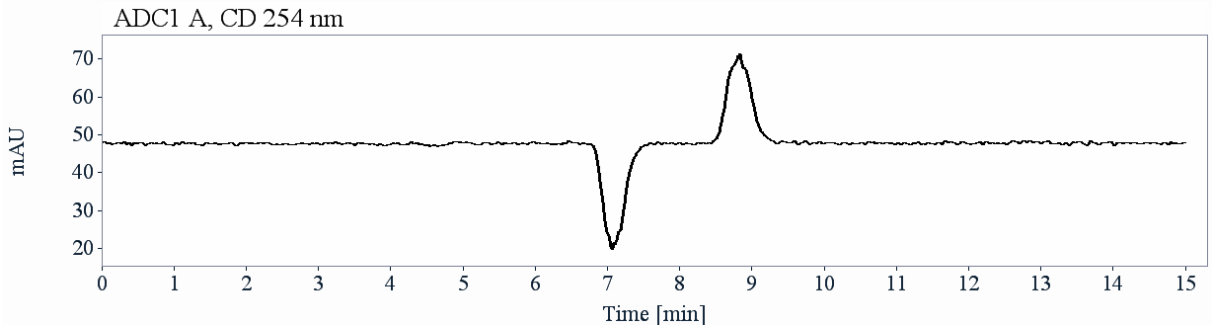
RT [min]	Area	Area%
6.92	210	2.97
7.88	6858	97.03
Sum	7068	100.00

• Recovered starting material: 87 mg

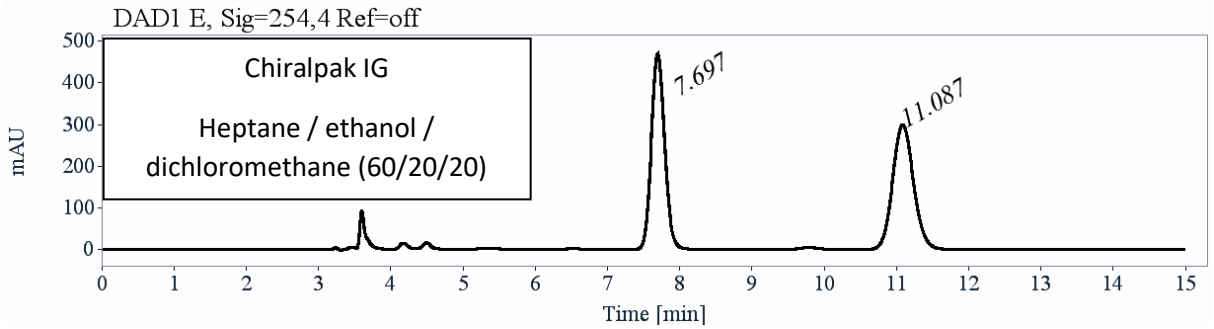
Analytical chiral HPLC separation for compound 4Br

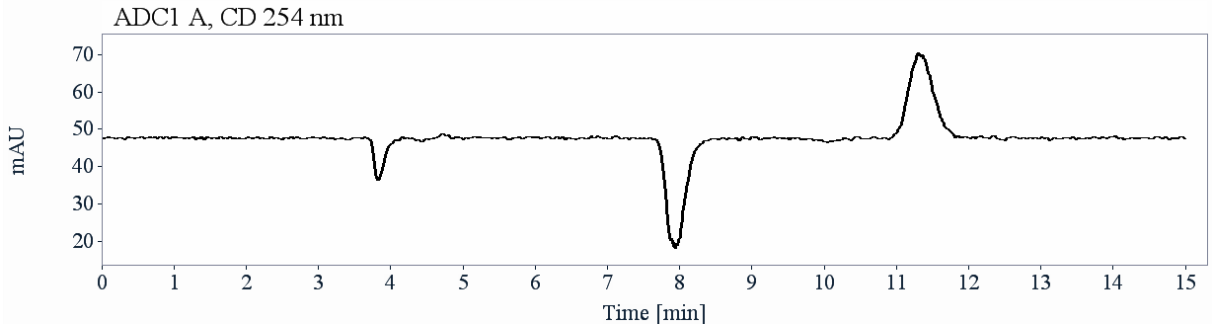
• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.85	5996	49.62	1.32		
8.58	6087	50.38	1.91	1.44	3.66
Sum	12082	100.00			





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.70	6008	49.94	1.61		
11.09	6022	50.06	2.76	1.71	7.81
Sum	12031	100.00			

Preparative separation for compound 4Br:

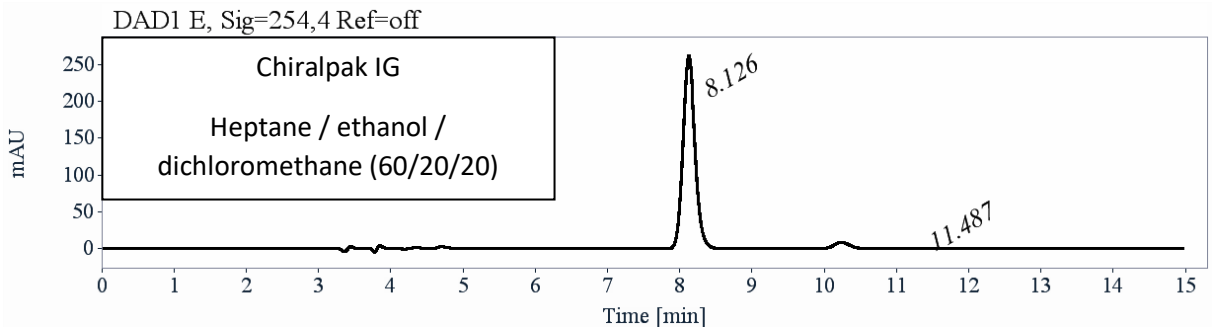
• Sample preparation: About 91 mg of purified compound **4Br** are dissolved in 18 mL of Dichloromethane.

• Chromatographic conditions: Chiralpak IF (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 320 nm.

• Injections (stacked): 45 times 400 □L, every 4 minutes.

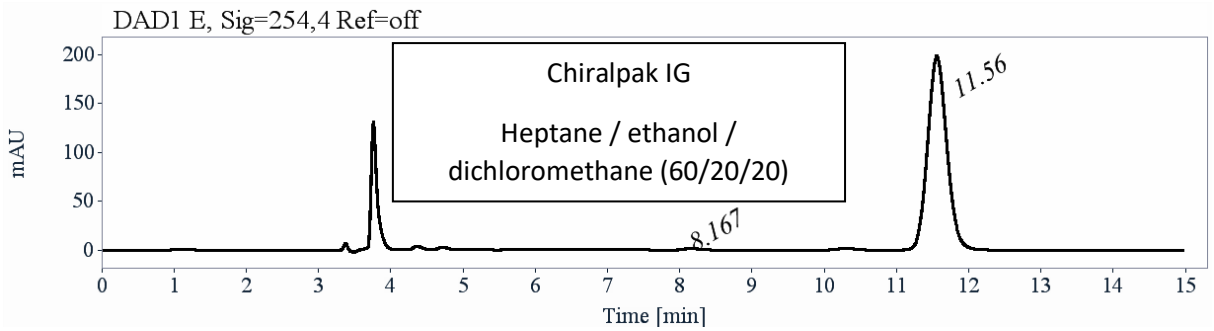
Collected fractions were placed in an ice bath and without light.

• Fraction1: 44 mg of the first eluted enantiomer with *ee* >99%



RT [min]	Area	Area%
8.13	3048	99.51
11.49	15	0.49
Sum	3063	100.00

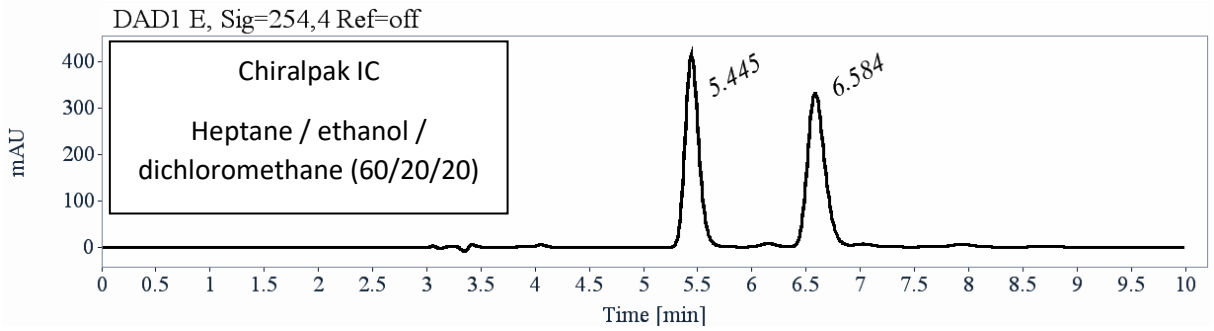
• Fraction 2: 43 mg of the second eluted enantiomer with *ee* >98.5%

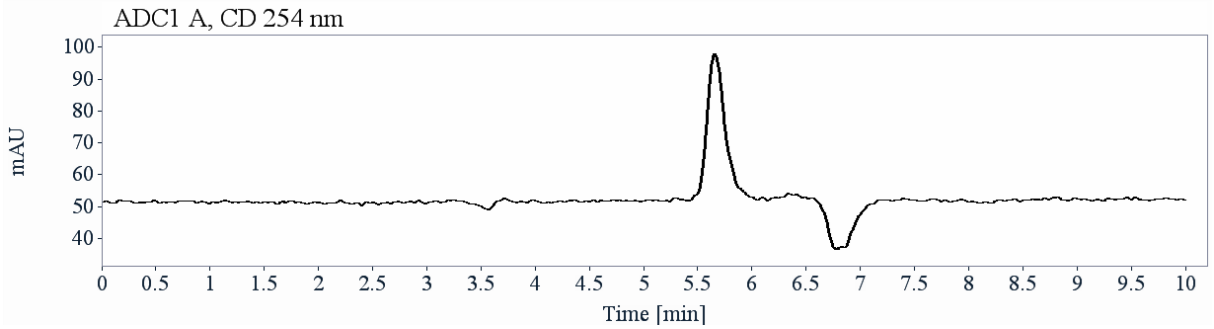


RT [min]	Area	Area%
8.17	24	0.65
11.56	3678	99.35
Sum	3702	100.00

Analytical chiral HPLC separation for compound 3Br

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.45	3681	49.63	0.85		
6.58	3736	50.37	1.23	1.46	4.31
Sum	7416	100.00			

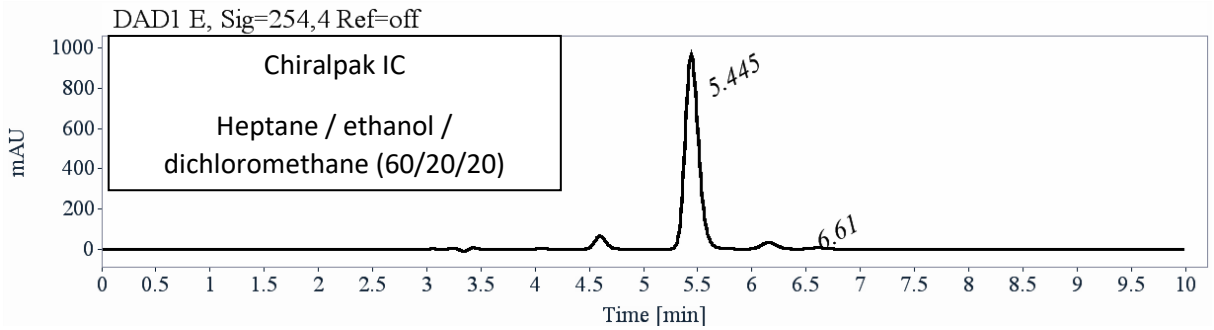
Preparative separation for compound 3Br:

• Sample preparation: About 54 mg of purified compound **3Br** are dissolved in 70 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IC (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

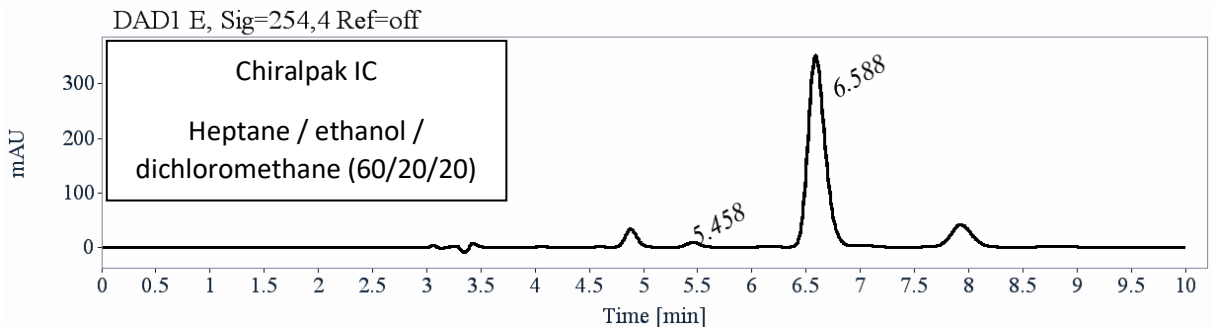
• Injections (stacked): 235 times 300 □L, every 5 minutes.

• Fraction 1: 24 mg of the first eluted enantiomer with *ee* >98%



RT [min]	Area	Area%
5.44	8462	99.09
6.61	78	0.91
Sum	8540	100.00

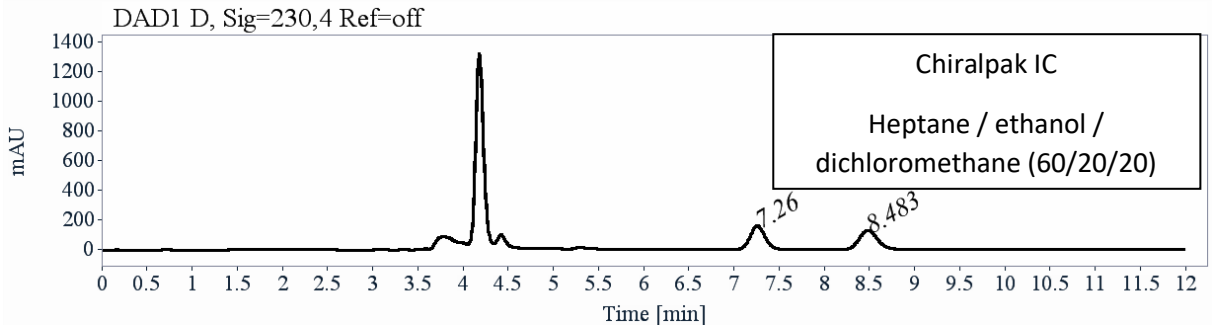
• Fraction 2: 24 mg of the second eluted enantiomer with *ee* >95%

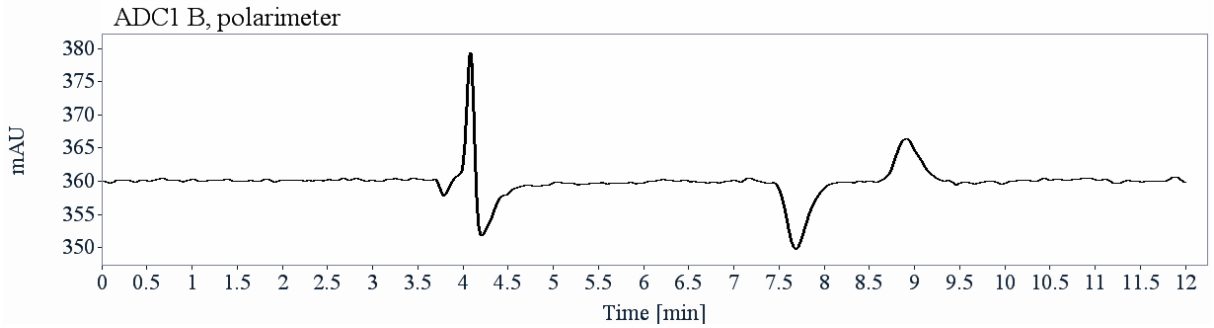


RT [min]	Area	Area%
5.46	82	2.07
6.59	3890	97.93
Sum	3973	100.00

Analytical chiral HPLC separation for compound 6Br

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a polarimetric detector. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.26	1881	49.78	1.46		
8.48	1898	50.22	1.88	1.28	3.62
Sum	3779	100.00			

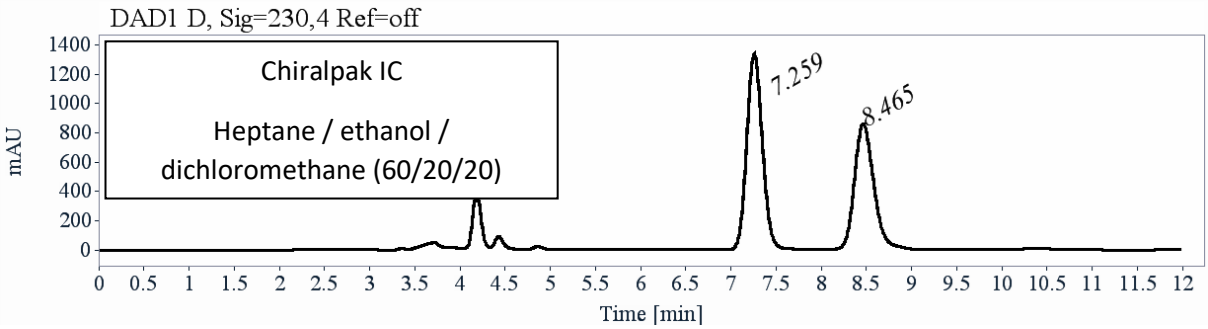
Preparative separation for compound 6Br:

• Sample preparation: About 90 mg of purified compound **6Br** are dissolved in 33 mL of dichloromethane.

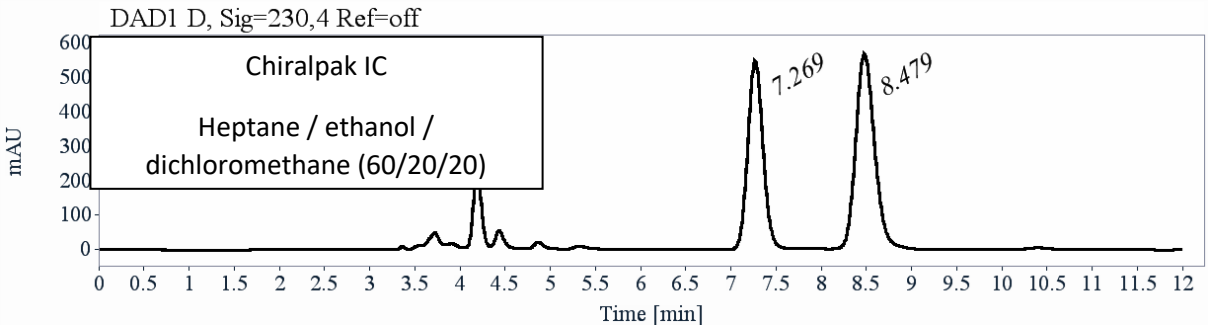
• Chromatographic conditions: Chiralpak IC (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 320 nm.

• Injections (stacked): 165 times 200 µL, every 3 minutes.

• Fraction 1: 38 mg, but racemized



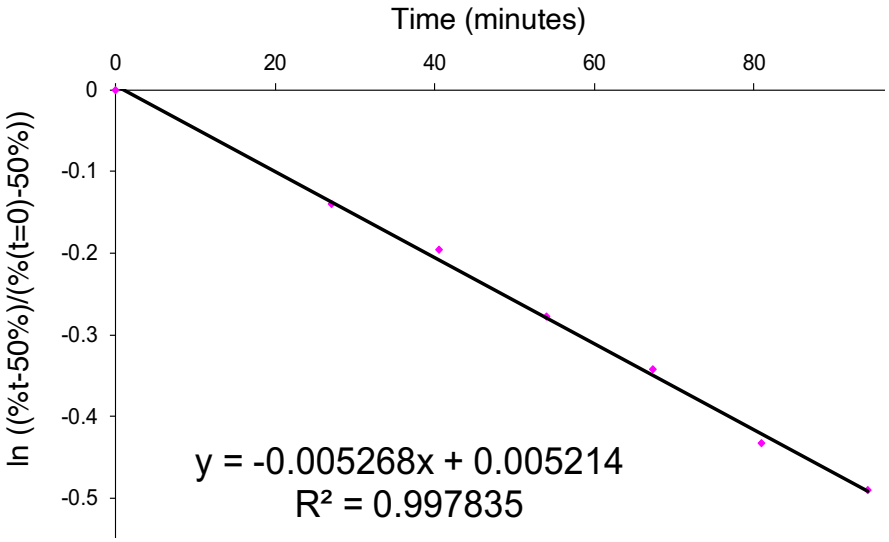
• Fraction-2: 40 mg, but racemized



Kinetic of enantiomerization of 6Br in the mobile phase

About 0.1 mg of the first eluted peak in 1.5 mL of hexane / ethanol / dichloromethane (6/2/2) is collected after separation on a preparative column (250 x 10 mm). This solution is thermostated at 25°C in the autosampler, 10 µL are taken and then injected on Chiralpak IC (6:2:2 heptane / ethanol / dichloromethane, 1 mL/min, UV 254 nm). The percentage decrease of the first eluted enantiomer is monitored.

Time (min)	% second eluted enantiomer	ln ((%t-50%)/(%(t=0)-50%))
0	99.213	0.00000
27	92.789	-0.13988
40	90.438	-0.19639
54	87.28	-0.27770
67	84.96	-0.34195
81	81.908	-0.43330
94	80.122	-0.49090



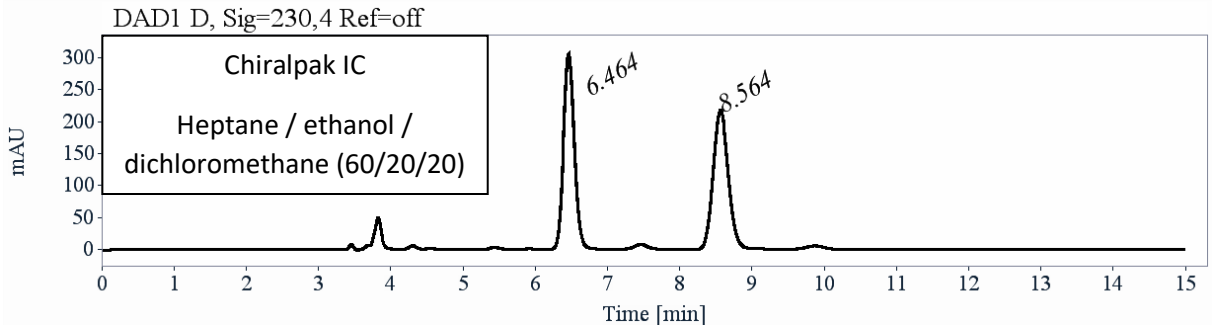
$k_{enantiomerisation} = 4.39.10^{-5}\ s^{-1}$ (25°C, hexane / ethanol / dichloromethane 6:2:2)

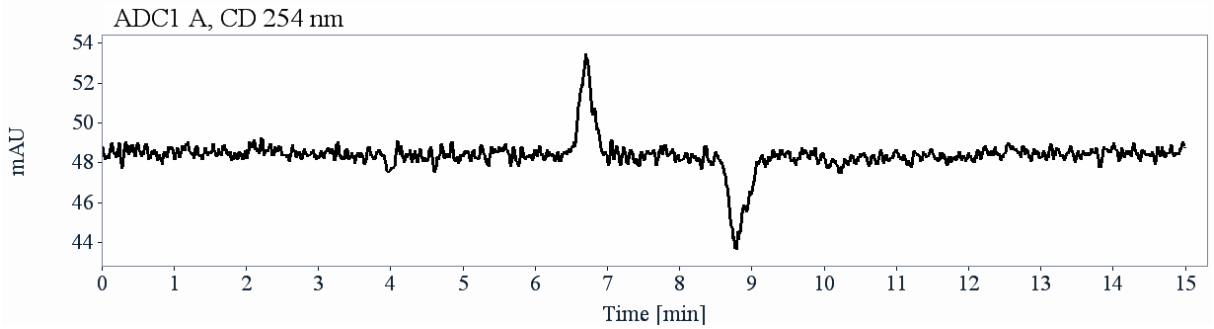
$\Delta G^{\neq} = 97.9\ kJ.mol^{-1}$ (25°C, hexane / ethanol / dichloromethane 6:2:2)

$t_{1/2} = 2.2$ hours (25°C, hexane / ethanol / dichloromethane 6:2:2)

Analytical chiral HPLC separation for compound 5Br

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.46	3172	49.84	1.19		
8.56	3192	50.16	1.90	1.60	6.40
Sum	6364	100.00			

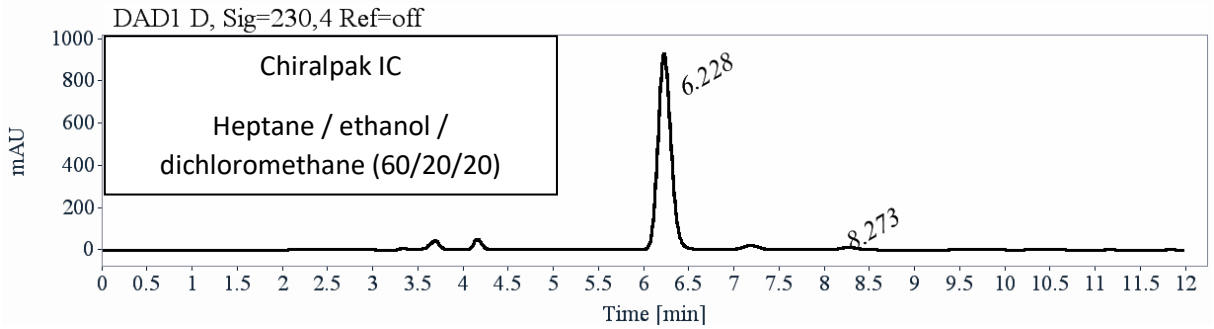
Preparative separation for compound 5Br:

• Sample preparation: About 55 mg of purified compound **5Br** are dissolved in 75 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IC (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 320 nm.

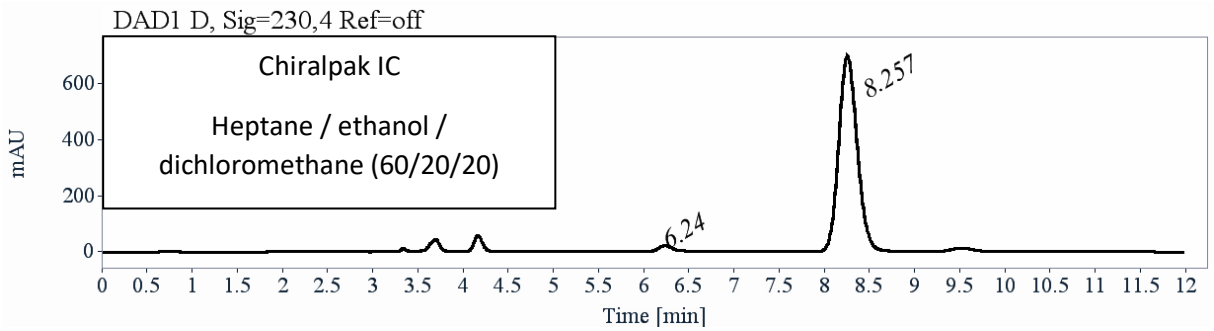
• Injections (stacked): 150 times 500 µL, every 6 minutes.

• Fraction1: 22 mg of the first eluted enantiomer with *ee* >96.5%



RT [min]	Area	Area%
6.23	9363	98.28
8.27	164	1.72
Sum	9527	100.00

• Fraction 2: 23 mg of the second eluted enantiomer with *ee* >94.5%

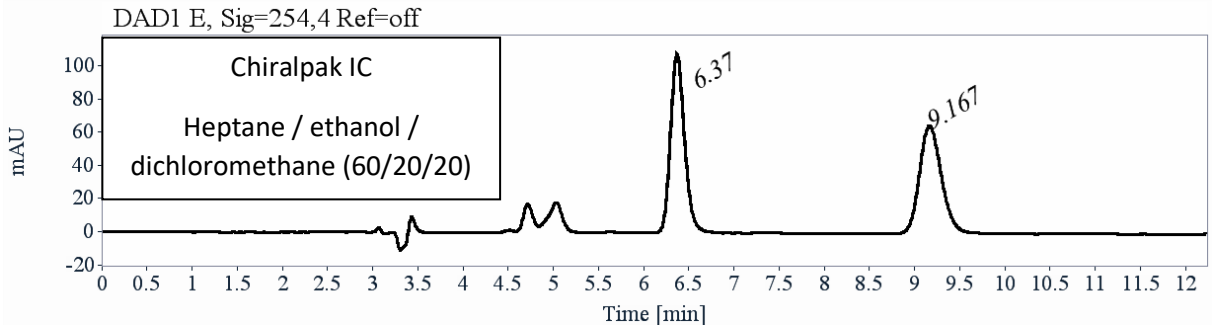


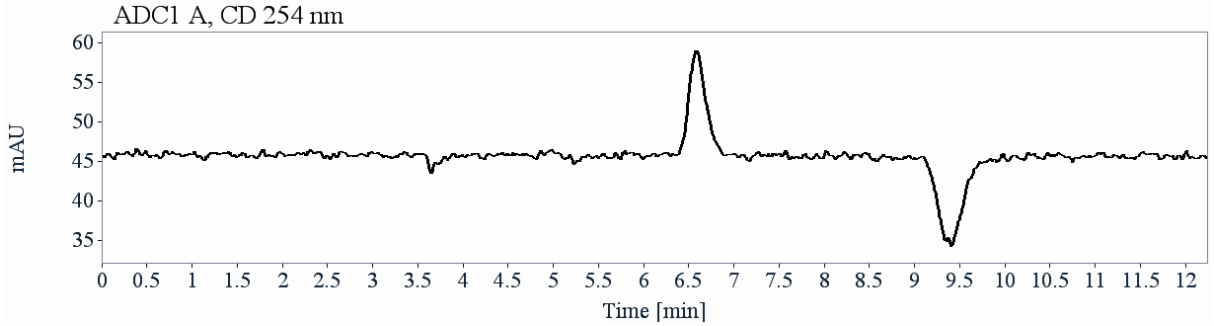
RT [min]	Area	Area%
6.24	260	2.55
8.26	9970	97.45
Sum	10230	100.00

The enantiomerization barrier is around 110 kJ/mol at 25°C in hexane / ethanol / dichloromethane (60/20/20) : in 4 days, the ee decreases from 96.5% to 80%.

Analytical chiral HPLC separation for compound 1l

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.37	1179	51.49	1.16		
9.17	1111	48.51	2.11	1.82	7.69
Sum	2290	100.00			

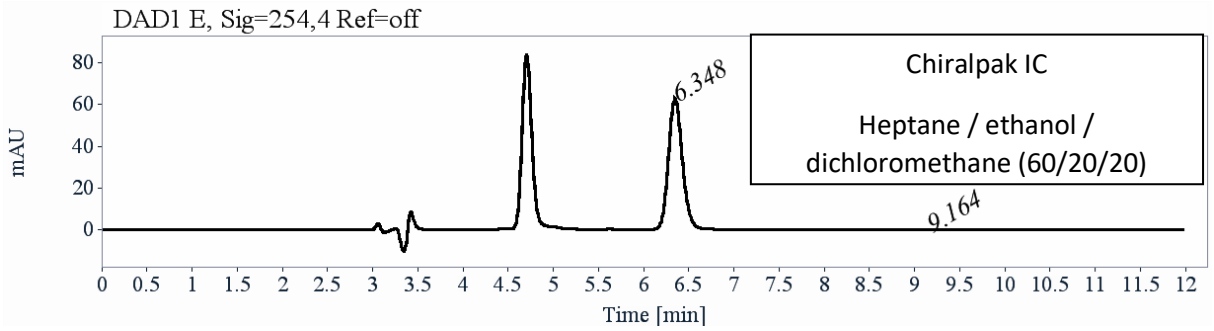
Preparative separation for compound 1l:

• Sample preparation: About 100 mg of purified compound **1l** are dissolved in 18 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IC (250 x 10 mm), hexane / ethanol / dichloromethane (60/20/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

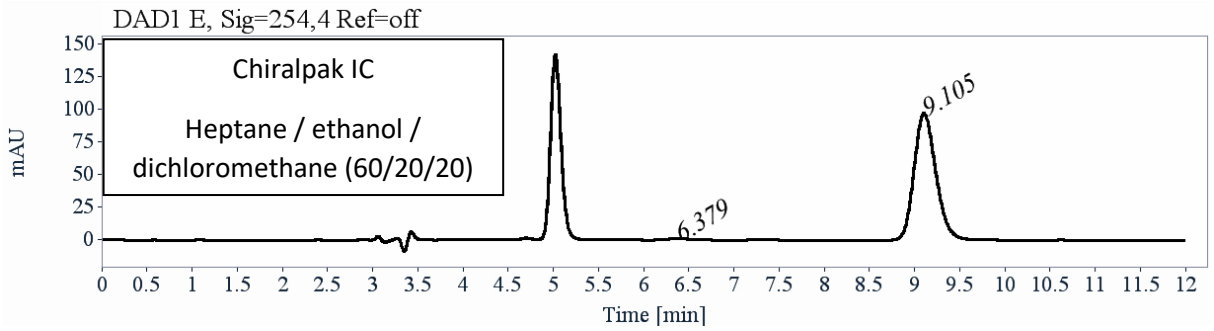
• Injections (stacked): 36 times 500 □L, every 8.5 minutes.

• Fraction1: 24 mg of the first eluted enantiomer with *ee* >99%



RT [min]	Area	Area%
6.35	676	99.76
9.16	2	0.24
Sum	677	100.00

• Fraction-2: 16 mg of the second eluted enantiomer with *ee* >97%



RT [min]	Area	Area%
6.38	22	1.32
9.11	1636	98.68
Sum	1658	100.00

Supplementary Data: photophysical characterization

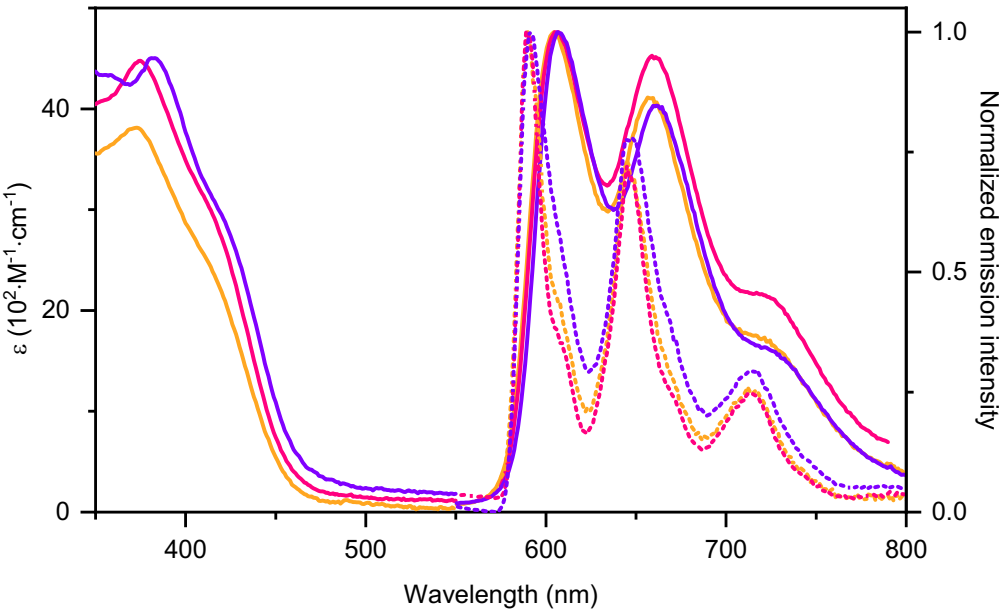


Figure S24. Electronic absorption and photoluminescence spectra of compounds **1Cl** (orange traces), **1Br** (magenta traces), and **1I** (purple traces) in acetone solution at a concentration of 2×10^{-5} M at room temperature (solid line) and 77 K (dashed line) in 2-MeTHF glassy matrix. Emission spectra were recorded upon excitation at λ_{exc} = 360 nm.

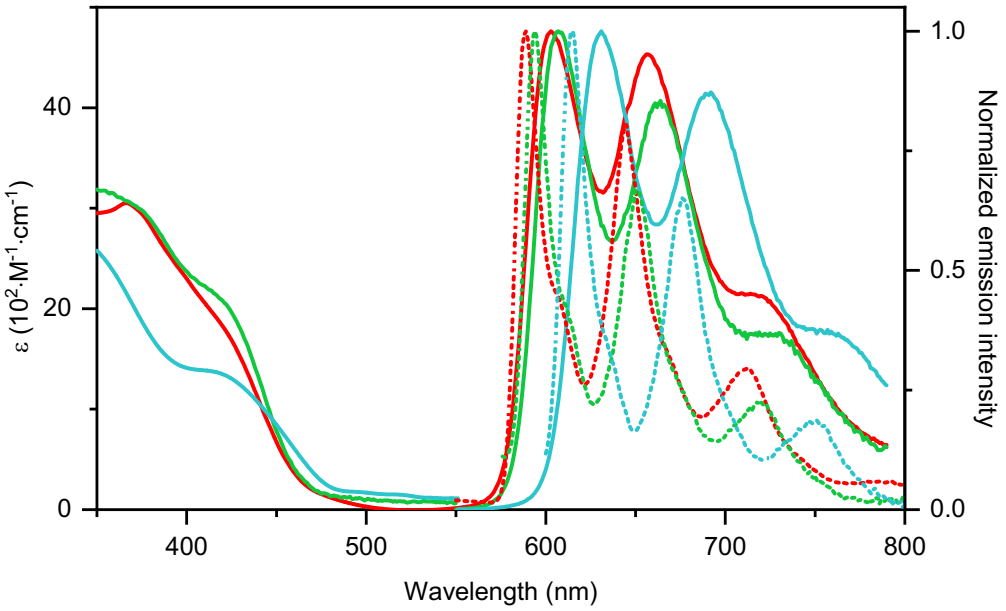


Figure S25. Electronic absorption and photoluminescence spectra of compounds **4Br** (red traces), **5Br** (green traces), and **6Br** (cyan traces) in acetone solution at a concentration of 2×10^{-5} M at room temperature (solid line) and 77 K (dashed line) in 2-MeTHF glassy matrix. Emission spectra were recorded upon excitation at λ_{exc} = 360 nm.

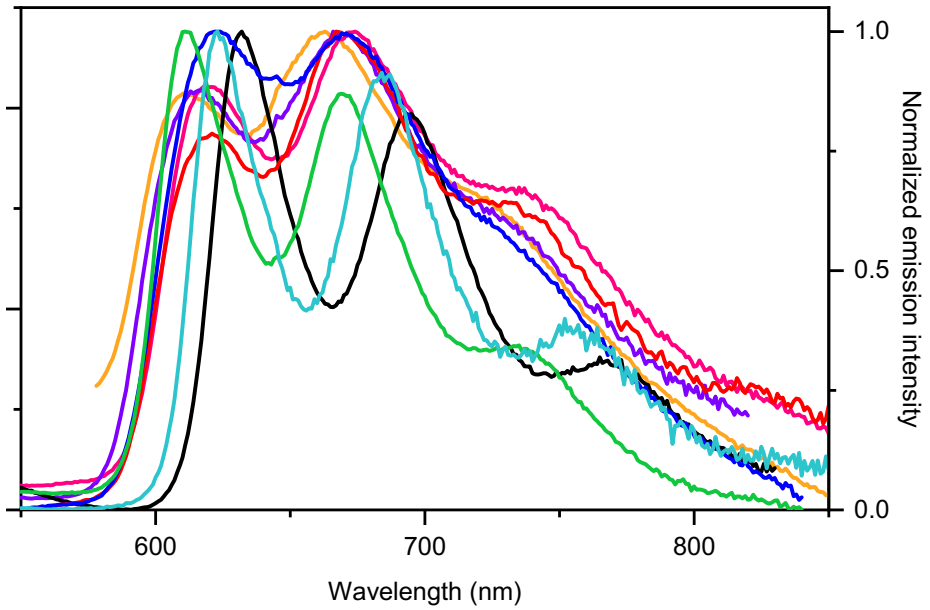


Figure S26. Photoluminescence spectra of compounds **1Cl** (orange), **1Br** (magenta), **1I** (purple), **2Br** (black), **3Br** (blue), **4Br** (red), **5Br** (green), and **6Br** (cyan) in solid state as neat powder. Emission spectra were recorded upon excitation at λ_{exc} = 360 nm.

Table S7. Photophysical properties of complexes **1**–**6** in the solid state as neat powder.

Compound	λ_{em} $[nm]$	$PLQY$ [%]	τ_{obs} $[\mu s]$ (%)	$\bar{\tau}_{obs}$ $[\mu s]$	k_r^a $[10^4 \cdot s^{-1}]$	k_{nr}^b $[10^4 \cdot s^{-1}]$
1Cl	611, 662, 722 *sh*	1	0.42 (82%) 1.29 (18%)	0.77	1.30	128
1Br	617, 671, 735 *sh*	1	0.70 (93%) 6.33 (7%)	2.99	0.33	33.1
1I	615, 670, 740 *sh*	1	1.26 (36%) 0.23 (64%)	1.01	0.99	98.1
2Br	632, 694, 767	1	1.10 (51%) 3.21 (49%)	2.66	0.38	37.2
3Br	621, 669, 735 *sh*	1	0.42 (73%) 1.59 (27%)	1.10	0.91	89.9
4Br	620, 670, 733 *sh*	1	1.27	-	0.79	78.3
5Br	611, 670, 737 *sh*	1	0.49 (65%) 2.41 (35%)	1.90	0.53	52.2
6Br	623, 684, 756	1	1.09 (68%) 4.41 (32%)	3.26	0.31	30.3

sh denotes a shoulder; [a] k_r = PLQY/τ; [b] k_{nr} = (1 – PLQY)/τ

Table S8. ECD, g_{abs} and g_{lum} data for the C_{Re} enantiomers of **1Cl**, **1Br**, **1I** and **2-4Br** in dilute (10^{-5}M) toluene solution at 298 K.[a]

Compound	$\Delta\varepsilon$ [M^{-1} cm^{-1}] (λ, [nm])	g_{abs} (λ, [nm])	g_{lum} (λ, [nm])	g_{lum} / g_{abs}	B_{CPL}
C_{Re}-**1Cl**	-2.1 (355), +1.8 (410), +1.8 (435)	7.3×10^{-4} (435)	-3.9×10^{-3} (620)	–5.3	3.56×10^{-2}
C_{Re}-**1Br**	-4.5 (355), +4.1 (412), +4.4 (438)	2.7×10^{-3} (438)	-4.4×10^{-3} (613)	–1.6	1.55×10^{-1}
C_{Re}-**1I**	-1.65 (358), +2.1 (414), +1.2 (453)	2.5×10^{-3} (453)	-4.4×10^{-3} (615)	–1.76	1.81×10^{-1}
C_{Re}-**2Br**	-2.1 (361), +2.4 (421), +2.5 (450)	1.1×10^{-3} (450)	-3.0×10^{-3} (640)	–2.7	5.84×10^{-2}
C_{Re}-**3Br**	-4.2 (354), +3.1 (413), +2.9 (442)	3.9×10^{-3} (442)	-3.3×10^{-3} - -1.1×10^{-3} (630)[b]	–0.3	1.22×10^{-1}
C_{Re}-**4Br**	-2.0 (346), +1.7 (406), +1.55 (430)	5.5×10^{-3} (430)	-3.2×10^{-3} (620)	–0.6	1.01×10^{-1}

[a] For CPL measurements, samples were degassed. [b] The measured signal was noisy.

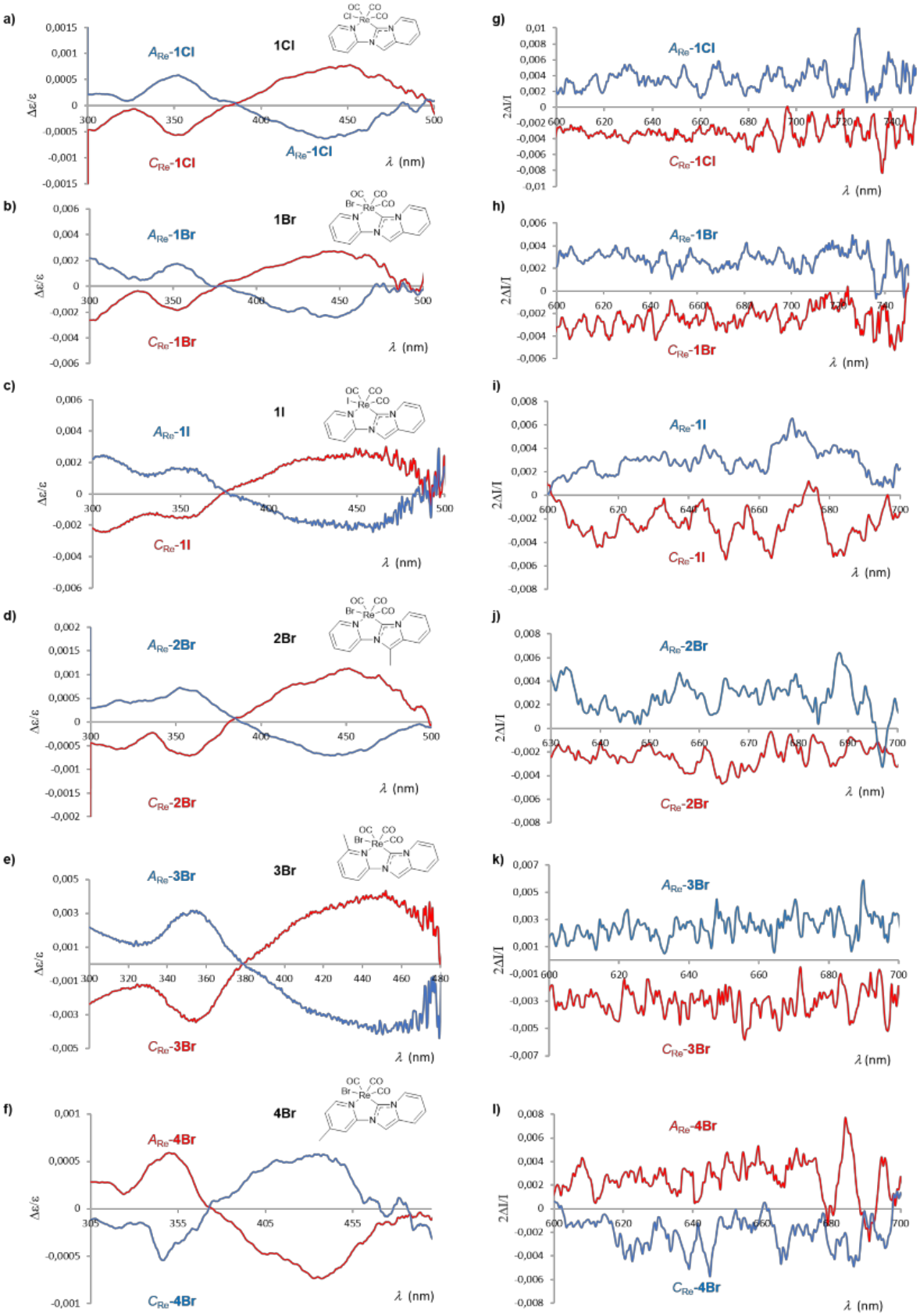
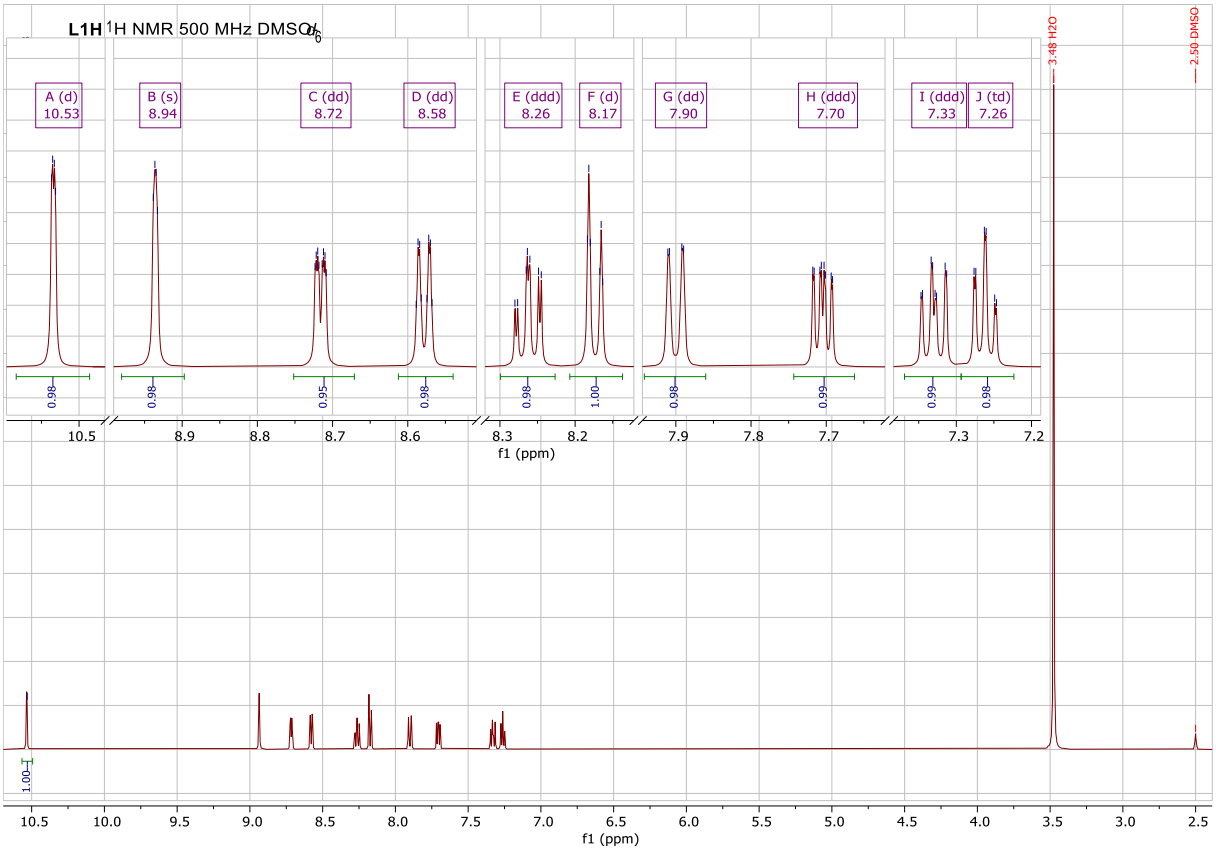
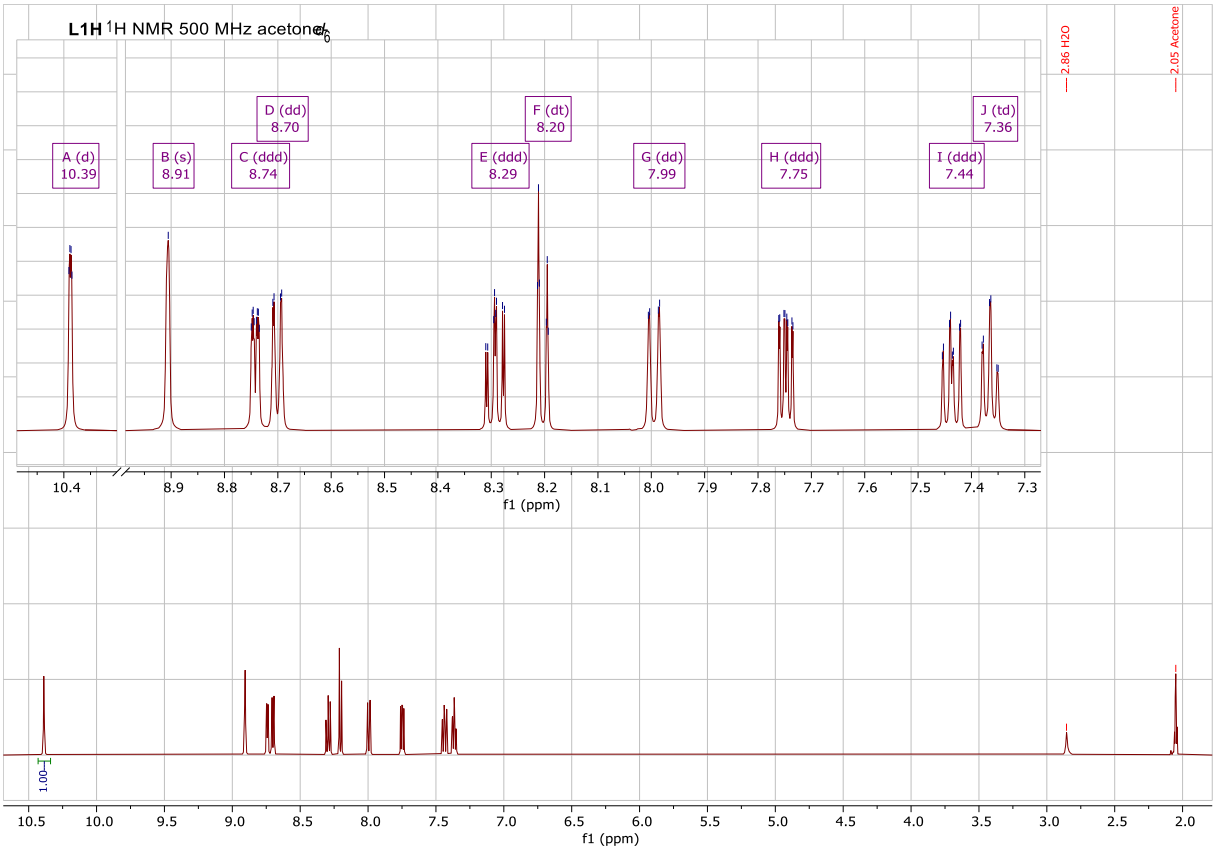


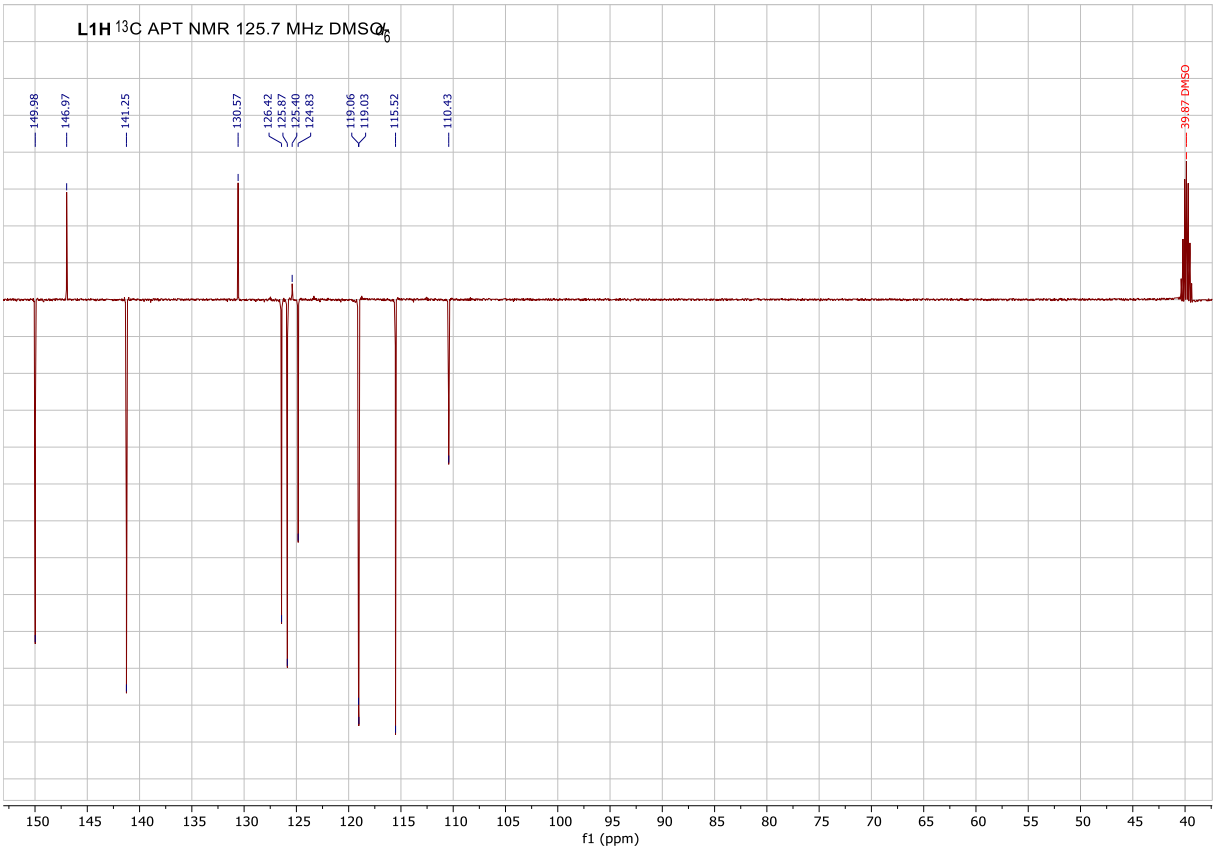
Figure S27. Absorption dissymmetry factors g_{abs} (a-f), and emission dissymmetry factors g_{lum} (g-l) spectra recorded for enantioenriched C_{Re} and A_{Re} complexes **1Cl**, **1Br**, **1I** and **2Br**–**4Br**. Red (blue) color depicts first (second) eluted enantiomers (see "chiral chromatographic separation" section above).

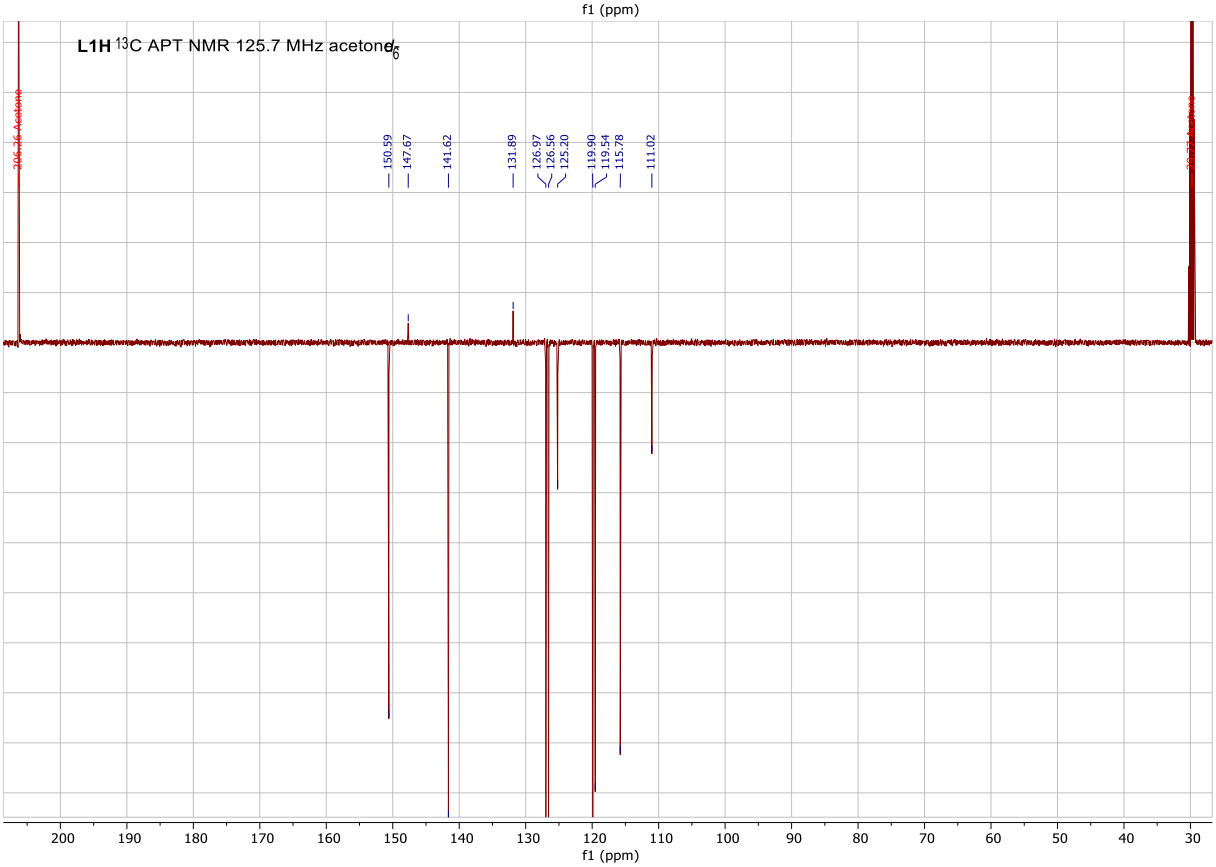
Supplementary Figures

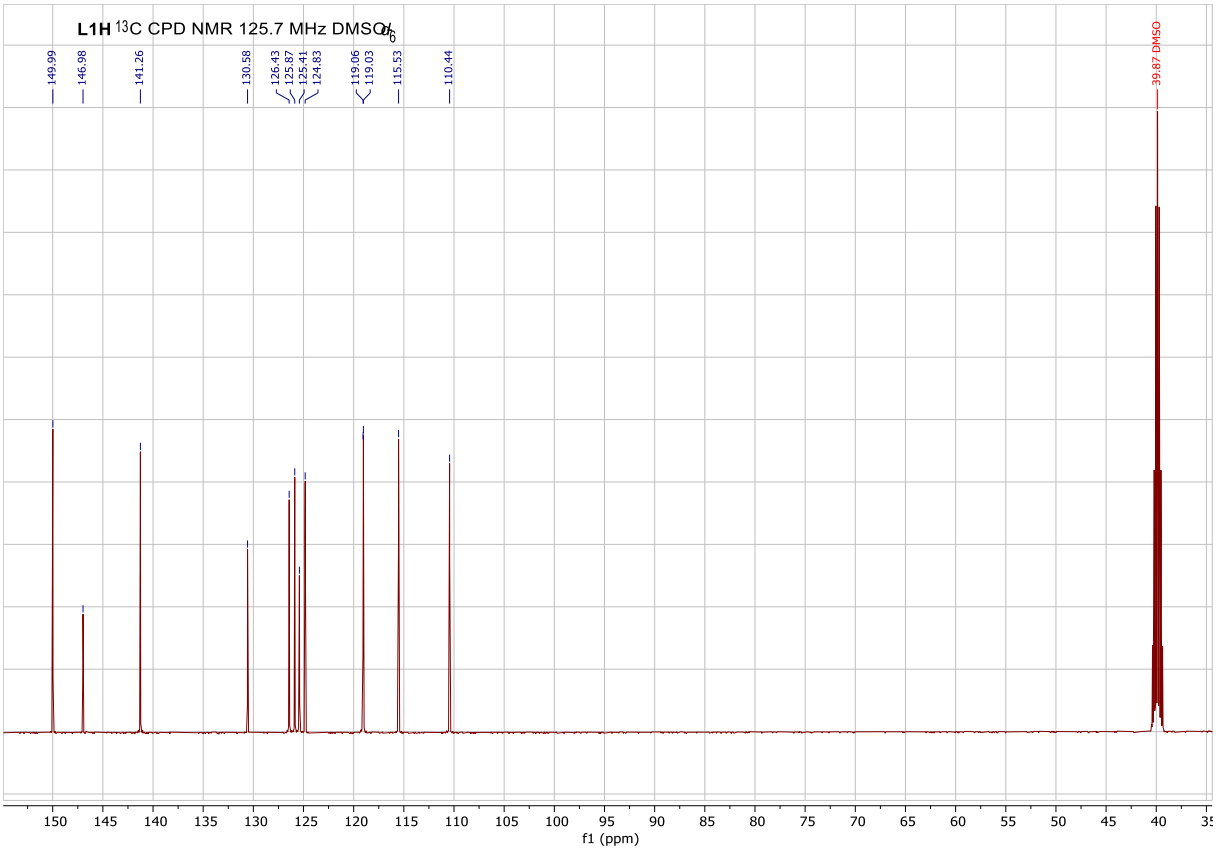
NMR Spectra

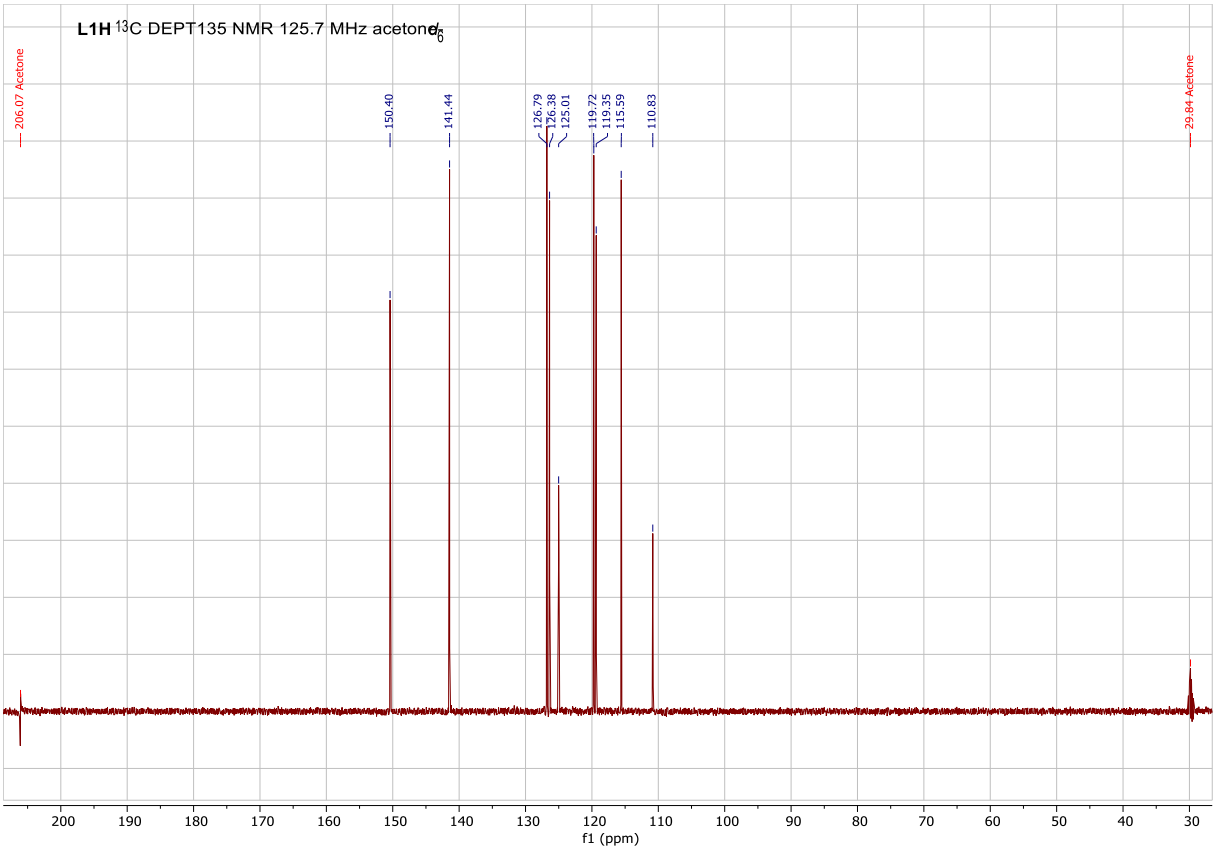


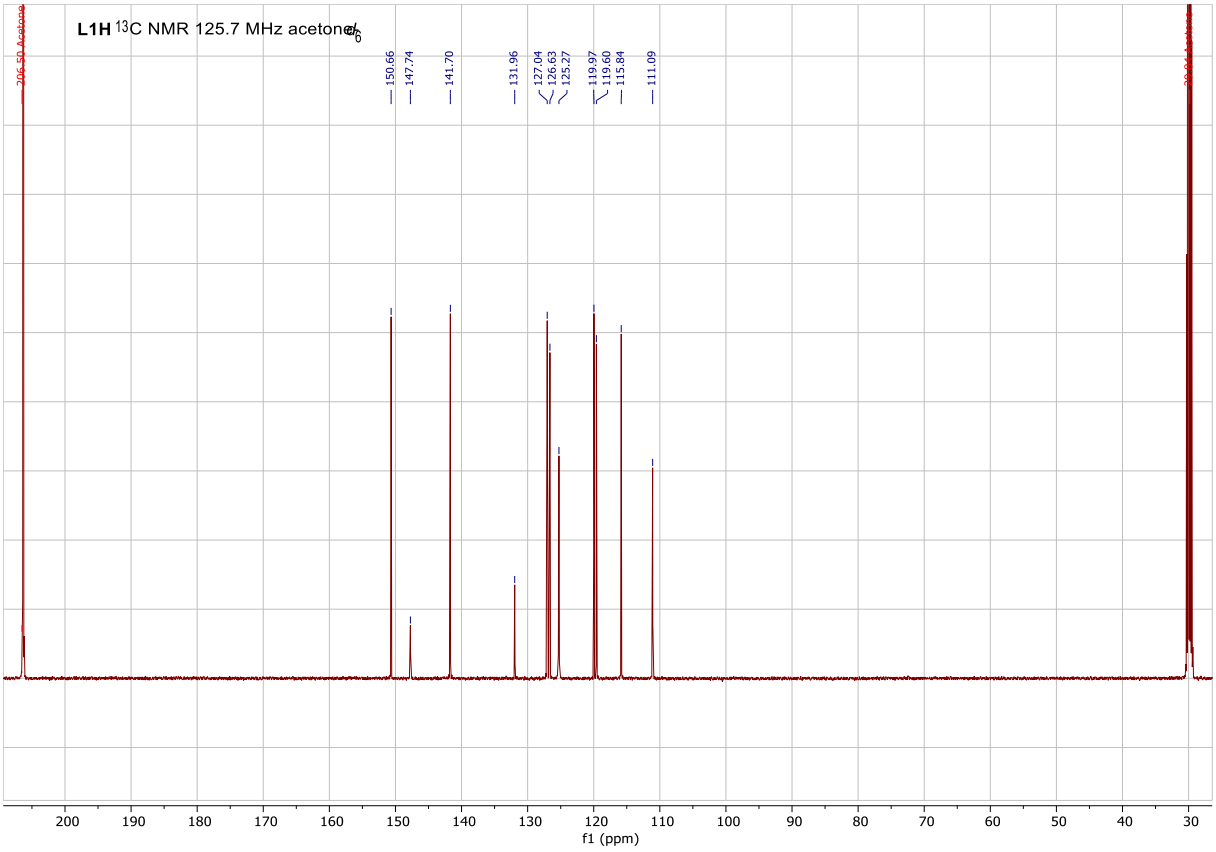


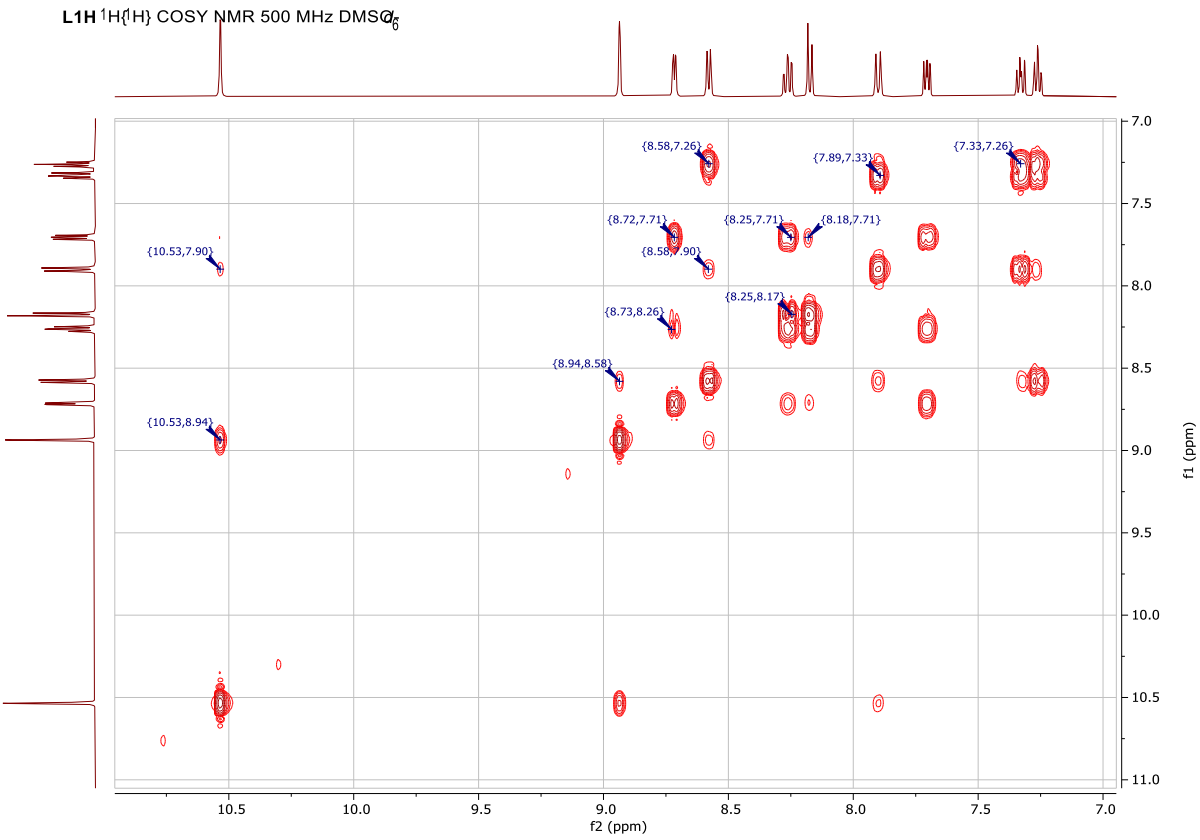

L1H 13C APT NMR 125.7 MHz DMSO-d6
149.98
146.97
141.25
130.57
126.42
125.87
125.40
124.83
119.06
119.03
115.52
110.43
39.87 DMSO
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

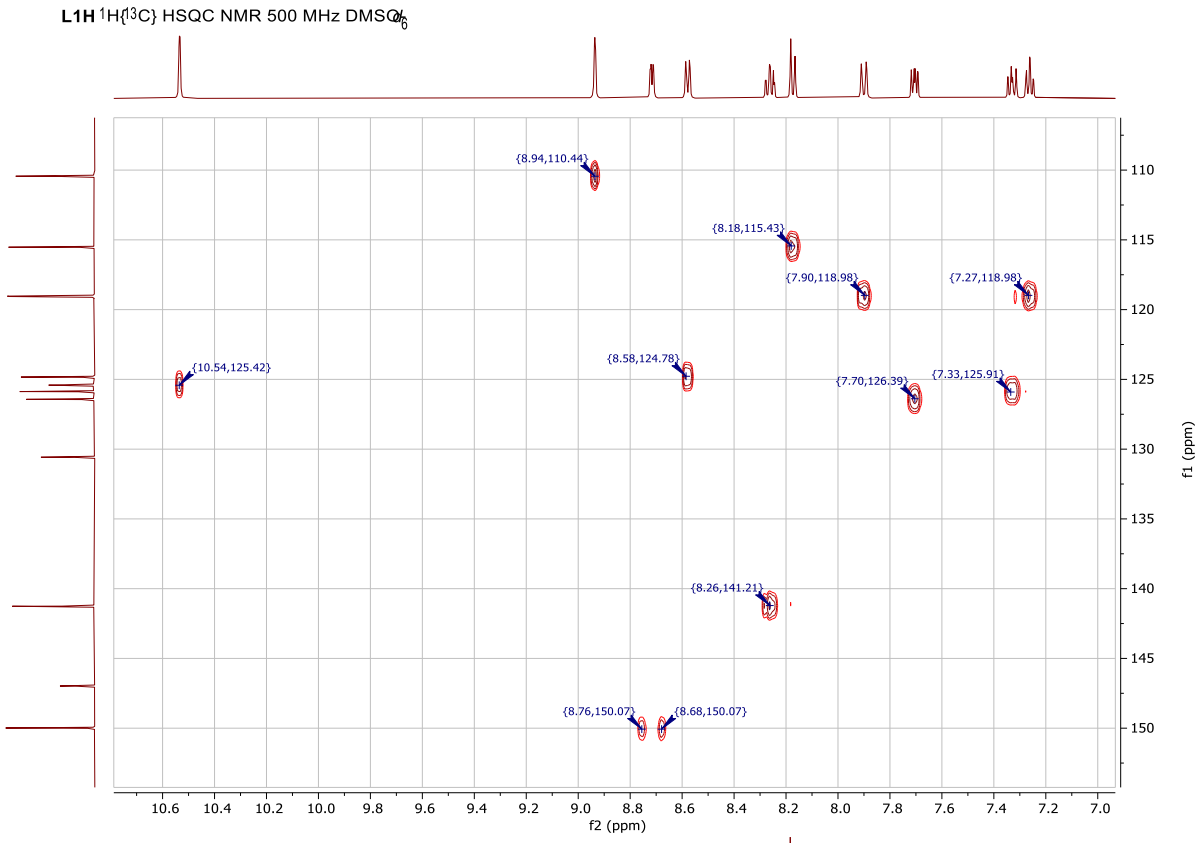

L1H 13C APT NMR 125.7 MHz acetone-d6
206.26 Acetone
150.59
147.67
141.62
131.89
126.97
126.56
125.20
119.90
119.54
115.78
111.02
29.84 Acetone
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)

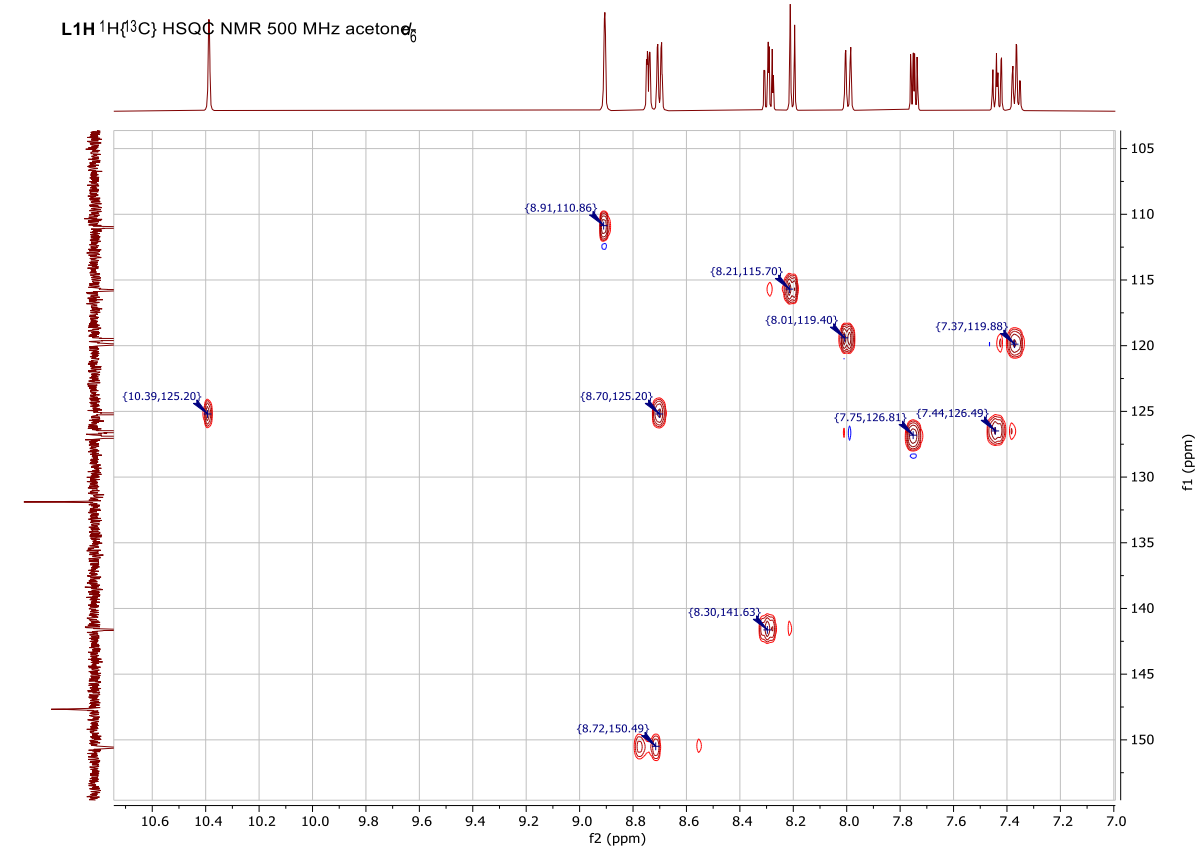

L1H 13C CPD NMR 125.7 MHz DMSO-d6
149.99
146.98
141.26
130.58
126.43
125.87
125.41
124.83
119.06
119.03
115.53
110.44
39.87 DMSO
f1 (ppm)


L1H 13C DEPT135 NMR 125.7 MHz acetone-d6
206.07 Acetone
150.40
141.44
126.79
126.38
125.01
119.72
119.35
115.59
110.83
29.84 Acetone
f1 (ppm)


L1H 13C NMR 125.7 MHz acetone-d6
206.55 Acetone
150.66
147.74
141.70
131.96
127.04
126.63
125.27
119.97
119.60
115.84
111.09
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


L1H 1H{1H} COSY NMR 500 MHz DMSO-d6
{8.58,7.26}
{7.89,7.33}
{7.33,7.26}
{8.72,7.71}
{8.25,7.71}
{8.18,7.71}
{10.53,7.90}
{8.58,7.90}
{8.25,8.17}
{8.73,8.26}
{8.94,8.58}
{10.53,8.94}
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
f2 (ppm)
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
f1 (ppm)


L1H $^{1}H\{^{13}C\}$ HSQC NMR 500 MHz DMSO-d_6
{8.94,110.44}
{8.18,115.43}
{7.90,118.98}
{7.27,118.98}
{10.54,125.42}
{8.58,124.78}
{7.70,126.39}
{7.33,125.91}
{8.26,141.21}
{8.76,150.07}
{8.68,150.07}
f2 (ppm)
f1 (ppm)


L1H $^{1}H\{^{13}C\}$ HSQC NMR 500 MHz acetone-d_6
{8.91,110.86}
{8.21,115.70}
{8.01,119.40}
{7.37,119.88}
{10.39,125.20}
{8.70,125.20}
{7.75,126.81}
{7.44,126.49}
{8.30,141.63}
{8.72,150.49}
f2 (ppm)
f1 (ppm)

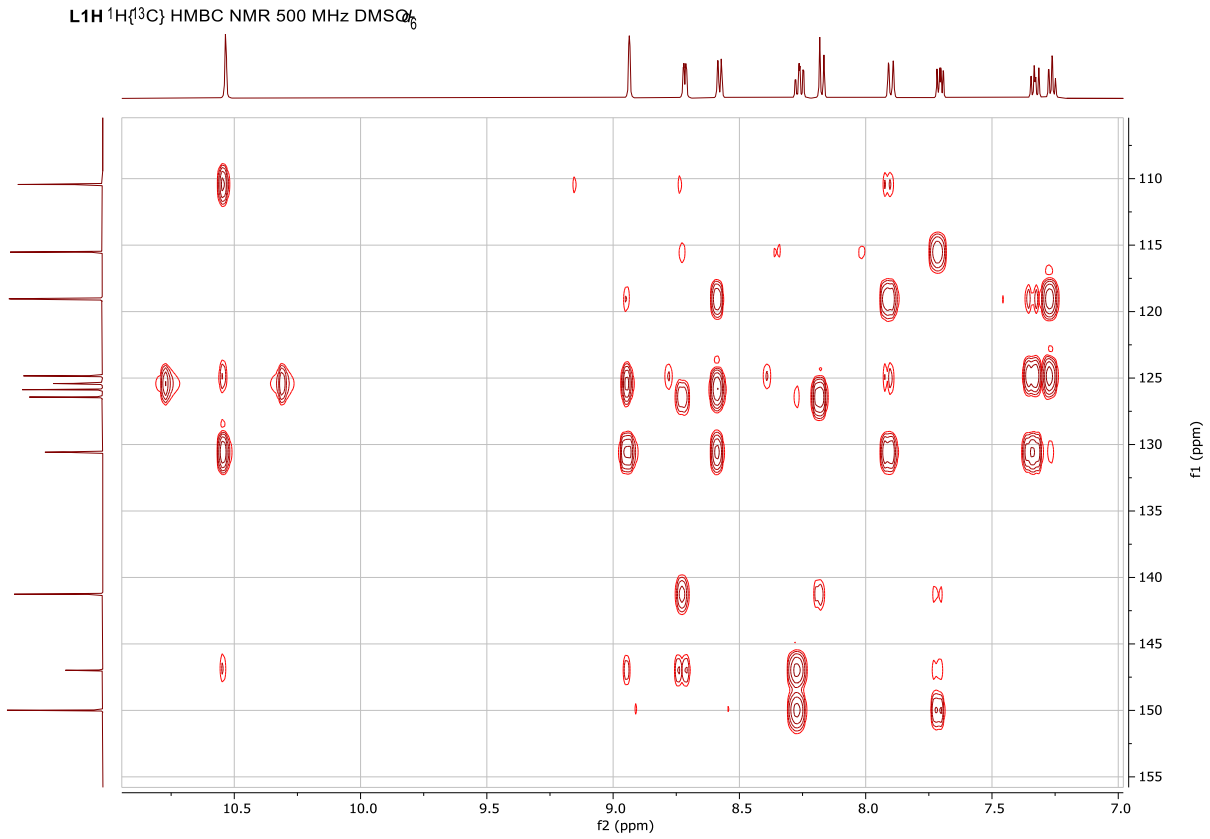
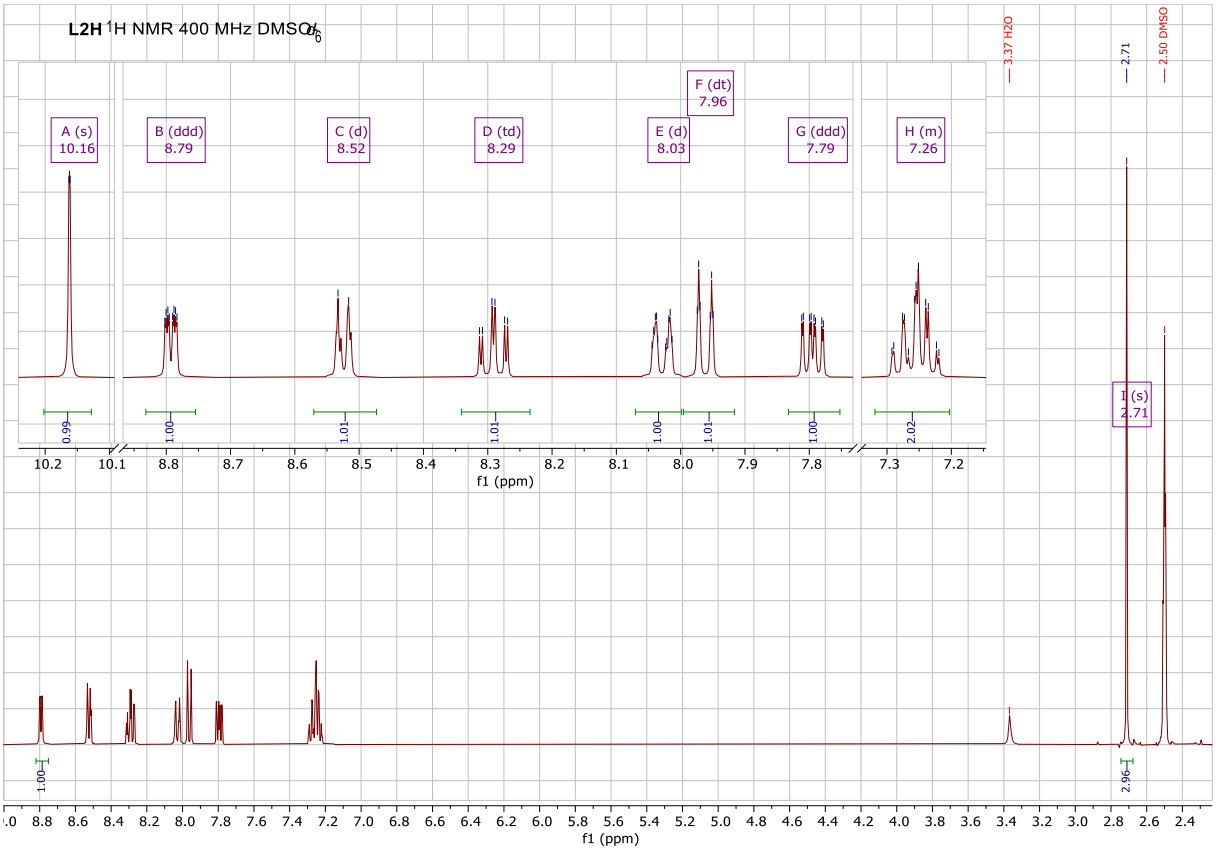
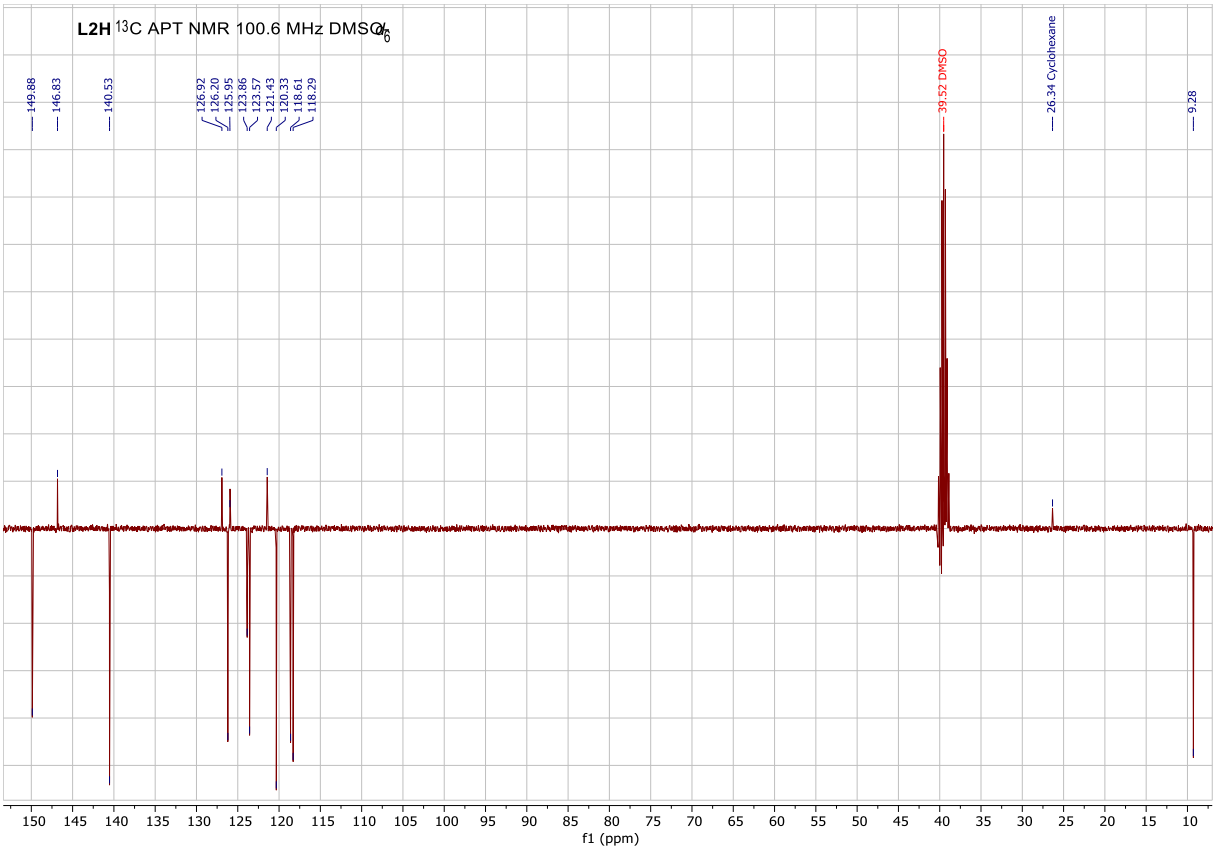
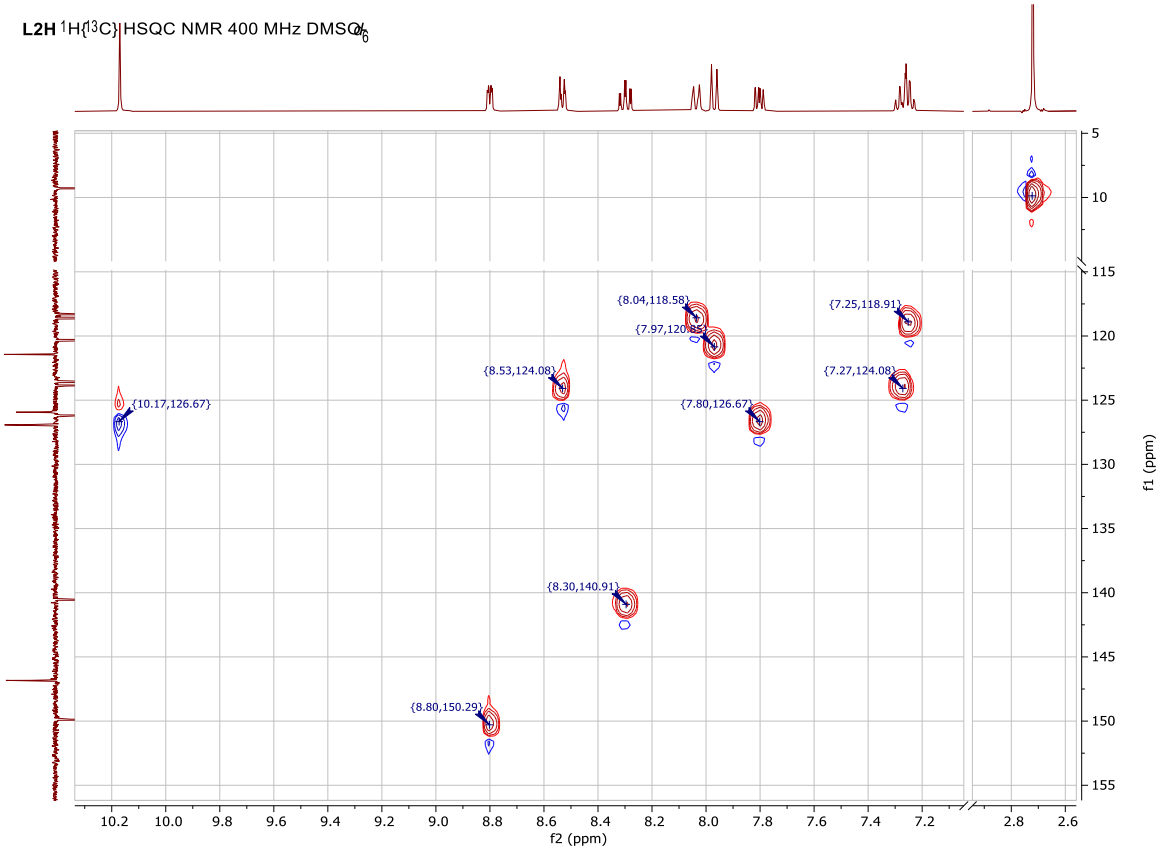


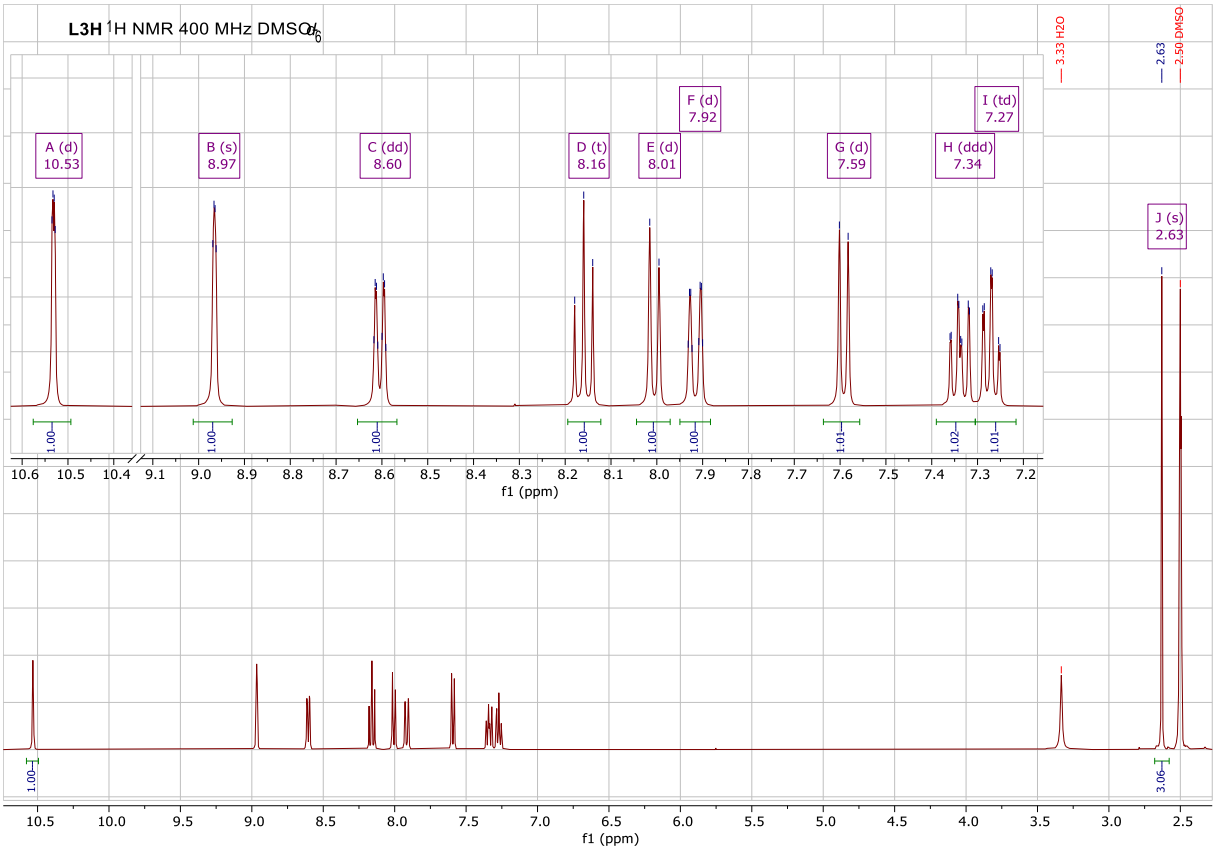
Figure S28 –NMR spectra for **L1H**: 1H, 13C APT, CPD, COSY, HBQC, HMBC in DMSO-d6 and 1H, APT, CPD, DEPT135, HBQC in acetone-d6.

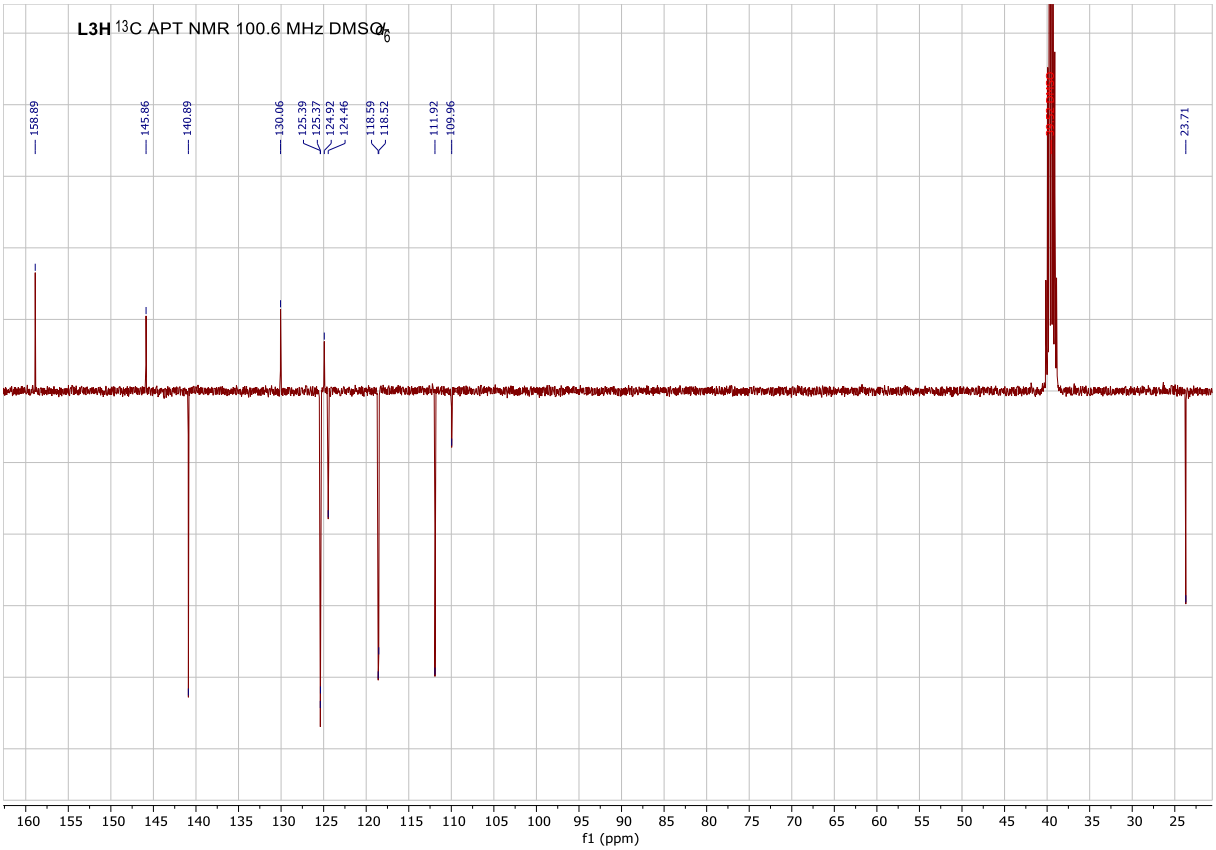

L2H 1H NMR 400 MHz DMSO-d6
A (s) 10.16
B (ddd) 8.79
C (d) 8.52
D (td) 8.29
E (d) 8.03
F (dt) 7.96
G (ddd) 7.79
H (m) 7.26
I (s) 2.71
3.37 H2O
2.71
2.50 DMSO
f1 (ppm)


L2H 13C APT NMR 100.6 MHz DMSO-d6
149.88
146.83
140.53
126.92
126.20
125.95
123.86
123.57
121.43
120.33
118.61
118.29
39.52 DMSO
26.34 Cyclohexane
9.28
f1 (ppm)



Figures S29 –NMR spectra for **L2H**: 1H, 13C APT, HBQC in DMSO-d6.


L3H 1H NMR 400 MHz DMSO-d6
A (d) 10.53
B (s) 8.97
C (dd) 8.60
D (t) 8.16
E (d) 8.01
F (d) 7.92
G (d) 7.59
H (ddd) 7.34
I (td) 7.27
J (s) 2.63
3.33 H2O
2.63
2.50 DMSO
f1 (ppm)


L3H 13C APT NMR 100.6 MHz DMSO-d6
158.89
145.86
140.89
130.06
125.39
125.37
124.92
124.46
118.59
118.52
111.92
109.96
23.71
f1 (ppm)

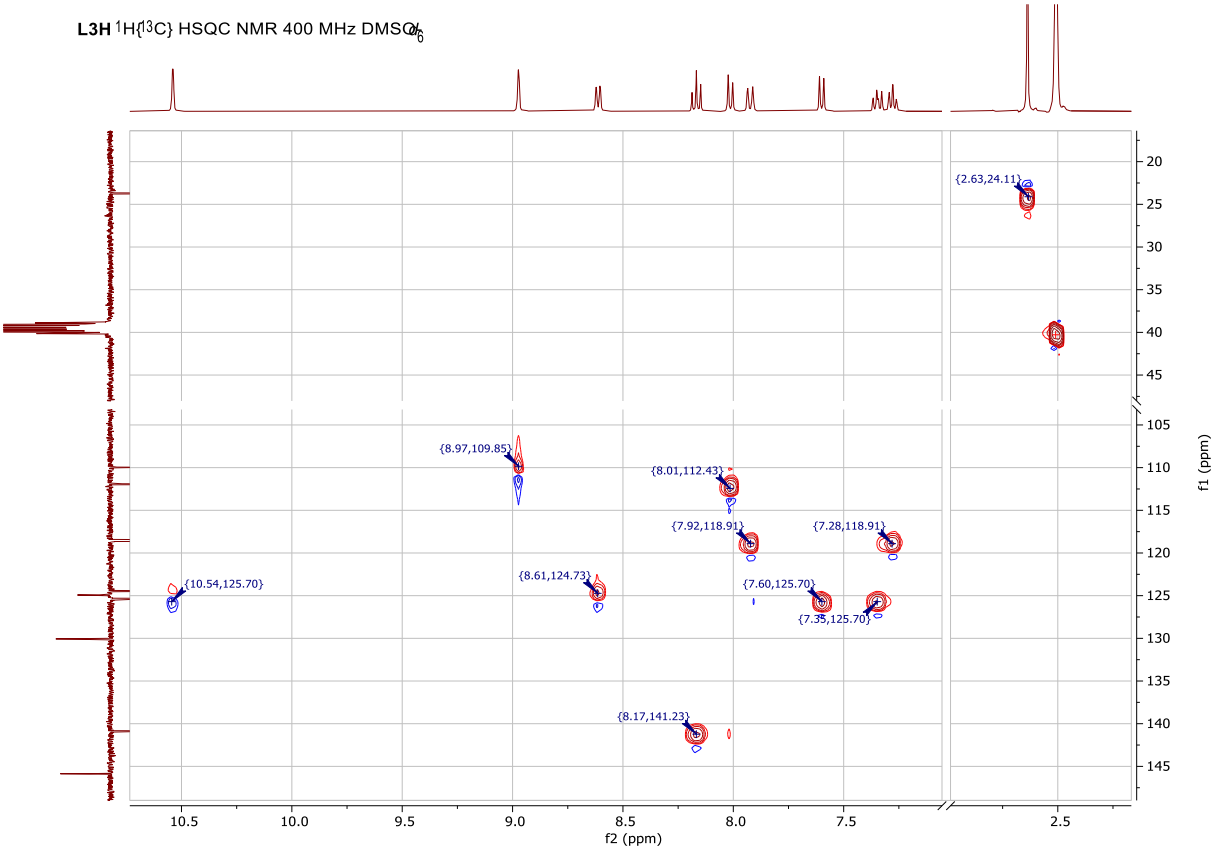
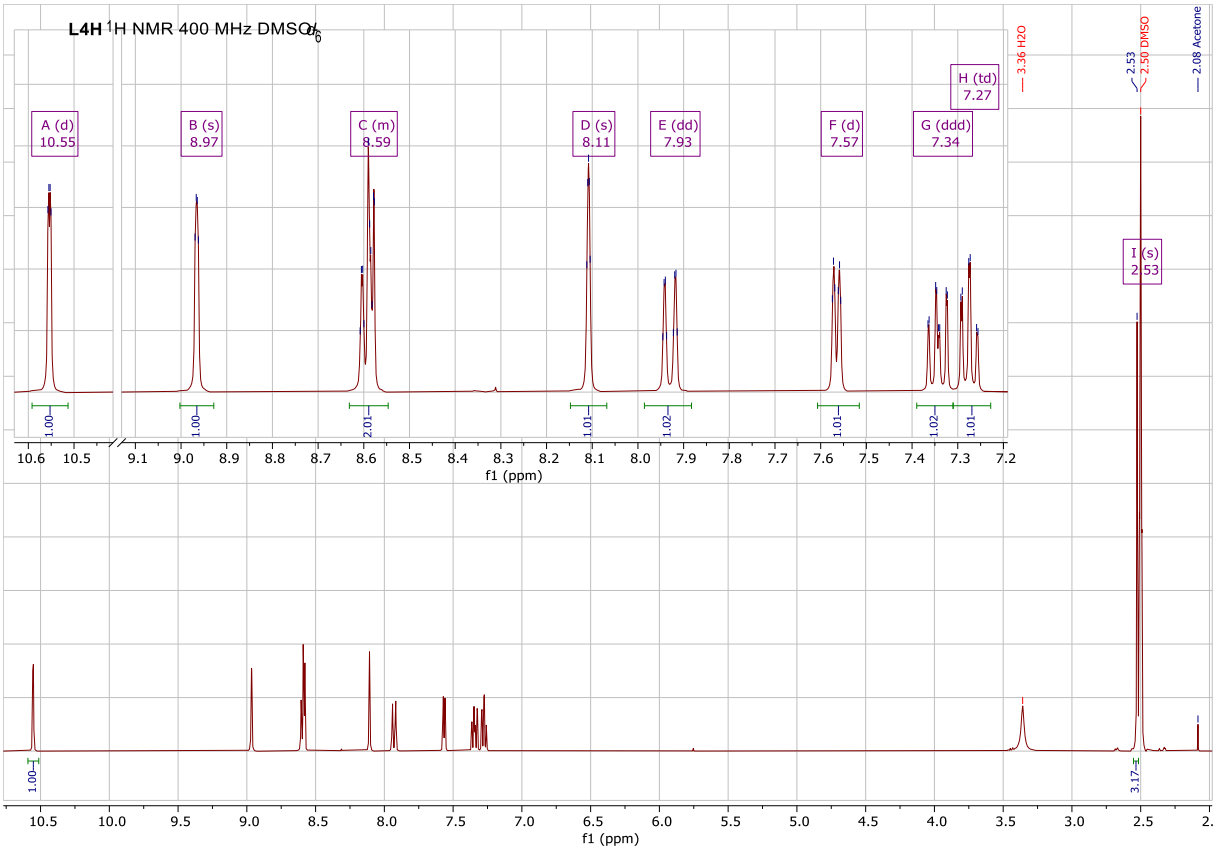
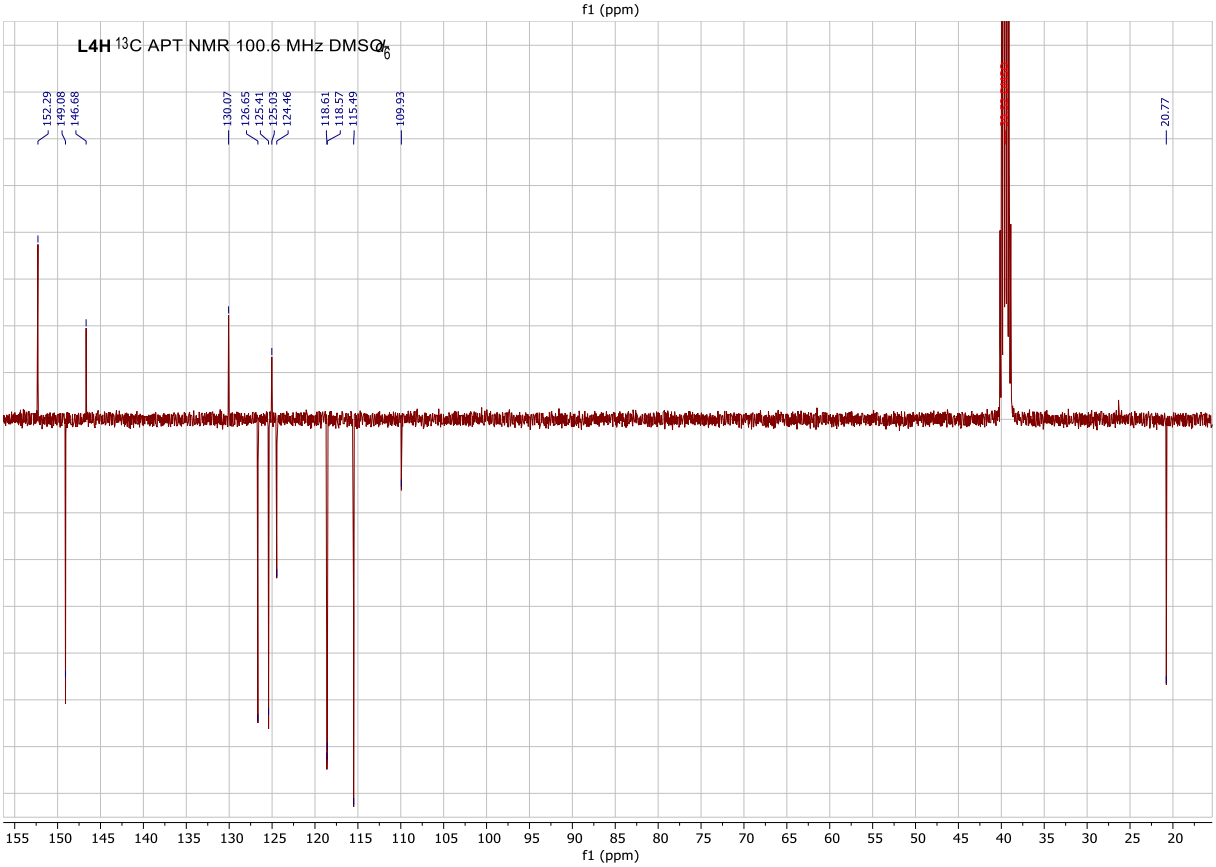


Figure S30 –NMR spectra for **L3H**: 1H, 13C APT, HBQC in DMSO-d6.


L4H 1H NMR 400 MHz DMSO-d6
A (d) 10.55
B (s) 8.97
C (m) 8.59
D (s) 8.11
E (dd) 7.93
F (d) 7.57
G (ddd) 7.34
H (td) 7.27
I (s) 2.53
3.36 H2O
2.53
2.50 DMSO
2.08 Acetone
1.00
1.00
2.01
1.01
1.02
1.01
1.02
1.01
1.00
3.17
f1 (ppm)


L4H 13C APT NMR 100.6 MHz DMSO-d6
152.29
149.08
146.68
130.07
126.65
125.41
125.03
124.46
118.61
118.57
115.49
109.93
20.77
f1 (ppm)

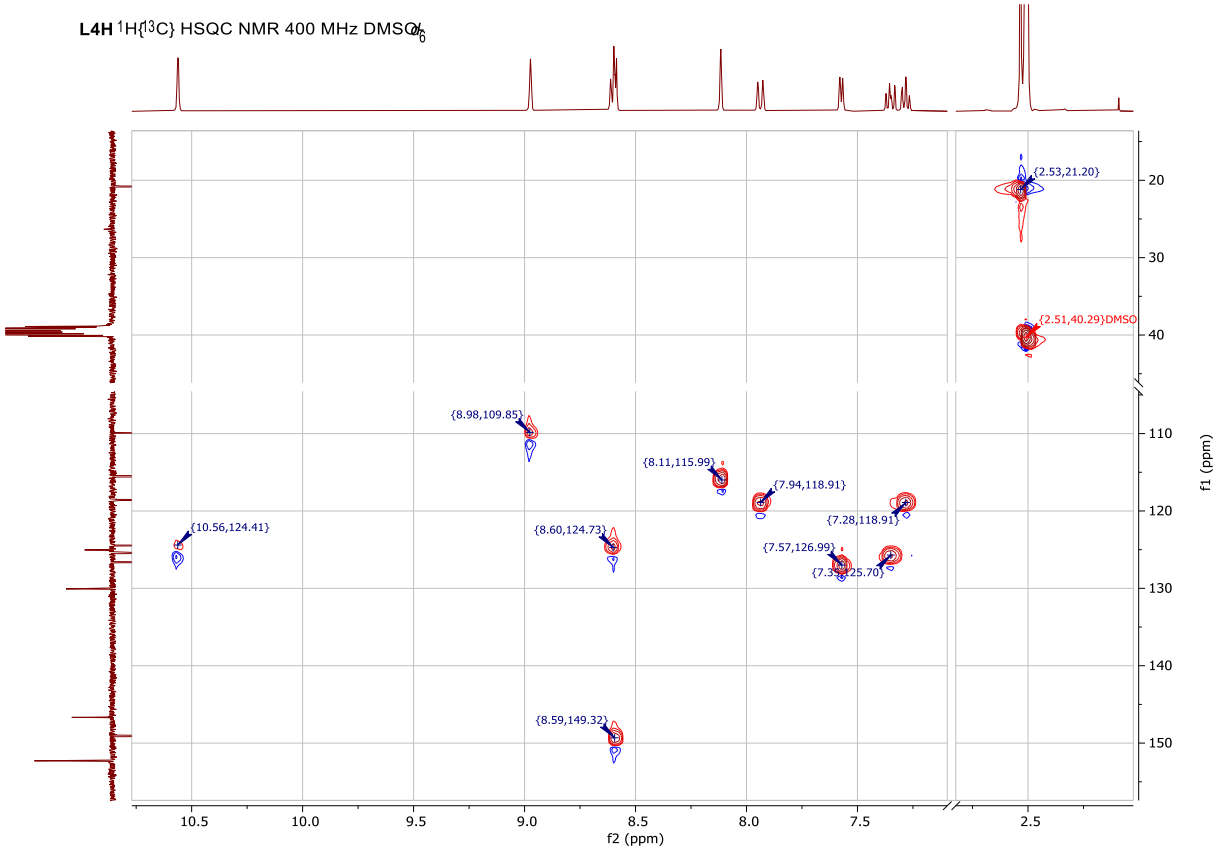
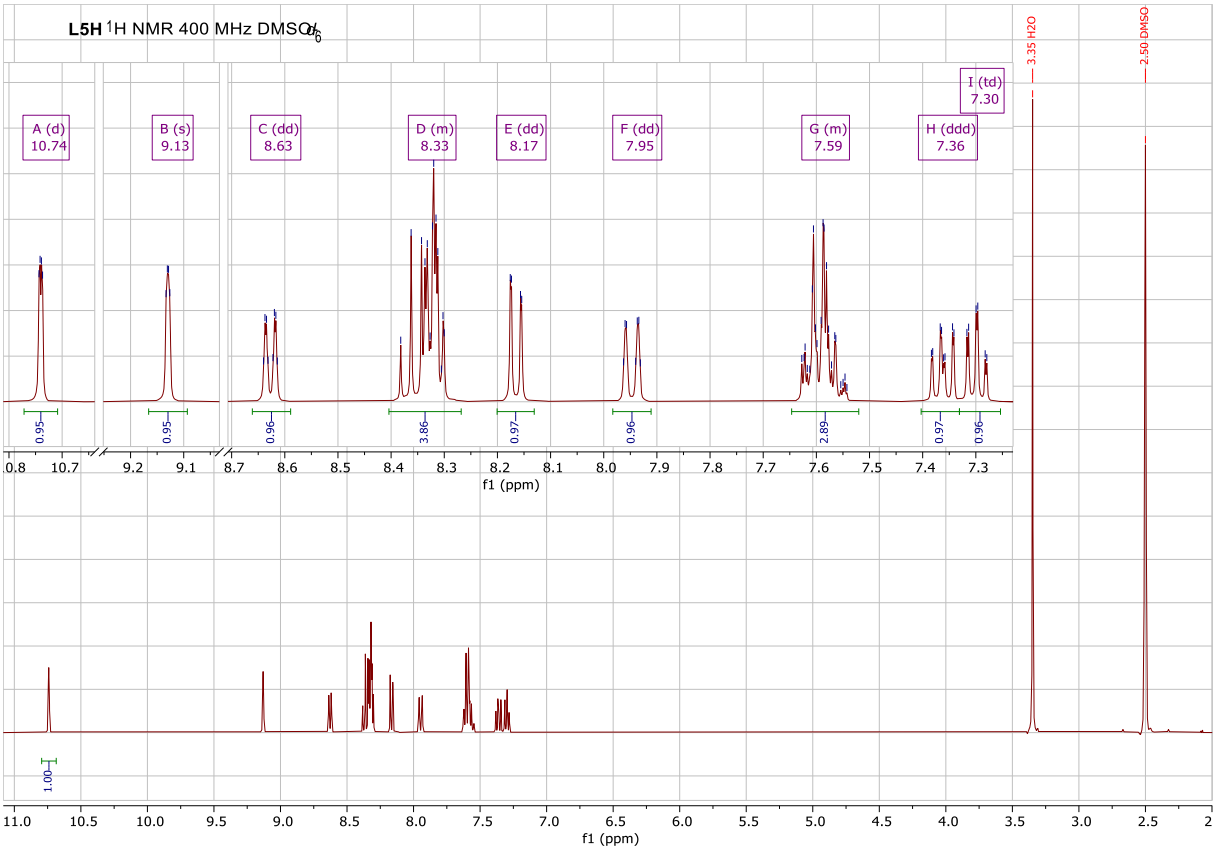
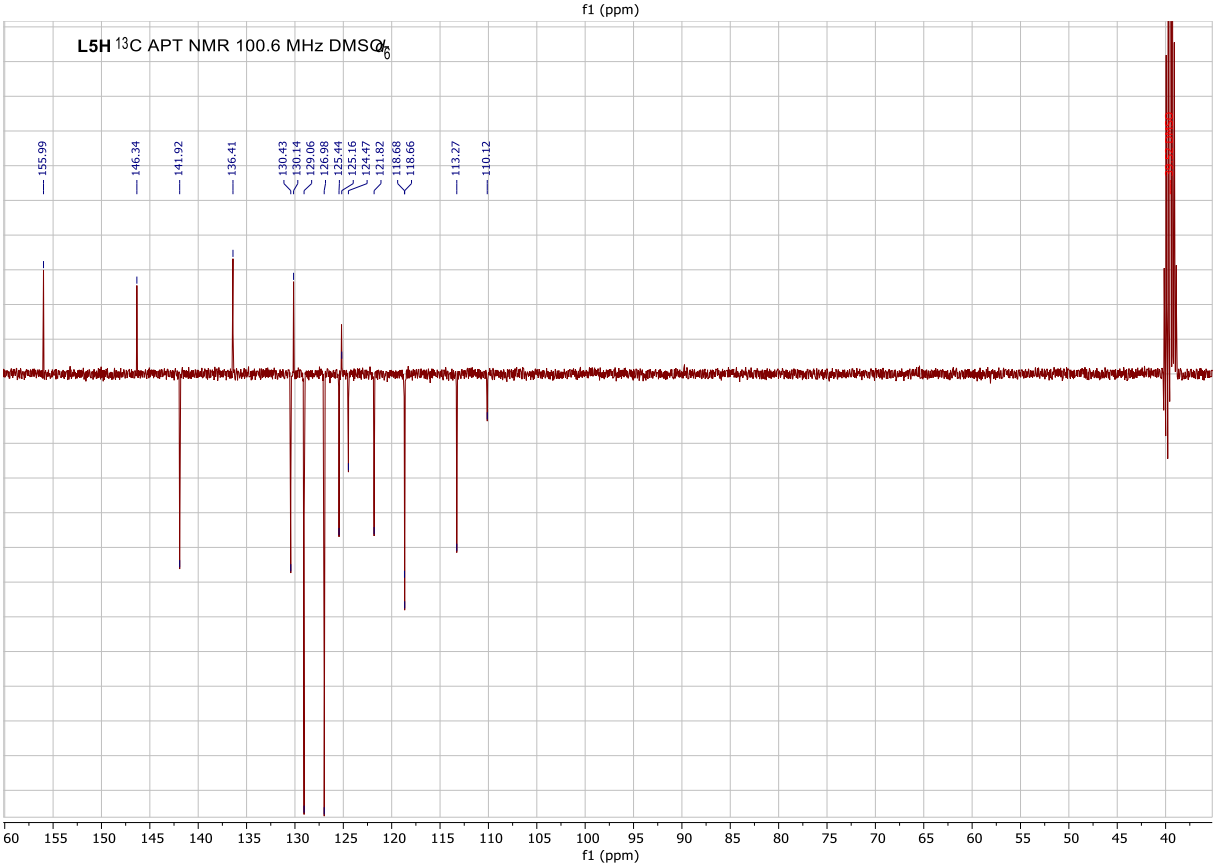


Figure S31 –NMR spectra for **L4H**: 1H, 13C APT, HBQC in DMSO-d6.


L5H 1H NMR 400 MHz DMSO-d6
A (d) 10.74
B (s) 9.13
C (dd) 8.63
D (m) 8.33
E (dd) 8.17
F (dd) 7.95
G (m) 7.59
H (ddd) 7.36
I (td) 7.30
3.35 H2O
2.50 DMSO
f1 (ppm)


L5H 13C APT NMR 100.6 MHz DMSO-d6
155.99
146.34
141.92
136.41
130.43
130.14
129.06
126.98
125.44
125.16
124.47
121.82
118.68
118.66
113.27
110.12
f1 (ppm)

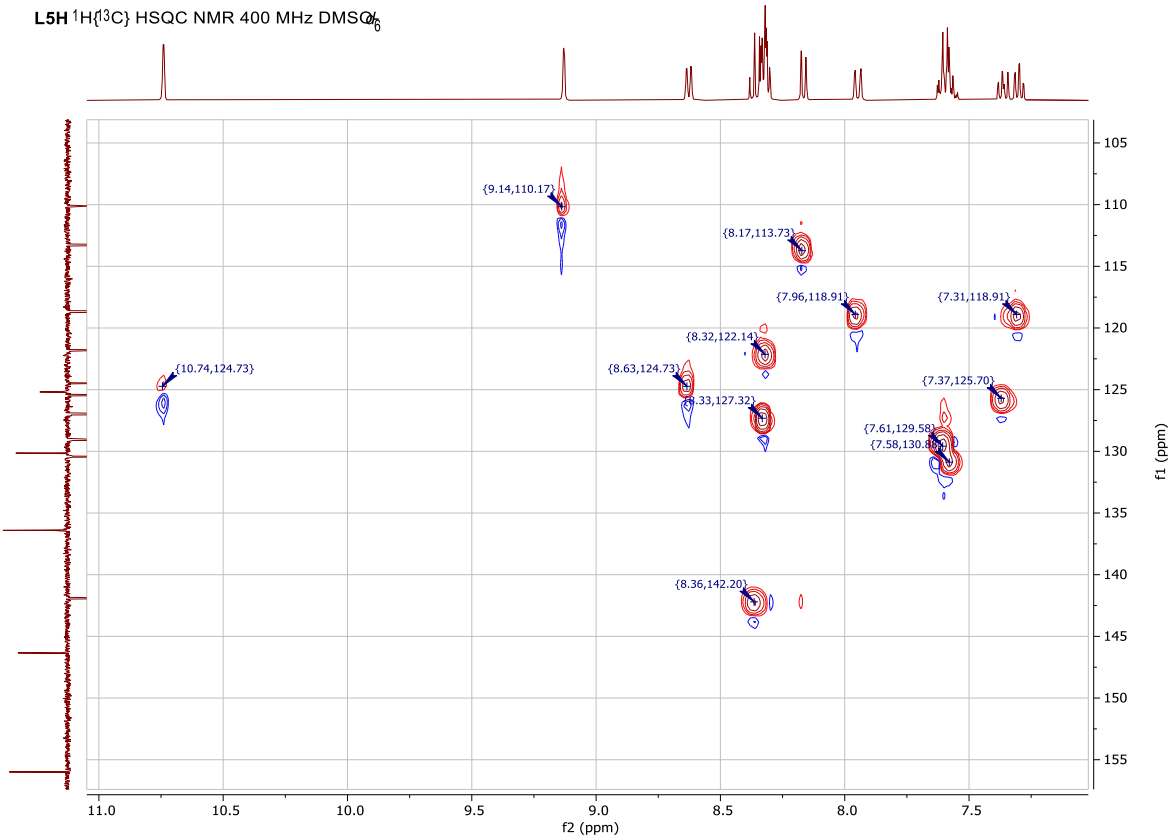
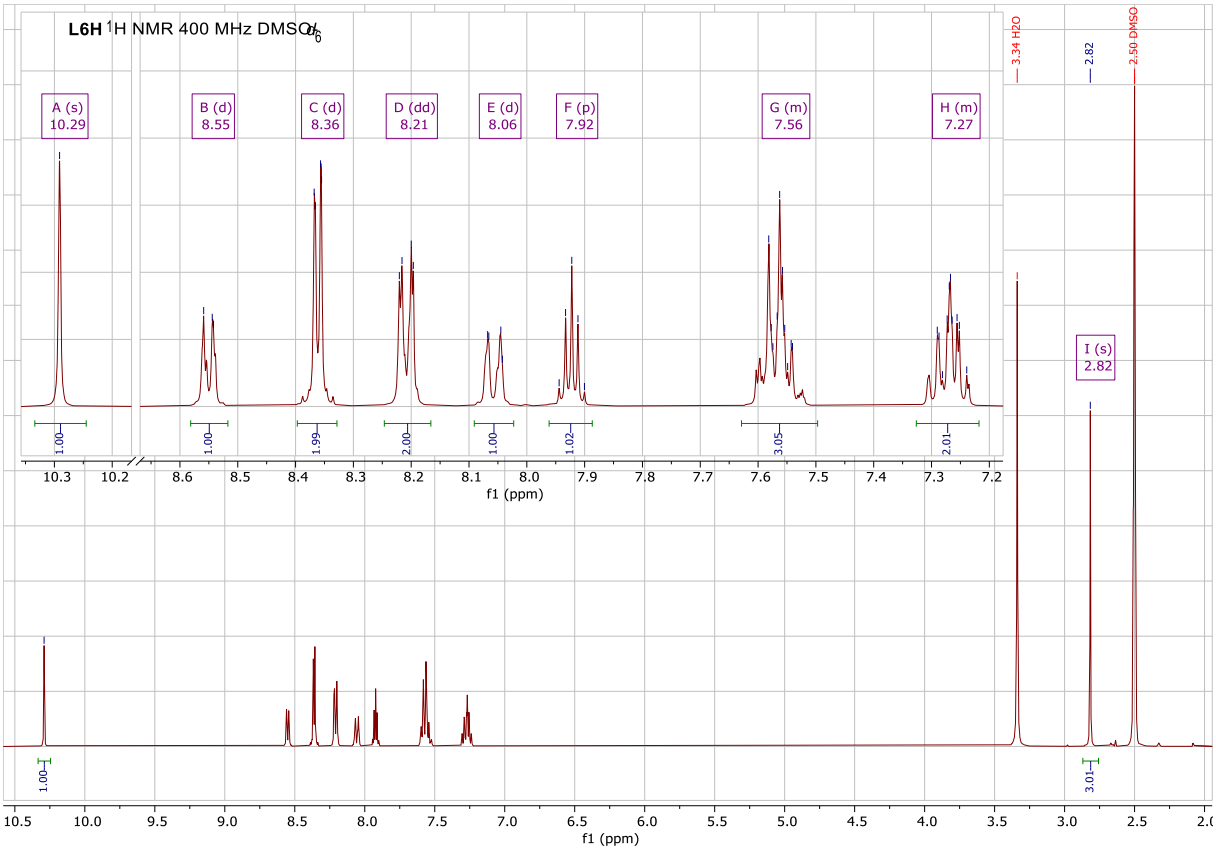
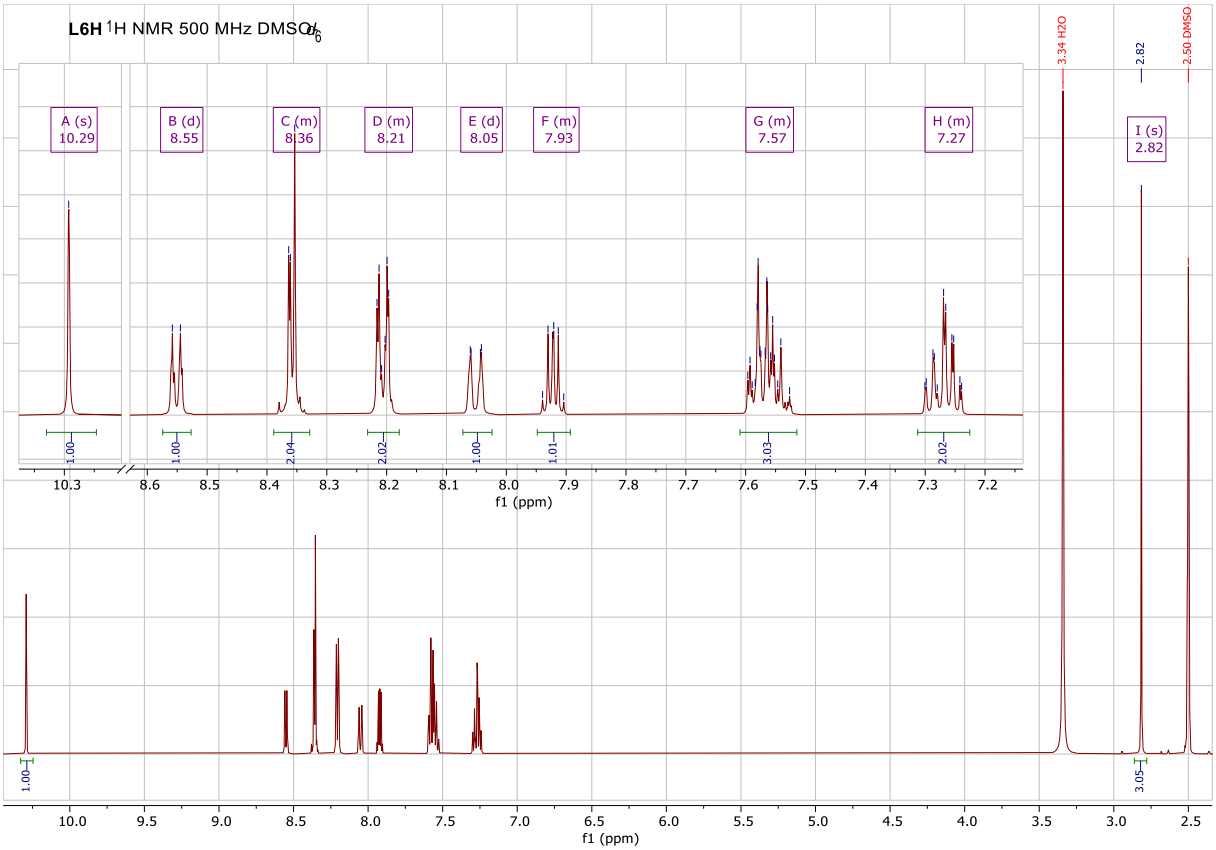
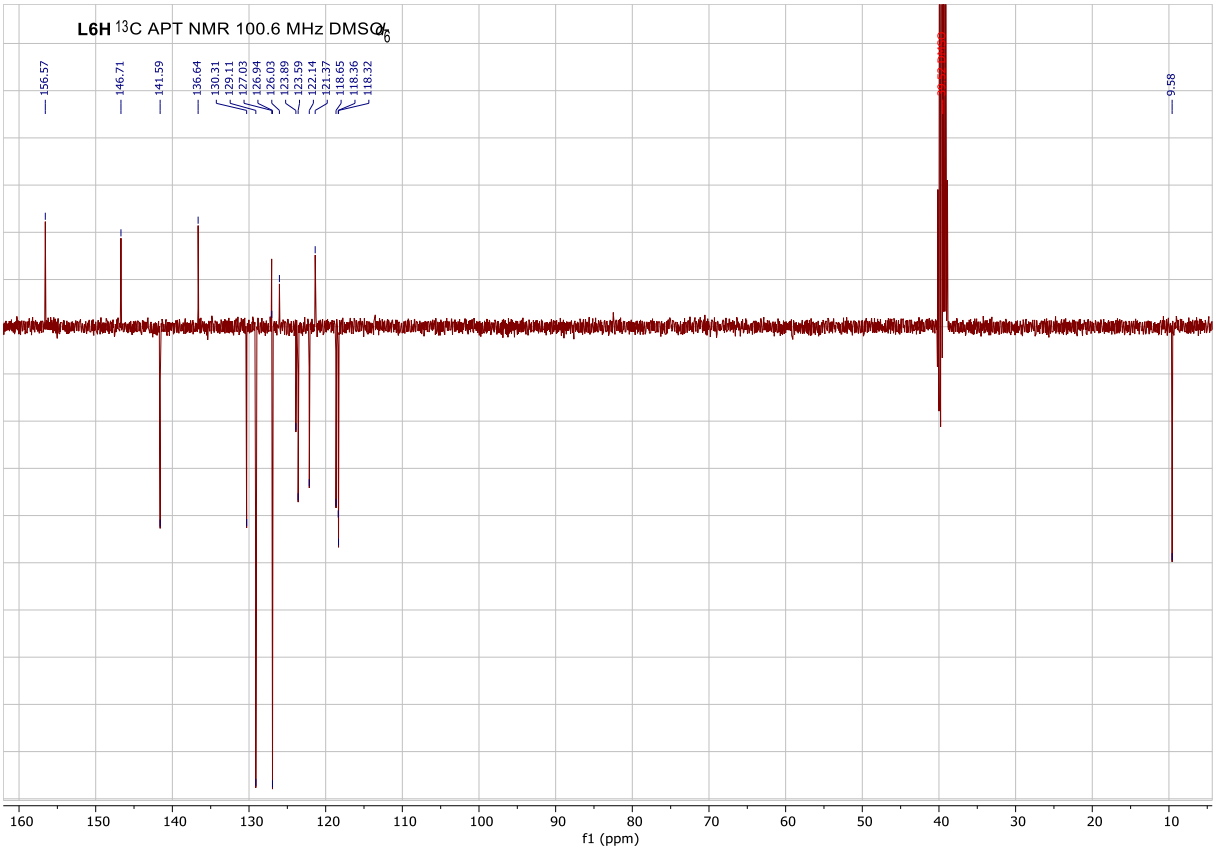
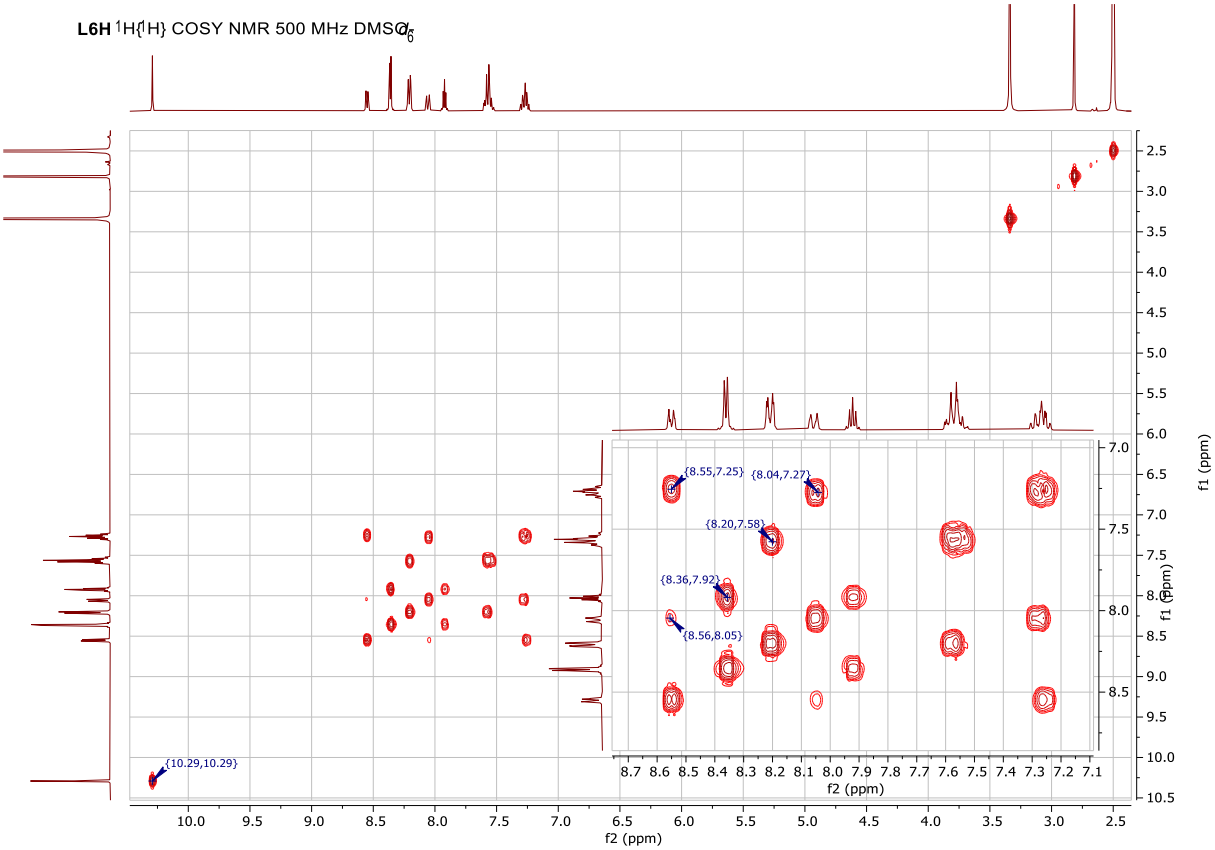


Figure S32 –NMR spectra for **L5H**: 1H, 13C APT, HBQC in DMSO-d6.


L6H 1H NMR 400 MHz DMSO-d6
A (s) 10.29
B (d) 8.55
C (d) 8.36
D (dd) 8.21
E (d) 8.06
F (p) 7.92
G (m) 7.56
H (m) 7.27
I (s) 2.82
3.34 H2O
2.82
2.50 DMSO
f1 (ppm)


L6H 1H NMR 500 MHz DMSO-d6
A (s) 10.29
B (d) 8.55
C (m) 8.36
D (m) 8.21
E (d) 8.05
F (m) 7.93
G (m) 7.57
H (m) 7.27
I (s) 2.82
3.34 H2O
2.82
2.50 DMSO
f1 (ppm)


L6H 13C APT NMR 100.6 MHz DMSO-d6
156.57
146.71
141.59
136.64
130.31
129.11
127.03
126.94
126.03
123.89
123.59
122.14
121.37
118.65
118.36
118.32
39.58
9.58
f1 (ppm)


L6H 1H{1H} COSY NMR 500 MHz DMSO-d6
{10.29,10.29}
{8.55,7.25}
{8.04,7.27}
{8.20,7.58}
{8.36,7.92}
{8.56,8.05}
f2 (ppm)
f1 (ppm)

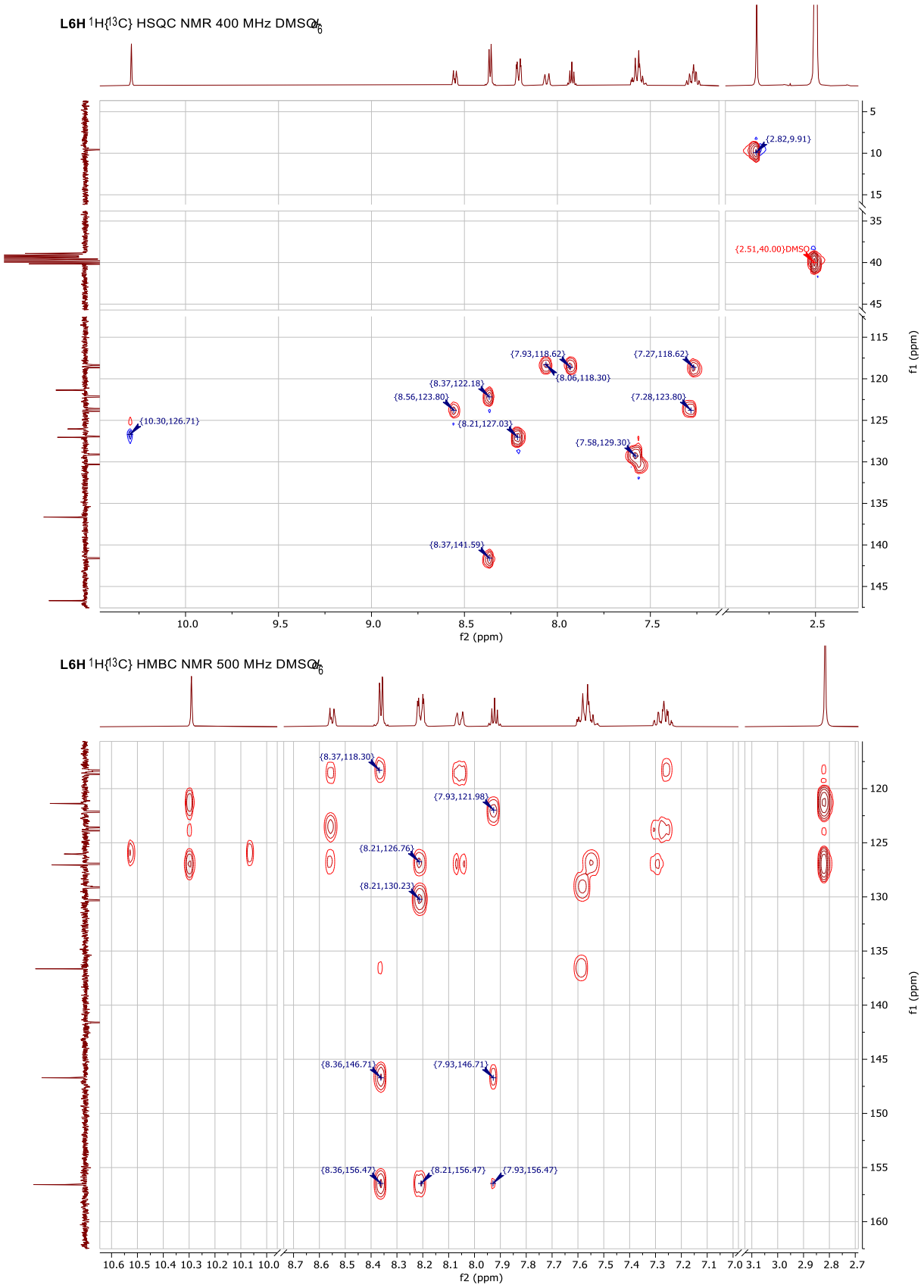


Figure S33 –NMR spectra for **L6H**: 1H, 13C APT, COSY, HBQC, HMBC in DMSO-d6.

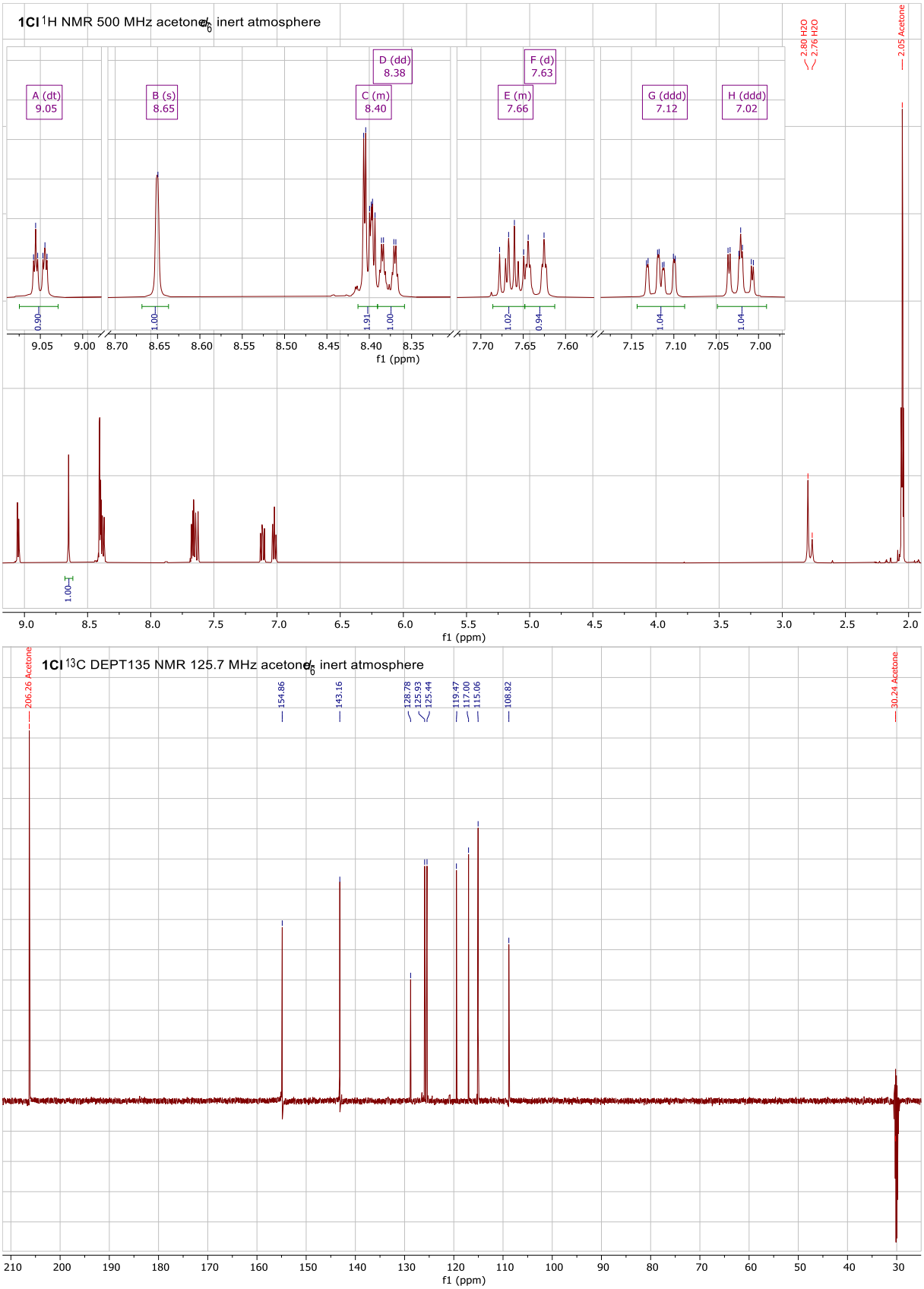


Figure S34 –NMR spectra for **1Cl**: 1H, 13C DEPT135 in acetone-d6.

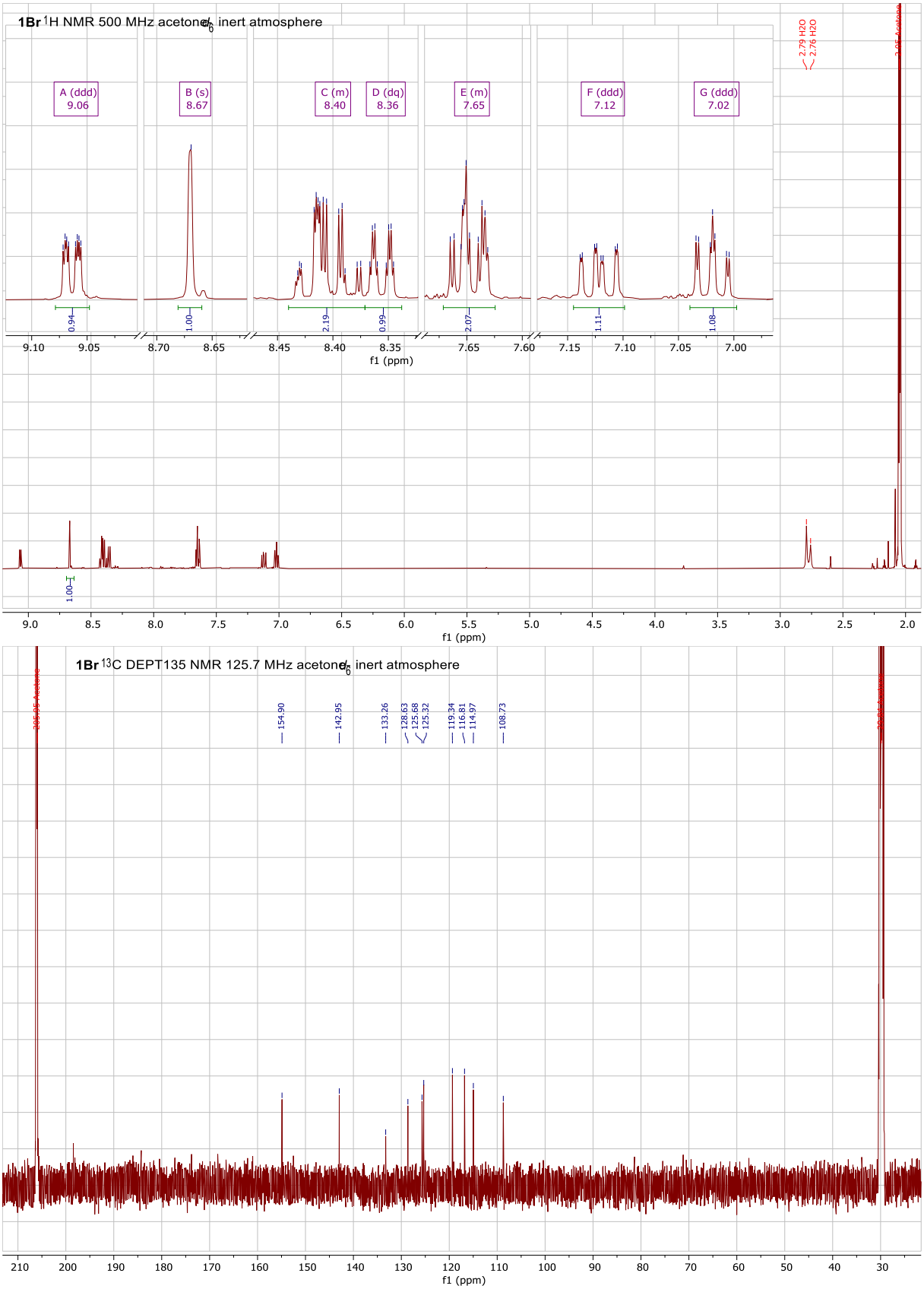


Figure S35 –NMR spectra for **1Br**: 1H, 13C DEPT135 in acetone-d6.

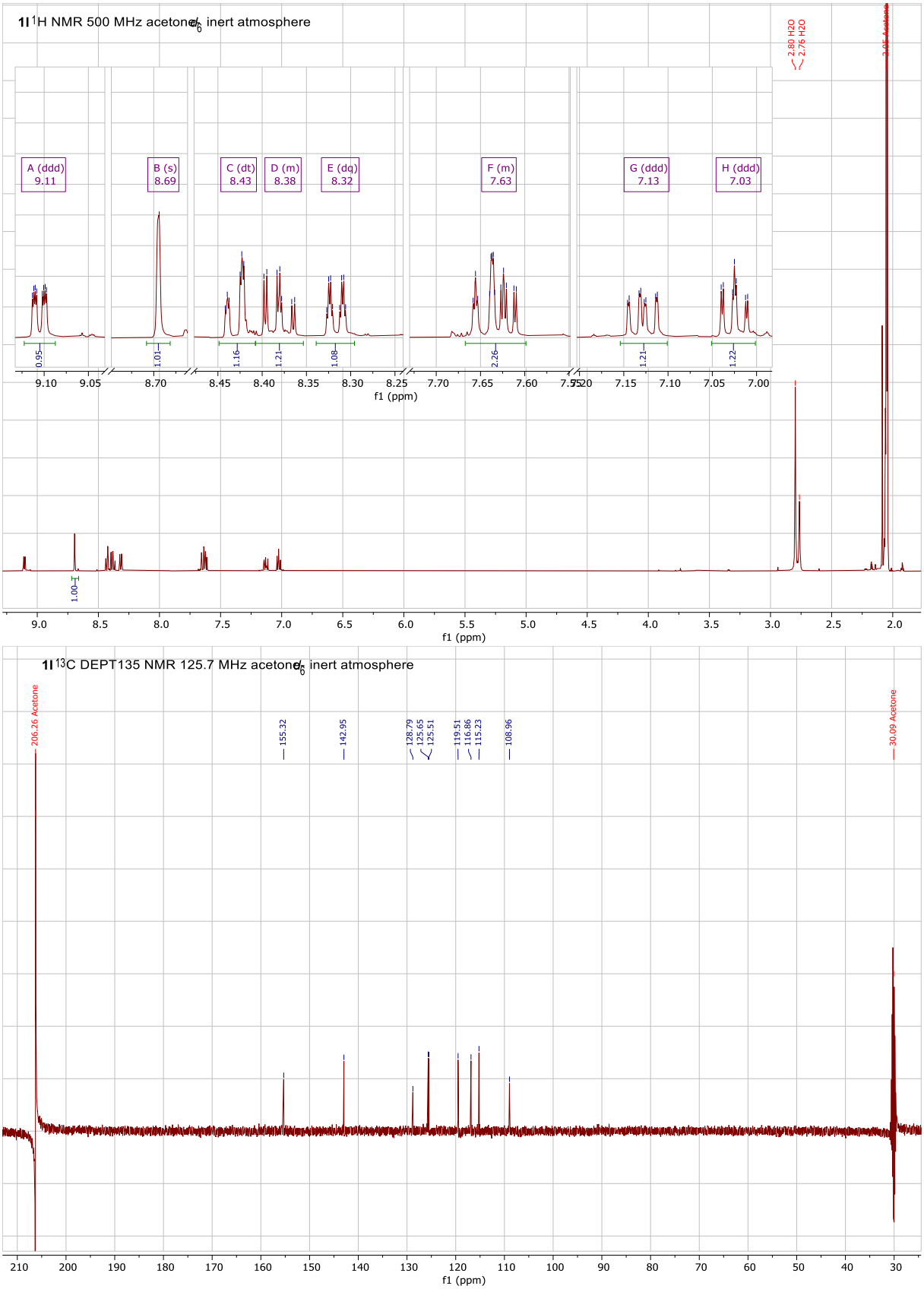


Figure S36 –NMR spectra for **1l**: 1H, 13C DEPT135 in acetone-d6.

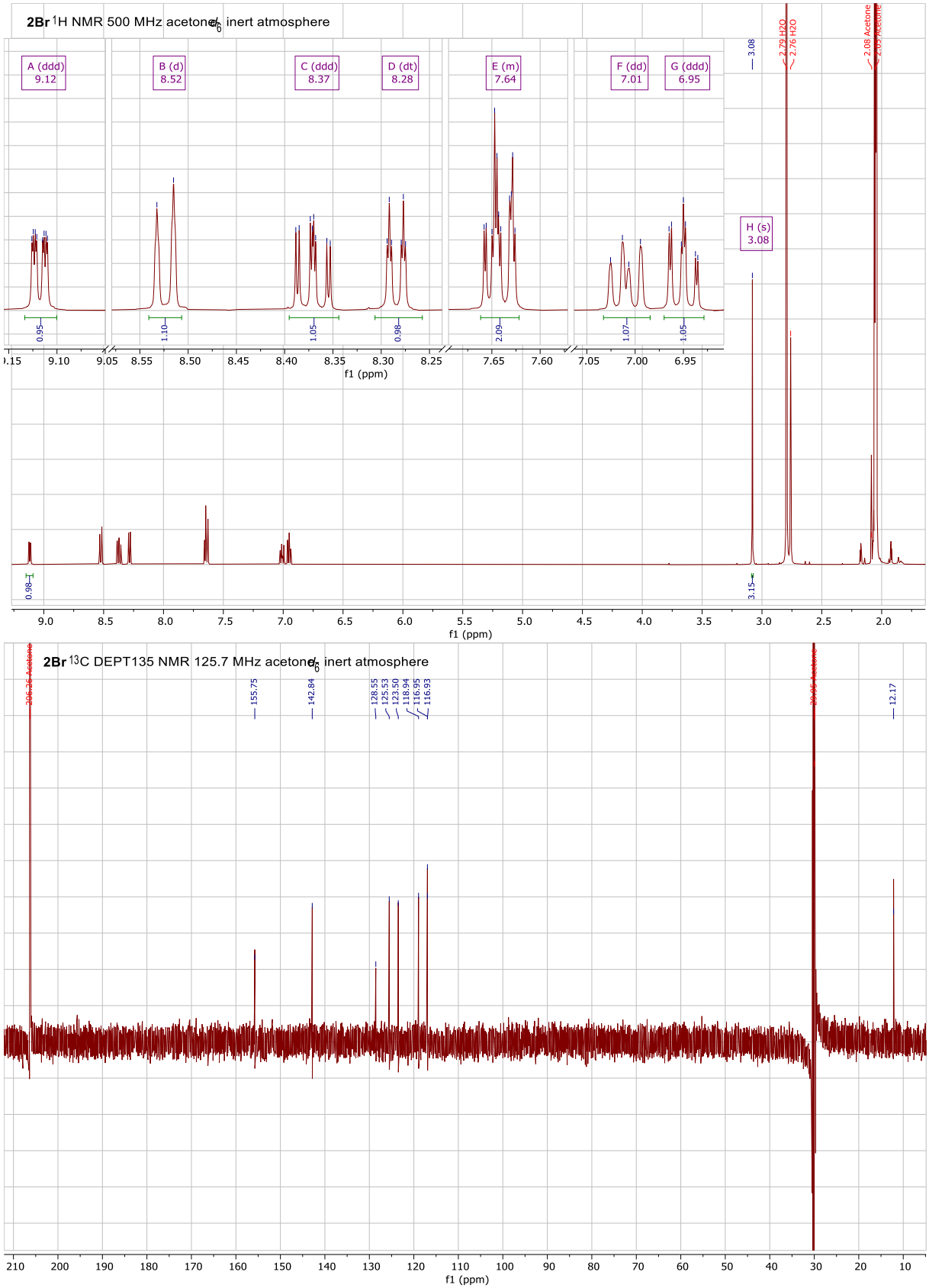


Figure S37 –NMR spectra for **2Br**: 1H, 13C DEPT135 in acetone-d6.

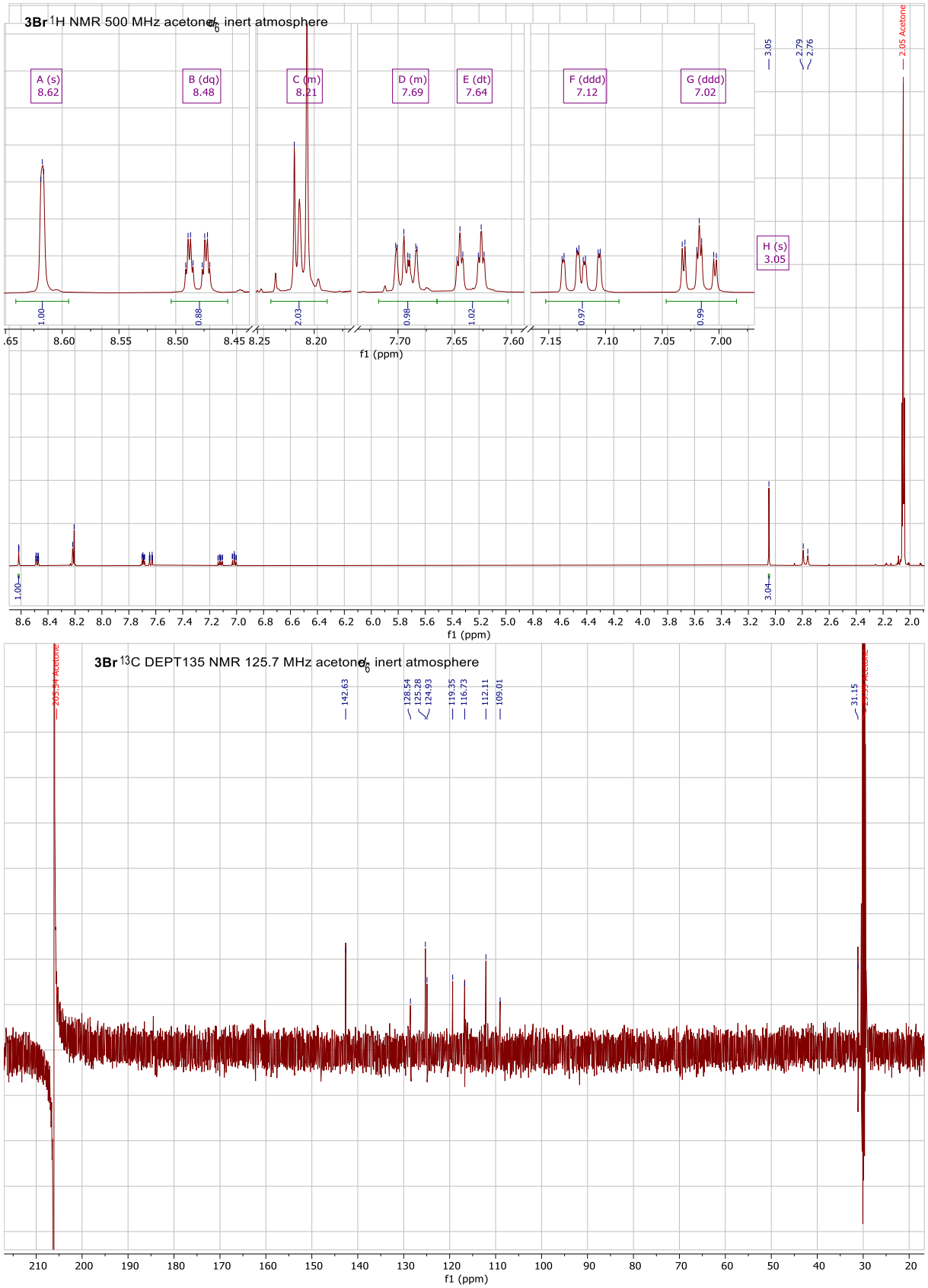


Figure S38 –NMR spectra for **3Br**: 1H, 13C DEPT135 in acetone-d6.

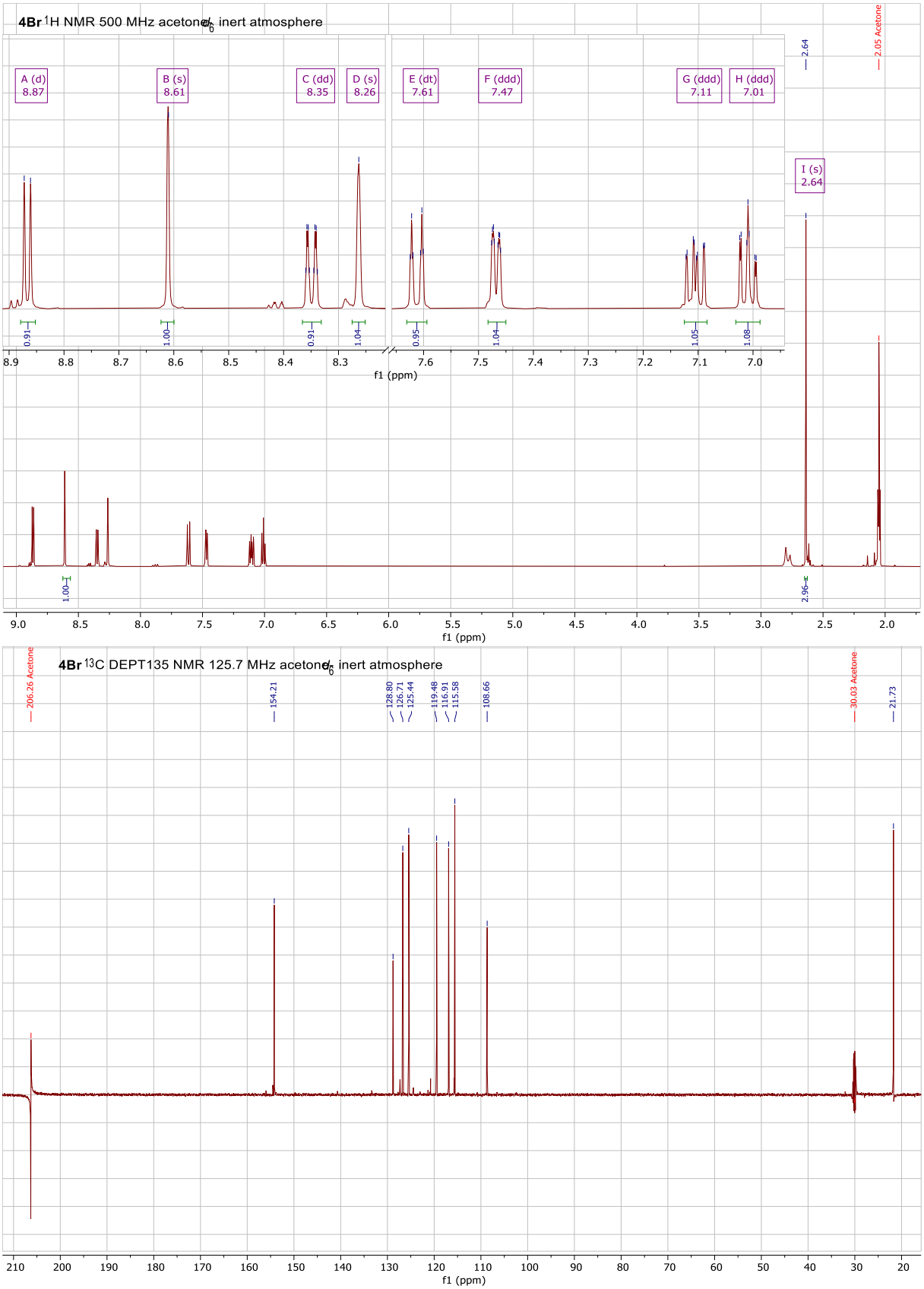


Figure S39 –NMR spectra for **4Br**: 1H, 13C DEPT135 in acetone-d6.

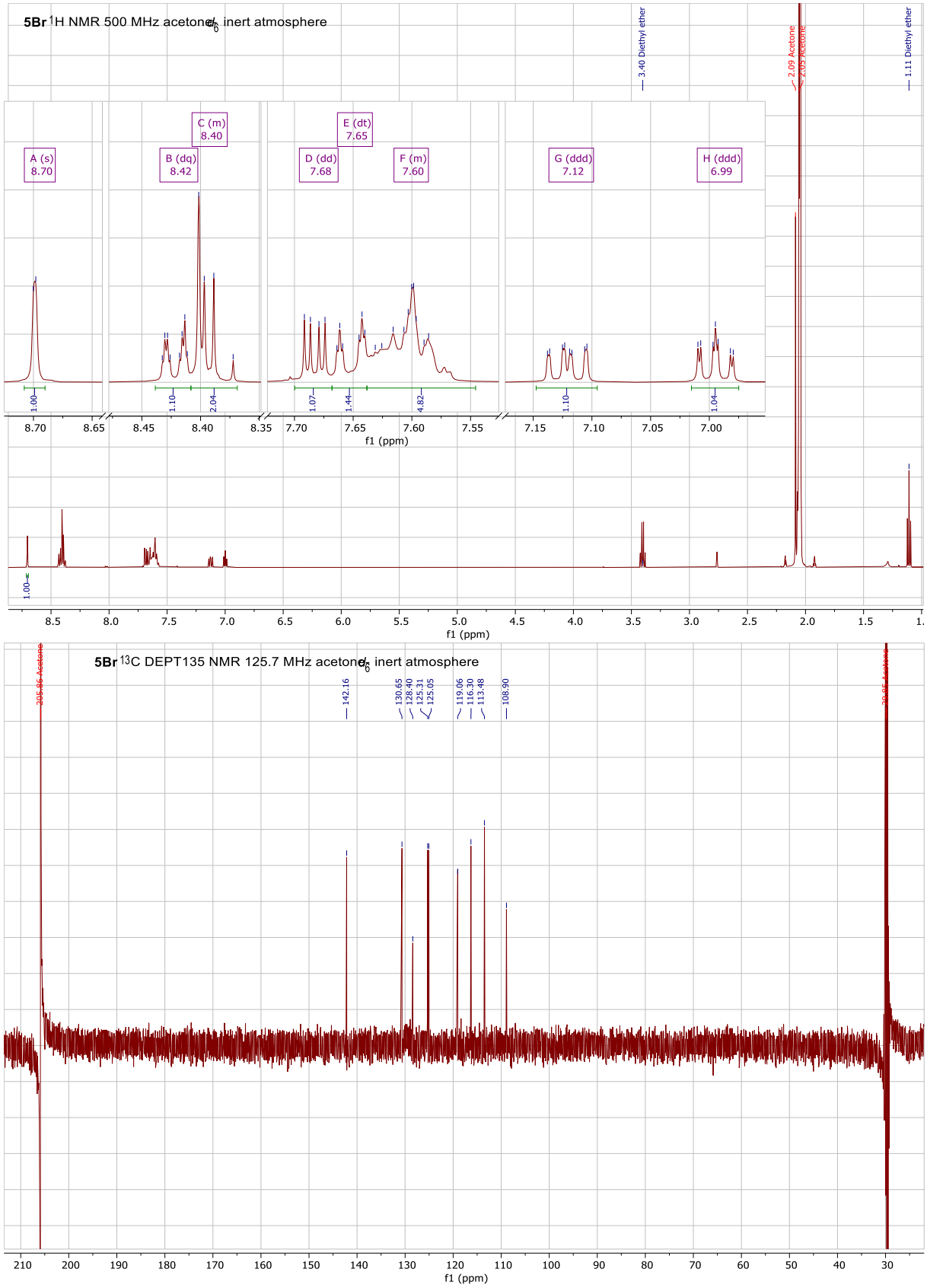


Figure S40 –NMR spectra for **5Br**: 1H, 13C DEPT135 in acetone-d6.

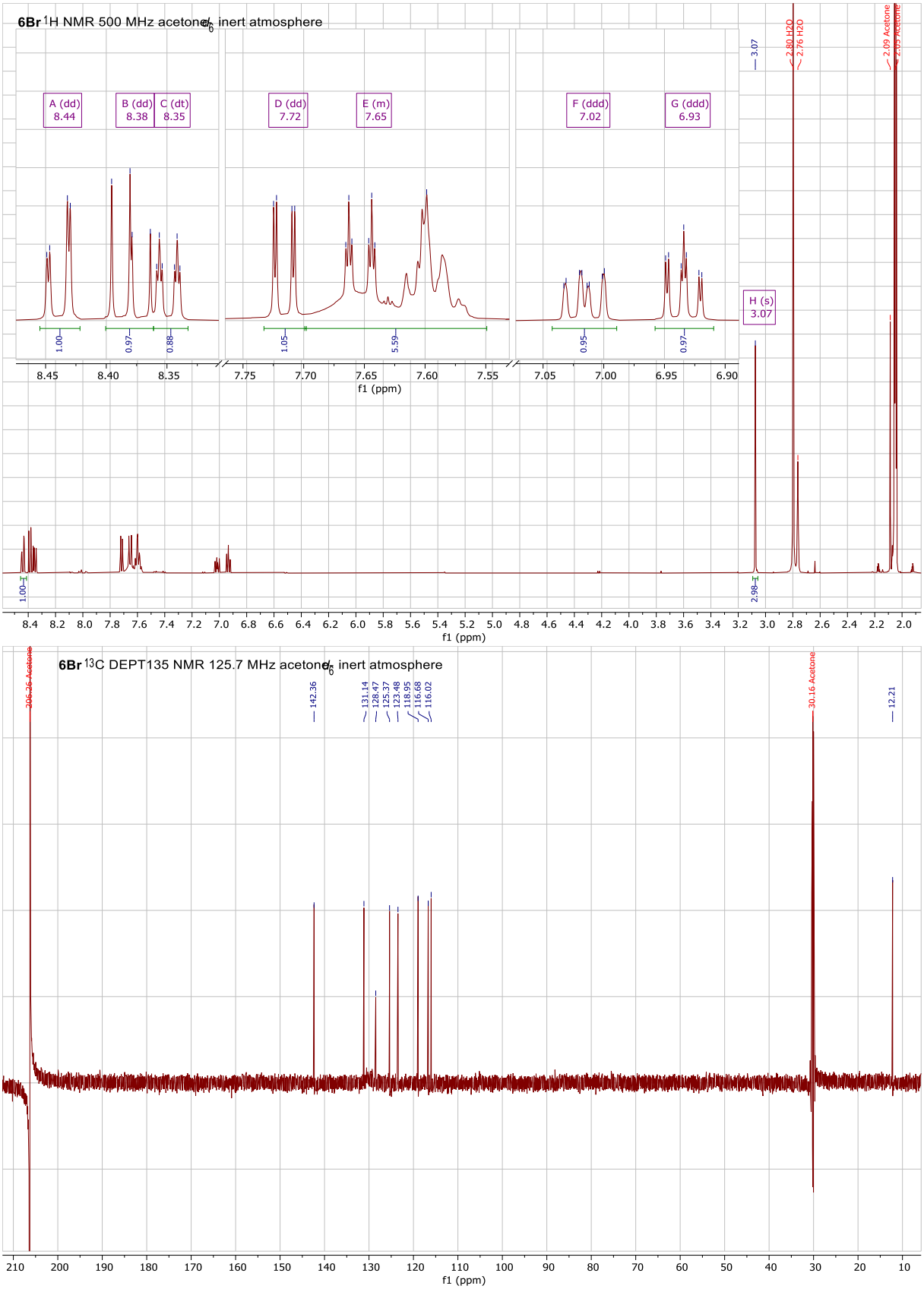


Figure S41 –NMR spectra for **6Br**: 1H, 13C DEPT135 in acetone-d6.

ESI-MS spectra

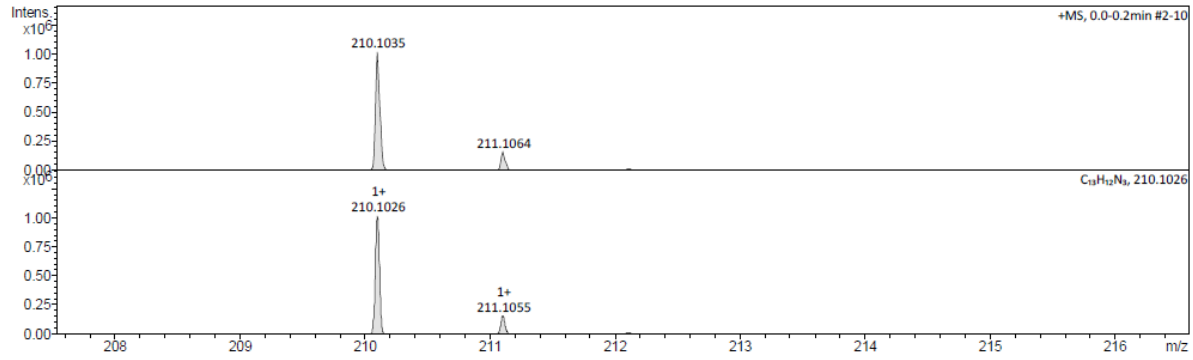
Mass Spectrum HR Report **L2H**

Analysis Info

Analysis Name	D:\Data\SMasse\2022\05_Mai 2022\F12514SK.d	Acquisition Date	5/19/2022 2:09:57 PM
Method	Tune_pos_Standard.m	Operator	BDAL@DE
Sample Name		Instrument	micrOTOF II 8213750.1045
Comment			1

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	49.7 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2020.0 V



Meas. m/z	#	Ion Formula	m/z err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I	VarNorm	Std m/z	Diff Std Comb	Dev
210.103506	1	C13H12N3	210.102574	-4.4	-4.4	9.5	ok	even	0.7	1.4	n.a.		n.a.	n.a.	n.a.

Figure S42 – HR-ESI-MS Spectrum of **L2H**

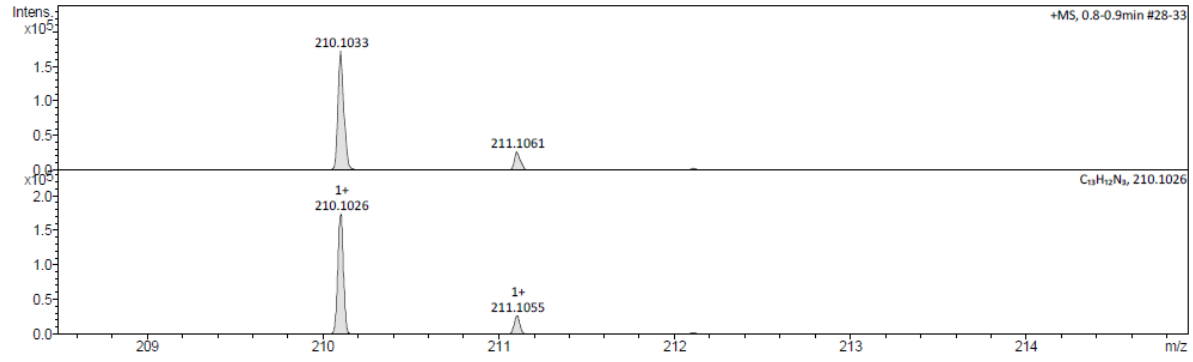
Mass Spectrum HR Report **L3H**

Analysis Info

Analysis Name	D:\Data\SMasse\2022\05_Mai 2022\F12286SK.d	Acquisition Date	5/2/2022 4:03:33 PM
Method	Tune_pos_Standard.m	Operator	BDAL@DE
Sample Name	VG13	Instrument	micrOTOF II 8213750.1045
Comment			1

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	49.7 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2020.0 V



Meas. m/z	#	Ion Formula	m/z err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I	VarNorm	Std m/z	Diff Std Comb	Dev
210.103316	1	C13H12N3	210.102574	-3.5	-4.1	9.5	ok	even	1.6	3.5	n.a.		n.a.	n.a.	n.a.

Figure S43 – HR-ESI-MS Spectrum of **L3H**

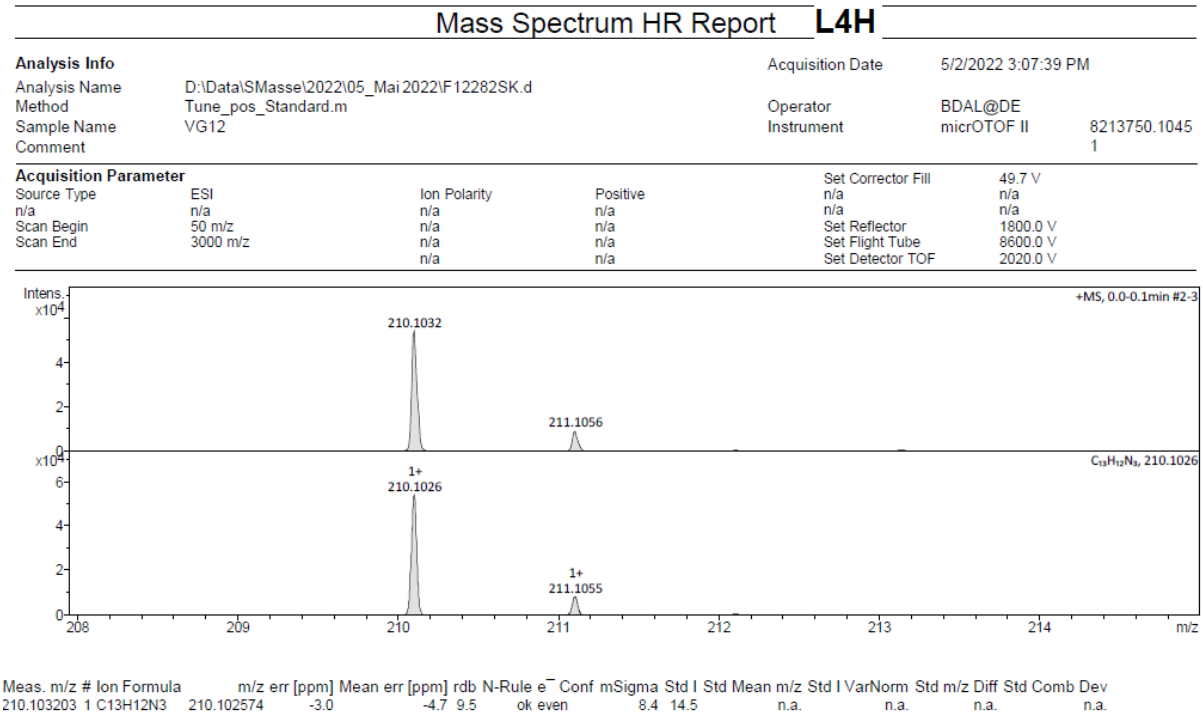


Figure S44 – HR-ESI-MS Spectrum of **L4H**

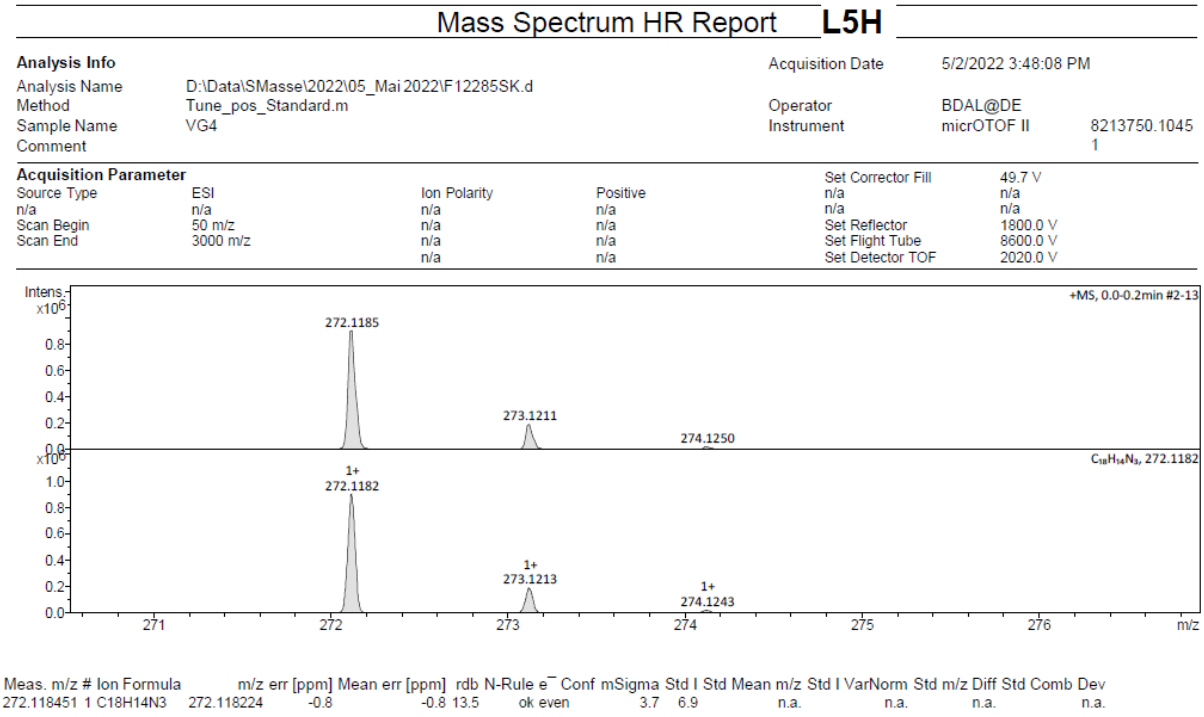
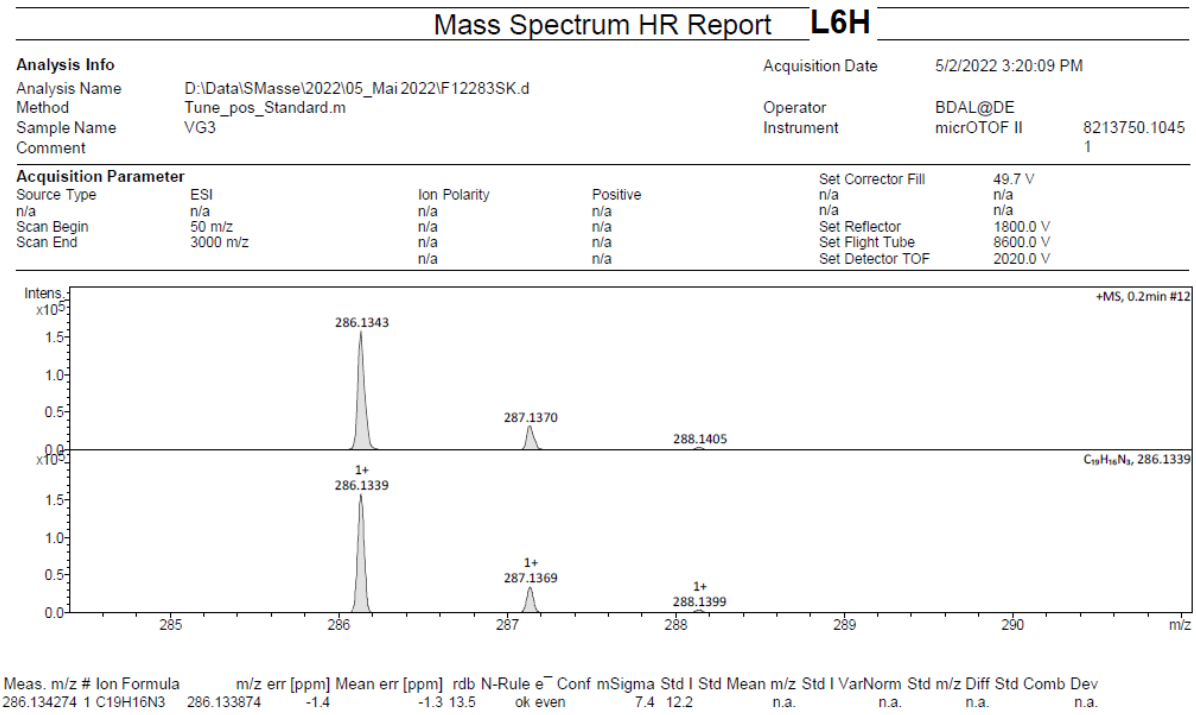
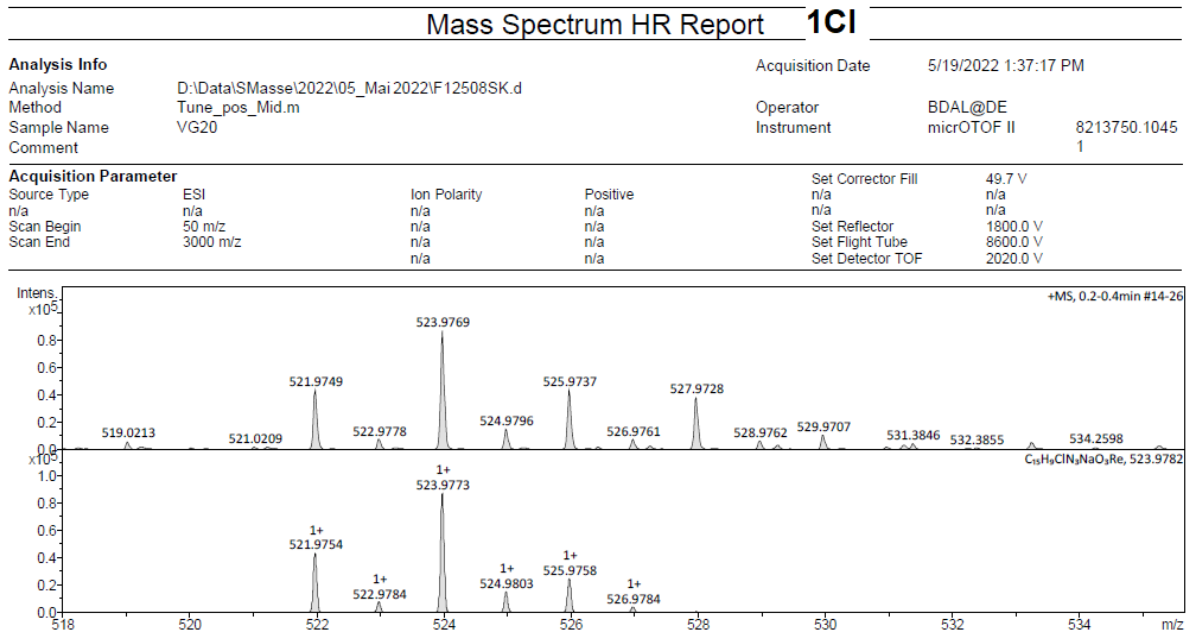


Figure S45 – HR-ESI-MS Spectrum of **L5H**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
286.134274	1	C19H16N3	286.133874	-1.4	-1.3	13.5	ok	even	7.4	12.2	n.a.	n.a.	n.a.	n.a.

Figure S46 – HR-ESI-MS Spectrum of **L6H**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
523.976886	1	C15H9ClN3NaO3Re	523.978218	0.9	1.9	13.0	-	odd	88.6	96.6	n.a.	n.a.	n.a.	n.a.

Figure S47– HR-ESI-MS Spectrum of **1Cl**

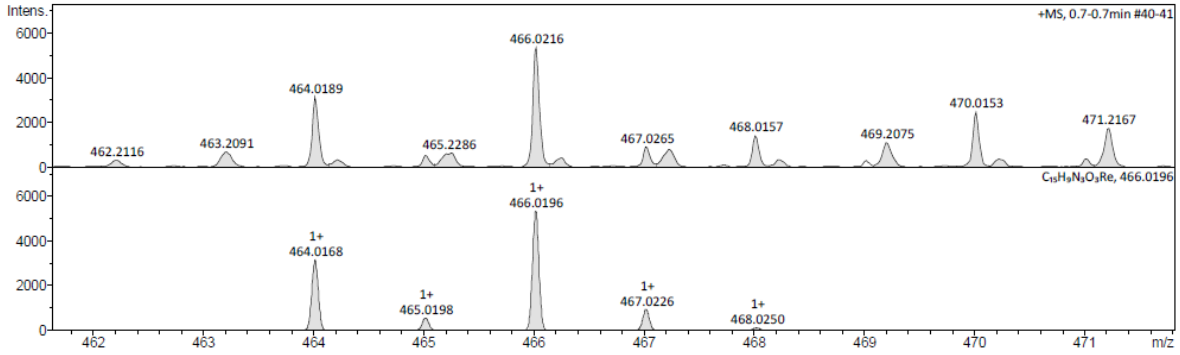
Mass Spectrum HR Report **1I**

Analysis Info

Analysis Name	D:\Data\SMasse\2022\10_Octobre 2022\F13486SK.d	Acquisition Date	10/13/2022 11:28:28 AM
Method	Tune_pos_Mid.m	Operator	BDAL@DE
Sample Name	VG35a	Instrument	micrOTOF II 8213750.1045
Comment			1

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	48.2 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	n/a	n/a
Scan End	3000 m/z	n/a	n/a	Set Reflector	1800.0 V
		n/a	n/a	Set Flight Tube	8600.0 V
				Set Detector TOF	2021.6 V



Meas. m/z	#	Ion Formula	m/z err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
466.021574	1	C15H9N3O3Re	466.019596	-4.2	1112.1	14.0	- odd	9.4	13.7	n.a.	n.a.	n.a.	n.a.

Figure S48 – HR-ESI-MS Spectrum of **1I**

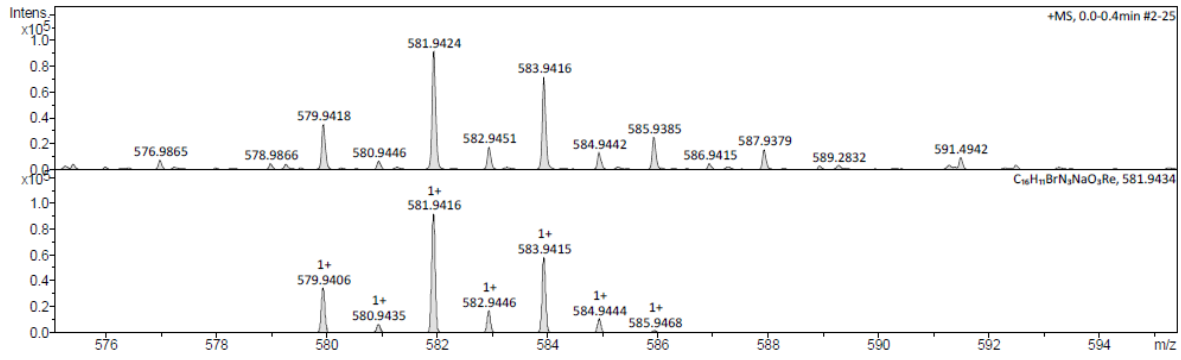
Mass Spectrum HR Report **2Br**

Analysis Info

Analysis Name	D:\Data\SMasse\2022\05_Mai 2022\F12509SK.d	Acquisition Date	5/19/2022 1:47:58 PM
Method	Tune_pos_Mid.m	Operator	BDAL@DE
Sample Name	VG21	Instrument	micrOTOF II 8213750.1045
Comment			1

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	49.7 V
n/a	n/a	n/a	n/a	n/a	n/a
Scan Begin	50 m/z	n/a	n/a	Set Reflector	1800.0 V
Scan End	3000 m/z	n/a	n/a	Set Flight Tube	8600.0 V
		n/a	n/a	Set Detector TOF	2020.0 V



Meas. m/z	#	Ion Formula	m/z err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
581.942388	1	C16H11BrN3NaO3Re	581.943352	-1.3	0.5	13.0	- odd	114.0	116.0	n.a.	n.a.	n.a.	n.a.

Figure S49 – HR-ESI-MS Spectrum of **2Br**

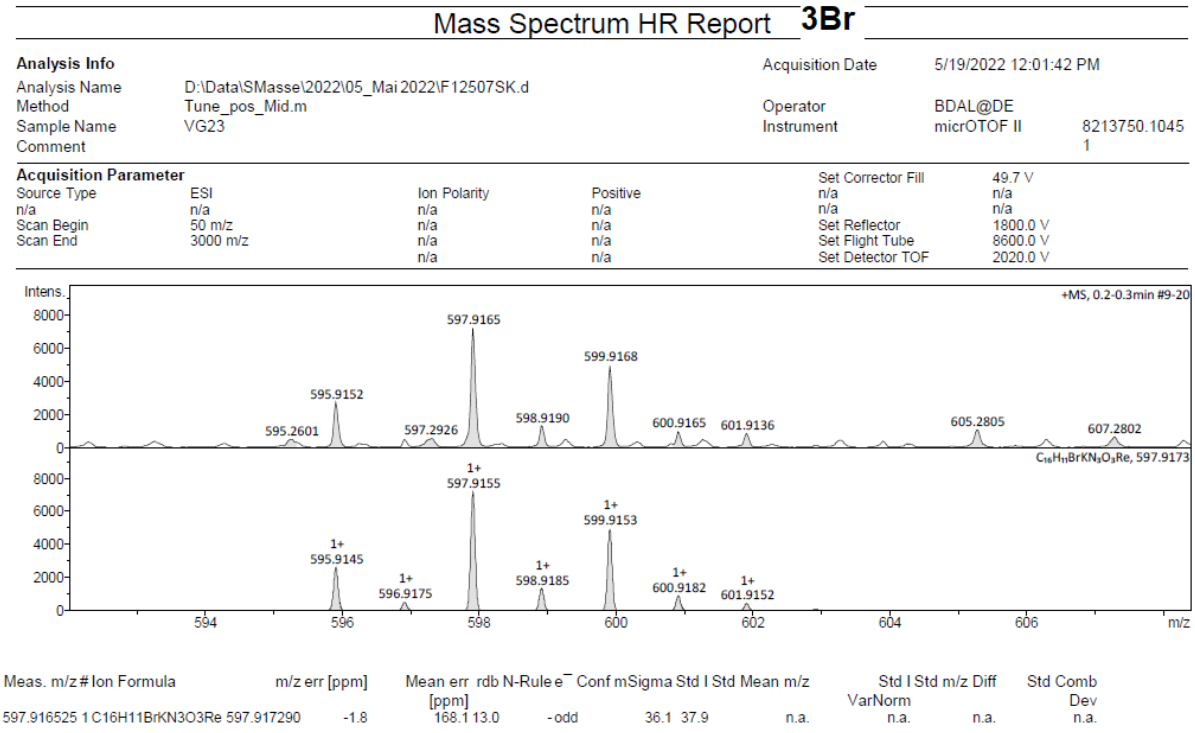


Figure S50 – HR-ESI-MS Spectrum of **3Br**

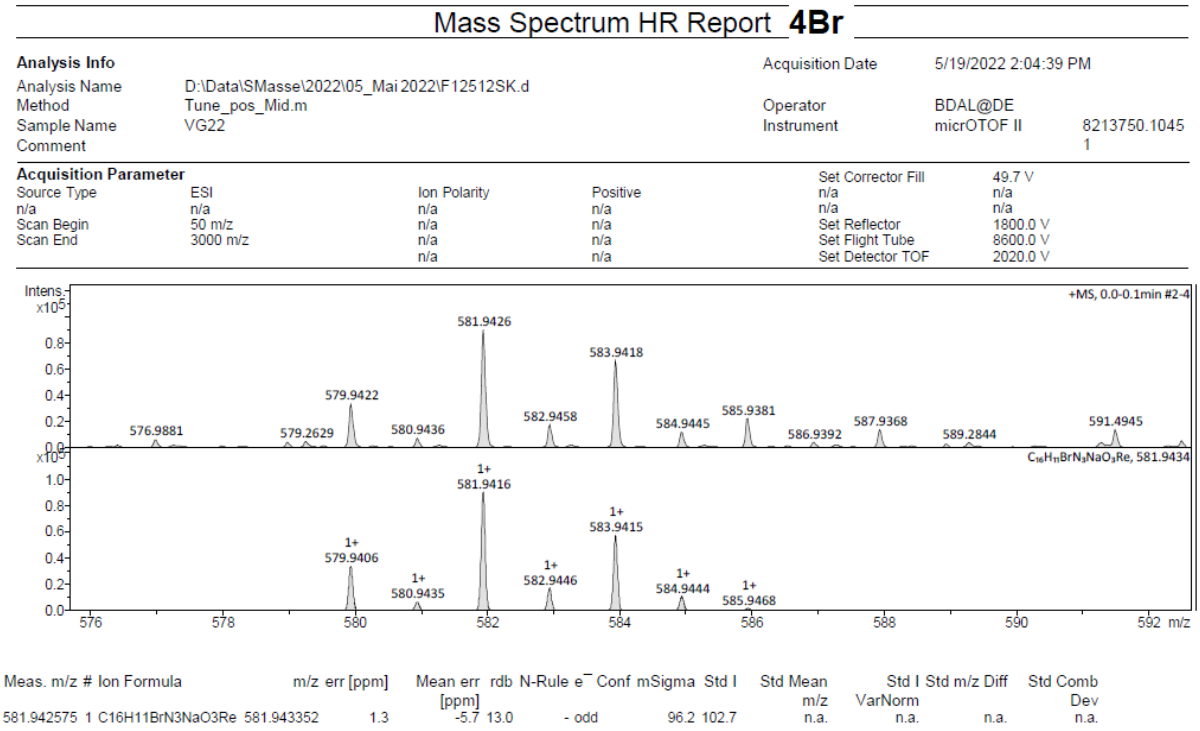


Figure S51 – HR-ESI-MS Spectrum of **4Br**

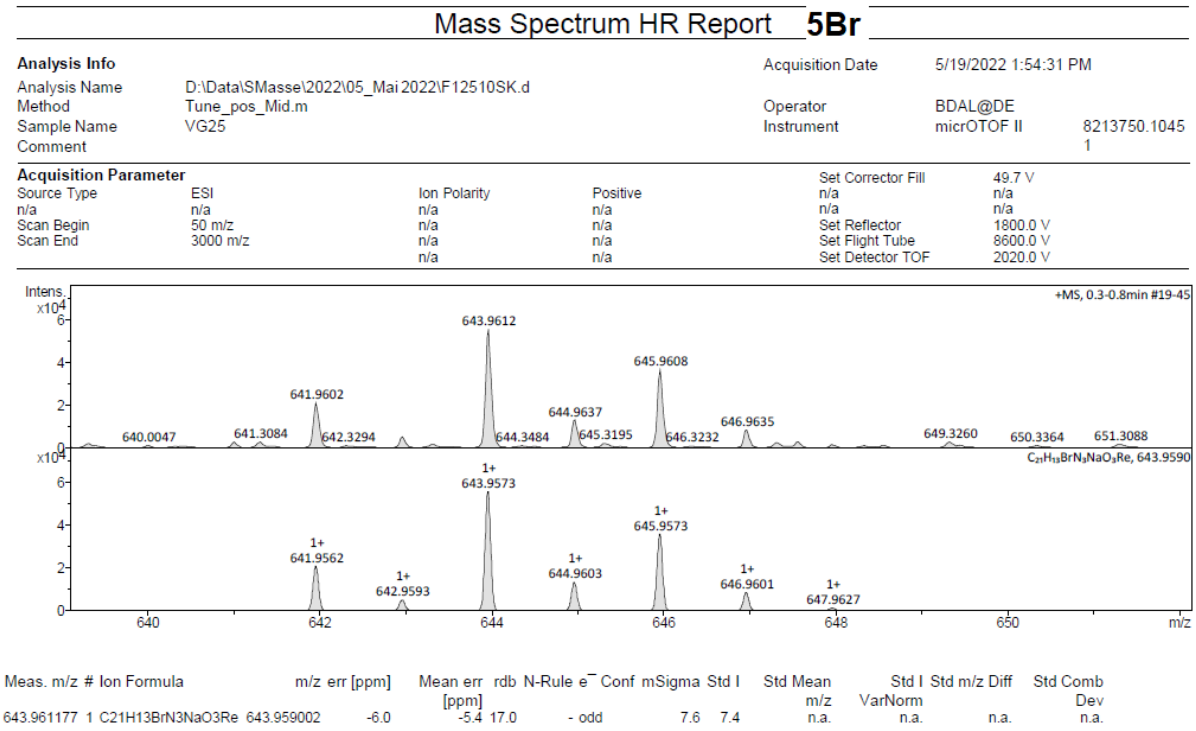


Figure S52 – HR-ESI-MS Spectrum of **5Br**

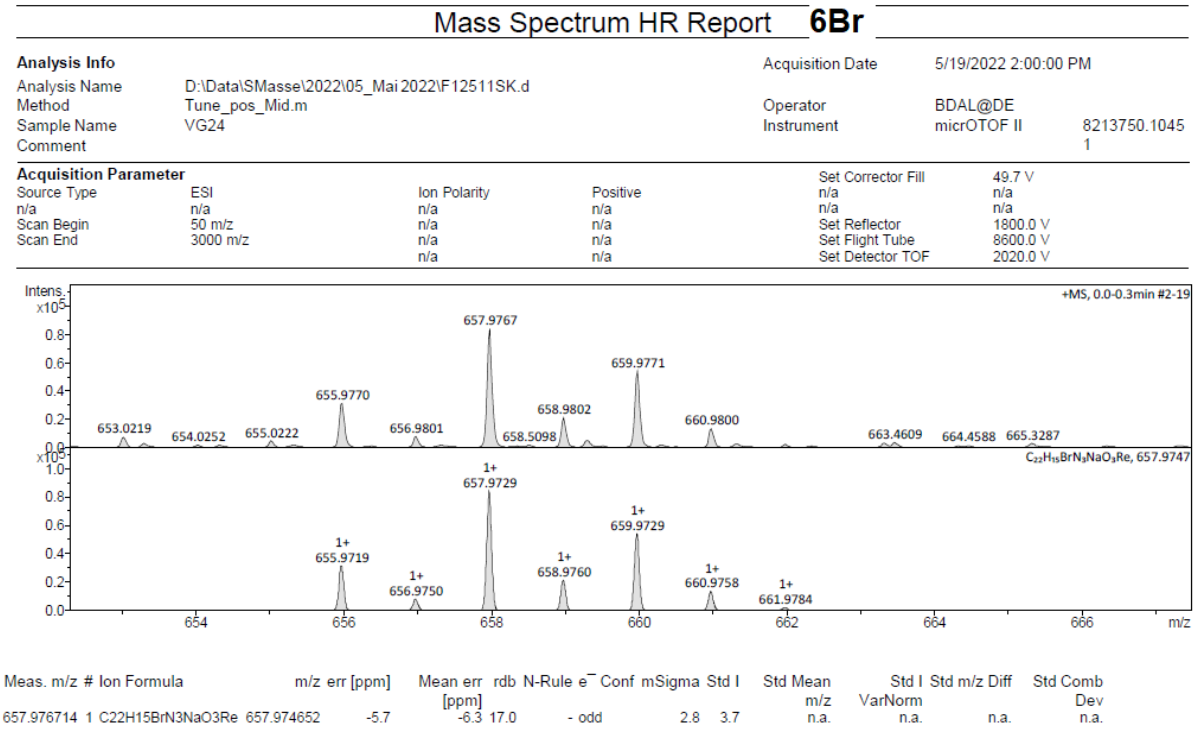


Figure S53 – HR-ESI-MS Spectrum of **6Br**

FT-ATR-IR Spectra

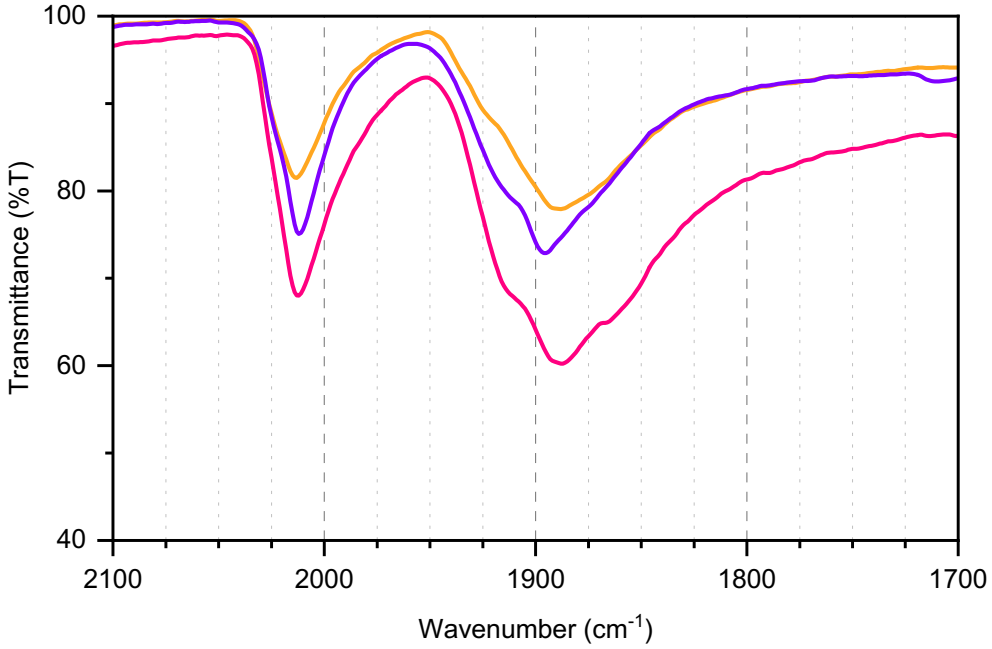


Figure S54 – FT-ATR-IR spectra of **1I** (yellow), **1Br** (magenta), **1I** (purple) in the region of interest for C=O bonds, 2100-1700 cm^{-1}.

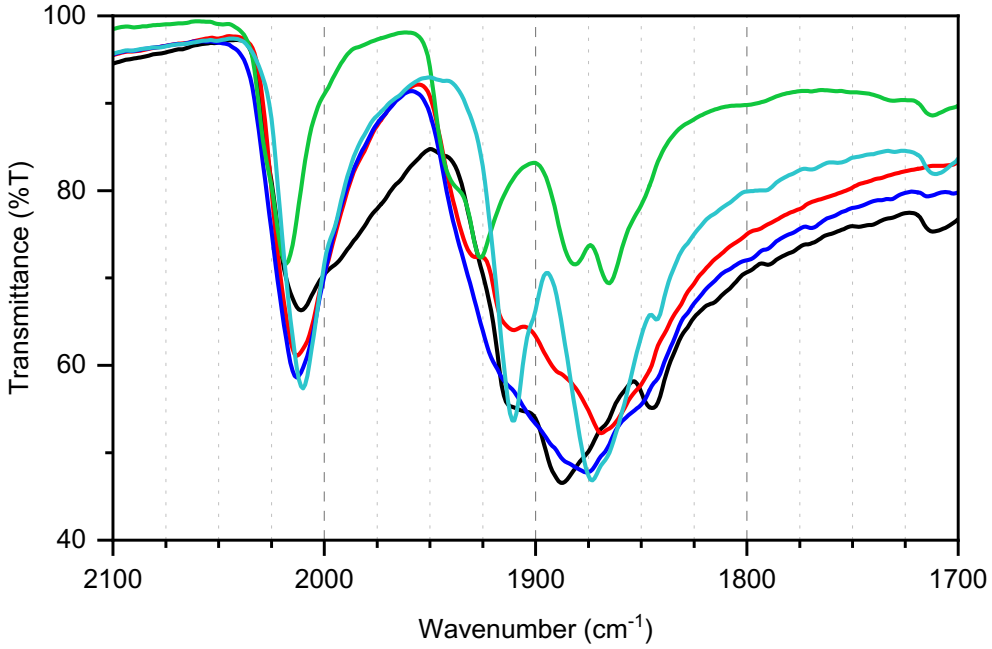


Figure S55 – FT-ATR-IR spectra of **2Br** (black), **3Br** (blue), **4Br** (red), **5Br** (green), and **6Br** (cyan) in the region of interest for C=O bonds, 2100-1700 cm^{-1}.