The photochemistry of rhenium(I) tricarbonyl *N*-heterocyclic carbene complexes

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Electronic Supplementary Information

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Bond Lengths and Angles Tables

Table S1. Selected bond lengths and angles for **2Cl**

Re(1)-C(3)	1.9123(10)
Re(1)-C(2)	1.9169(11)
Re(1)-C(1)	1.9552(11)
Re(1)-C(12)	2.1488(10)
Re(1)-N(21)	2.2117(8)
Re(1)-Cl(4)	2.4956(2)
C(3)-Re(1)-C(2)	88.78(5)
C(3)-Re(1)-C(1)	91.37(4)
C(2)-Re(1)-C(1)	87.66(4)
C(3)-Re(1)-C(12)	95.71(4)
C(2)-Re(1)-C(12)	99.91(4)
C(1)-Re(1)-C(12)	169.71(4)
C(3)-Re(1)-N(21)	93.78(4)
C(2)-Re(1)-N(21)	173.94(4)
C(1)-Re(1)-N(21)	97.76(4)
C(12)-Re(1)-N(21)	74.38(3)
C(3)-Re(1)-Cl(4)	178.13(3)
C(2)-Re(1)-Cl(4)	92.98(3)
C(1)-Re(1)-Cl(4)	88.06(3)
C(12)-Re(1)-Cl(4)	84.62(3)
N(21)-Re(1)-Cl(4)	84.53(2)

Table S2. Selected bond lengths and angles for **2Br**

Re(1)-C(3)	1.917(4)
Re(1)-C(2)	1.923(4)
Re(1)-C(1)	1.957(3)
Re(1)-C(12)	2.145(3)
Re(1)-N(21)	2.210(3)
Re(1)-Br(4)	2.6255(4)
C(3)-Re(1)-C(2)	89.42(15)
C(3)-Re(1)-C(1)	92.06(14)
C(2)-Re(1)-C(1)	87.94(14)
C(3)-Re(1)-C(12)	96.25(13)
C(2)-Re(1)-C(12)	100.14(13)
C(1)-Re(1)-C(12)	168.43(14)
C(3)-Re(1)-N(21)	93.24(13)
C(2)-Re(1)-N(21)	174.42(12)
C(1)-Re(1)-N(21)	96.86(12)
C(12)-Re(1)-N(21)	74.70(12)
C(3)-Re(1)-Br(4)	177.81(11)
C(2)-Re(1)-Br(4)	92.66(11)
C(1)-Re(1)-Br(4)	87.32(10)
C(12)-Re(1)-Br(4)	84.07(9)
N(21)-Re(1)-Br(4)	84.75(7)

Table S3. Selected bond lengths and angles for **3Cl**

Re(1)-C(201)	1.908(4)
Re(1)-C(101)	1.949(5)
Re(1)-C(301)	1.977(6)
Re(1)-C(2)	2.119(4)
Re(1)-N(21)	2.277(3)
Re(1)-Cl(1)	2.4799(13)
C(201)-Re(1)-C(101)	85.75(18)
C(201)-Re(1)-C(301)	91.65(19)
C(101)-Re(1)-C(301)	88.6(2)
C(201)-Re(1)-C(2)	95.88(17)
C(101)-Re(1)-C(2)	177.60(18)
C(301)-Re(1)-C(2)	89.60(19)
C(201)-Re(1)-N(21)	168.61(17)
C(101)-Re(1)-N(21)	104.68(15)
C(301)-Re(1)-N(21)	93.14(16)
C(2)-Re(1)-N(21)	73.84(14)
C(201)-Re(1)-Cl(1)	92.14(16)
C(101)-Re(1)-Cl(1)	93.60(14)
C(301)-Re(1)-Cl(1)	175.74(13)
C(2)-Re(1)-Cl(1)	88.09(13)
N(21)-Re(1)-Cl(1)	82.78(10)

Table S4. Selected bond lengths and angles for **3Br**

Re(1)-C(201)	1.913(4)
Re(1)-C(101)	1.955(4)
Re(1)-C(301)	2.058(5)
Re(1)-C(2)	2.114(4)
Re(1)-N(21)	2.275(3)
Re(1)-Br(1)	2.6243(5)
C(201)-Re(1)-C(101)	85.28(15)
C(201)-Re(1)-C(301)	92.03(18)
C(101)-Re(1)-C(301)	88.77(17)
C(201)-Re(1)-C(2)	95.91(14)
C(101)-Re(1)-C(2)	178.61(15)
C(301)-Re(1)-C(2)	90.46(17)
C(201)-Re(1)-N(21)	168.85(14)
C(101)-Re(1)-N(21)	104.79(13)
C(301)-Re(1)-N(21)	92.97(13)
C(2)-Re(1)-N(21)	74.10(11)
C(201)-Re(1)-Br(1)	91.74(14)
C(101)-Re(1)-Br(1)	94.00(12)
C(301)-Re(1)-Br(1)	175.50(11)
C(2)-Re(1)-Br(1)	86.70(12)
N(21)-Re(1)-Br(1)	82.90(8)

Table S5. Selected bond lengths and angles for *cis*,*cis*-[Re(CO)$_2$(**PyImPh**)(NCCH$_3$)Cl]

Re(1)-C(102)	1.886(3)
Re(1)-C(101)	1.888(5)
Re(1)-C(103)	1.937(14)
Re(1)-C(2)	2.062(2)
Re(1)-N(31)	2.119(2)
Re(1)-N(21)	2.215(2)
Re(1)-Cl(2)	2.416(4)
Re(1)-Cl(1)	2.4914(12)
C(102)-Re(1)-C(101)	84.83(15)
C(102)-Re(1)-C(103)	90.8(5)
C(102)-Re(1)-C(2)	98.38(9)
C(101)-Re(1)-C(2)	91.70(14)
C(103)-Re(1)-C(2)	90.5(4)
C(102)-Re(1)-N(31)	94.10(9)
C(101)-Re(1)-N(31)	90.06(14)
C(103)-Re(1)-N(31)	88.7(4)
C(2)-Re(1)-N(31)	167.50(9)
C(102)-Re(1)-N(21)	172.96(9)
C(101)-Re(1)-N(21)	93.89(14)
C(103)-Re(1)-N(21)	90.7(5)
C(2)-Re(1)-N(21)	74.71(8)
N(31)-Re(1)-N(21)	92.83(8)
C(102)-Re(1)-Cl(2)	91.26(13)
C(103)-Re(1)-Cl(2)	177.4(4)
C(2)-Re(1)-Cl(2)	90.87(11)
N(31)-Re(1)-Cl(2)	89.49(10)
N(21)-Re(1)-Cl(2)	87.52(12)
C(102)-Re(1)-Cl(1)	95.12(8)
C(101)-Re(1)-Cl(1)	177.13(13)
C(2)-Re(1)-Cl(1)	91.15(7)

N(31)-Re(1)-Cl(1)	87.08(6)
N(21)-Re(1)-Cl(1)	86.51(6)

Table S6. Anisotropic displacement parameters ($Å^2x10^3$)for *cis*,*cis*-[$Re(CO)_2$(**PyImPh**)($NCCH_3$)Cl]; the anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	22(1)	20(1)	15(1)	1(1)	8(1)	0(1)
Cl(1)	21(1)	27(1)	23(1)	4(1)	8(1)	-2(1)
C(103)	27(7)	34(7)	30(6)	4(5)	8(6)	-6(5)
O(103)	27(6)	52(6)	48(6)	16(5)	13(5)	-6(5)
C(101)	27(2)	19(2)	20(2)	1(1)	10(2)	-1(2)
O(101)	25(1)	33(2)	31(1)	1(1)	7(1)	-10(1)
Cl(2)	29(2)	40(2)	25(2)	4(1)	10(2)	-5(2)
C(102)	29(1)	30(1)	17(1)	-2(1)	9(1)	-2(1)
O(102)	53(1)	22(1)	35(1)	-1(1)	13(1)	4(1)
N(1)	23(1)	21(1)	17(1)	2(1)	10(1)	0(1)
C(11)	26(1)	24(1)	15(1)	1(1)	6(1)	3(1)
C(12)	29(1)	37(1)	26(1)	6(1)	13(1)	8(1)
C(13)	41(2)	51(2)	29(1)	5(1)	13(1)	22(1)
C(14)	58(2)	30(1)	25(1)	1(1)	6(1)	17(1)
C(15)	50(2)	23(1)	26(1)	1(1)	4(1)	0(1)
C(16)	30(1)	26(1)	22(1)	3(1)	6(1)	-2(1)
C(2)	20(1)	21(1)	17(1)	1(1)	7(1)	-1(1)
N(21)	21(1)	20(1)	19(1)	2(1)	6(1)	-2(1)
C(22)	21(1)	19(1)	21(1)	1(1)	6(1)	-2(1)
C(23)	32(1)	19(1)	29(1)	-1(1)	11(1)	0(1)
C(24)	33(1)	19(1)	36(1)	2(1)	8(1)	2(1)
C(25)	34(1)	25(1)	30(1)	9(1)	7(1)	1(1)
C(26)	30(1)	25(1)	21(1)	5(1)	6(1)	-1(1)
N(3)	24(1)	19(1)	17(1)	1(1)	8(1)	-1(1)
C(4)	27(1)	24(1)	19(1)	-4(1)	11(1)	-4(1)
C(5)	26(1)	27(1)	17(1)	-1(1)	9(1)	-1(1)
N(31)	26(1)	26(1)	20(1)	-1(1)	9(1)	-3(1)
C(31)	32(1)	28(1)	21(1)	1(1)	10(1)	-5(1)
C(32)	42(2)	48(2)	19(1)	0(1)	11(1)	-9(1)
N(41)	72(2)	54(2)	46(2)	10(1)	35(2)	25(2)
C(41)	56(2)	21(1)	24(1)	3(1)	12(1)	4(1)
C(42)	87(3)	73(3)	44(2)	7(2)	6(2)	-47(3)

Table S7. Selected bond lengths and angles for *cis*,*cis*-[$Re(CO)_2$(**PyImPh**)Br($P(OEt)_3$)]

Re(1)-C(20)	1.890(4)
Re(1)-C(10)	1.899(4)
Re(1)-C(2)	2.117(4)
Re(1)-N(22)	2.236(3)
Re(1)-P(1)	2.3457(10)
Re(1)-Br(1)	2.6557(4)
C(20)-Re(1)-C(10)	87.45(16)
C(20)-Re(1)-C(2)	101.57(15)
C(10)-Re(1)-C(2)	94.62(15)
C(20)-Re(1)-N(22)	174.12(14)
C(10)-Re(1)-N(22)	96.94(14)
C(2)-Re(1)-N(22)	74.25(13)
C(20)-Re(1)-P(1)	87.15(12)
C(10)-Re(1)-P(1)	91.45(11)
C(2)-Re(1)-P(1)	169.56(10)
N(22)-Re(1)-P(1)	96.61(9)
C(20)-Re(1)-Br(1)	91.50(12)
C(10)-Re(1)-Br(1)	176.42(11)
C(2)-Re(1)-Br(1)	82.23(10)
N(22)-Re(1)-Br(1)	83.88(8)
P(1)-Re(1)-Br(1)	91.92(2)

Table S8. Selected bond lengths and angles for *cis*,*trans*-[$Re(CO)_2$(**PyImPh**)Br($P(OEt)_3$)]

Re(1)-C(102)	1.907(6)
Re(1)-C(101)	1.927(6)
Re(1)-C(2)	2.140(5)
Re(1)-N(21)	2.209(5)
Re(1)-P(1)	2.2793(16)
Re(1)-Br(1)	2.6602(6)
C(102)-Re(1)-C(101)	88.2(2)
C(102)-Re(1)-C(2)	103.7(2)
C(101)-Re(1)-C(2)	167.3(2)
C(102)-Re(1)-N(21)	176.0(2)
C(101)-Re(1)-N(21)	94.3(2)
C(2)-Re(1)-N(21)	74.18(19)
C(102)-Re(1)-P(1)	91.89(18)
C(101)-Re(1)-P(1)	86.38(17)
C(2)-Re(1)-P(1)	88.61(15)
N(21)-Re(1)-P(1)	91.49(12)
C(102)-Re(1)-Br(1)	90.97(18)
C(101)-Re(1)-Br(1)	97.39(16)
C(2)-Re(1)-Br(1)	87.14(14)
N(21)-Re(1)-Br(1)	85.52(12)
P(1)-Re(1)-Br(1)	175.34(4)

Excitation and Emission Profiles

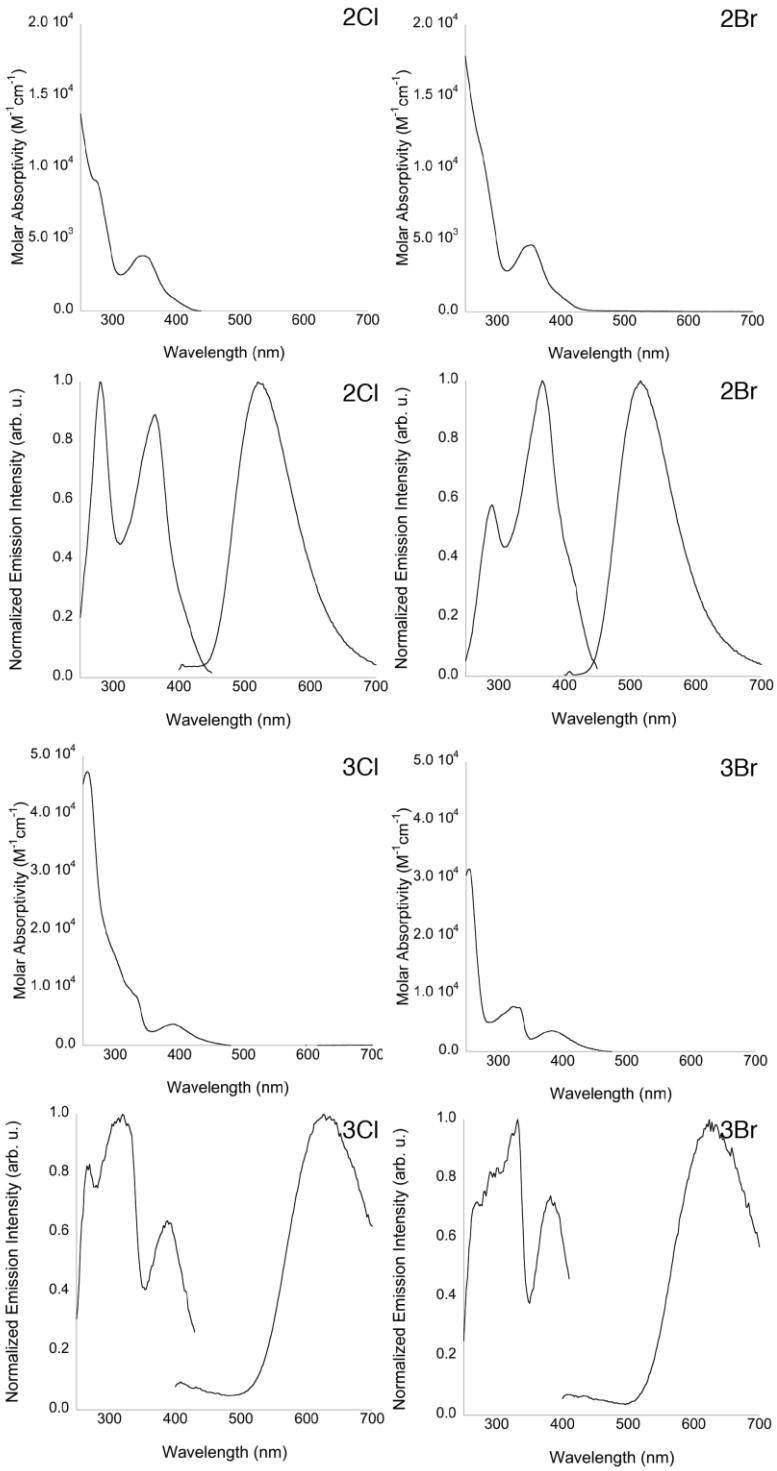

Figure S1. Absorption, excitation and emission profiles for all the complexes from a ca. 10^{-5} M solution in dichloromethane.

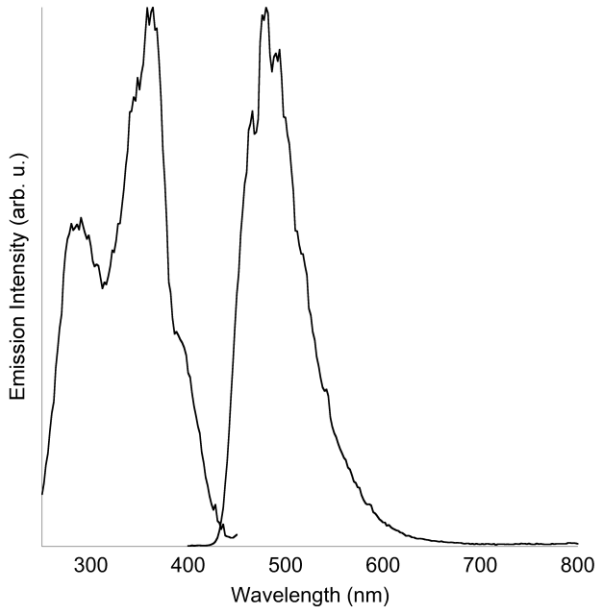

Figure S2. Excitation and emission profiles for **2Cl** at 77 K from a ca. 10^{-5} M solution in dichloromethane.

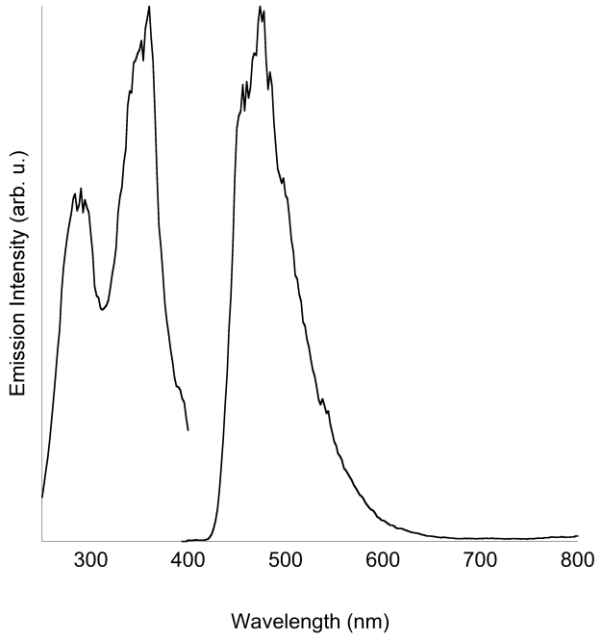

Figure S3. Excitation and emission profiles for **2Br** at 77 K from a ca. 10^{-5} M solution in dichloromethane.

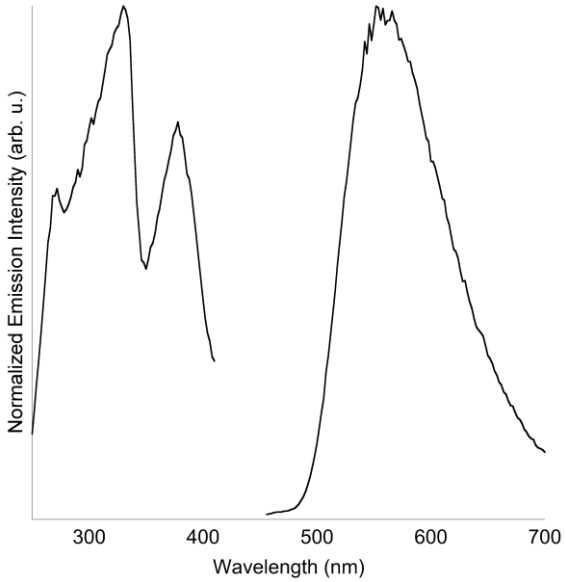

Figure S4. Excitation and emission profiles for **3Cl** at 77 K from a ca. 10^{-5} M solution in dichloromethane.

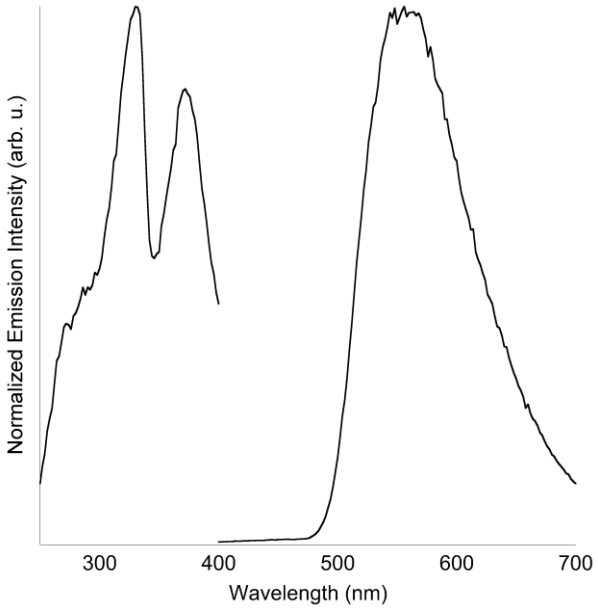

Figure S5. Excitation and emission profiles for **3Br** at 77 K from a ca. 10^{-5} M solution in dichloromethane.

Calculated Orbitals Contours

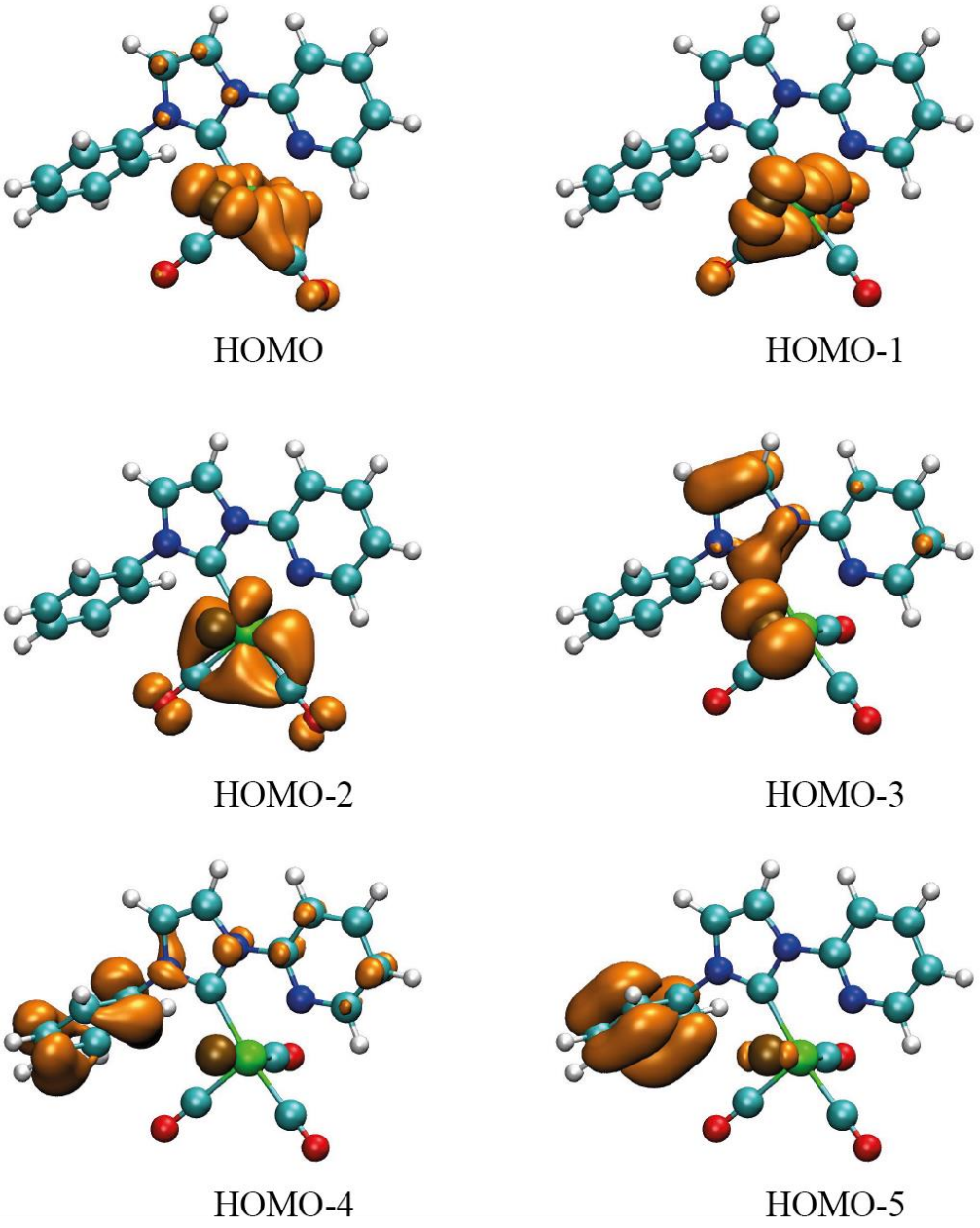

Figure S6. Selected occupied orbital contours of **2Cl**.

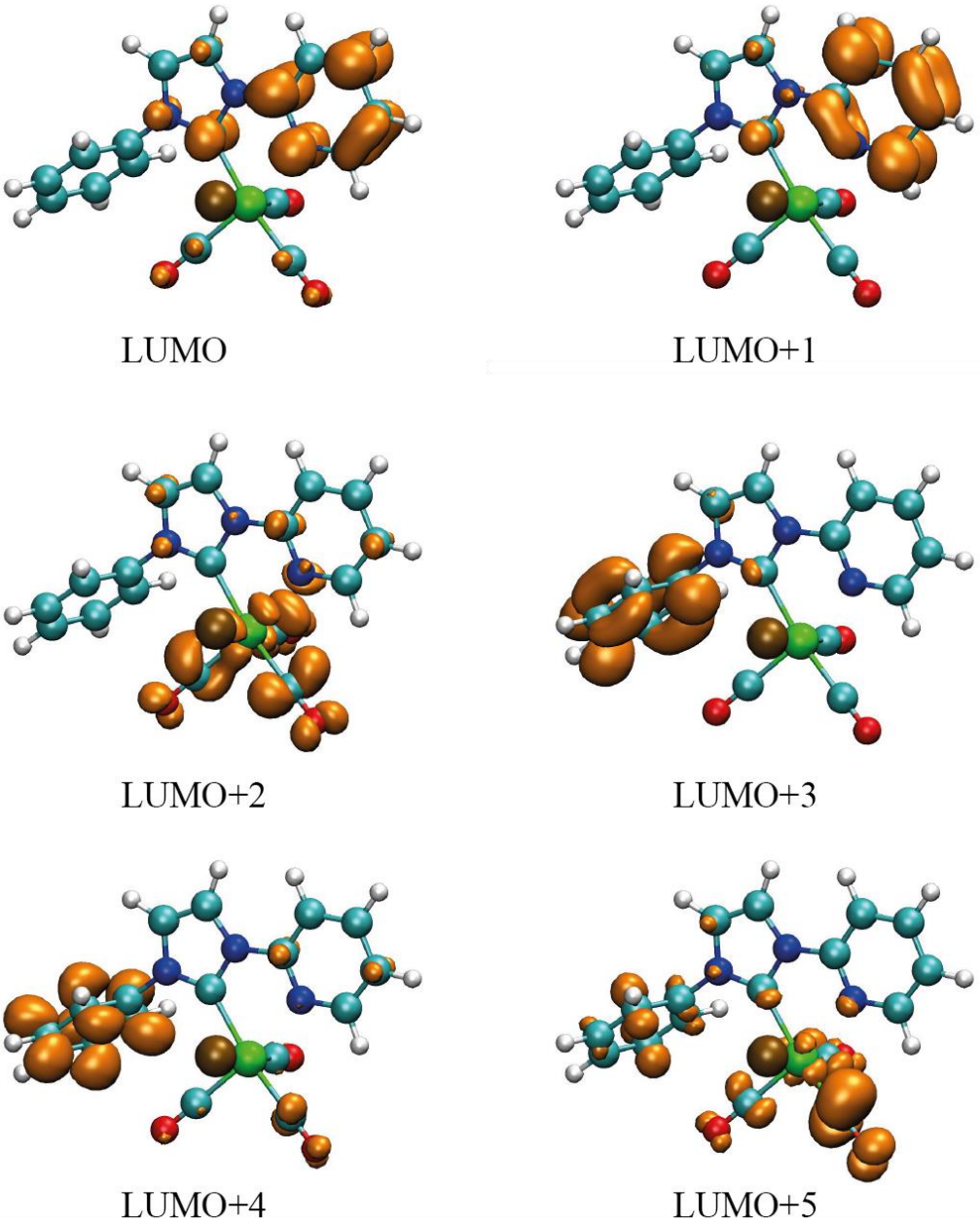

Figure S7. Selected unoccupied orbital contours of **2Cl**.

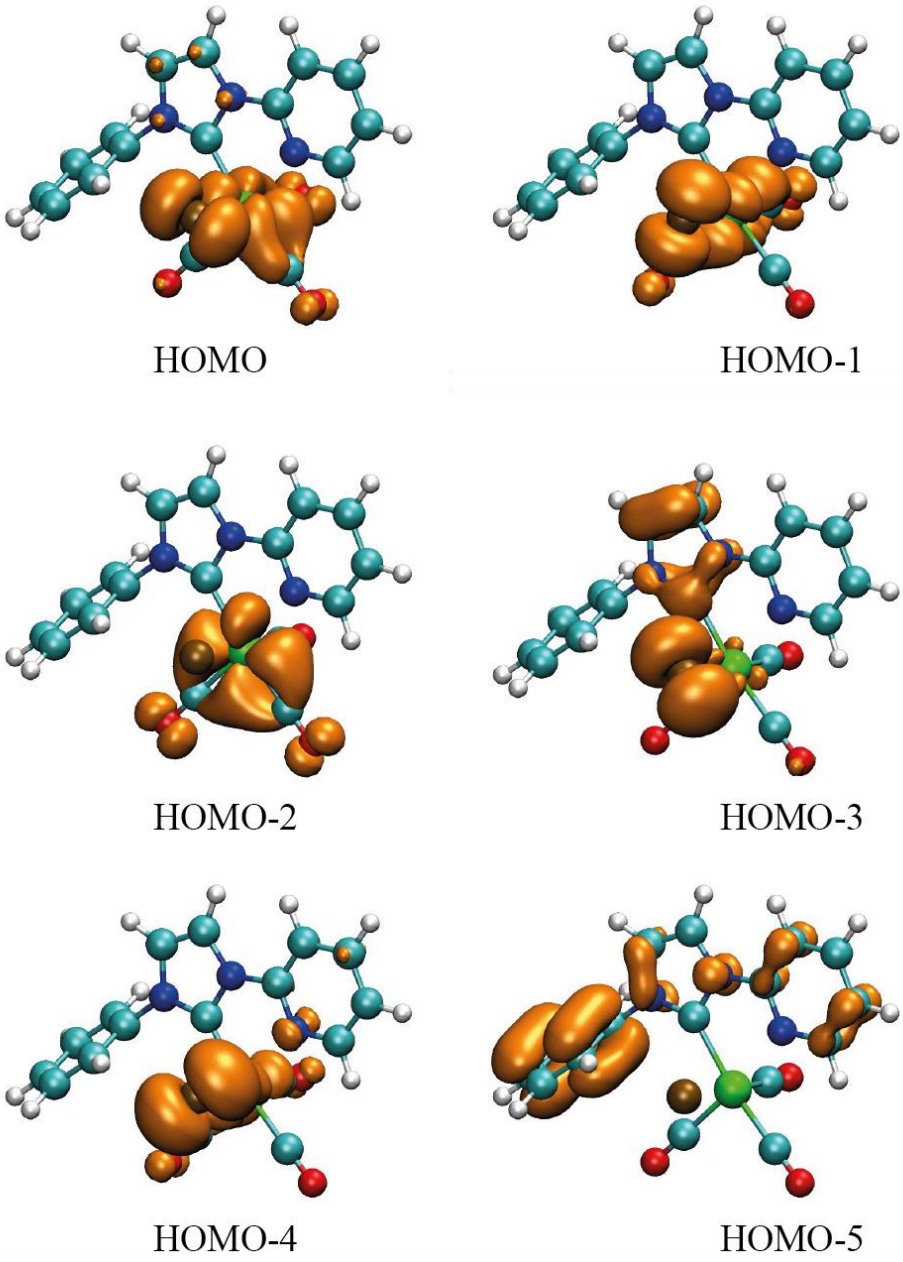

Figure S8. Selected occupied orbital contours of **2Br**.

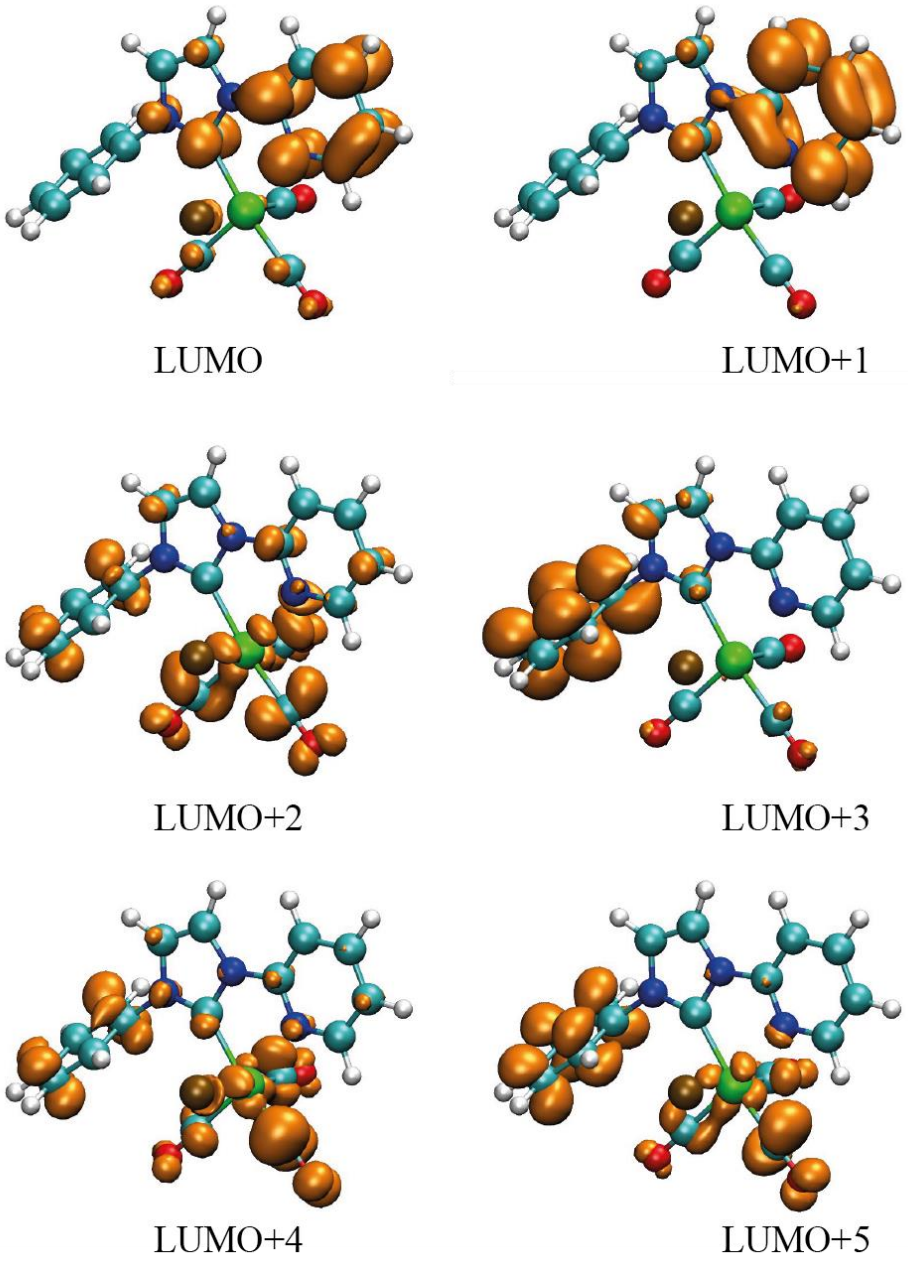

Figure S9. Selected unoccupied orbital contours of **2Br**.

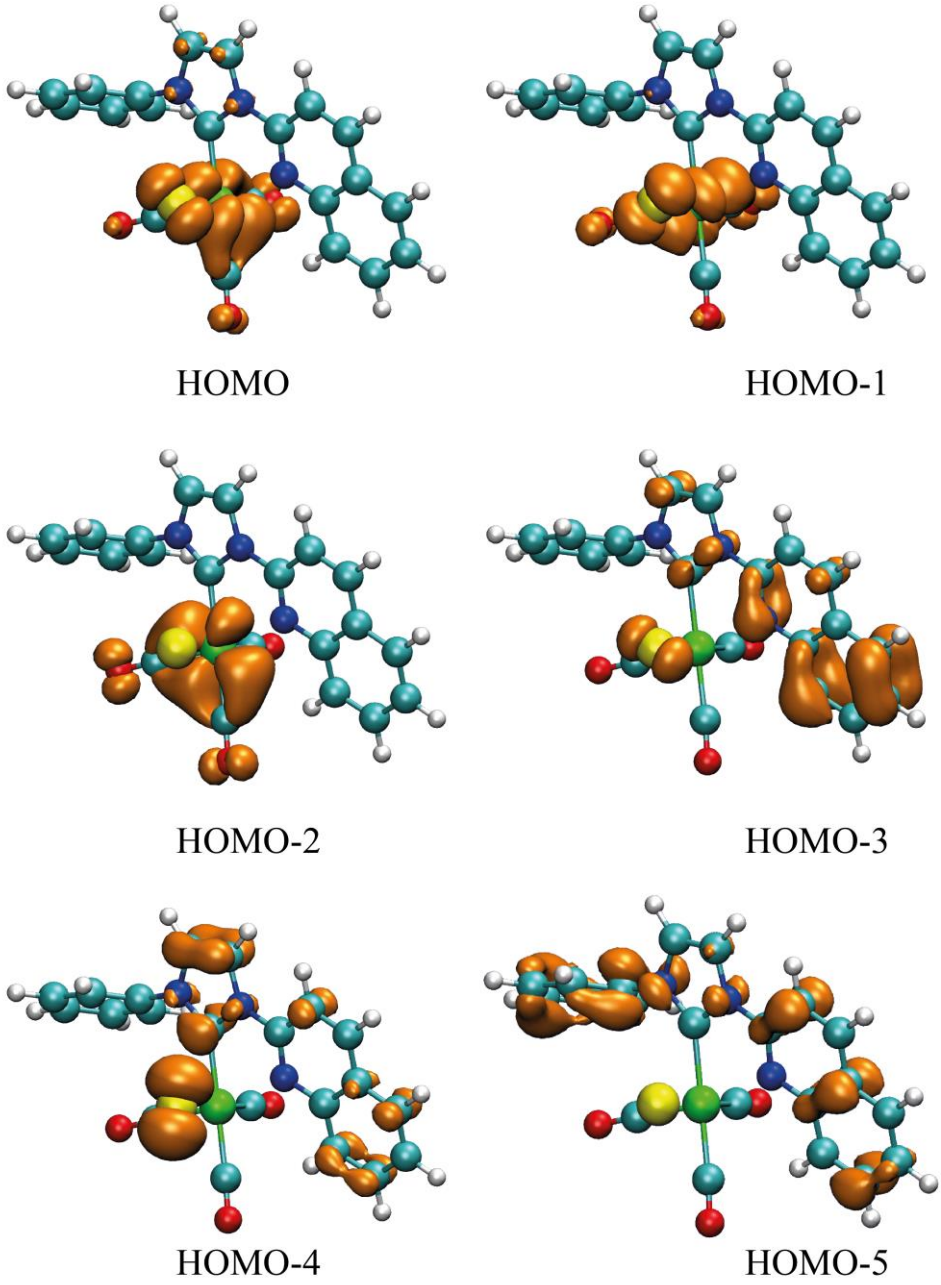

Figure S10. Selected occupied orbitals contours of **3Cl.**

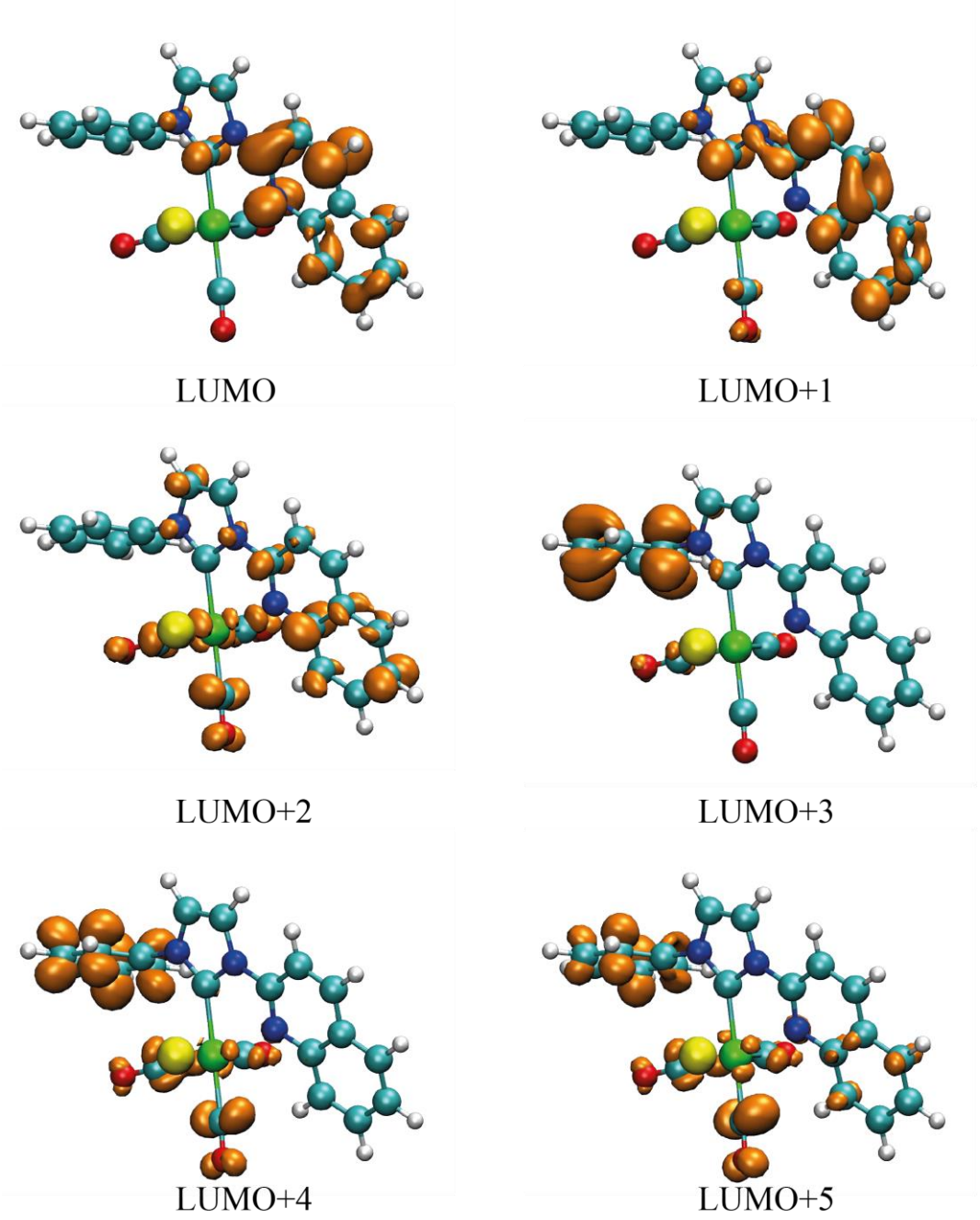

Figure S11. Selected unoccupied orbitals contours of **3Cl.**

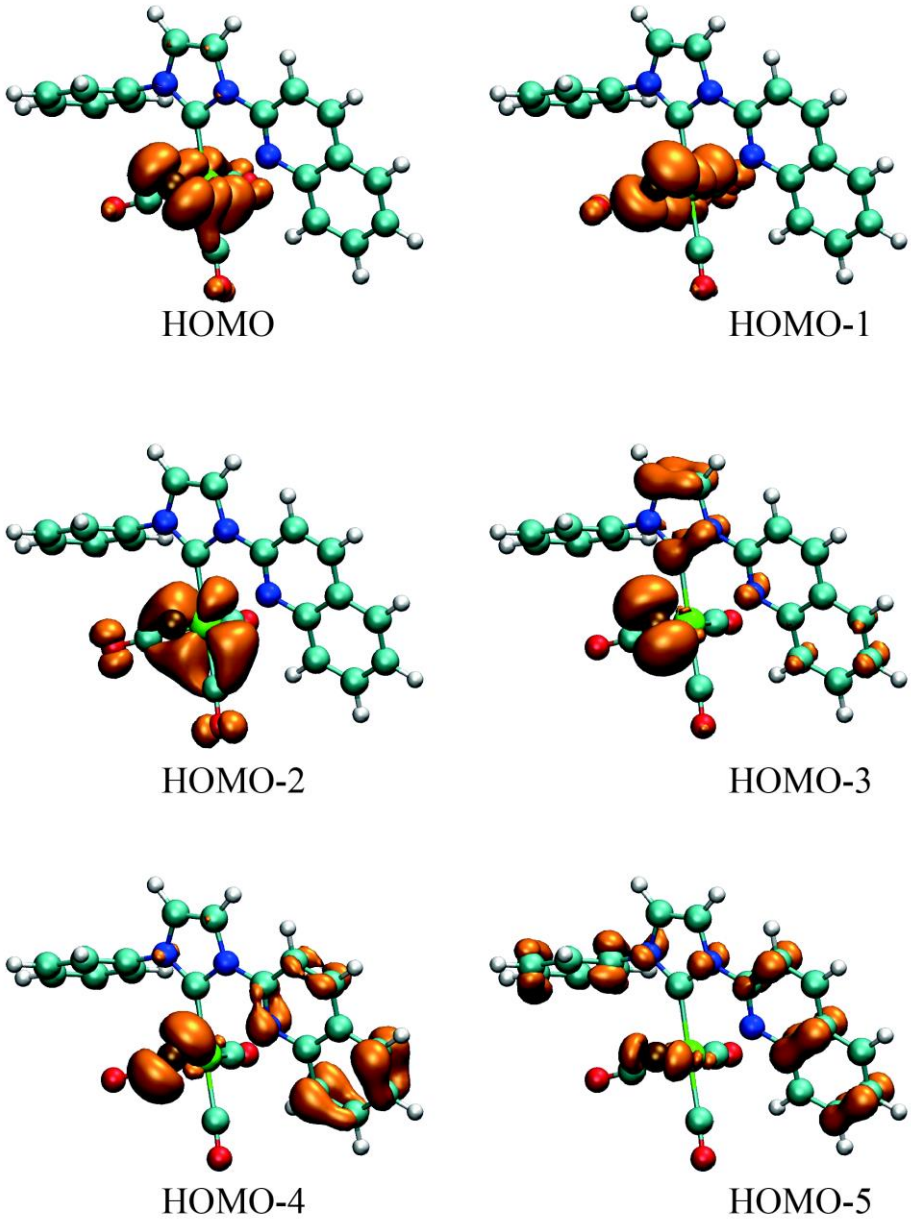

Figure S12. Selected occupied orbital contours of **3Br**.

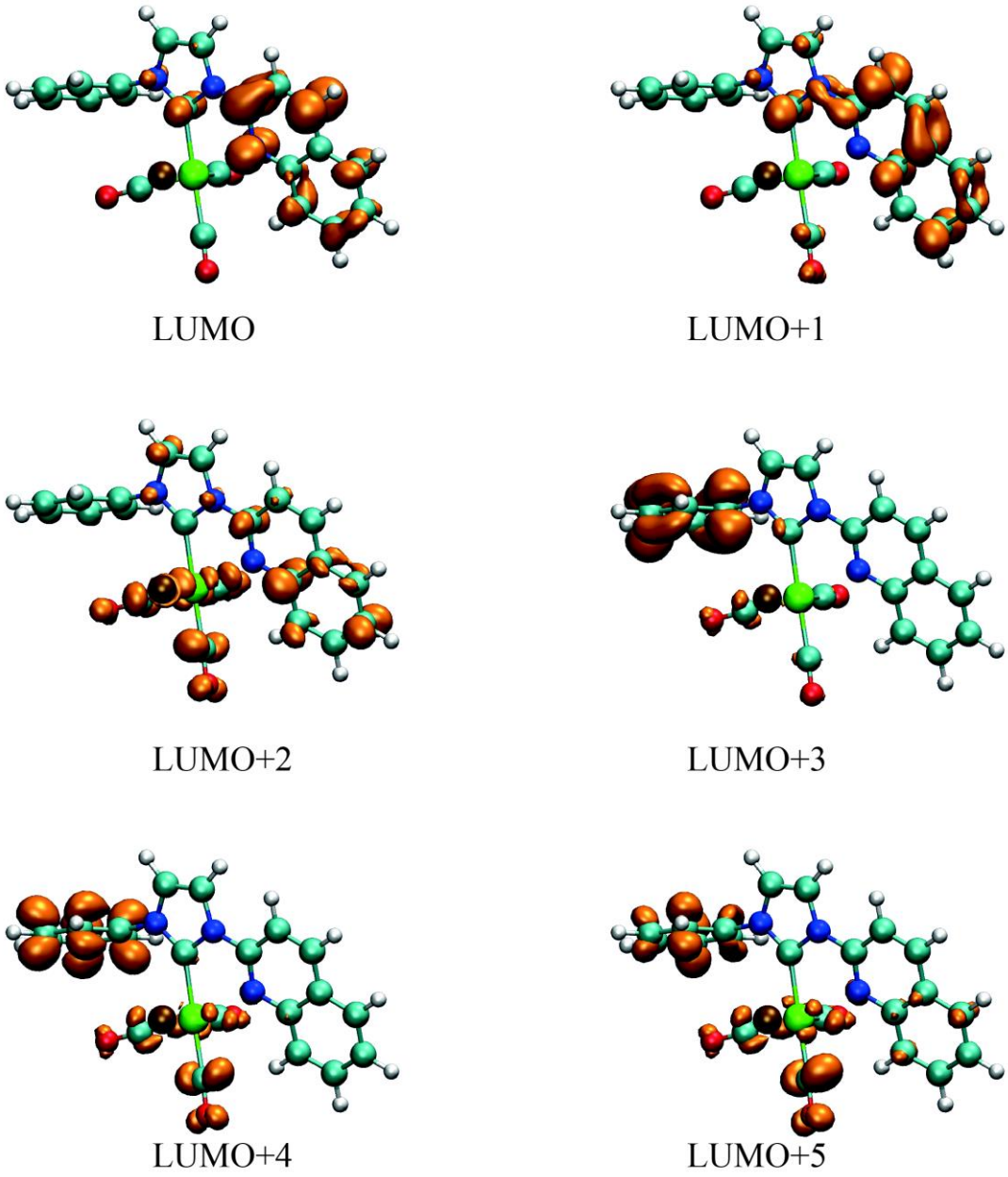

Figure S13. Selected unoccupied orbital contours of **3Br**.

Calculated Transitions

Table S9. Calculated transitions for **2Cl**

Wavelength	Intensity	Levels	Character
399.47 nm	0.0107	HOMO -> LUMO	96.5 %
376.08 nm	0.1112	HOMO-1 -> LUMO	95.0 %
354.04 nm	0.0021	HOMO-2 -> LUMO	96.4 %
327.41 nm	0.0309	HOMO -> LUMO+1	96.6 %
316.59 nm	0.0116	HOMO-1 -> LUMO+1	95.8 %
301.27 nm	0.0085	HOMO -> LUMO+2	83.5 %
293.46 nm	0.0007	HOMO-2 -> LUMO+1	73.7 %
		HOMO-1 -> LUMO+2	12.8 %
292.70 nm	0.0063	HOMO-2 -> LUMO+1	19.8 %
		HOMO-1 -> LUMO+2	48.7 %
290.22 nm	0.0512	HOMO-3 -> LUMO	91.6 %
281.10 nm	0.0204	HOMO-1 -> LUMO+2	10.6 %
273.68 nm	0.0147	HOMO-1 -> LUMO+2	13.8 %
270.05 nm	0.0061	HOMO -> LUMO+3	75.1 %

269.74 nm	0.0377	HOMO-6 -> LUMO	59.4 %
		HOMO-2 -> LUMO+2	11.2 %
267.92 nm	0.0047	HOMO-6 -> LUMO	13.8 %
		HOMO-2 -> LUMO+2	52.4 %
265.94 nm	0.2067	HOMO-4 -> LUMO	77.7 %
262.54 nm	0.0082	HOMO-1 -> LUMO+3	82.4 %
260.99 nm	0.0041	HOMO-6 -> LUMO	11.7 %
258.93 nm	0.0021	HOMO-5 -> LUMO	84.3 %
254.76 nm	0.0079	HOMO-7 -> LUMO	31.1 %
253.60 nm	0.0370	HOMO-3 -> LUMO+1	20.8 %

Table S10. Calculated transitions for **2Br**

Wavelength	Intensity	Levels	Character
404.80 nm	0.0073	HOMO -> LUMO	97.1 %
384.74 nm	0.0774	HOMO-1 -> LUMO	96.1 %
353.09 nm	0.0050	HOMO-2 -> LUMO	96.6 %
331.18 nm	0.0212	HOMO -> LUMO+1	97.2 %
322.04 nm	0.0108	HOMO-1 -> LUMO+1	96.4 %
308.51 nm	0.0434	HOMO-3 -> LUMO	96.1 %
303.88 nm	0.0100	HOMO -> LUMO+2	72.4 %
		HOMO -> LUMO+3	6.9 %
		HOMO -> LUMO+5	12.9 %
296.23 nm	0.0106	HOMO-4 -> LUMO	2.4 %
		HOMO-1 -> LUMO+2	50.9 %
		HOMO-1 -> LUMO+3	4.5 %
		HOMO-1 -> LUMO+5	10.5 %
		HOMO -> LUMO+2	3.0 %
		HOMO -> LUMO+4	15.8 %
		HOMO -> LUMO+5	3.1 %
292.96 nm	0.0014	HOMO-2 -> LUMO+1	92.3 %
		HOMO-2 -> LUMO+4	2.2 %

290.74 nm	0.0742	HOMO-4 -> LUMO	89.7 %
		HOMO-2 -> LUMO+1	2.1 %
		HOMO-1 -> LUMO+2	2.6 %
285.01 nm	0.0269	HOMO-2 -> LUMO+2	2.1 %
		HOMO-1 -> LUMO+2	11.4 %
		HOMO-1 -> LUMO+4	8.6 %
		HOMO-1 -> LUMO+5	6.3 %
		HOMO -> LUMO+3	3.3 %
		HOMO -> LUMO+4	45.2 %
		HOMO -> LUMO+5	10.1 %
278.51 nm	0.0126	HOMO-1 -> LUMO+2	14.3 %
		HOMO-1 -> LUMO+3	5.3 %
		HOMO-1 -> LUMO+4	55.4 %
		HOMO-1 -> LUMO+5	11.5 %
		HOMO -> LUMO+4	3.3 %
272.19 nm	0.0029	HOMO-5 -> LUMO	6.4 %
		HOMO -> LUMO+2	9.9 %
		HOMO -> LUMO+3	73.0 %
		HOMO -> LUMO+4	5.6 %
270.80 nm	0.1328	HOMO-7 -> LUMO	3.9 %
		HOMO-5 -> LUMO	53.1 %
		HOMO-3 -> LUMO+1	2.4 %
		HOMO-2 -> LUMO+2	15.8 %
		HOMO-2 -> LUMO+4	4.5 %
		HOMO -> LUMO+3	7.0 %
		HOMO -> LUMO+4	2.4 %

268.38 nm	0.1069	HOMO-5 -> LUMO	24.1 %
		HOMO-2 -> LUMO+1	2.6 %
		HOMO-2 -> LUMO+2	40.2 %
		HOMO-2 -> LUMO+4	19.5 %
265.43 nm	0.0361	HOMO-3 -> LUMO+1	72.6 %
		HOMO-2 -> LUMO+4	2.2 %
		HOMO-1 -> LUMO+3	15.7 %
		HOMO-1 -> LUMO+4	3.4 %
264.89 nm	0.0372	HOMO-3 -> LUMO+1	20.3 %
		HOMO-1 -> LUMO+2	4.5 %
		HOMO-1 -> LUMO+3	60.0 %
		HOMO-1 -> LUMO+4	7.4 %
262.87 nm	0.0048	HOMO -> LUMO+2	8.6 %
		HOMO -> LUMO+3	7.0 %
		HOMO -> LUMO+4	12.2 %
		HOMO -> LUMO+5	66.3 %
260.39 nm	0.0052	HOMO-6 -> LUMO	91.9 %
257.63 nm	0.0176	HOMO-7 -> LUMO	35.8 %
		HOMO-6 -> LUMO	2.2 %
		HOMO-5 -> LUMO	5.3 %
		HOMO-4 -> LUMO+1	3.6 %
		HOMO-2 -> LUMO+4	9.7 %
		HOMO-2 -> LUMO+5	4.2 %
		HOMO-1 -> LUMO+3	2.9 %
		HOMO-1 -> LUMO+4	6.0 %
		HOMO-1 -> LUMO+5	16.4 %

Table S11. Calculated transitions for **3Cl**

Wavelength	Intensity	Levels	Character
440.48 nm	0.0021	HOMO -> LUMO	97.8 %
410.61 nm	0.0984	HOMO-1 -> LUMO	97.5 %
382.95 nm	0.0003	HOMO-2 -> LUMO	97.3 %
328.79 nm	0.0131	HOMO-3 -> LUMO	4.8 %
		HOMO -> LUMO+1	81.0 %
		HOMO -> LUMO+2	7.6 %
323.64 nm	0.0434	HOMO-4 -> LUMO	6.6 %
		HOMO-3 -> LUMO	82.1 %
		HOMO-1 -> LUMO+1	5.3 %
		HOMO -> LUMO+1	2.7 %
314.94 nm	0.0277	HOMO-5 -> LUMO	2.3 %
		HOMO-3 -> LUMO	4.2 %
		HOMO-1 -> LUMO+1	81.0 %
		HOMO-1 -> LUMO+2	5.4 %
313.08 nm	0.1007	HOMO-5 -> LUMO	5.0 %
		HOMO-4 -> LUMO	83.9 %
		HOMO-3 -> LUMO	5.5 %
301.11 nm	0.0795	HOMO-7 -> LUMO	3.5 %
		HOMO-5 -> LUMO	38.4 %
		HOMO-4 -> LUMO	5.2 %

		HOMO-3 -> LUMO+1	2.5 %
		HOMO-2 -> LUMO+1	7.5 %
		HOMO-1 -> LUMO+2	2.3 %
		HOMO -> LUMO+1	5.4 %
		HOMO -> LUMO+2	24.1 %
		HOMO -> LUMO+3	2.7 %
298.08 nm	0.1358	HOMO-5 -> LUMO	28.3 %
		HOMO-3 -> LUMO+1	2.6 %
		HOMO-2 -> LUMO+1	33.3 %
		HOMO-2 -> LUMO+2	8.7 %
		HOMO -> LUMO+1	2.3 %
		HOMO -> LUMO+2	6.7 %
		HOMO -> LUMO+4	4.2 %
		HOMO -> LUMO+5	2.2 %
297.15 nm	0.0477	HOMO-5 -> LUMO	0.1 %
		HOMO-2 -> LUMO+1	36.4 %
		HOMO-2 -> LUMO+2	5.6 %
		HOMO -> LUMO+1	3.9 %
		HOMO -> LUMO+2	27.1 %
		HOMO -> LUMO+3	3.9 %
		HOMO -> LUMO+4	7.7 %
		HOMO -> LUMO+5	3.0 %
289.66 nm	0.0516	HOMO-5 -> LUMO	4.8 %
		HOMO-1 -> LUMO+1	7.0 %
		HOMO-1 -> LUMO+2	18.4 %
		HOMO-1 -> LUMO+3	3.1 %
		HOMO-1 -> LUMO+4	12.1 %
		HOMO-1 -> LUMO+5	6.1 %

		HOMO -> LUMO+2	7.6 %
		HOMO -> LUMO+4	19.8 %
		HOMO -> LUMO+5	13.0 %
		HOMO -> LUMO+6	2.5 %
282.62 nm	0.0247	HOMO-1 -> LUMO+2	25.8 %
		HOMO-1 -> LUMO+3	2.5 %
		HOMO-1 -> LUMO+4	8.7 %
		HOMO-1 -> LUMO+5	3.2 %
		HOMO -> LUMO+2	10.2 %
		HOMO -> LUMO+4	24.8 %
		HOMO -> LUMO+5	10.6 %
281.97 nm	0.0078	HOMO-8 -> LUMO	78.7 %
		HOMO-6 -> LUMO	14.3 %
278.23 nm	0.0298	HOMO-7 -> LUMO	9.8 %
		HOMO-5 -> LUMO	3.9 %
		HOMO-1 -> LUMO+2	24.3 %
		HOMO-1 -> LUMO+4	31.3 %
		HOMO-1 -> LUMO+5	19.8 %
		HOMO-1 -> LUMO+6	5.6 %
277.18 nm	0.0031	HOMO-8 -> LUMO	12.0 %
		HOMO-7 -> LUMO	4.9 %
		HOMO-6 -> LUMO	79.3 %
274.89 nm	0.0446	HOMO-8 -> LUMO	3.0 %
		HOMO-7 -> LUMO	55.7 %
		HOMO-6 -> LUMO	3.4 %
		HOMO-5 -> LUMO	6.8 %

		HOMO-3 -> LUMO+1	9.4 %
		HOMO-1 -> LUMO+2	6.4 %
		HOMO-1 -> LUMO+4	3.4 %
		HOMO-1 -> LUMO+5	2.4 %
271.52 nm	0.0166	HOMO -> LUMO+2	7.8 %
		HOMO -> LUMO+3	83.9 %
		HOMO -> LUMO+4	2.6 %
269.30 nm	0.0144	HOMO-2 -> LUMO+1	18.5 %
		HOMO-2 -> LUMO+2	64.7 %
		HOMO-2 -> LUMO+3	6.2 %
262.55 nm	0.0110	HOMO-1 -> LUMO+2	5.8 %
		HOMO-1 -> LUMO+3	84.2 %
260.78 nm	0.0076	HOMO-9 -> LUMO	11.0 %
		HOMO-3 -> LUMO+1	6.9 %
		HOMO-2 -> LUMO+4	6.6 %
		HOMO-2 -> LUMO+5	3.7 %
		HOMO-1 -> LUMO+3	2.4 %
		HOMO -> LUMO+4	24.2 %
		HOMO -> LUMO+5	37.1 %
		HOMO -> LUMO+5	37.1 %

Table S12. Calculated transitions for **3Br**

Wavelength	Intensity	Levels	Character
445.85 nm	0.0012	HOMO -> LUMO	98.0 %
420.40 nm	0.0758	HOMO-1 -> LUMO	97.8 %
382.29 nm	0.0002	HOMO-2 -> LUMO	97.3 %
340.23 nm	0.0258	HOMO-4 -> LUMO	4.5 %
		HOMO-3 -> LUMO	93.4 %
332.70 nm	0.0065	HOMO-4 -> LUMO	7.7 %
		HOMO -> LUMO+1	78.8 %
		HOMO -> LUMO+2	7.6 %
324.35 nm	0.0950	HOMO-4 -> LUMO	79.7 %
		HOMO-3 -> LUMO	3.3 %
		HOMO-1 -> LUMO+1	5.6 %
		HOMO -> LUMO+1	6.3 %
320.36 nm	0.0281	HOMO-5 -> LUMO	2.6 %
		HOMO-4 -> LUMO	3.3 %
		HOMO-1 -> LUMO+1	82.9 %
		HOMO-1 -> LUMO+2	4.9 %
303.78 nm	0.0916	HOMO-8 -> LUMO	2.8 %
		HOMO-6 -> LUMO	3.6 %
		HOMO-5 -> LUMO	48.2 %
		HOMO-4 -> LUMO+1	2.4 %

		HOMO-1 -> LUMO+2	2.4 %
		HOMO -> LUMO+1	4.0 %
		HOMO -> LUMO+2	24.6 %
		HOMO -> LUMO+3	2.3 %
301.32 nm	0.0648	HOMO-6 -> LUMO	22.0 %
		HOMO-5 -> LUMO	17.0 %
		HOMO-2 -> LUMO+1	2.7 %
		HOMO -> LUMO+1	6.1 %
		HOMO -> LUMO+2	31.1 %
		HOMO -> LUMO+3	4.3 %
		HOMO -> LUMO+4	4.8 %
		HOMO -> LUMO+5	2.5 %
298.90 nm	0.1038	HOMO-8 -> LUMO	2.0 %
		HOMO-6 -> LUMO	49.9 %
		HOMO-5 -> LUMO	7.7 %
		HOMO-2 -> LUMO+1	9.9 %
		HOMO-1 -> LUMO+2	4.4 %
		HOMO -> LUMO+2	6.1 %
		HOMO -> LUMO+3	2.1 %
		HOMO -> LUMO+4	3.8 %
		HOMO -> LUMO+5	2.1 %
297.86 nm	0.0163	HOMO-6 -> LUMO	12.5 %
		HOMO-2 -> LUMO+1	62.5 %
		HOMO-2 -> LUMO+2	14.1 %
292.75 nm	0.0471	HOMO-6 -> LUMO	3.0 %
		HOMO-5 -> LUMO	4.5 %
		HOMO-1 -> LUMO+1	6.4 %

		HOMO-1 -> LUMO+2	24.9 %
		HOMO-1 -> LUMO+3	5.3 %
		HOMO-1 -> LUMO+4	10.8 %
		HOMO-1 -> LUMO+5	6.1 %
		HOMO -> LUMO+2	6.3 %
		HOMO -> LUMO+4	13.6 %
		HOMO -> LUMO+5	10.0 %
285.79 nm	0.0245	HOMO-1 -> LUMO+2	29.7 %
		HOMO-1 -> LUMO+3	2.1 %
		HOMO-1 -> LUMO+4	2.2 %
		HOMO -> LUMO+2	10.1 %
		HOMO -> LUMO+3	6.7 %
		HOMO -> LUMO+4	25.1 %
		HOMO -> LUMO+5	12.7 %
281.71 nm	0.0147	HOMO-1 -> LUMO+2	22.6 %
		HOMO-1 -> LUMO+3	4.9 %
		HOMO-1 -> LUMO+4	34.6 %
		HOMO-1 -> LUMO+5	23.4 %
		HOMO-1 -> LUMO+6	5.5 %
278.84 nm	0.0134	HOMO-9 -> LUMO	5.3 %
		HOMO-8 -> LUMO	23.4 %
		HOMO-7 -> LUMO	59.1 %
		HOMO-6 -> LUMO	4.1 %
276.03 nm	0.0441	HOMO-8 -> LUMO	47.4 %
		HOMO-7 -> LUMO	32.8 %
		HOMO-5 -> LUMO	7.2 %
		HOMO-4 -> LUMO+1	2.6 %

		HOMO-3 -> LUMO+1	4.3 %
272.94 nm	0.0066	HOMO -> LUMO+2	3.4 %
		HOMO -> LUMO+3	77.8 %
		HOMO -> LUMO+4	12.5 %
270.26 nm	0.0412	HOMO-9 -> LUMO	2.1 %
		HOMO-8 -> LUMO	3.4 %
		HOMO-3 -> LUMO+1	6.3 %
		HOMO-2 -> LUMO+1	18.0 %
		HOMO-2 -> LUMO+2	59.1 %
		HOMO-2 -> LUMO+3	3.7 %
269.25 nm	0.0511	HOMO-9 -> LUMO	76.7 %
		HOMO-7 -> LUMO	2.2 %
		HOMO-4 -> LUMO+1	7.7 %
		HOMO-3 -> LUMO+1	3.2 %
267.70 nm	0.0471	HOMO-8 -> LUMO	5.4 %
		HOMO-4 -> LUMO+1	4.2 %
		HOMO-3 -> LUMO+1	73.9 %
		HOMO-2 -> LUMO+2	7.9 %
		HOMO-2 -> LUMO+2	7.9 %

^{1}H-NMR Progressions for the Photochemical Studies

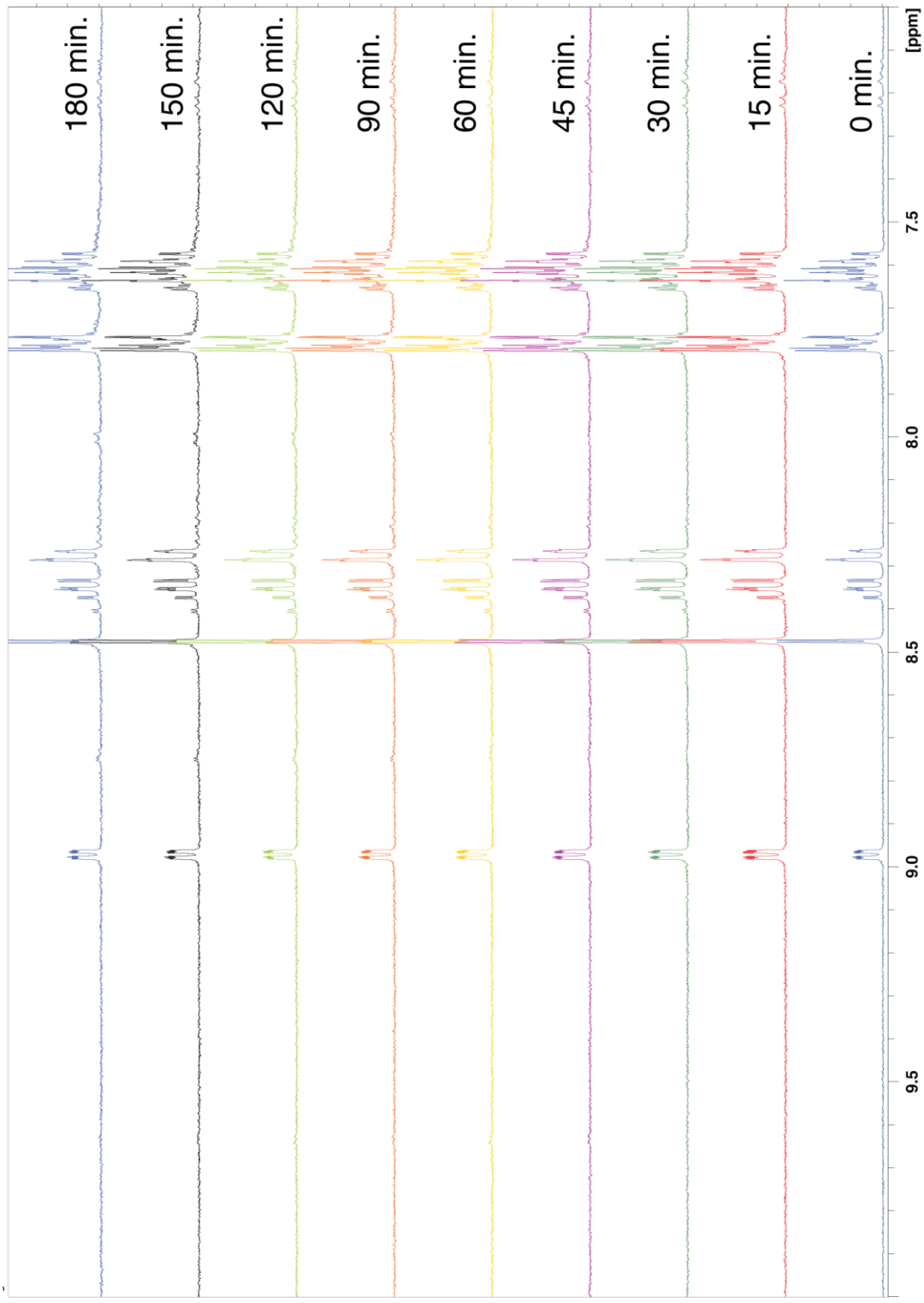

Figure S14. Photolysis of **2Cl** in a deuterated acetone solution.

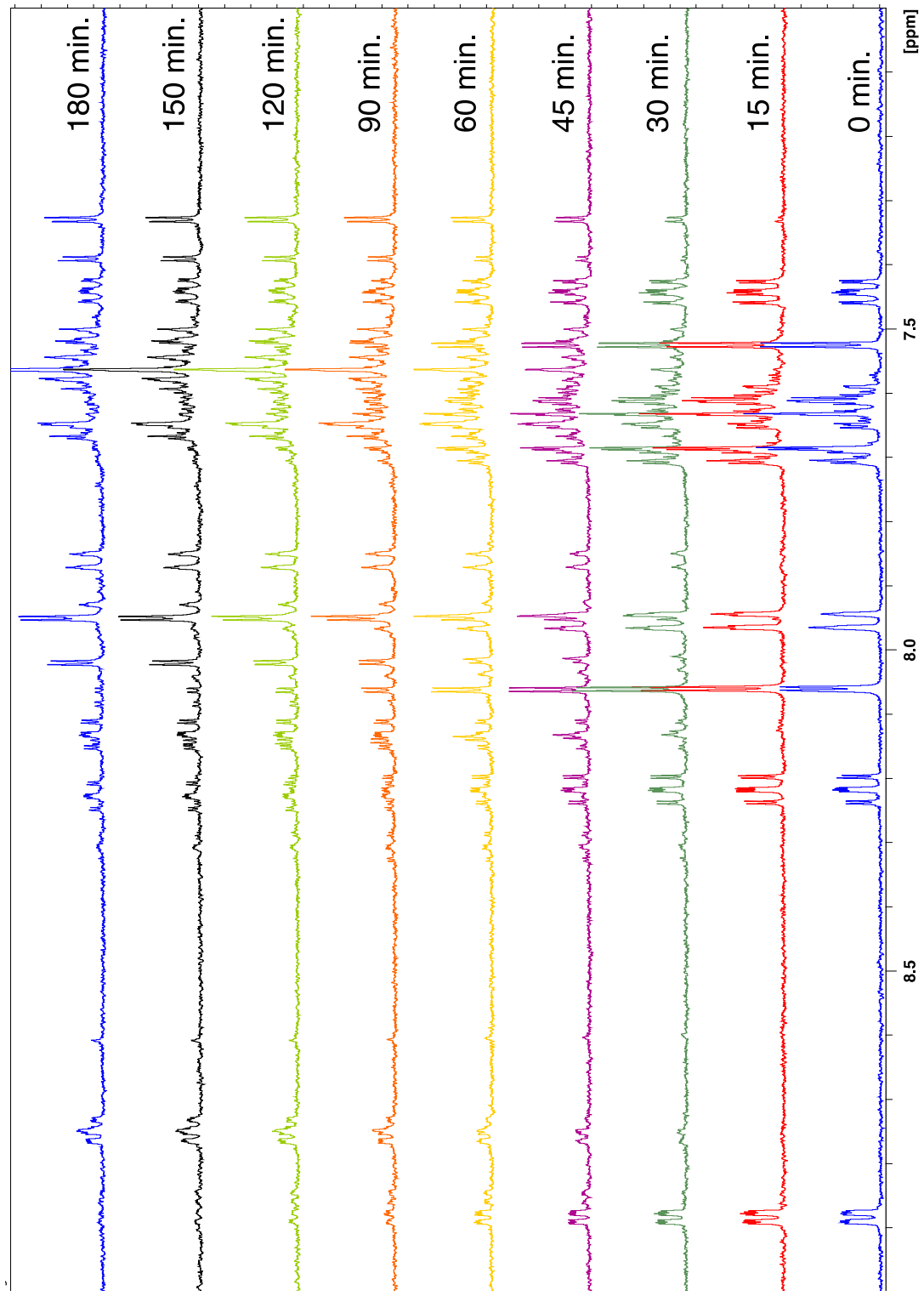

Figure S15. Photolysis of **2Cl** in a deuterated acetonitrile solution.

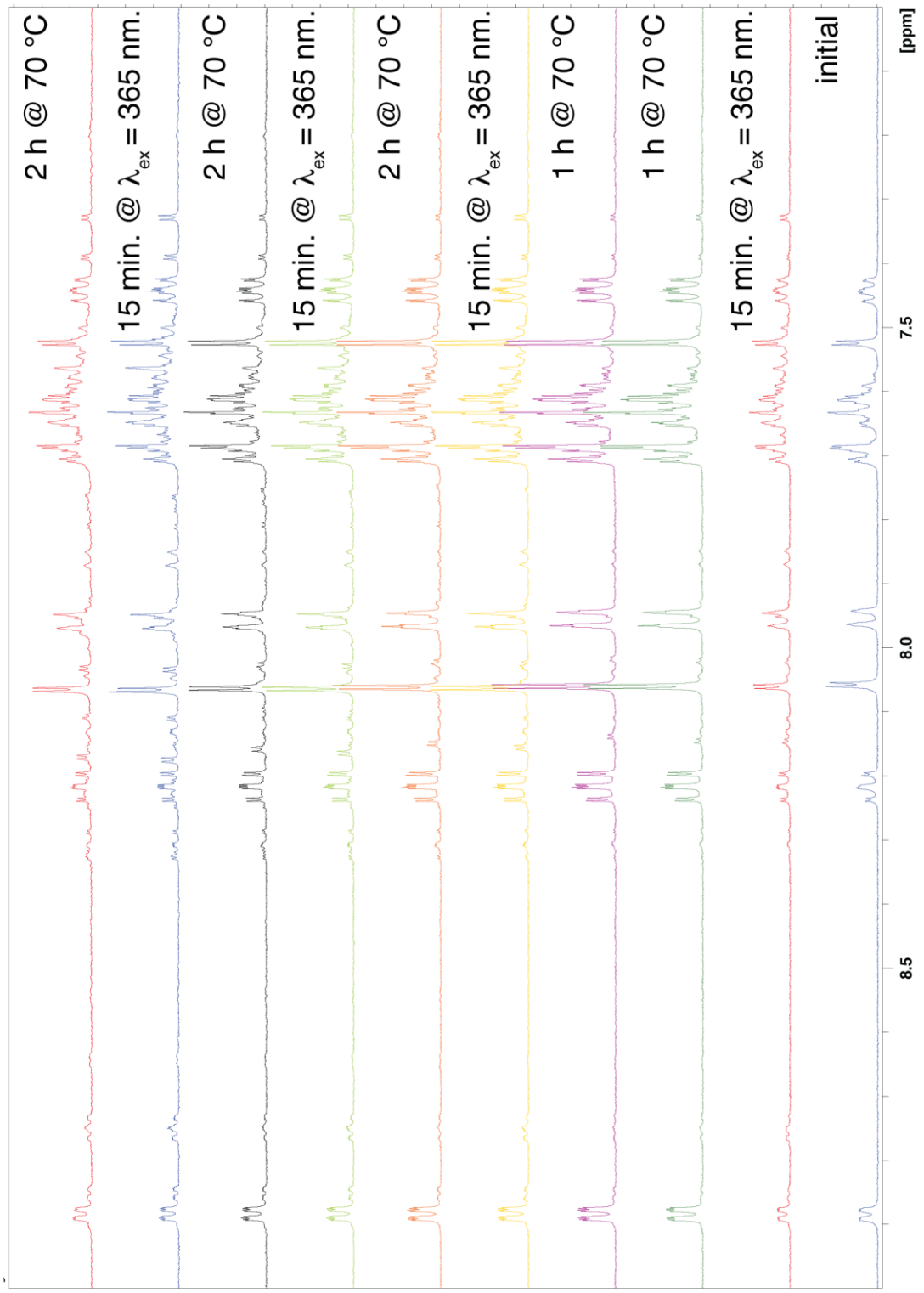

Figure S16. Photochemical and thermal steps of **2Cl** in a deuterated acetonitrile solution. The thermal steps were performed in darkness.

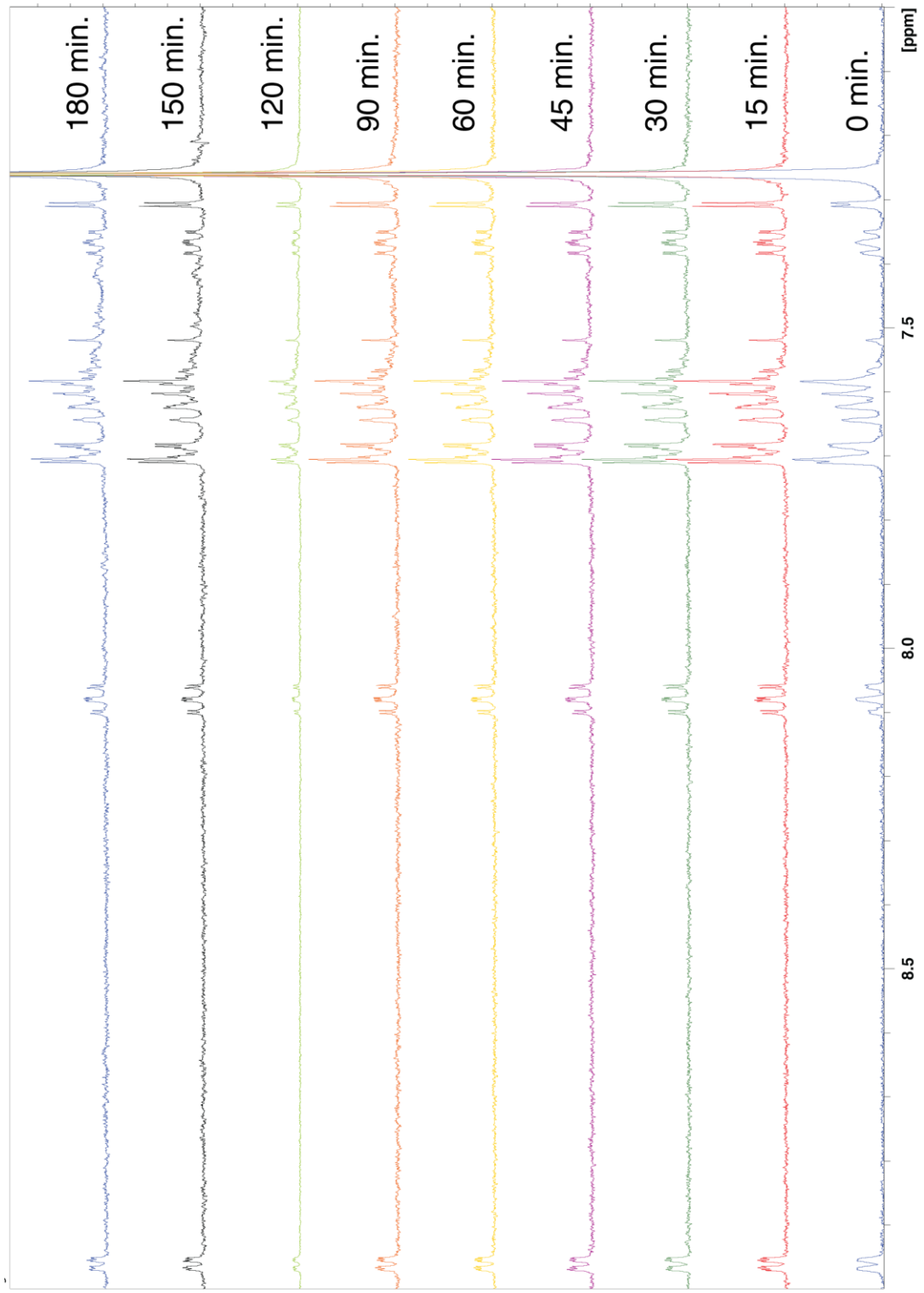

Figure S17. Photolysis of **2Cl** in a deuterated chloroform solution.

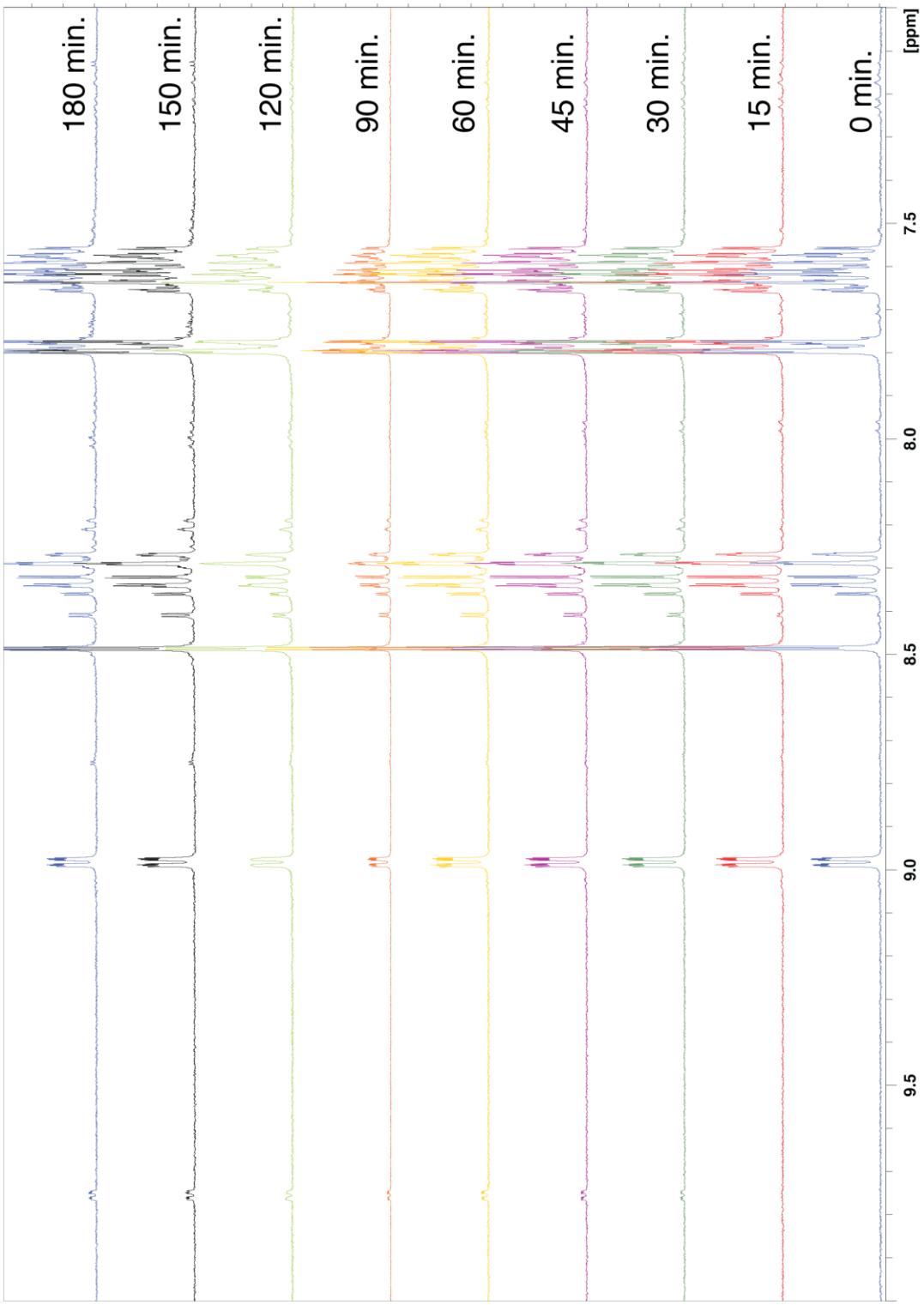

Figure S18. Photolysis of **2Br** in a deuterated acetone solution.

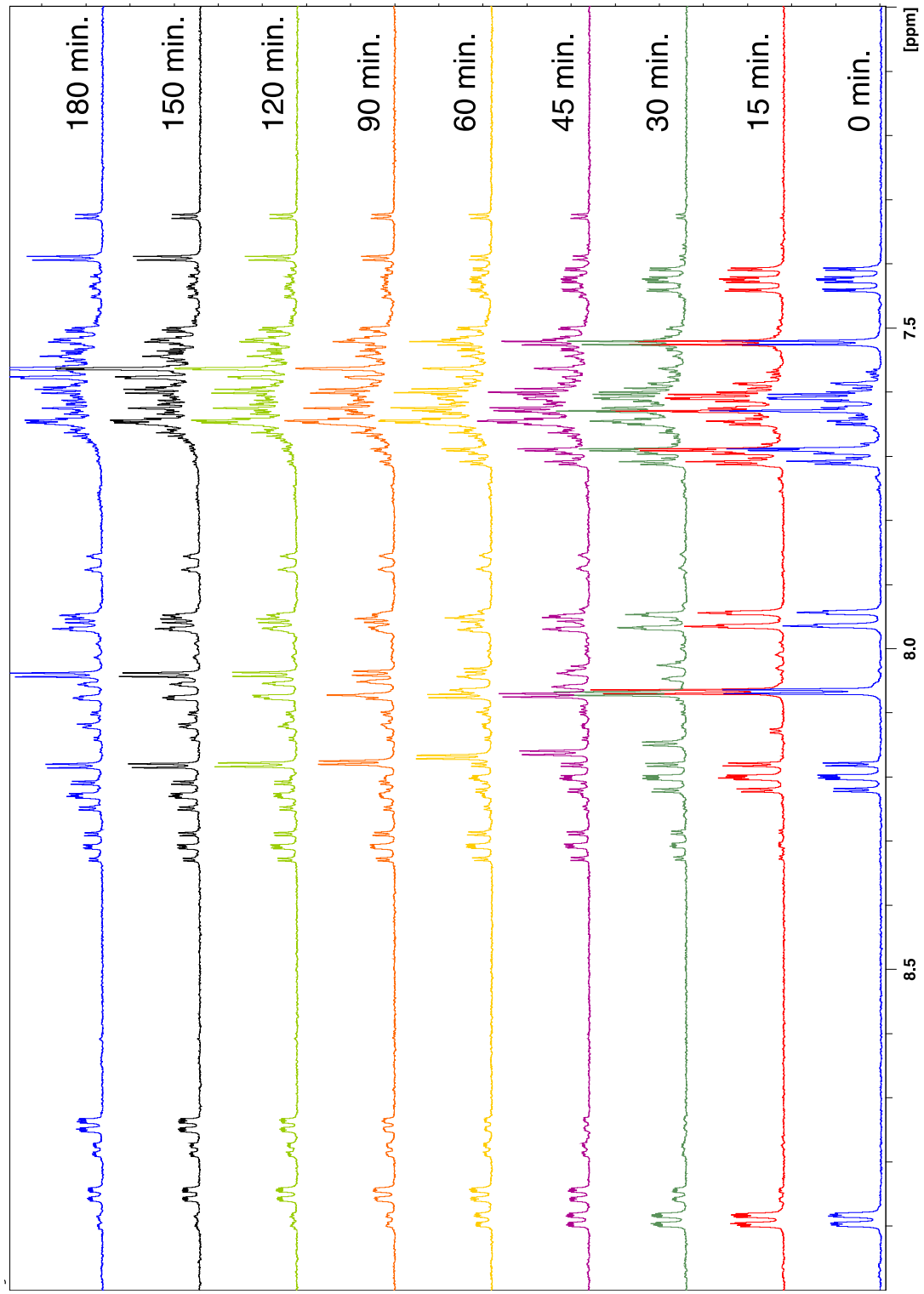

Figure S19. Photolysis of **2Br** in a deuterated acetonitrile solution.

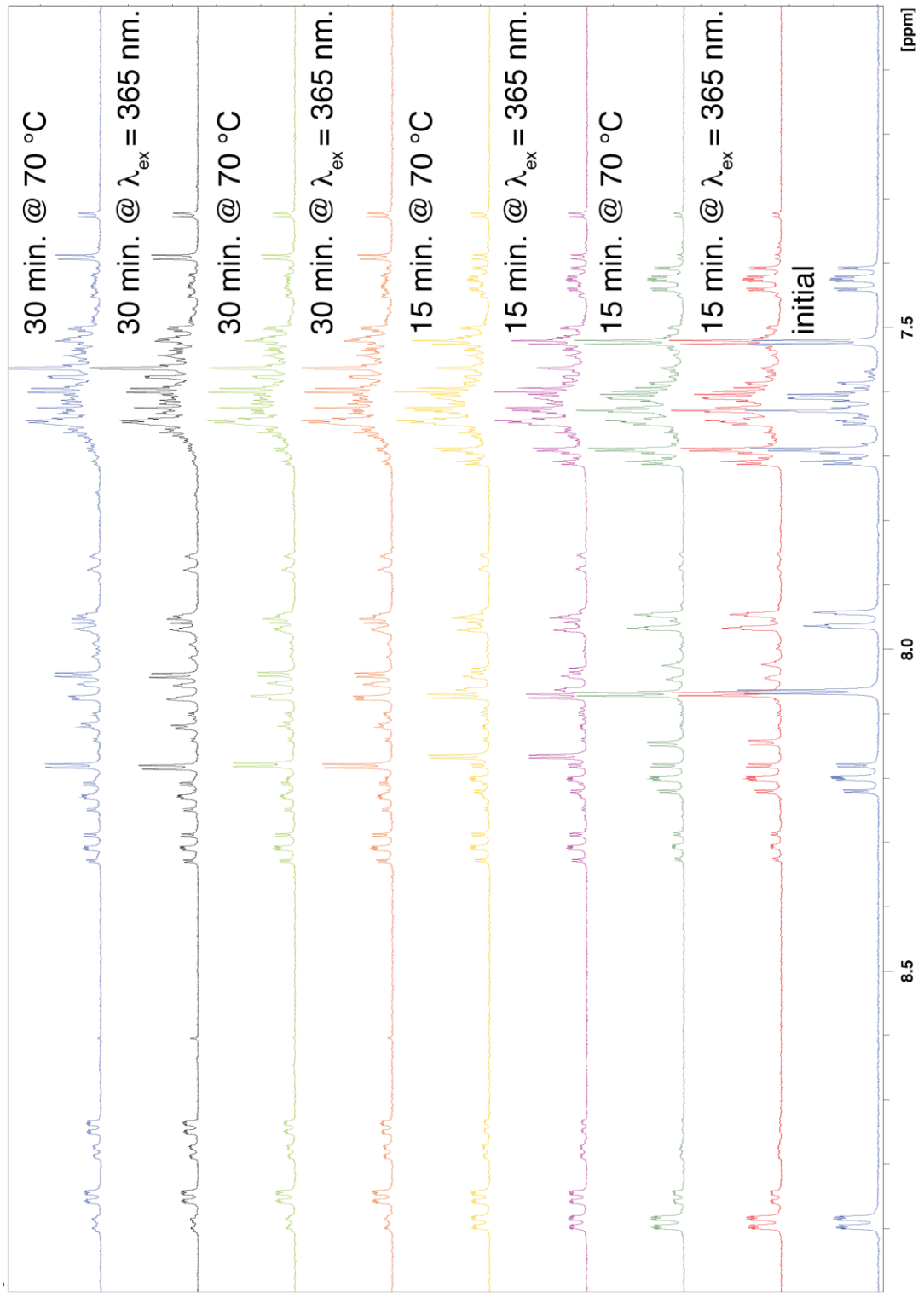

Figure S20. Photochemical and thermal steps of **2Br** in a deuterated acetonitrile solution. The thermal steps were performed in darkness.

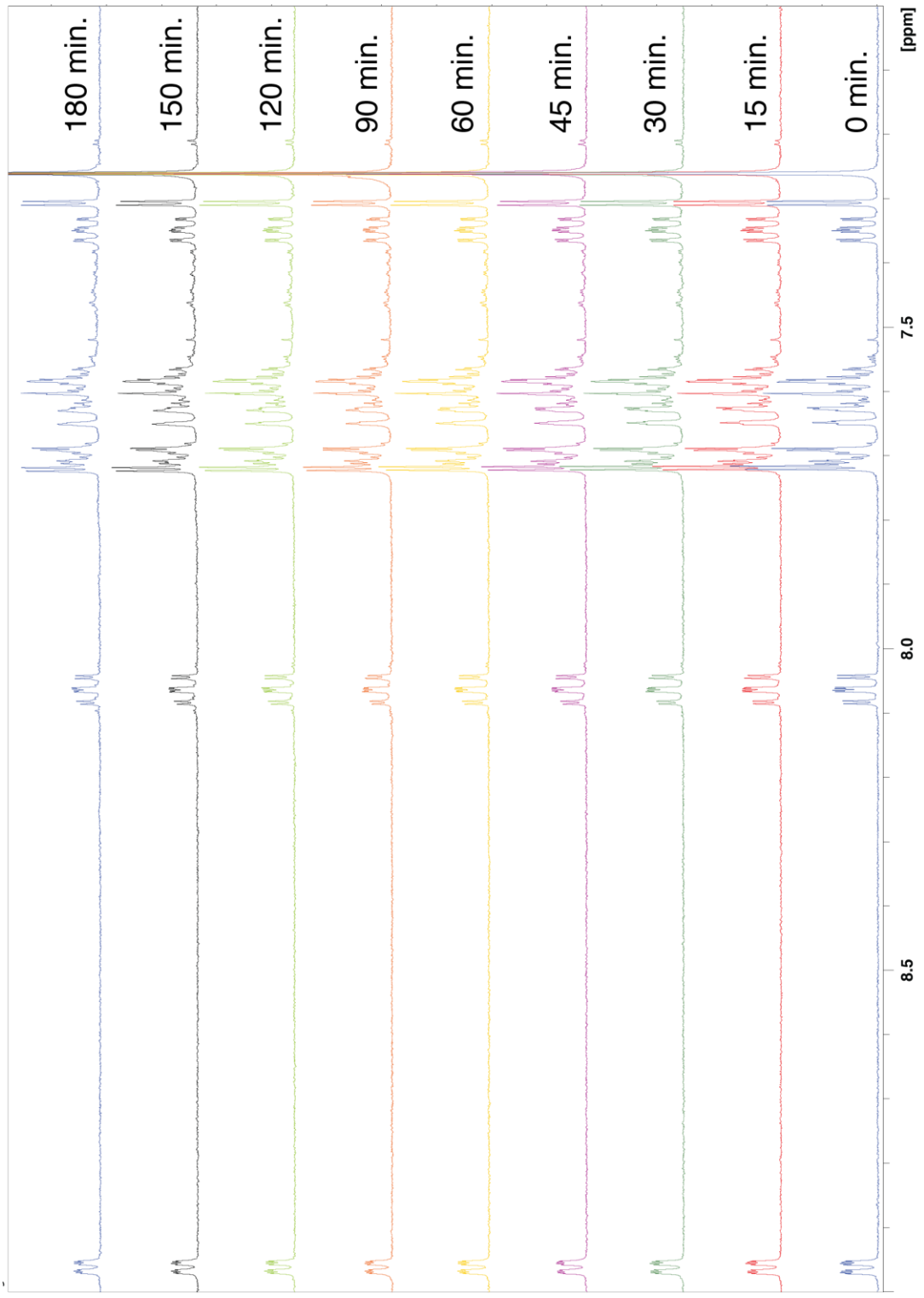

Figure S21. Photolysis of **2Br** in a deuterated chloroform solution.

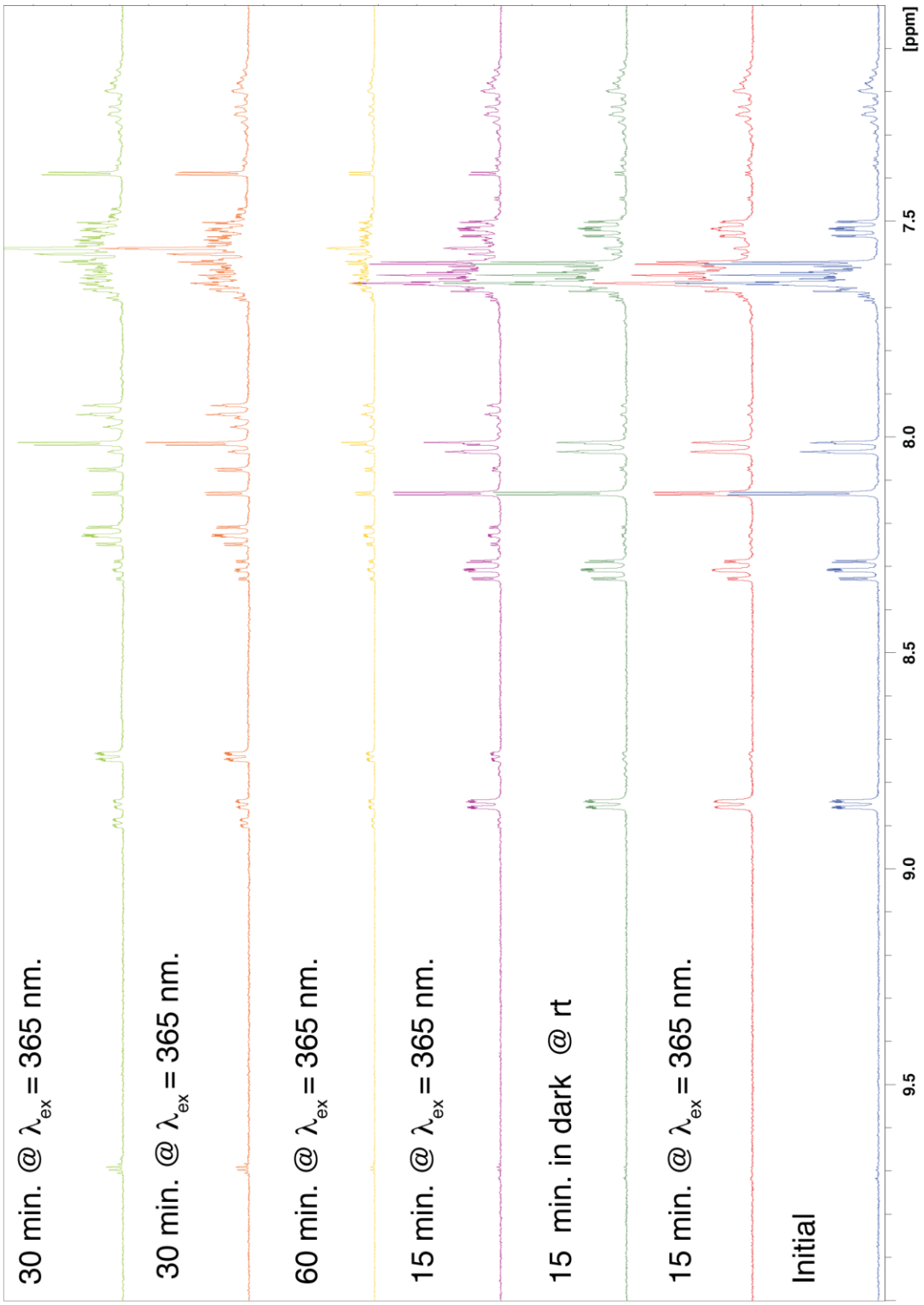

Figure S22. Photolysis of *fac*-[Re(CO)$_3$(**PyImPh**)(NCCD$_3$)]BF$_4$ in a deuterated acetonitrile solution.

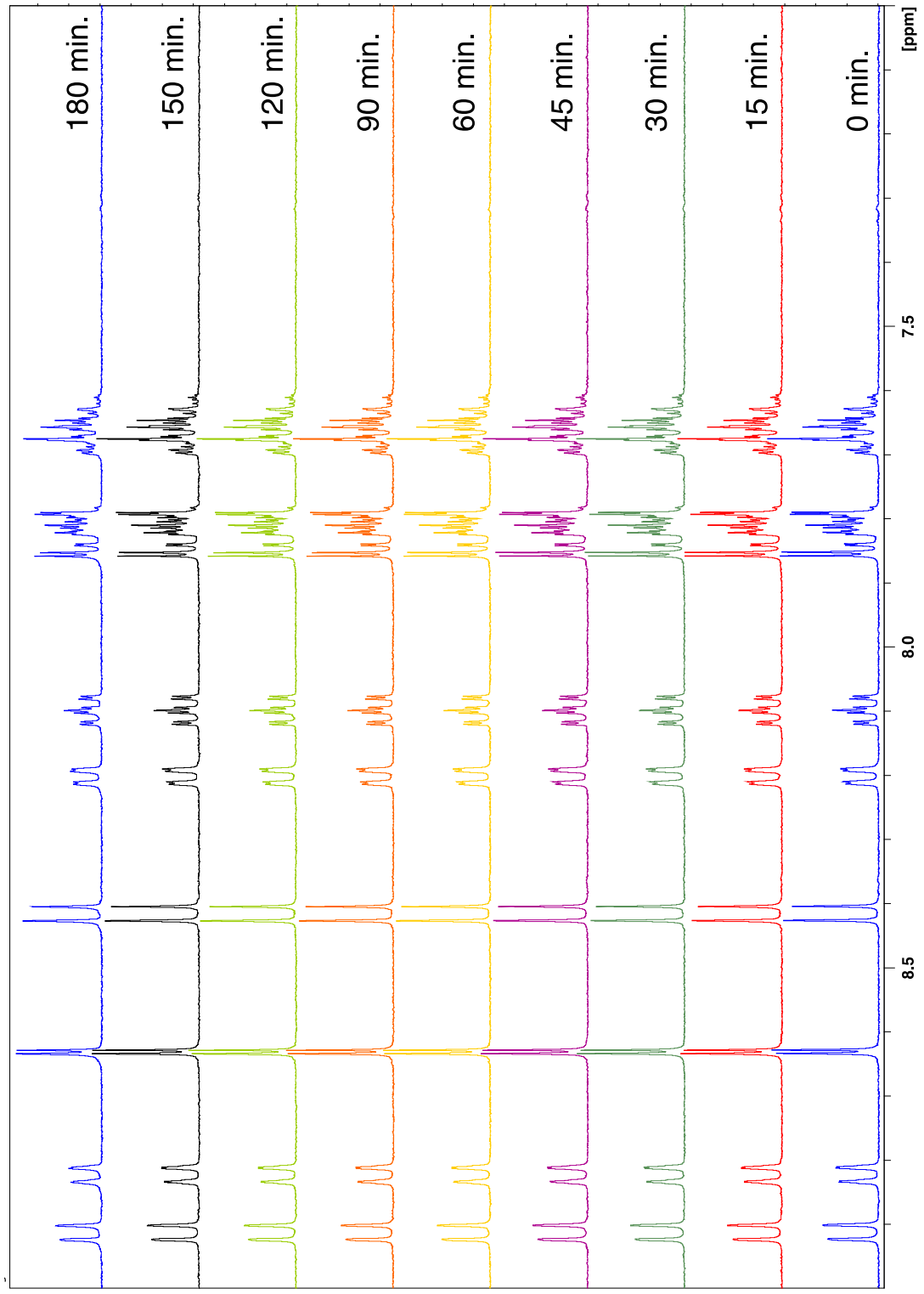

Figure S23. Photolysis of **3Cl** in a deuterated acetone solution.

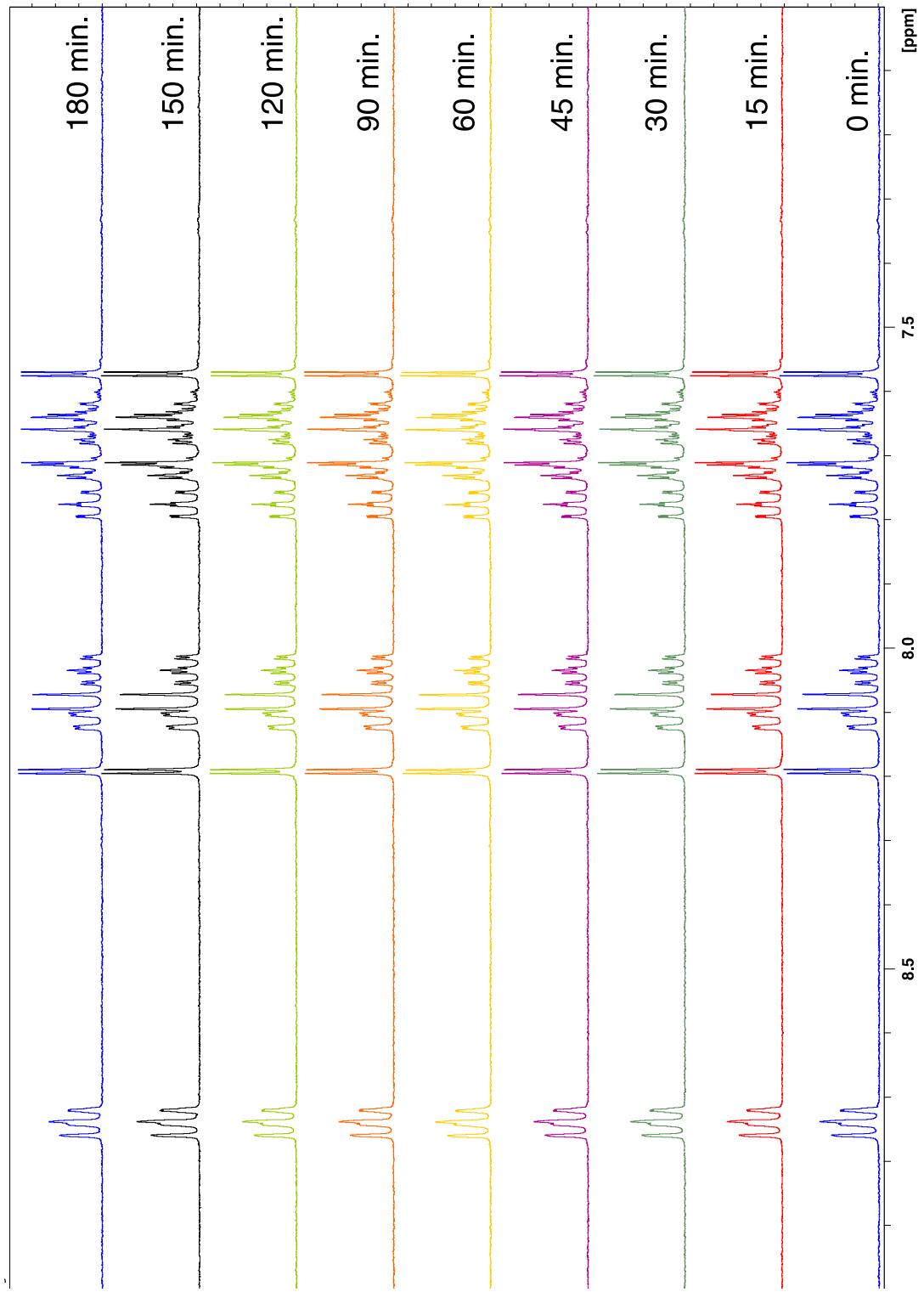

Figure S24. Photolysis of **3Cl** in a deuterated acetonitrile solution.

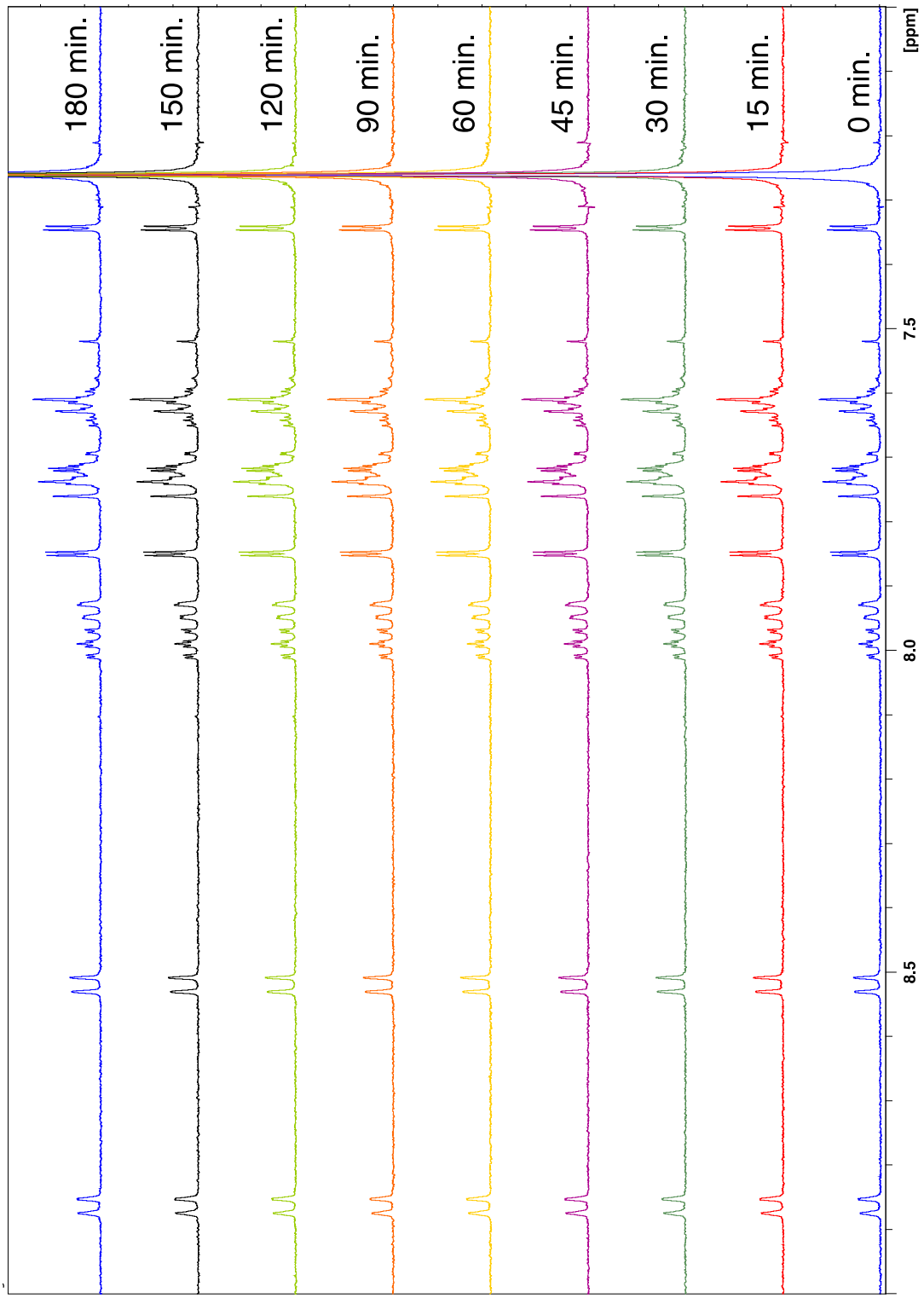

Figure S25. Photolysis of **3Cl** in a deuterated chloroform solution.

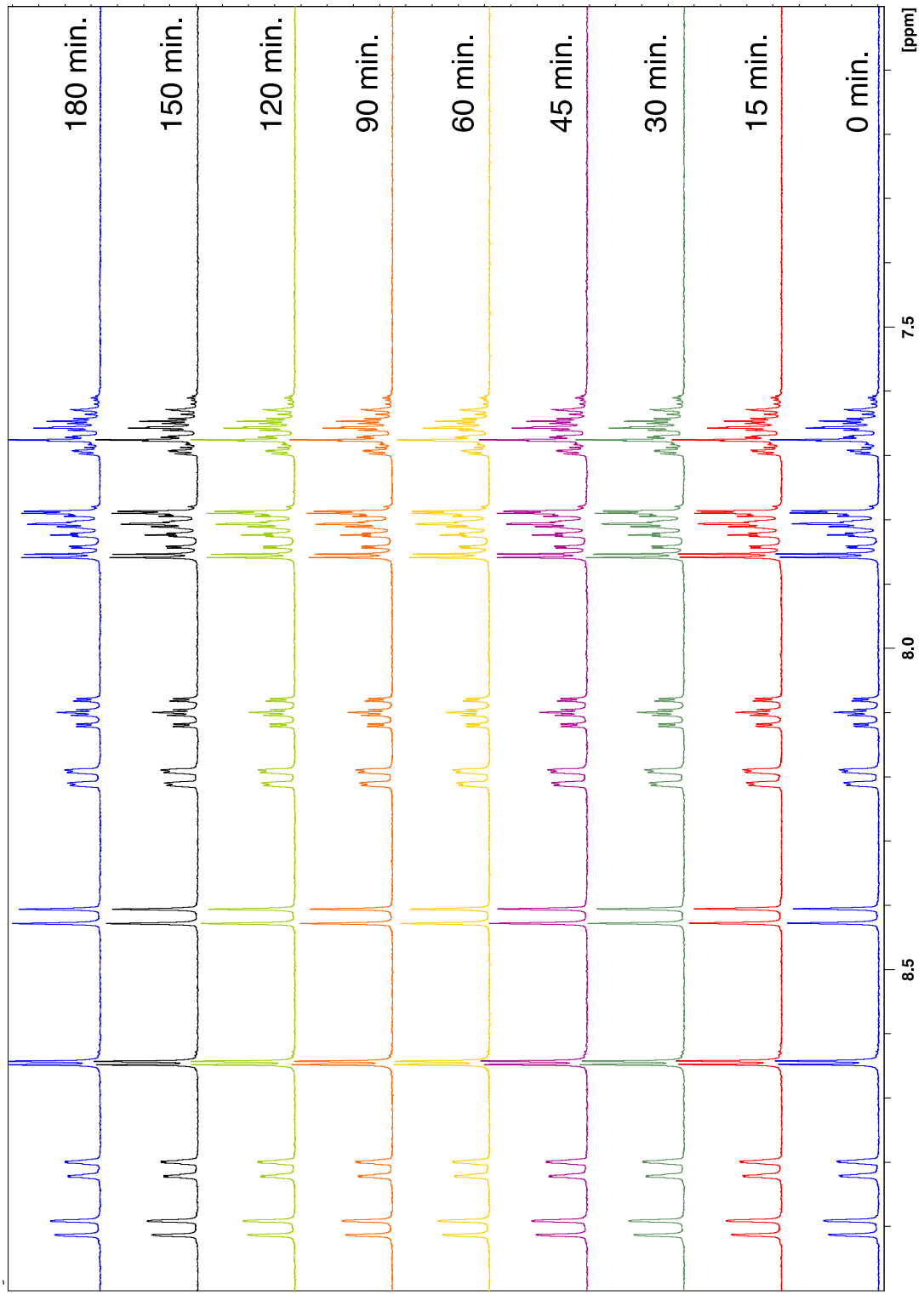

Figure S26. Photolysis of **3Br** in a deuterated acetone solution.

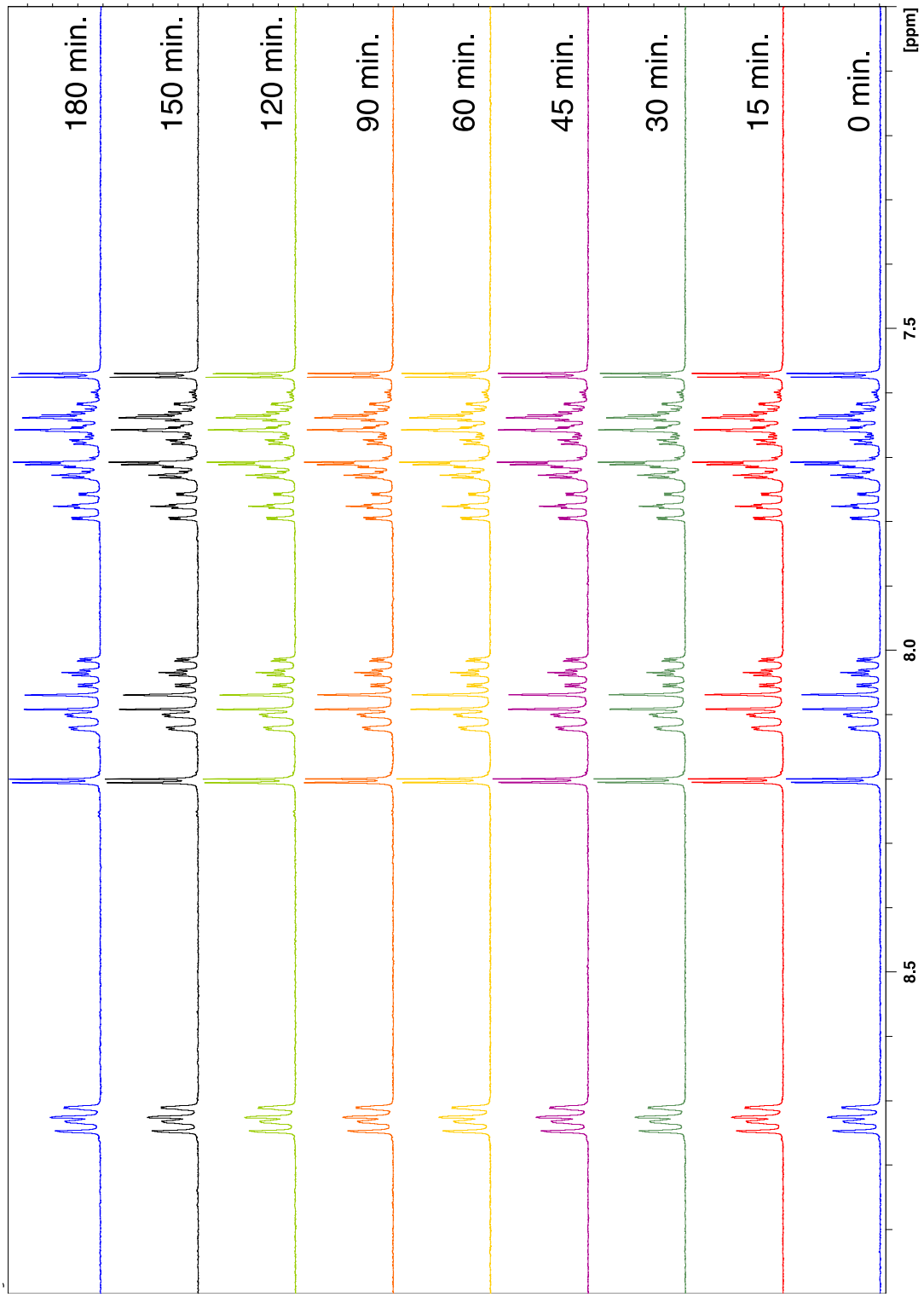

Figure S27. Photolysis of **3Br** in a deuterated acetonitrile solution.

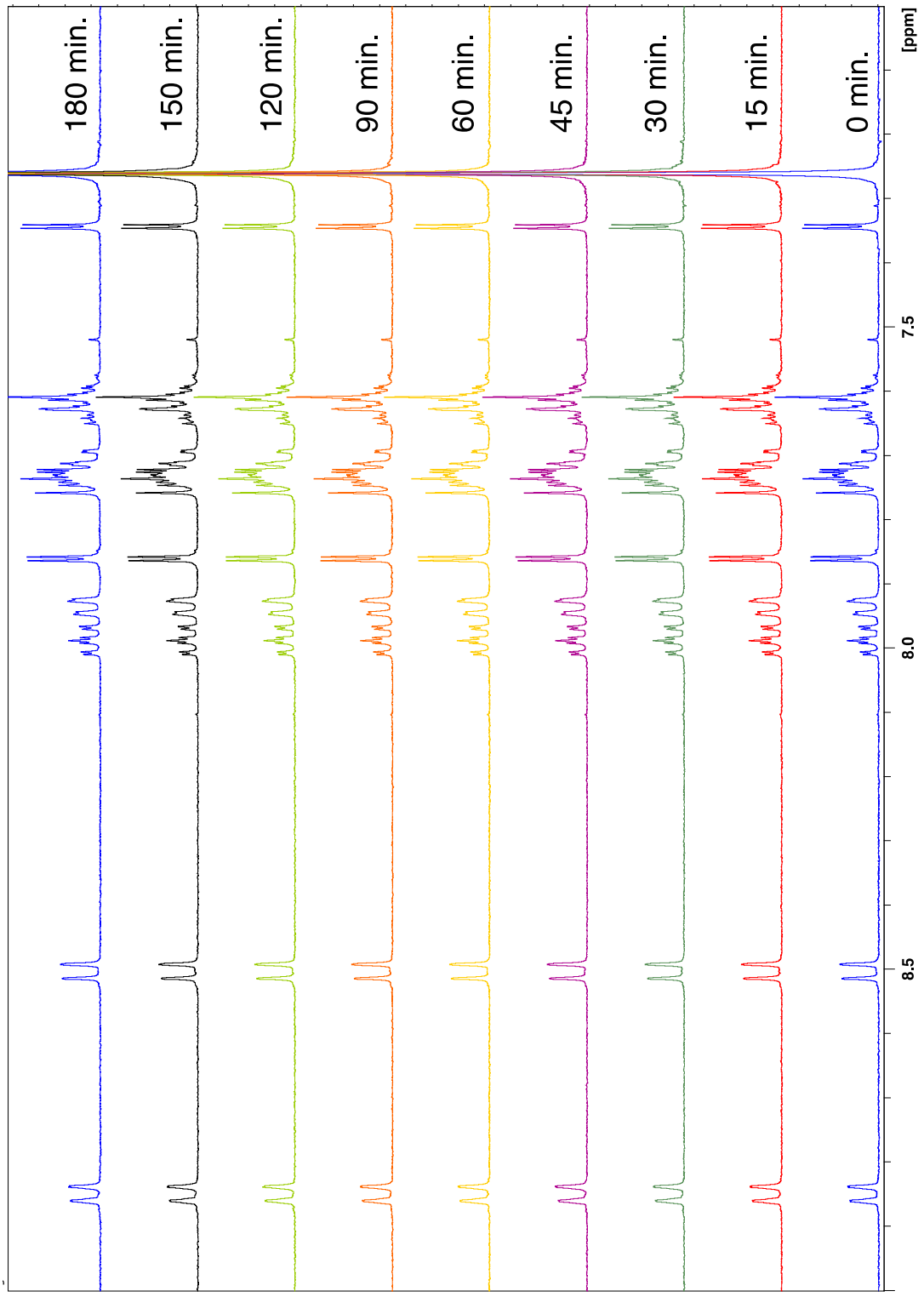

Figure S28. Photolysis of **3Br** in a deuterated chloroform solution.

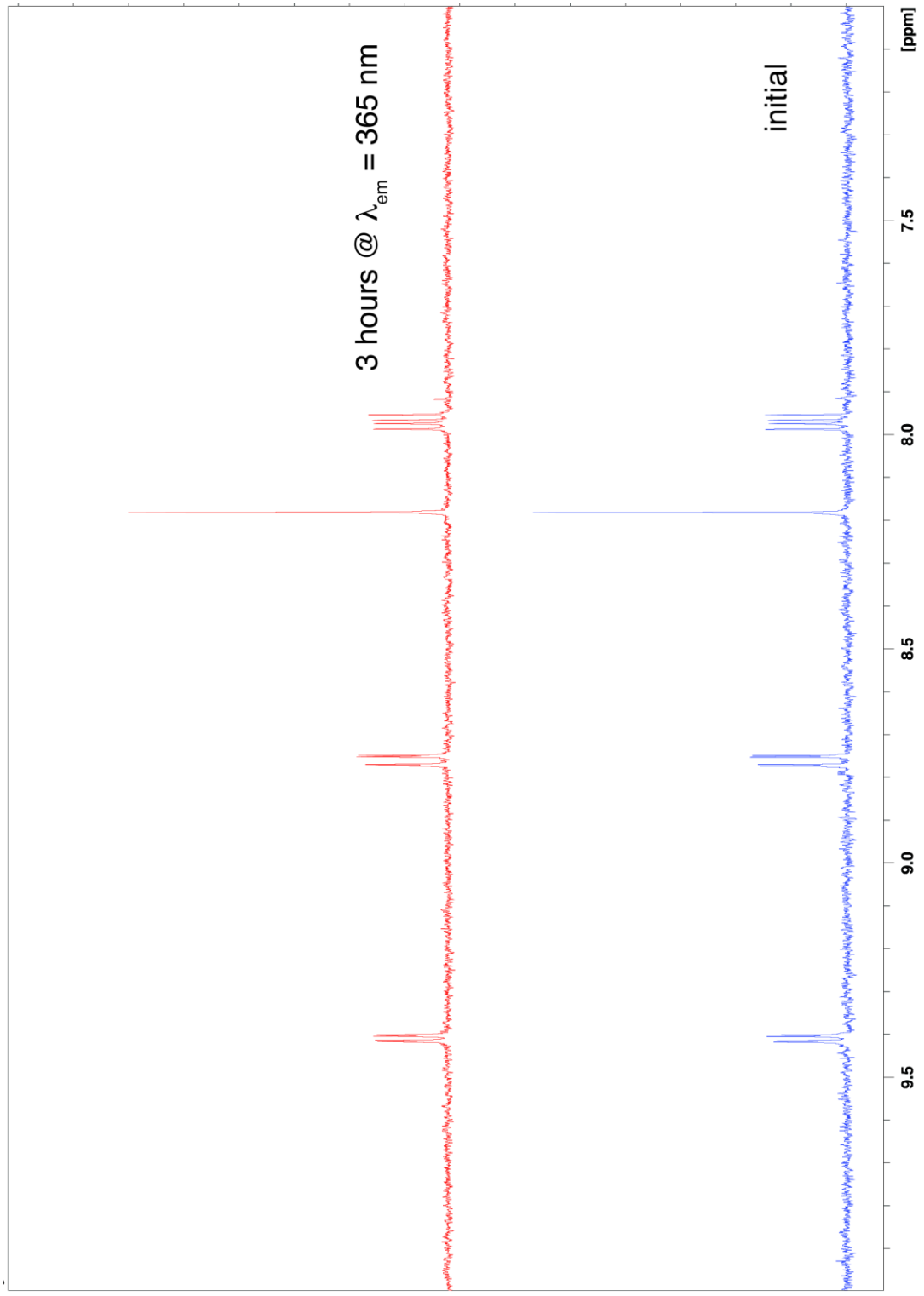

Figure S29. Photolysis of *fac*-[Re(CO)$_3$(**phen**)Br] in a deuterated acetonitrile solution.