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1. Synthesis and Characterization of 1,3-Diethylbenzimidazol-2-ium salts (1-3)

1,3-Diethylbenzimidazol-2-ium iodide (1)

To a stirred solution of benzimidazole 2000 mg (16.93 mmol, 1 equiv.) in 30 mL of anhydrous ACN, 744.9 mg (18.62 mmol, 1.1 equiv.) of NaH was added. After forming the benzimidazole-2-ium sodium salt under the release of H_2, 20.52 mL (253.90 mmol, 15 equiv.) of iodoethane was applied and the reaction mixture was stirred under an argon atmosphere at 82°C for 72 h in the dark. The solvent was removed under reduced pressure and the residue was taken up in DCM and filtered over celite to remove NaI salt. The solvent was evaporated and the product was recrystallized from EtOH to yield compound **1** as a yellowish solid, 3125 mg (61% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.87 (s, 1H, NCHN), 7.79 – 7.71 (m, 2H, Ar-H), 7.71 – 7.63 (m, 2H, Ar-H), 4.55 (q, *J* = 7.3 Hz, 4H, CH_2), 1.57 (t, *J* = 7.3 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, DMSO-d_6): δ 142.1 (NCN), 131.4 (Ar-C_q), 126.93 (Ar-CH), 114.1 (Ar-CH), 42.6 (CH_2), 14.7 (CH_3). IR (ATR, cm^{-1}): 3025 bw, 2980 bw; 1562 s, 1428 w, 1215 m; 751 s, 552 m.

1,3-Diethylbenzimidazol-2-ium chloride (2)

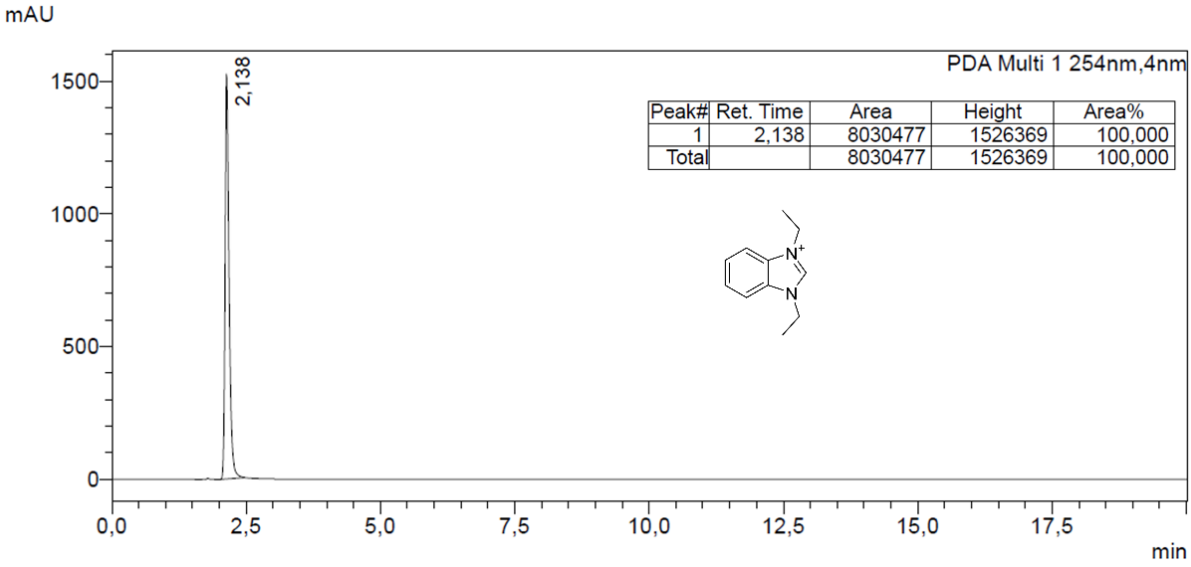
2330 mg (7.71 mmol, 1 equiv.) of **1** was dissolved in 30 mL of water. 1202 mg (3.86 mmol, 0.5 equiv.) of Ag_2SO_4 was added and the resulting yellowish suspension was stirred overnight under light protection. The AgI formed was removed by filtration over celite and the filtrate was supplemented with 803 mg (3.86 mmol, 0.5 equiv.) of $BaCl_2$. The solution was stirred for another 2 h, the formed $BaSO_4$ was removed *via* filtration over celite and the filtrate was evaporated under reduced pressure to dryness. The off-white residue was taken up in DCM and filtered again over celite. Et_2O was added to the DCM solution to precipitate the product. The latter was collected *via* filtration, washed with Et_2O, and dried *in vacuo* to yield **2** as a white solid, 1398 mg (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.94 (s, 1H, NCHN), 7.75 – 7.69 (m, 2H, Ar-H), 7.69 – 7.62 (m, 2H, Ar-H), 4.71 (q, *J* = 7.3 Hz, 4H, CH_2), 1.74 (t, *J* = 7.3 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.3 (NCN), 131.3 (Ar-C_q), 127.1 (Ar-CH), 113.0 (Ar-CH), 42.88 (CH_2), 15.0 (CH_3). ESI-HRMS(+) found (calculated): *m/z* [M-Cl^-]$^+$, 175.1213 (175.1235). IR (ATR, cm^{-1}): 3414 bm, 3363 bm; 3031 bw, 2981 bw; 1561 s, 1432 w, 1208 m; 761 s, 514 bm. Purity calculated using HPLC (peak area): 100.0%.

1,3-Diethylbenzimidazolium hexafluorophosphate (3)

1997 mg (6.61 mmol, 1 equiv.) of **1** was dissolved in 10 mL of MeOH. 10 mL of an aqueous saturated KPF_6 solution was added dropwise to the solution under vigorous stirring. After 2 h of stirring the precipitate formed was filtered, and washed with 10 mL water and Et_2O, respectively. The product was subsequently dried in high vacuum to yield compound **3** as a white solid, 2000 mg (95% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.75 (s, 1H, NCHN), 8.13 – 8.04 (m, 2H, Ar-H), 7.75 – 7.65 (m, 2H, Ar-H), 4.51 (q, *J* = 7.3 Hz, 4H, CH_2), 1.55 (t, *J* = 7.3 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, DMSO-d_6): δ 142.0 (NCN), 131.5 (Ar-C_q), 127.0 (Ar-CH), 114.1 (Ar-CH), 42.5 (CH_2), 14.6 (CH_3). IR (ATR, cm^{-1}): 3165 w, 3111 bw, 2985 w; 1568 m, 1432 w 1213 m; 827 bs (ν_{P-F}); 754 s, 555 s.

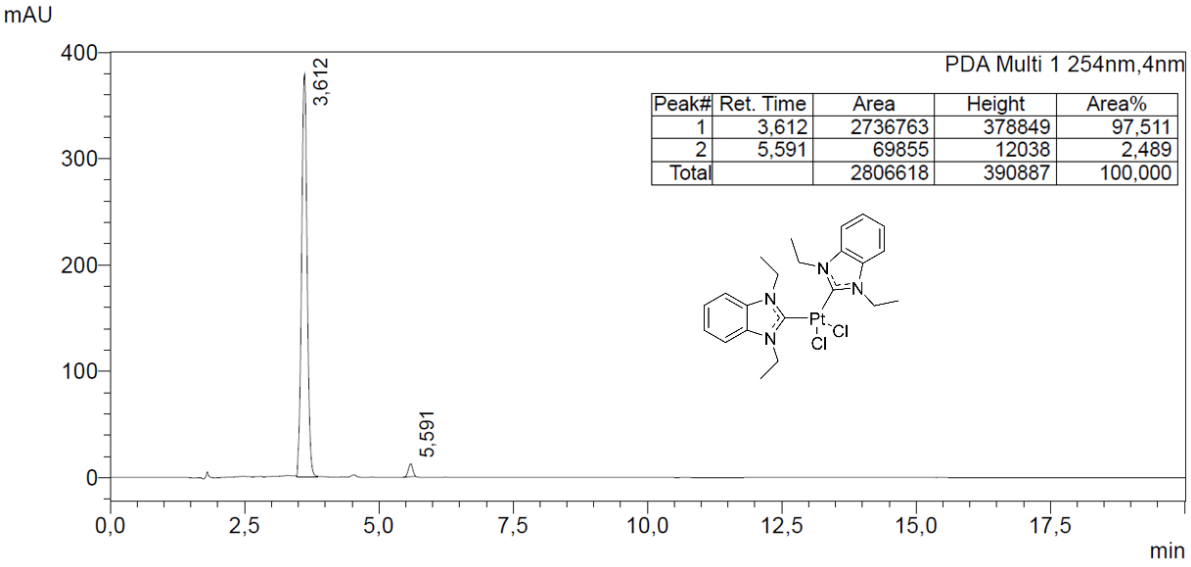
2. HPLC purity of 2, 5, 7, and 9-12

Complexes **2**, **5**, **7**, and **9**-**12** (approximately 0.5 mg) were dissolved in 0.5 mL of ACN (HPLC-grade) and 20 µL were injected into a Shimadzu prominence HPLC with autosampler SIL-20A HT, column oven CTO-10AS VP, degassers DGU-20A, detector SPD-M20A, and pumps LC-20AD. As column, a KNAUER Eurospher 100-5 C18, 250 x 4 mm was used. For the gold(I) complexes **9**-**12** gradient elution (70:30 (v/v) to 90:10 (v/v)) of ACN/water (0.1% TFA) was used. While for the platinum(II) complexes **5**, **7**, and **9**, as well as for ligand **2** the gradient was modified as follows: (60:40 (v/v) to 90:10 (v/v)) of ACN/water (0.1% TFA). The software LabSolutions was used for data processing. Purity was calculated using the peak area % at 254 nm.



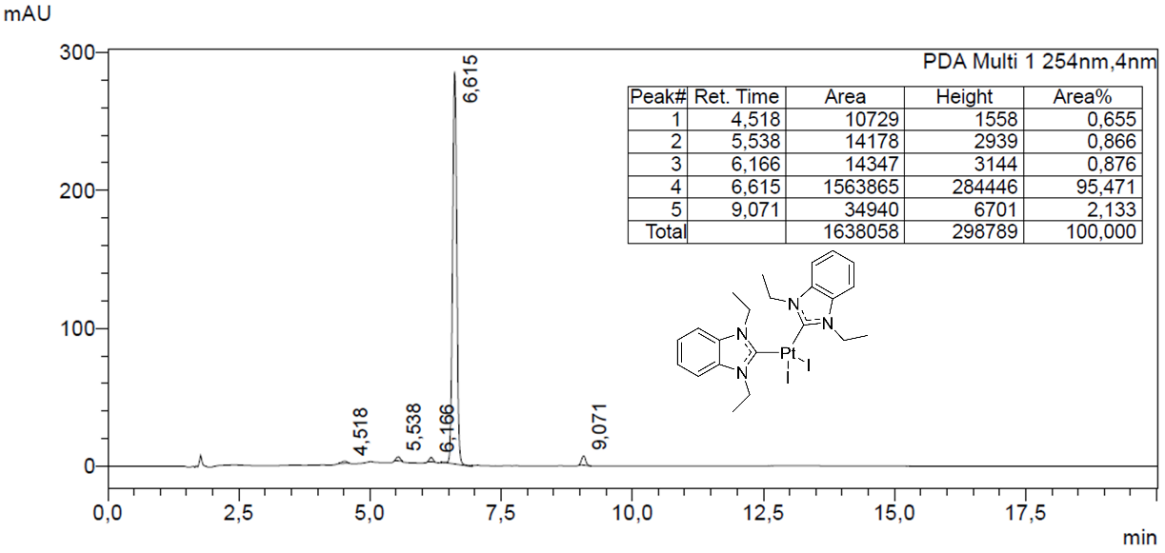
Peak#	Ret. Time	Area	Height	Area%
1	2,138	8030477	1526369	100,000
Total		8030477	1526369	100,000

Figure S1. HPLC chromatogram of **2** dissolved in ACN (purity: 100.00%).



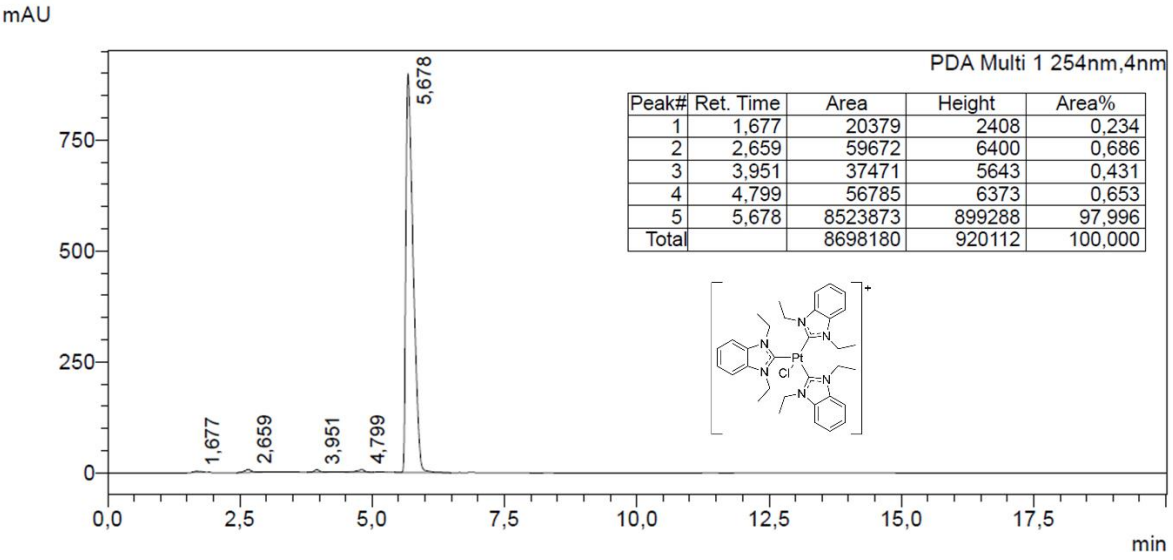
Peak#	Ret. Time	Area	Height	Area%
1	3,612	2736763	378849	97,511
2	5,591	69855	12038	2,489
Total		2806618	390887	100,000

Figure S2. HPLC chromatogram of **5** dissolved in ACN (purity: 97.51%).



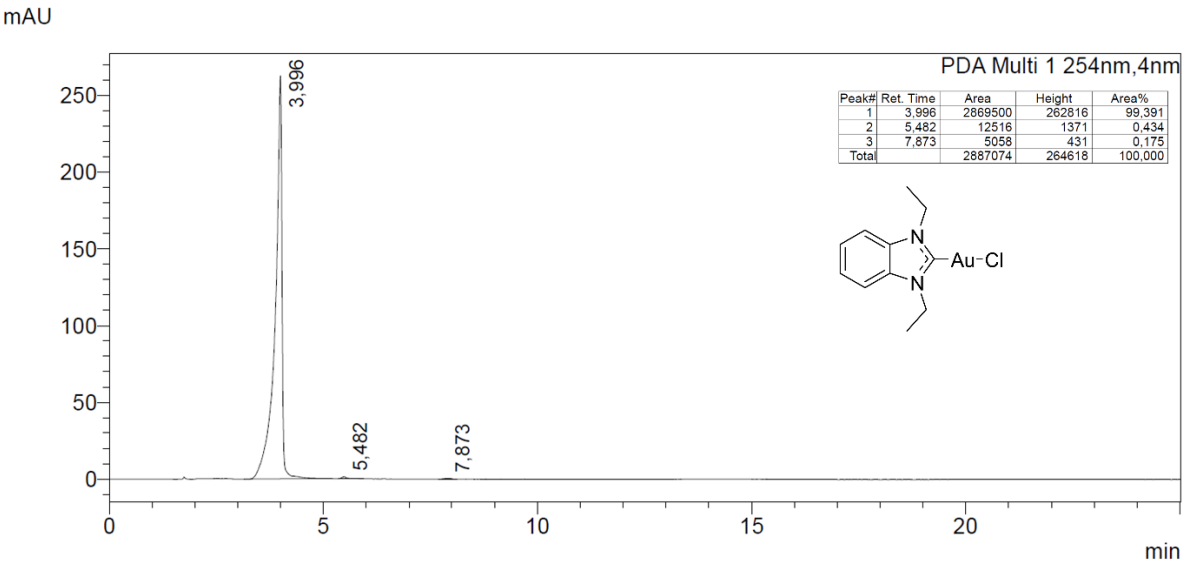
Peak#	Ret. Time	Area	Height	Area%
1	4,518	10729	1558	0,655
2	5,538	14178	2939	0,866
3	6,166	14347	3144	0,876
4	6,615	1563865	284446	95,471
5	9,071	34940	6701	2,133
Total		1638058	298789	100,000

Figure S3. HPLC chromatogram of **7** dissolved in ACN (purity: 95.47%).



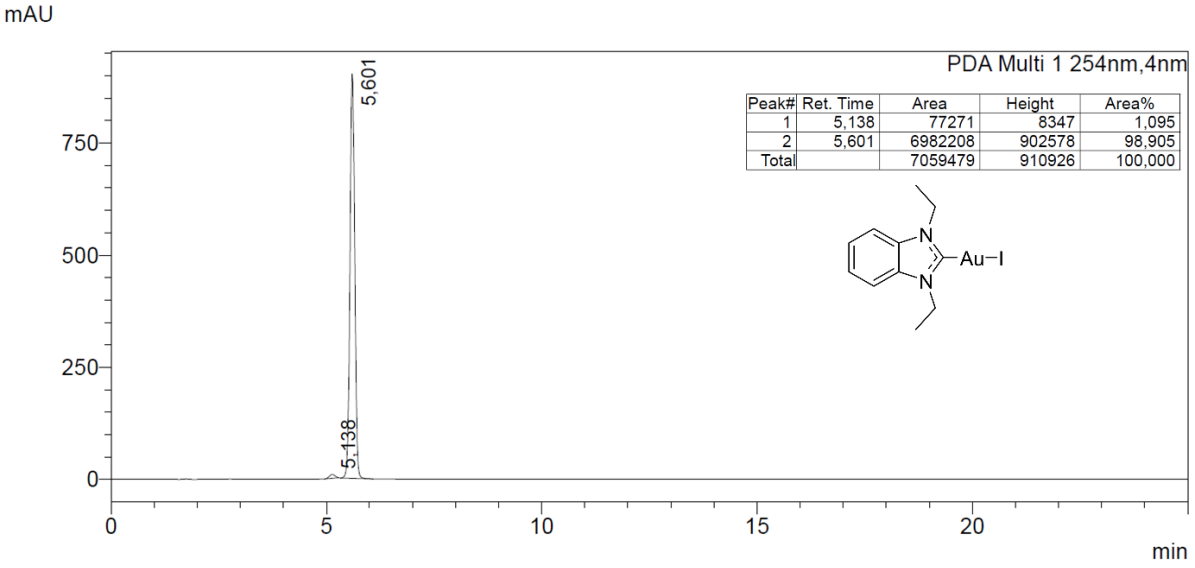
Peak#	Ret. Time	Area	Height	Area%
1	1,677	20379	2408	0,234
2	2,659	59672	6400	0,686
3	3,951	37471	5643	0,431
4	4,799	56785	6373	0,653
5	5,678	8523873	899288	97,996
Total		8698180	920112	100,000

Figure S4. HPLC chromatogram of **9** dissolved in ACN (purity: 98.00%).



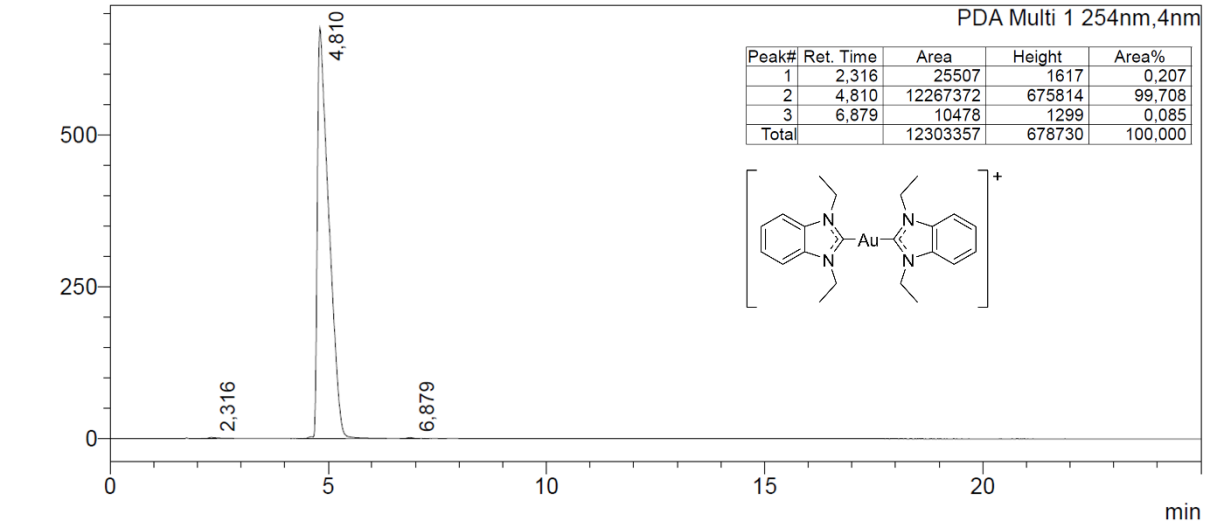
Peak#	Ret. Time	Area	Height	Area%
1	3,996	2869500	262816	99,391
2	5,482	12516	1371	0,434
3	7,873	5058	431	0,175
Total		2887074	264618	100,000

Figure S5. HPLC chromatogram of **10** dissolved in ACN (purity: 99.39%).



Peak#	Ret. Time	Area	Height	Area%
1	5,138	77271	8347	1,095
2	5,601	6982208	902578	98,905
Total		7059479	910926	100,000

Figure S6. HPLC chromatogram of **11** dissolved in ACN (purity: 98.91%).



Peak#	Ret. Time	Area	Height	Area%
1	2,316	25507	1617	0,207
2	4,810	12267372	675814	99,708
3	6,879	10478	1299	0,085
Total		12303357	678730	100,000

Figure S7. HPLC chromatogram of **12** dissolved in ACN (purity: 99.71%).

3. ^{1}H NMR Spectra of **2** and **4**-**12**

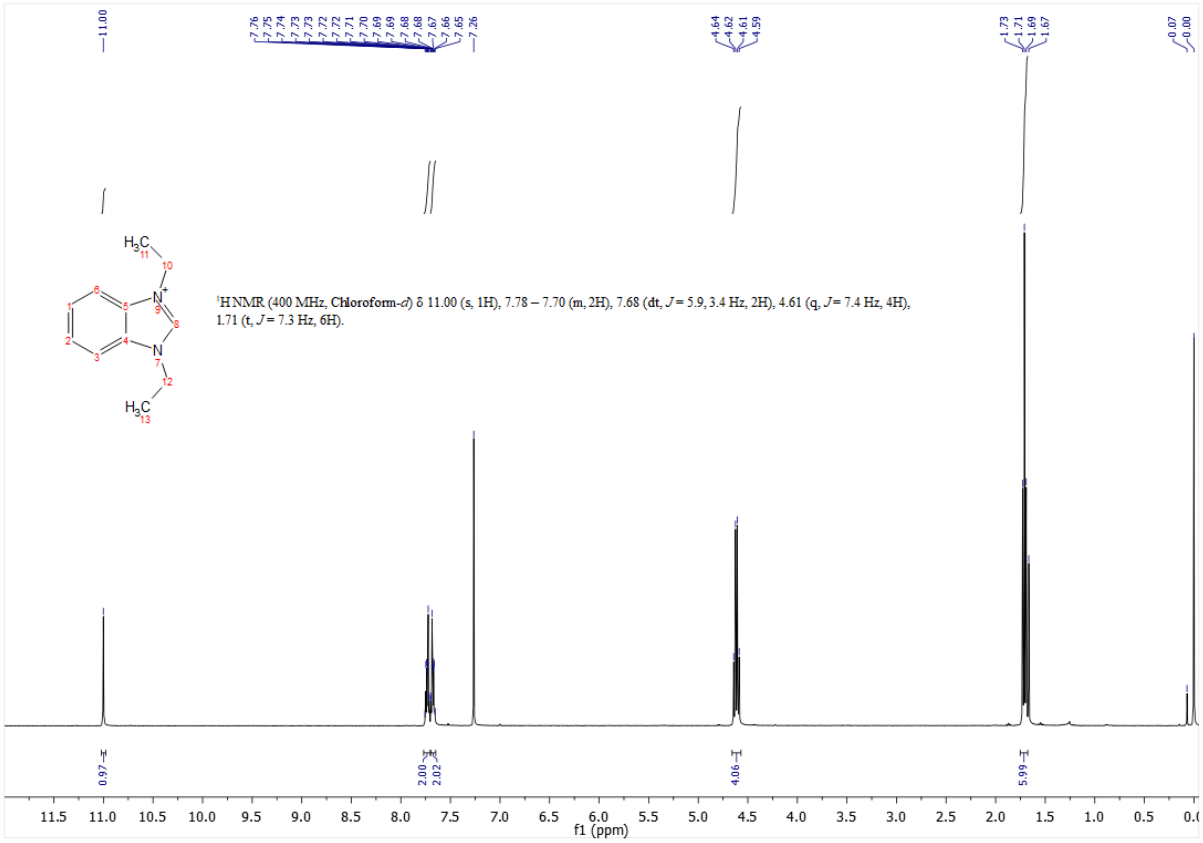


Figure S8. ^{1}H NMR spectrum (400 MHz) of **2** recorded in $CDCl_3$.

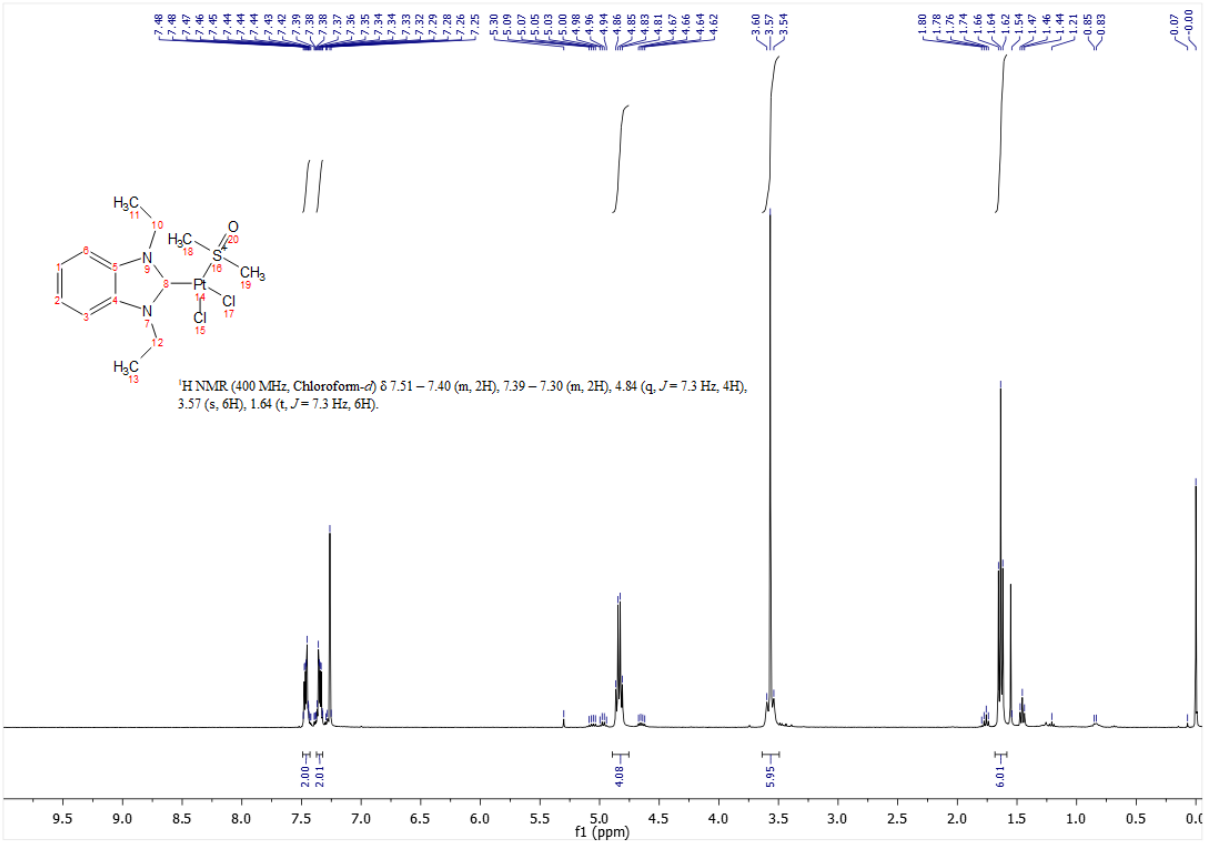


Figure S9. ^{1}H NMR spectrum (400 MHz) of **4** recorded in $CDCl_3$.

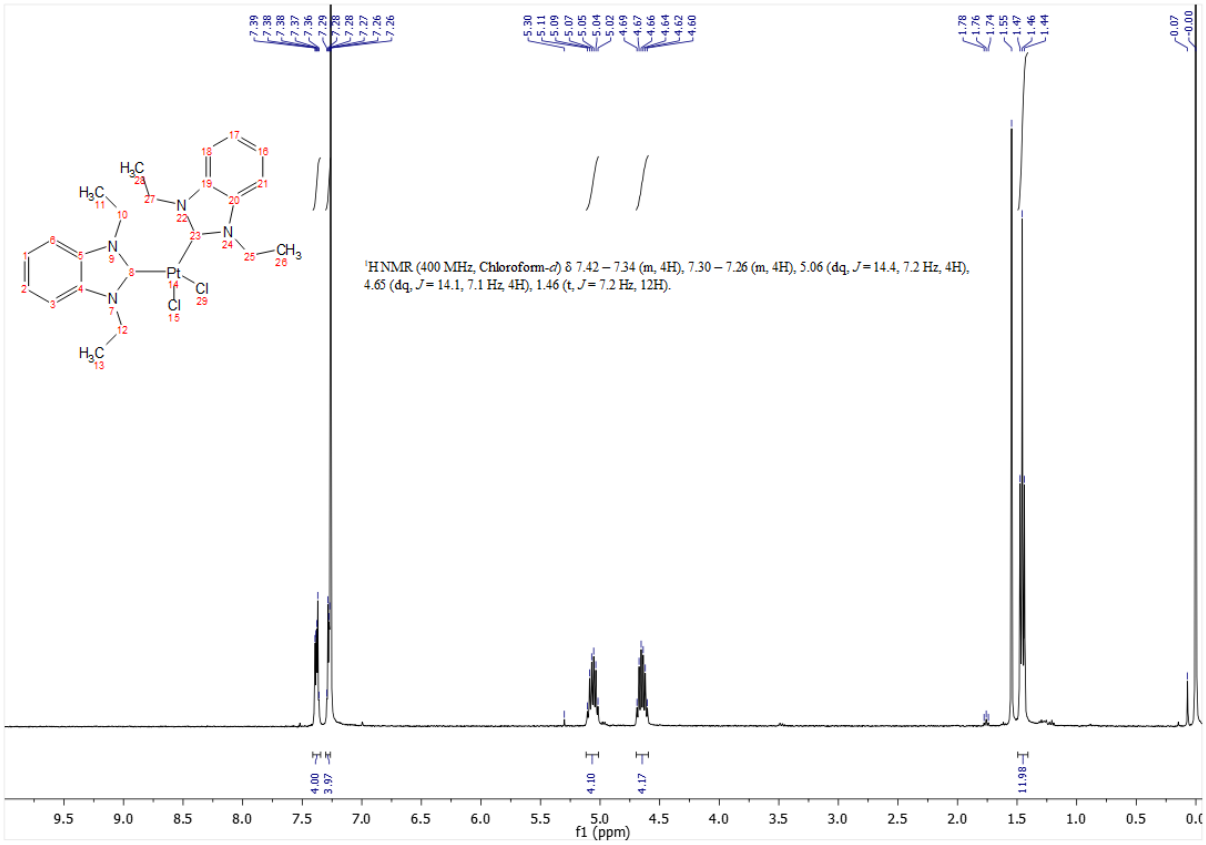


Figure S10. ^{1}H NMR spectrum (400 MHz) of **5** recorded in $CDCl_3$.

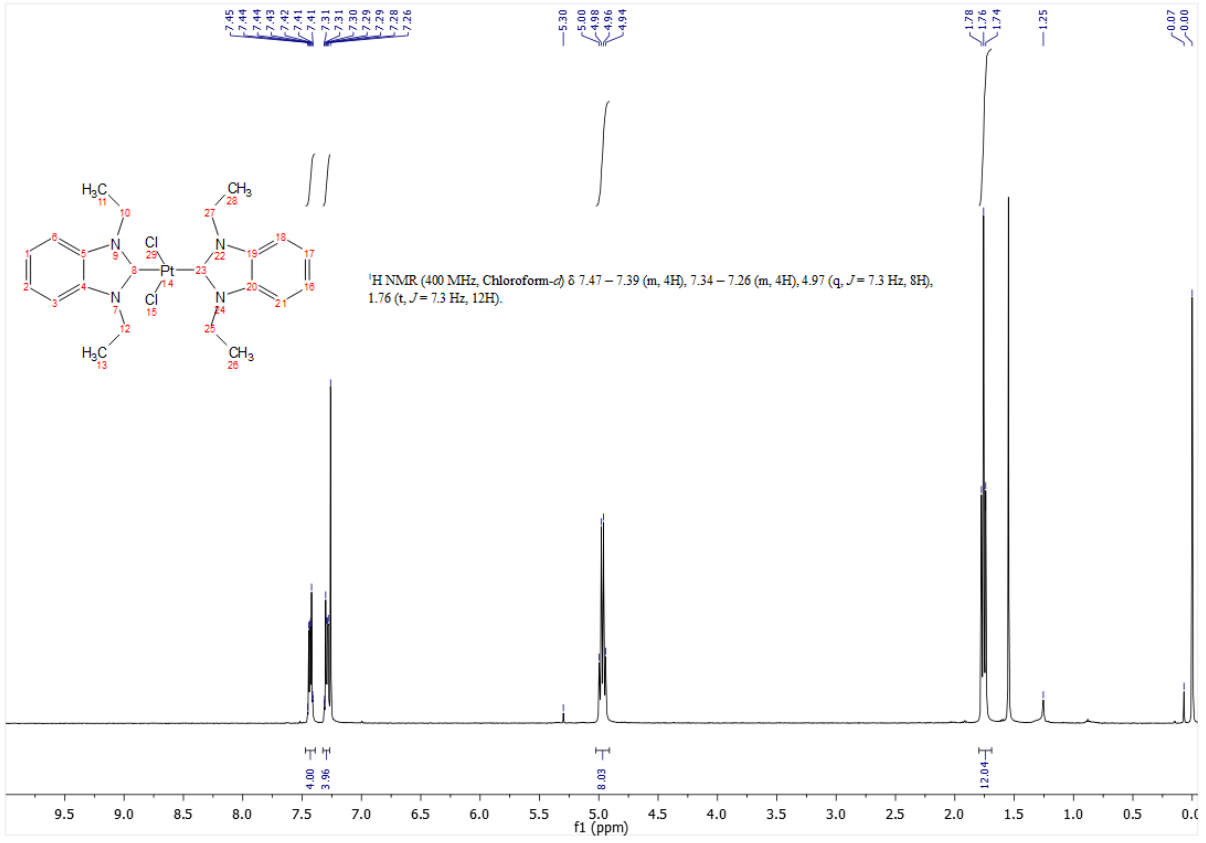


Figure S11. ^{1}H NMR spectrum (400 MHz) of **6** recorded in $CDCl_3$.

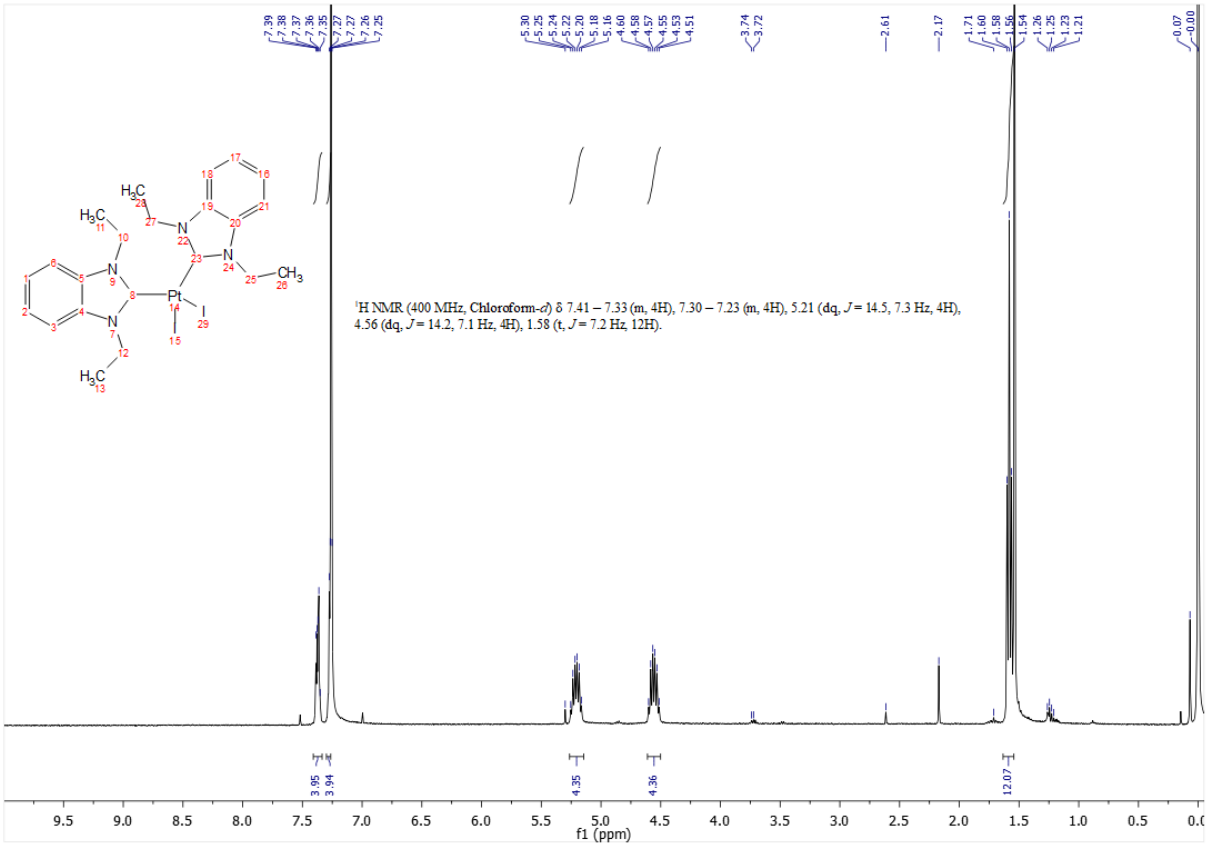


Figure S12. ^{1}H NMR spectrum (400 MHz) of **7** recorded in $CDCl_3$.

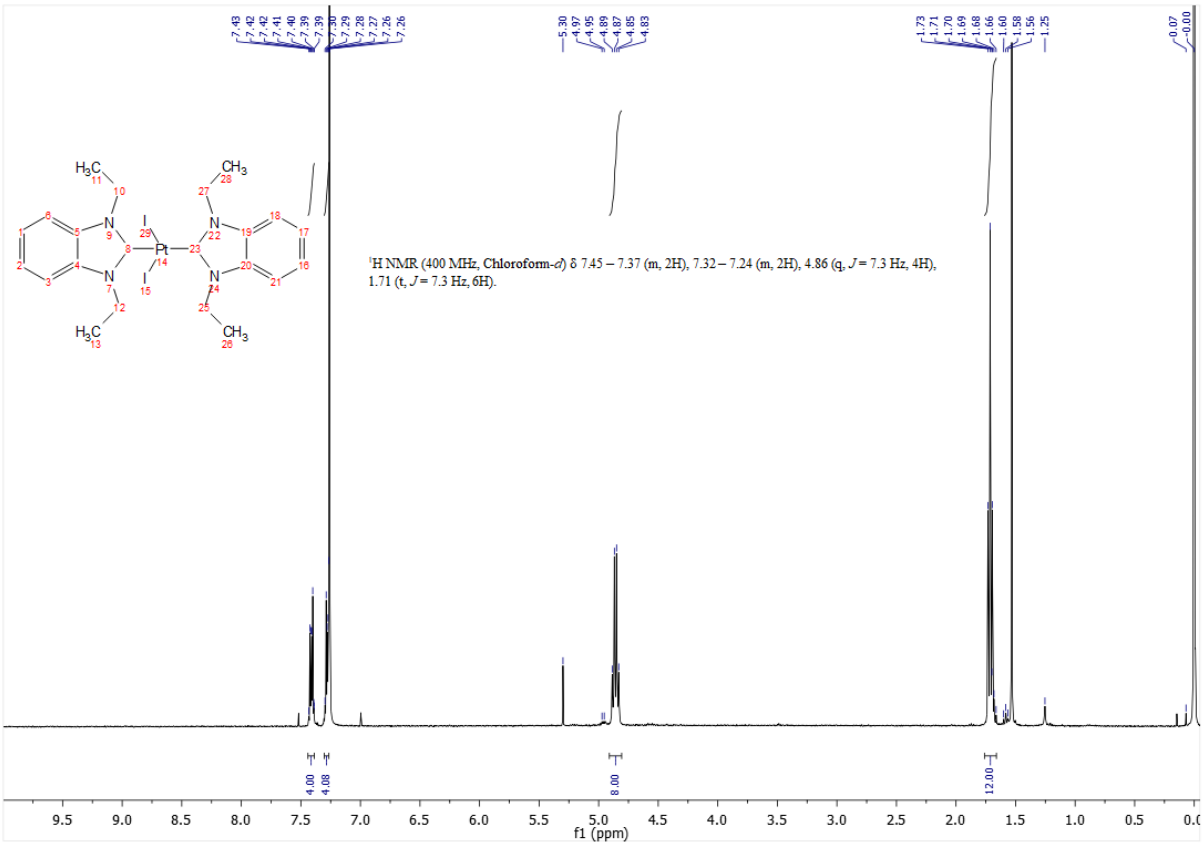


Figure S13. ^{1}H NMR spectrum (400 MHz) of **8** recorded in $CDCl_3$.

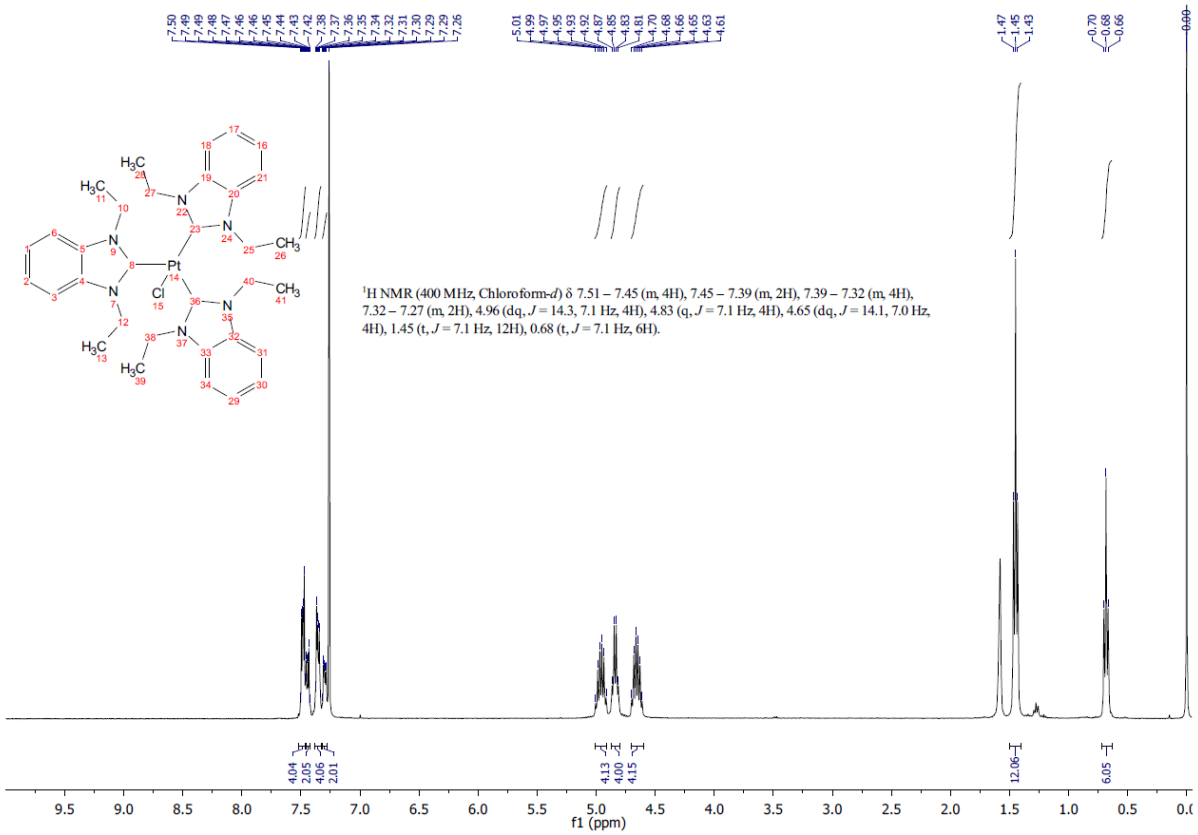


Figure S14. ^{1}H NMR spectrum (400 MHz) of **9** recorded in $CDCl_3$.

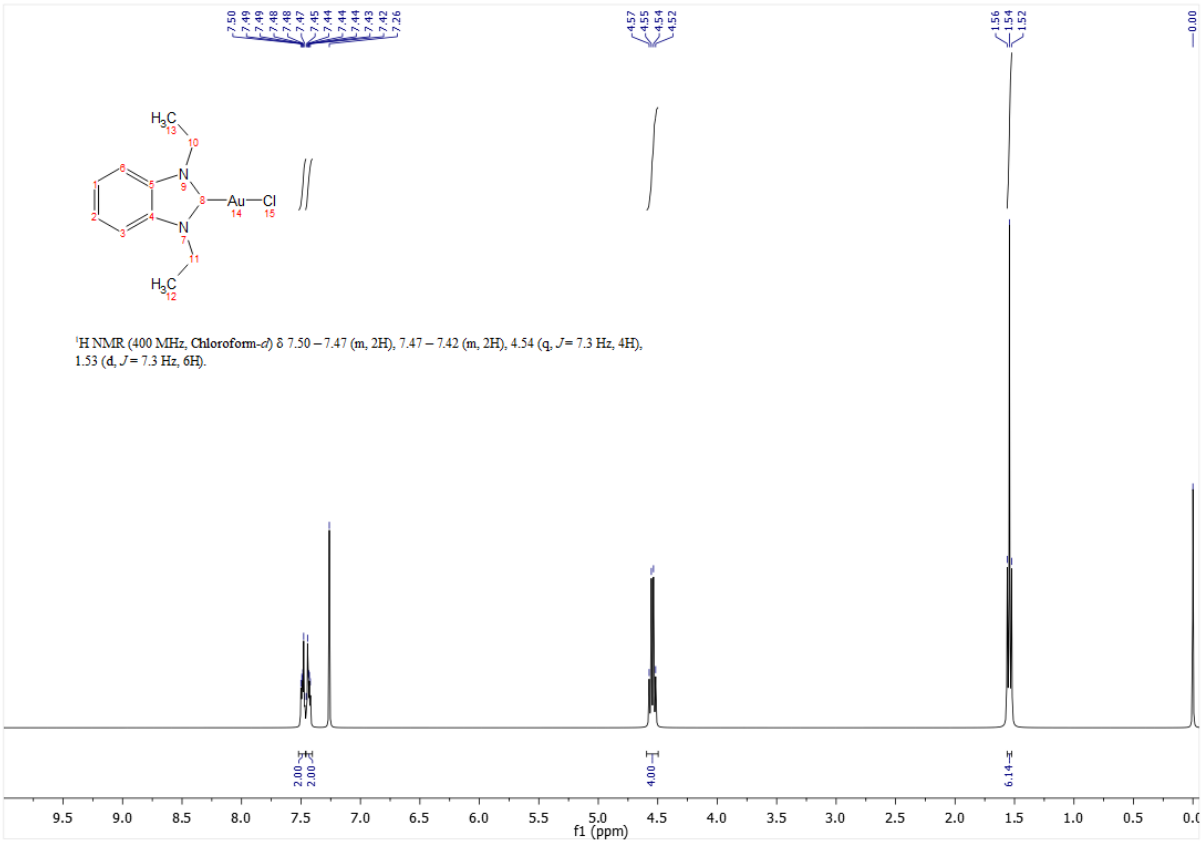


Figure S15. ^{1}H NMR spectrum (400 MHz) of **10** recorded in $CDCl_3$.

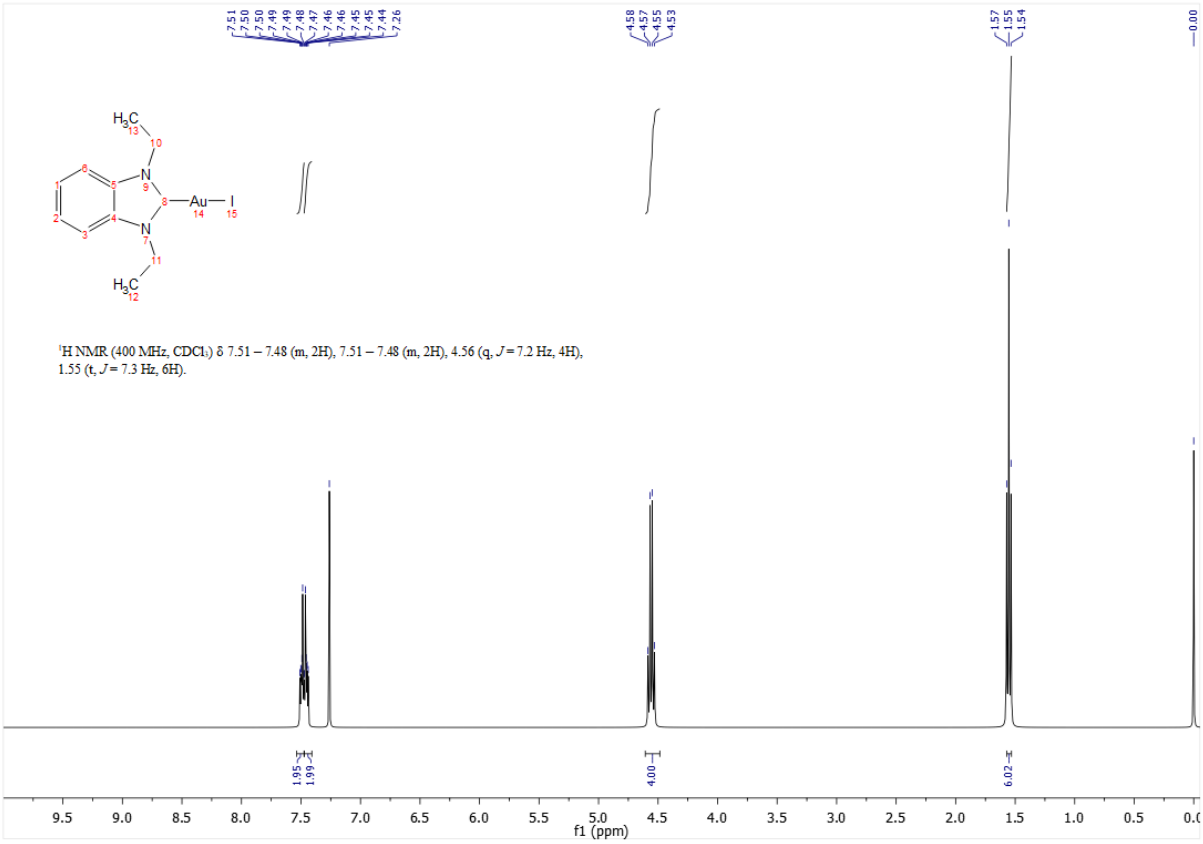


Figure S16. ^{1}H NMR spectrum (400 MHz) of **11** recorded in $CDCl_3$.

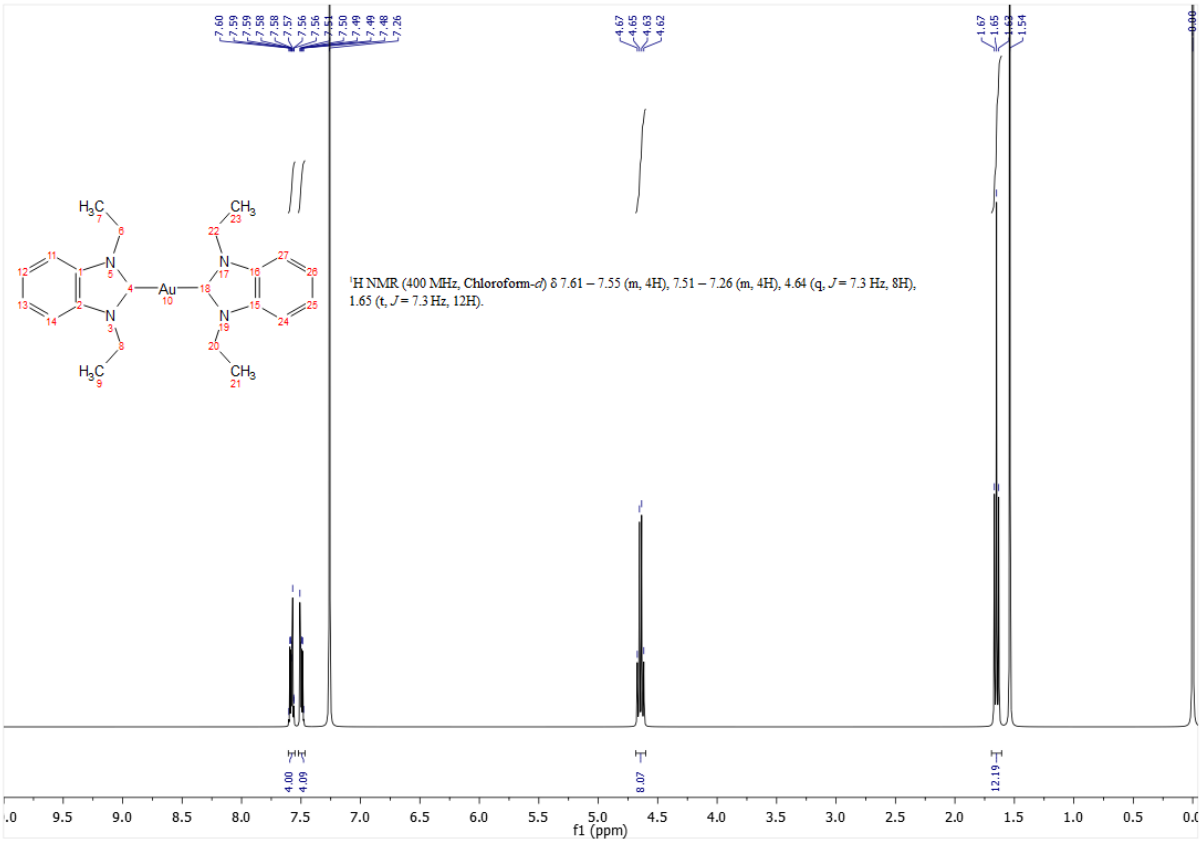


Figure S17. ^{1}H NMR spectrum (400 MHz) of **12** recorded in $CDCl_3$.

4. ^{13}C NMR Spectra of **2**, **4**-**6**, and **9**-**12**

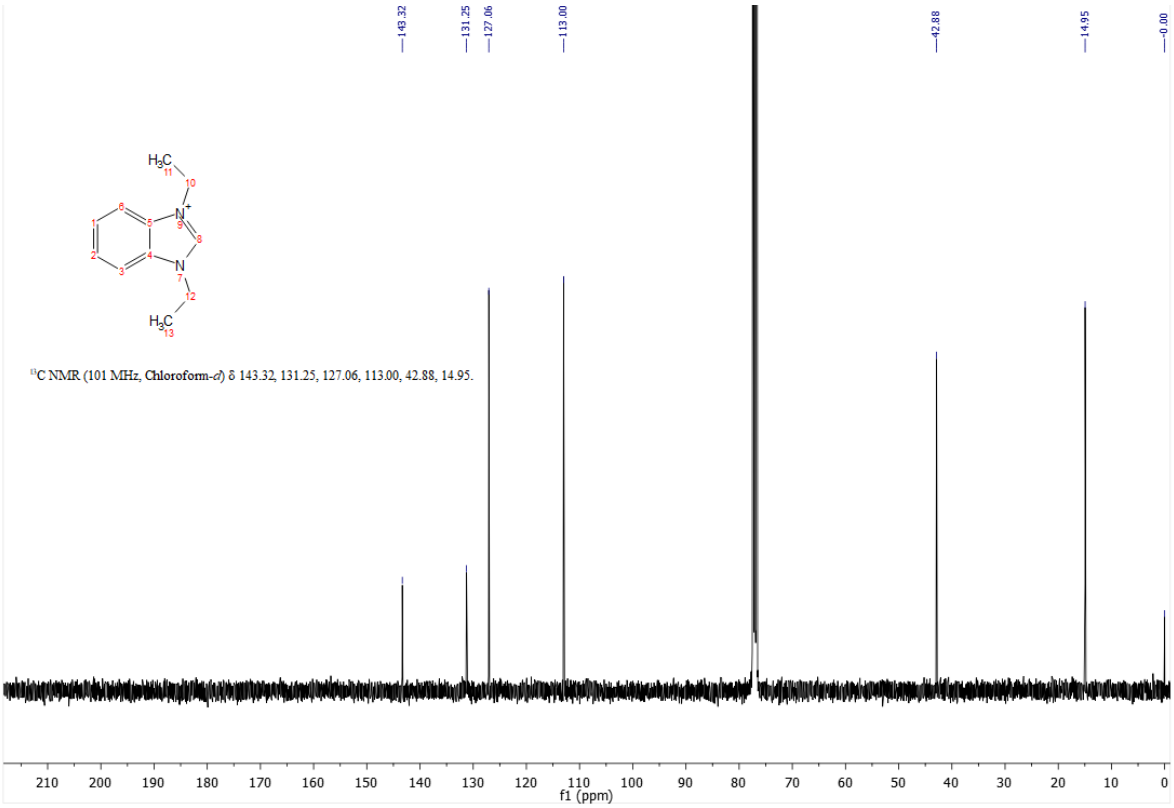


Figure S18. ^{13}C NMR spectrum (101 MHz) of **2** recorded in $CDCl_3$.

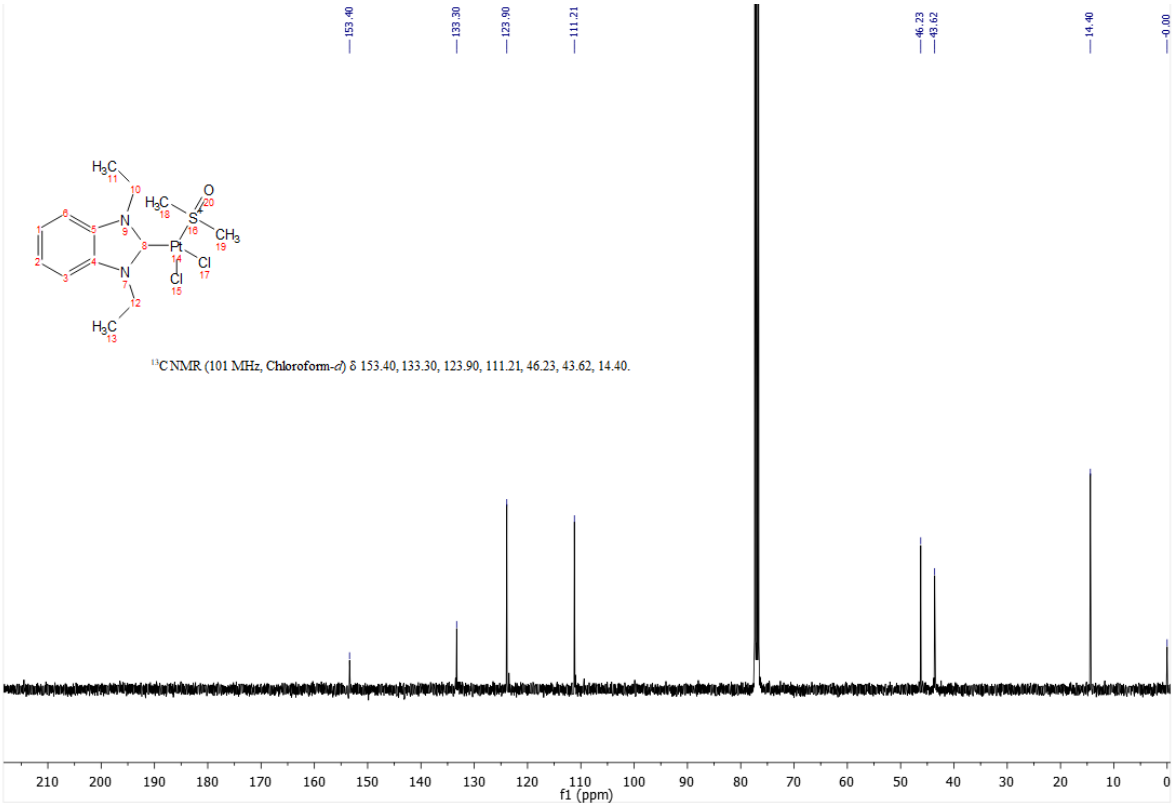


Figure S19. ^{13}C NMR spectrum (101 MHz) of **4** recorded in $CDCl_3$.

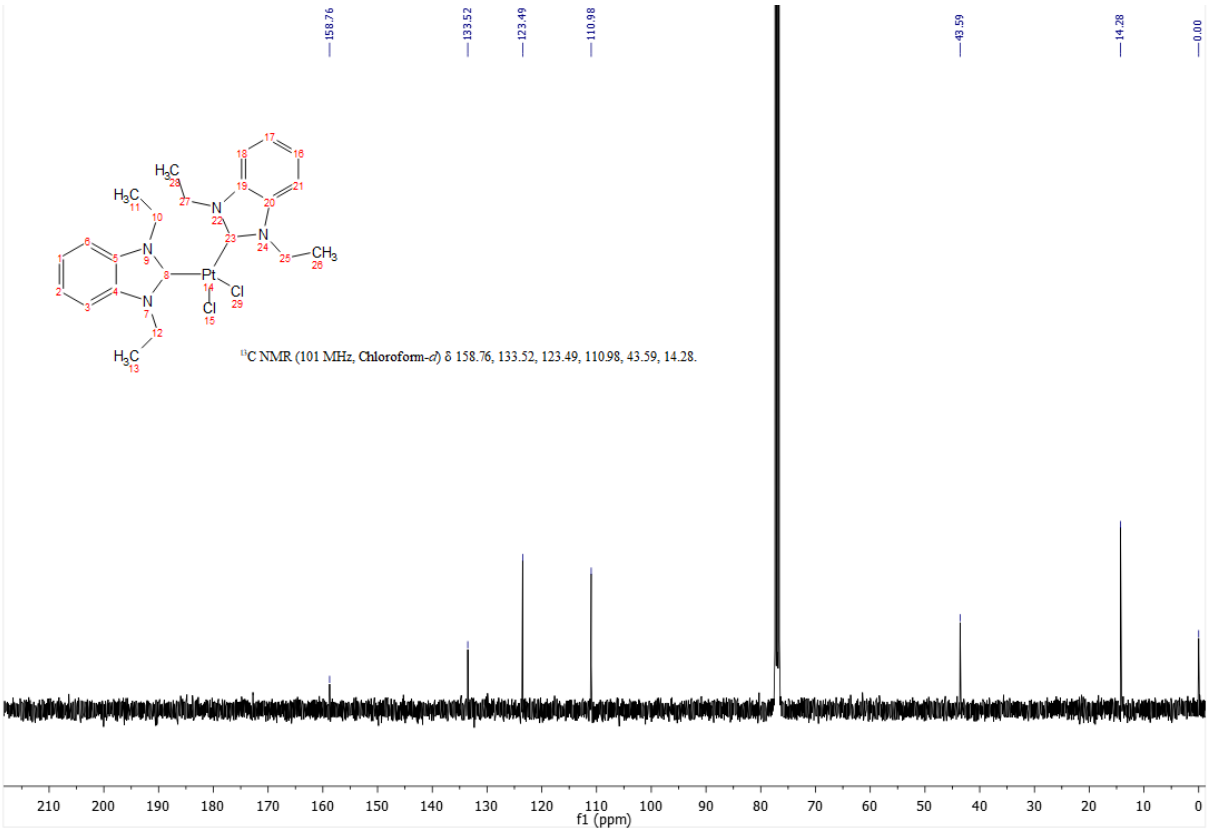


Figure S20. ^{13}C NMR spectrum (101 MHz) of **5** recorded in $CDCl_3$.

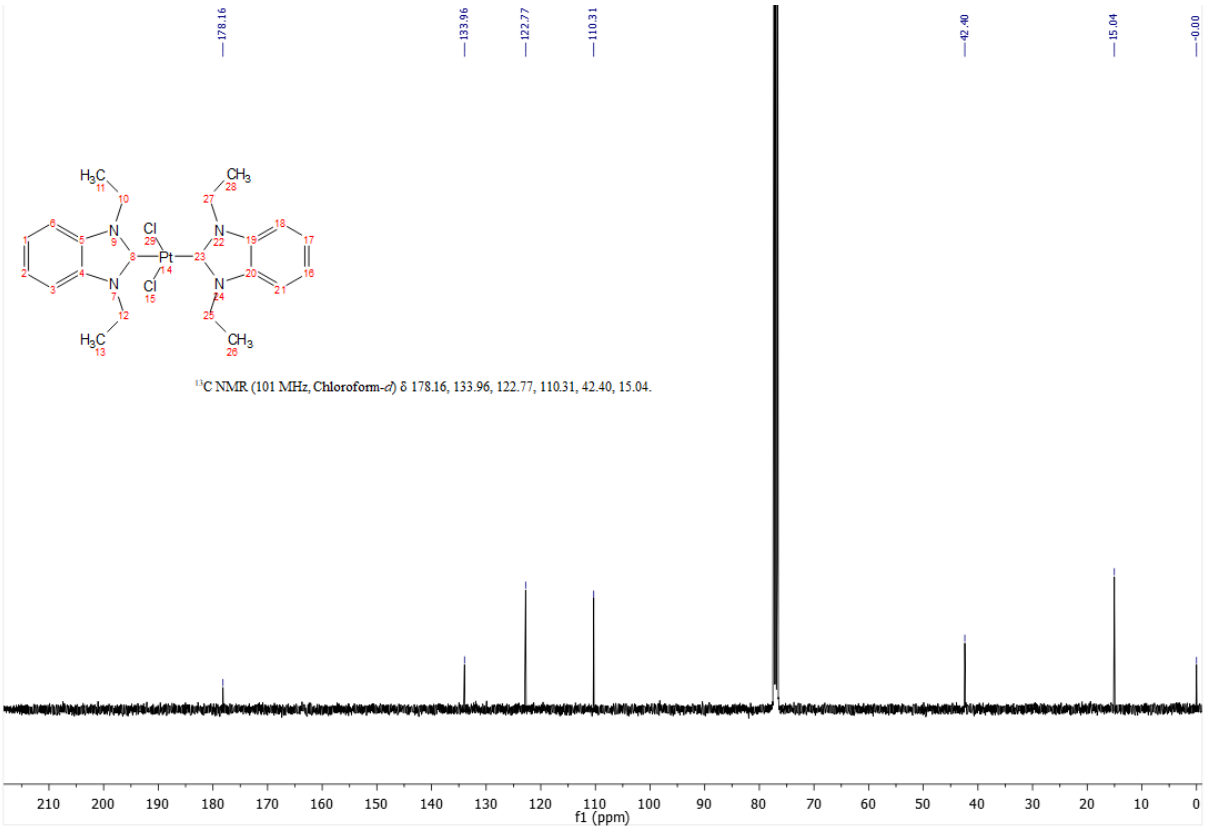


Figure S21. ^{13}C NMR spectrum (101 MHz) of **6** recorded in $CDCl_3$.

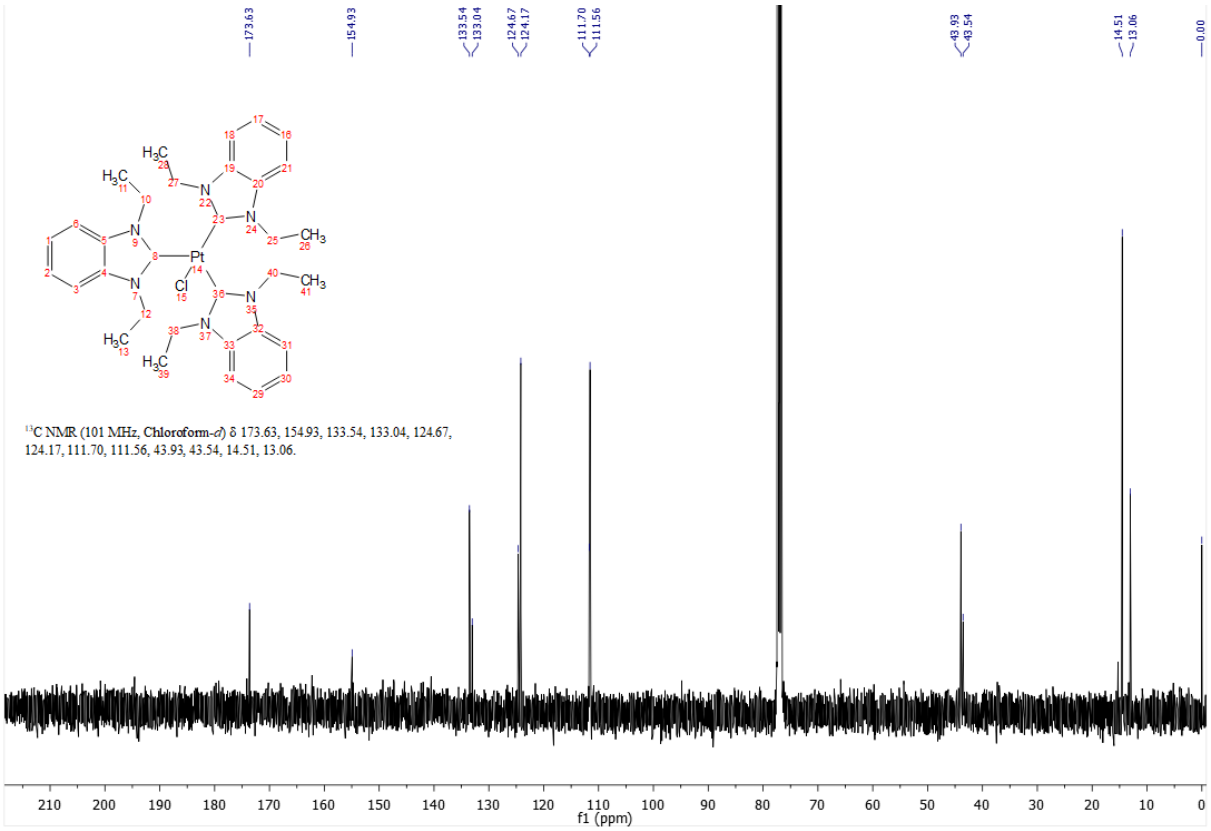


Figure S22. ^{13}C NMR spectrum (101 MHz) of **9** recorded in $CDCl_3$.

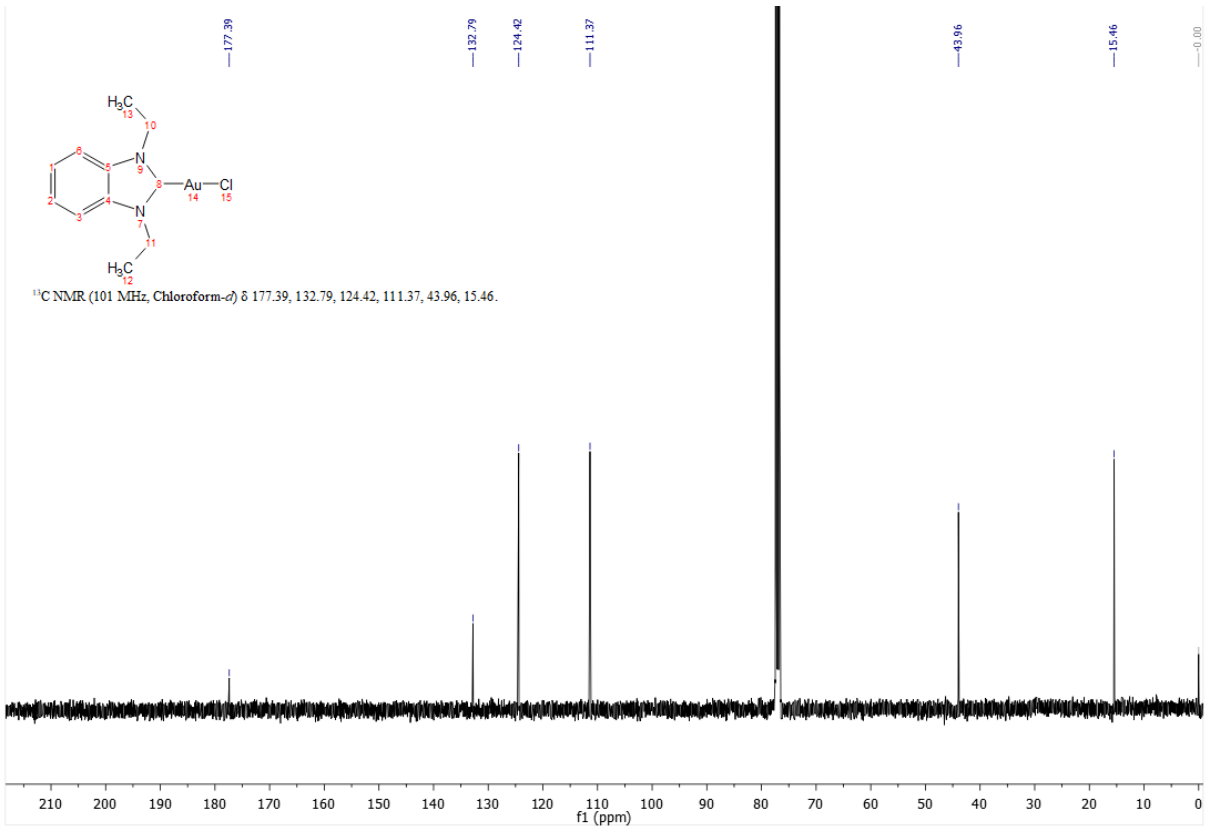


Figure S23. ^{13}C NMR spectrum (101 MHz) of **10** recorded in $CDCl_3$.

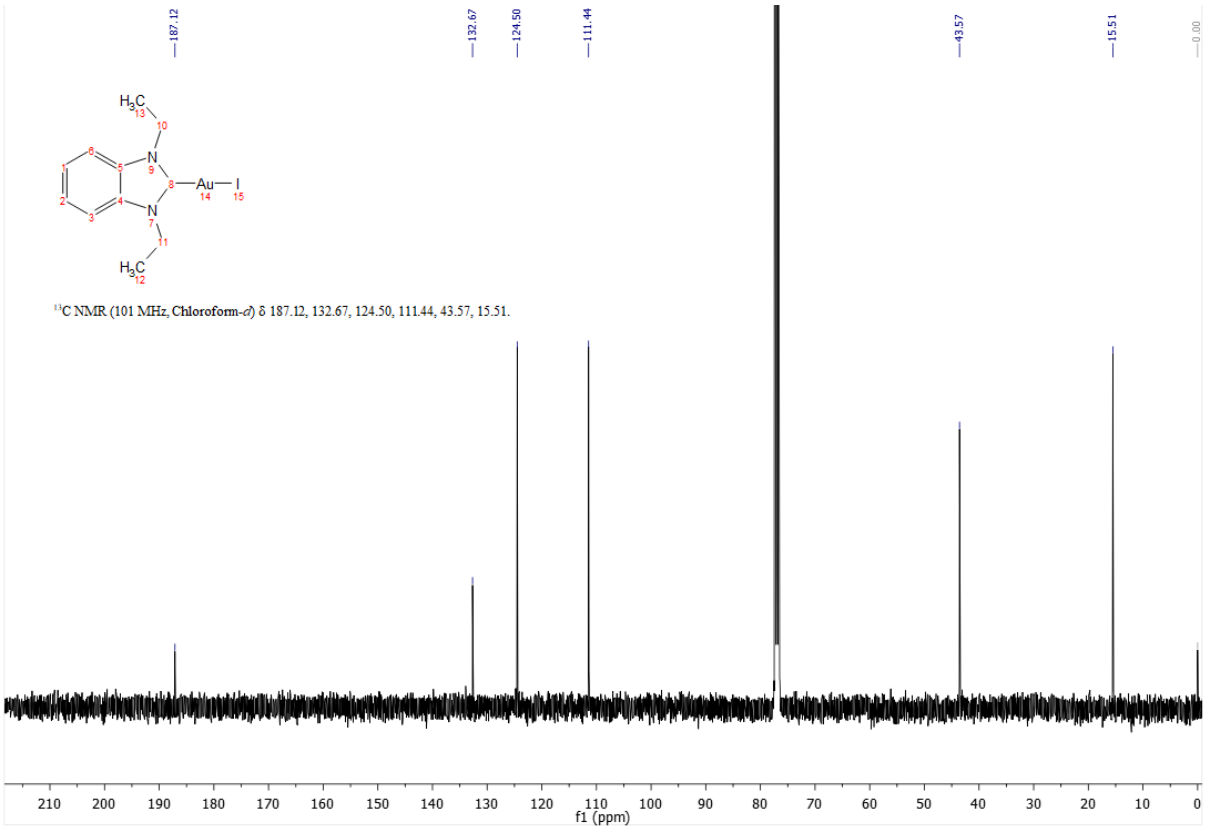


Figure S24. ^{13}C NMR spectrum (101 MHz) of **11** recorded in $CDCl_3$.

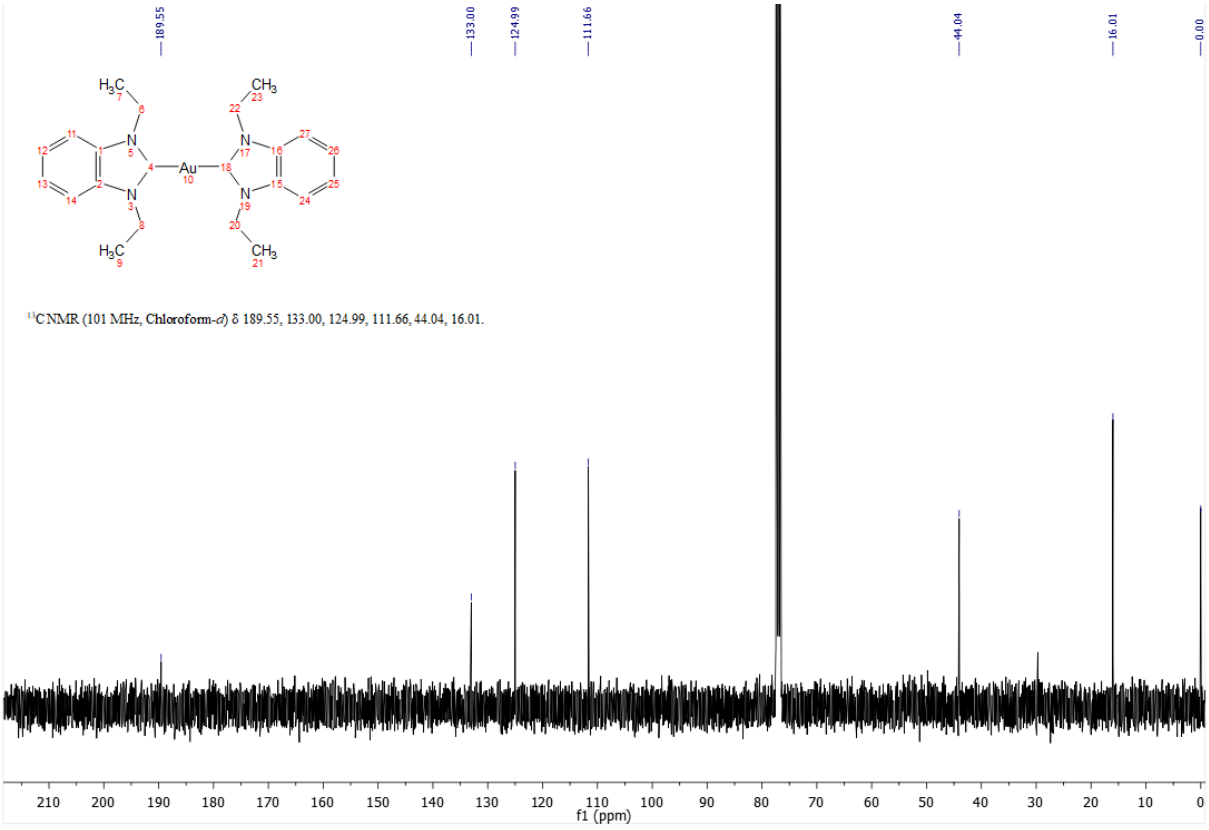


Figure S25. ^{13}C NMR spectrum (101 MHz) of **12** recorded in $CDCl_3$.

5. ^{195}Pt NMR Spectra of **5**, **6**, and **9**

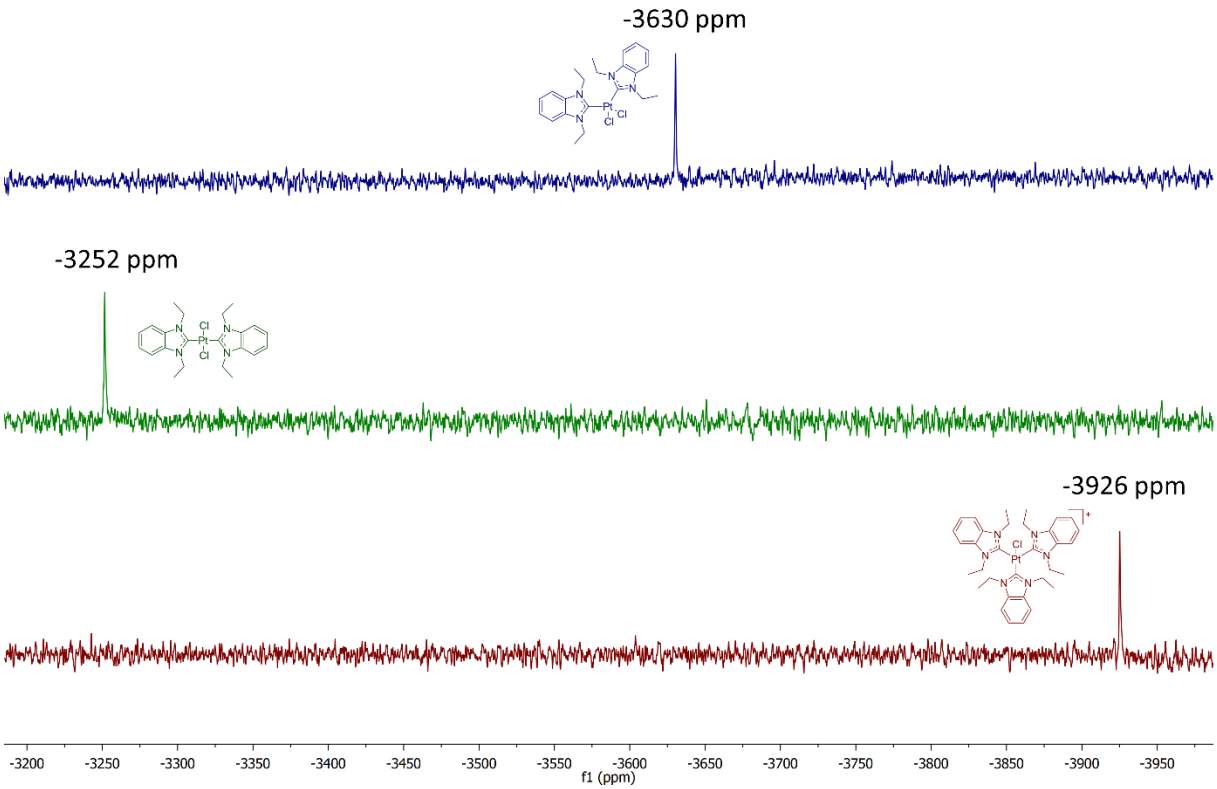


Figure S26. ^{195}Pt NMR spectra (86 MHz) of **5** (top), **6** (middle), and **9** (bottom) recorded in $CDCl_3$. The spectra were processed with a line broadening factor of 40 Hz.

6. ESI-HRMS spectrum of **9**

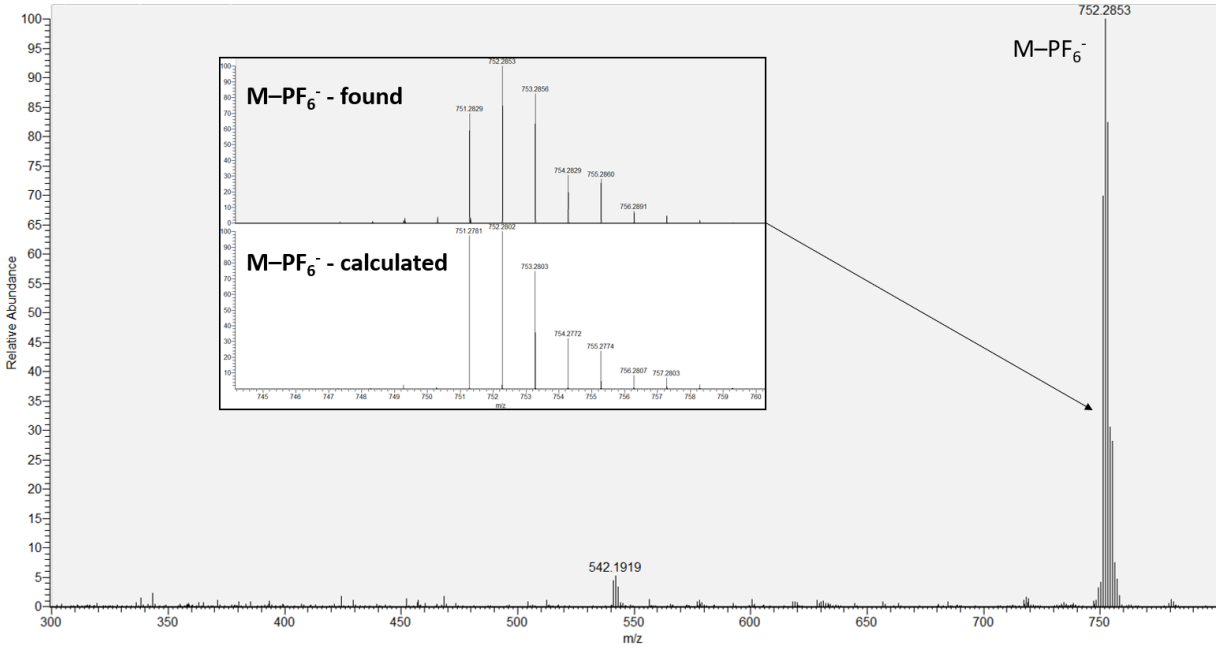


Figure S27. ESI-HRMS(+) spectrum of complex **9**.

7. X-ray Analysis of 1, 5, 6, 8, and 10

7.1. Crystal Structures

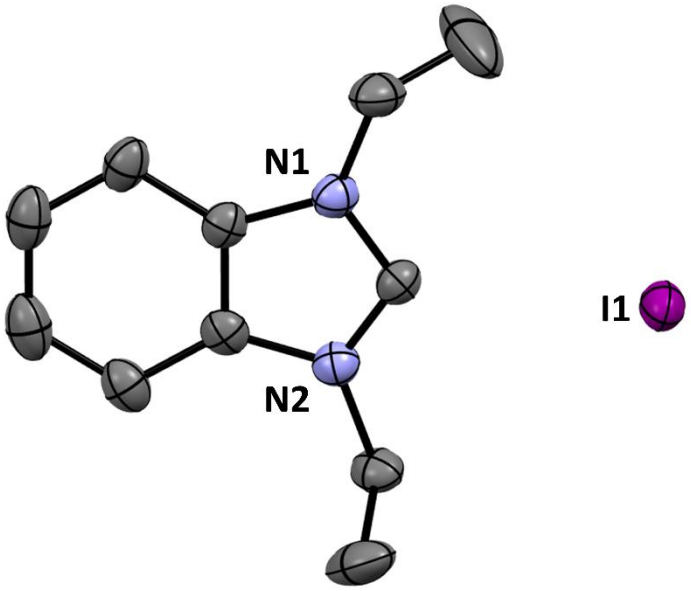


Figure S28. X-ray structure of the NHC ligand **1**. The thermal ellipsoids have been drawn at the 50% probability level.

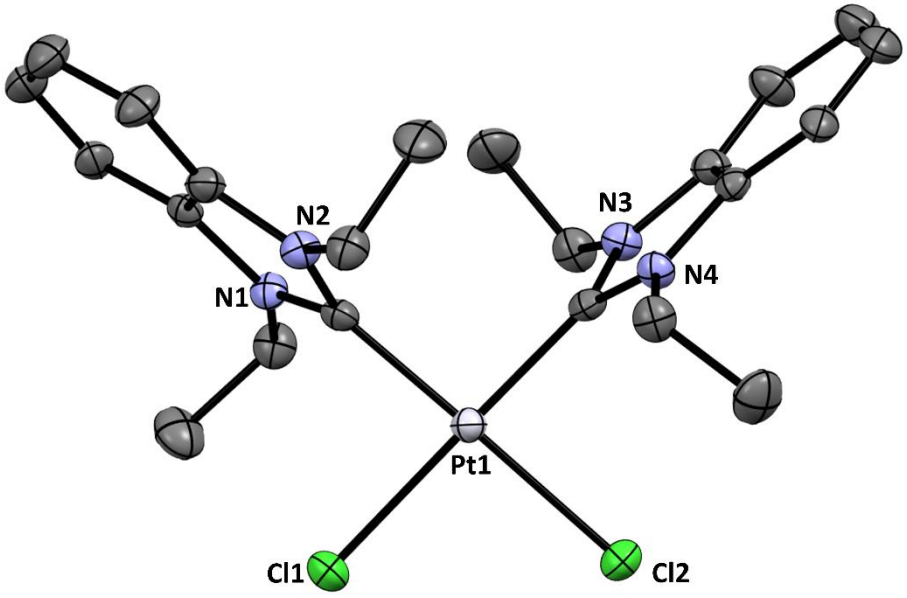


Figure S29. X-ray structure of *cis*-[PtL_2Cl_2] **5**. The thermal ellipsoids have been drawn at the 50% probability level.

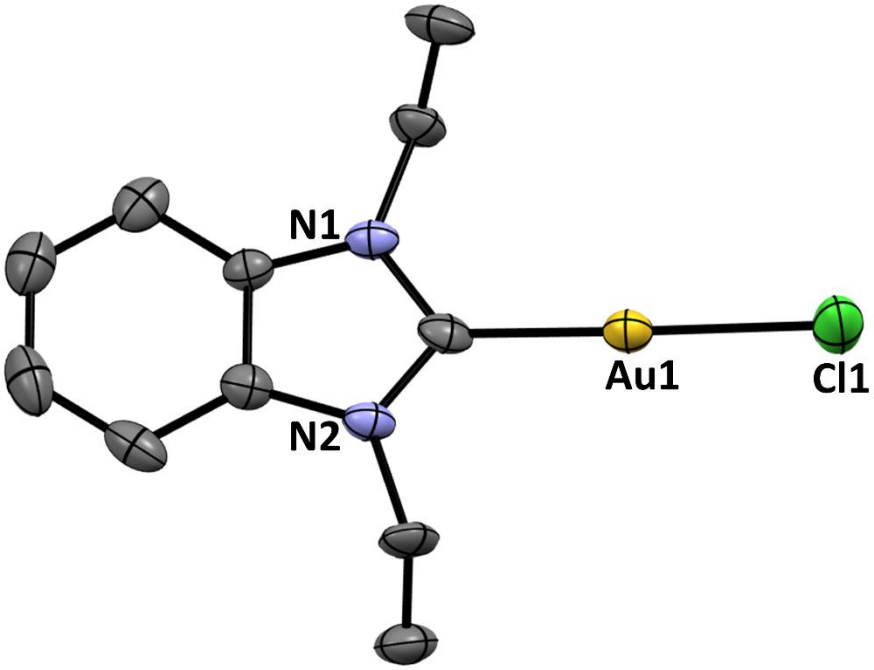


Figure S30. X-ray structure of [AuLCl] **10**. The thermal ellipsoids have been drawn at the 50% probability level.

7.2. Crystallographic Data

Table S1. Crystal data and structure refinement for **1**.

CCDC number	2267764	
Empirical formula	$C_{11}H_{15}IN_2$	
Formula weight	302.15	
Temperature	173.00 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (no. 14)	
Unit cell dimensions	a = 11.0644(4) Å	α = 90°
	b = 14.5146(5) Å	β = 90.3710(10)°
	c = 15.1226(5) Å	γ = 90°
Volume	2428.57(15) $Å^3$	
Z	8	
Density (calculated)	1.653 mg/m^3	
Absorption coefficient	2.604 mm^{-1}	
F(000)	1184	
Crystal size	0.16 x 0.08 x 0.04 mm^3	
Theta range for data collection	1.841 to 28.328°	
Index ranges	-14<=h<=14, -19<=k<=19, -20<=l<=20	
Reflections collected	58918	
Independent reflections	6048 [R(int) = 0.0366]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.7406	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6048 / 0 / 257	
Goodness-of-fit on F^2	1.180	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR_2 = 0.0877	
R indices (all data)	R1 = 0.0459, wR_2 = 0.0893	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.113 and -0.858 e.$Å^{-3}$	

Table S2. Crystal data and structure refinement for **5**.

CCDC number	2267765	
Empirical formula	$C_{22}H_{28}Cl_2N_4Pt$	
Formula weight	614.47	
Temperature	173.00 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fdd2 (no. 43)	
Unit cell dimensions	a = 12.7666(4) Å	α = 90°
	b = 29.7845(9) Å	β = 90°
	c = 11.9548(4) Å	γ = 90°
Volume	4545.8(2) $Å^3$	
Z	8	
Density (calculated)	1.796 mg/m^3	
Absorption coefficient	6.424 mm^{-1}	
F(000)	2400	
Crystal size	0.12 x 0.06 x 0.03 mm^3	
Theta range for data collection	2.432 to 27.897°	
Index ranges	-16<=h<=16, -39<=k<=39, -15<=l<=15	
Reflections collected	24151	
Independent reflections	2712 [R(int) = 0.0629]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8014 and 0.5966	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2712 / 1 / 134	
Goodness-of-fit on F^2	0.932	
Final R indices [I>2sigma(I)]	R1 = 0.0160, wR_2 = 0.0312	
R indices (all data)	R1 = 0.0192, wR_2 = 0.0316	
Absolute structure parameter	0.008(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.570 and -0.506 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **6**.

CCDC number	2267766	
Empirical formula	$C_{22}H_{28}Cl_2N_4Pt$	
Formula weight	614.47	
Temperature	173.00 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1(no. 2)	
Unit cell dimensions	a = 8.1511(4) Å	α = 106.5240(10)°
	b = 8.8139(4) Å	β = 92.733(2)°
	c = 8.9475(4) Å	γ = 113.6690(10)°
Volume	554.75(4) $Å^3$	
Z	1	
Density (calculated)	1.839 mg/m^3	
Absorption coefficient	6.580 mm^{-1}	
F(000)	300	
Crystal size	0.21 x 0.17 x 0.12 mm^3	
Theta range for data collection	2.416 to 28.368°	
Index ranges	-10<=h<=10, -11<=k<=11, -11<=l<=11	
Reflections collected	20548	
Independent reflections	2748 [R(int) = 0.0629]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6944 and 0.4617	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2748 / 0 / 136	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0177, wR_2 = 0.0381	
R indices (all data)	R1 = 0.0177, wR_2 = 0.0381	
Extinction coefficient	0.0128(12)	
Largest diff. peak and hole	1.249 and -0.986 e.$Å^{-3}$	

Table S4. Crystal data and structure refinement for **8**.

CCDC number	2267767	
Empirical formula	$C_{22}H_{28}I_2N_4Pt$	
Formula weight	797.37	
Temperature	295.15 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca (no. 61)	
Unit cell dimensions	a = 12.5666(5) Å	α = 90°
	b = 9.2622(4) Å	β = 90°
	c = 21.4634(9) Å	γ = 90°
Volume	2498.22(18) $Å^3$	
Z	4	
Density (calculated)	2.120 mg/m^3	
Absorption coefficient	8.103 mm^{-1}	
F(000)	1488	
Crystal size	0.29 x 0.18 x 0.14 mm^3	
Theta range for data collection	2.496 to 28.751°	
Index ranges	-16<=h<=16, -12<=k<=12, -29<=l<=29	
Reflections collected	71184	
Independent reflections	3228 [R(int) = 0.0651]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7247 and 0.2446	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3228 / 0 / 136	
Goodness-of-fit on F^2	1.145	
Final R indices [I>2sigma(I)]	R1 = 0.0222, wR_2 = 0.0531	
R indices (all data)	R1 = 0.0247, wR_2 = 0.0548	
Extinction coefficient	0.00177(13)	
Largest diff. peak and hole	1.109 and -0.881 e.$Å^{-3}$	

Table S5. Crystal data and structure refinement for **9**.

CCDC number	2267768	
Empirical formula	$C_{33}H_{42}ClF_6N_6PPt$ x 0.25 CH_3OH	
Formula weight	905.74	
Temperature	153.00 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c (no. 14)	
Unit cell dimensions	a = 14.0281(7) Å	α = 90°
	b = 12.7311(6) Å	β = 94.5881(17)°
	c = 41.196(2) Å	γ = 90°
Volume	7333.7(6) $Å^3$	
Z	8	
Density (calculated)	1.641 mg/m^3	
Absorption coefficient	4.007 mm^{-1}	
F(000)	3600	
Crystal size	0.14 x 0.05 x 0.03 mm^3	
Theta range for data collection	1.882 to 25.497°	
Index ranges	-16<=h<=16, -15<=k<=15, -49<=l<=49	
Reflections collected	140487	
Independent reflections	13612 [R(int) = 0.0459]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8748 and 0.6484	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13612 / 0 / 910	
Goodness-of-fit on F^2	1.259	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR_2 = 0.0838	
R indices (all data)	R1 = 0.0430, wR_2 = 0.0847	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.316 and -2.142 e.$Å^{-3}$	

Table S6. Crystal data and structure refinement for **10**.

CCDC number	2267769	
Empirical formula	$C_{11}H_{14}AuClN_2$	
Formula weight	406.66	
Temperature	173.00 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1 (no. 2)	
Unit cell dimensions	a = 7.3500(3) Å	α = 114.7106(14)°
	b = 9.3720(4) Å	β = 96.1579(15)°
	c = 9.7743(5) Å	γ = 90.3251(15)°
Volume	607.16(5) $Å^3$	
Z	2	
Density (calculated)	2.224 mg/m^3	
Absorption coefficient	12.304 mm^{-1}	
F(000)	380	
Crystal size	0.14 x 0.04 x 0.03 mm^3	
Theta range for data collection	2.311 to 25.749°	
Index ranges	-8<=h<=8, -11<=k<=10, 0<=l<=11	
Reflections collected	2314	
Independent reflections	2314 [R(int) = ?]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5620 and 0.3012	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2314 / 0 / 139	
Goodness-of-fit on F^2	1.148	
Final R indices [I>2sigma(I)]	R1 = 0.0230, wR_2 = 0.0546	
R indices (all data)	R1 = 0.0254, wR_2 = 0.0568	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.378 and -0.677 $e.Å^{-3}$	

Table S7. Crystal data and structure refinement for **12**.

CCDC number*	2267770	
Empirical formula	$C_{22}H_{28}AuF_6N_4P$	
Formula weight	690.42	
Temperature	173.00 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$ (no. 33)	
Unit cell dimensions	a = 11.4102(6) Å	α = 90°
	b = 21.7489(11) Å	β = 90°
	c = 10.1452(4) Å	γ = 90°
Volume	2517.6(2) $Å^3$	
Z	4	
Density (calculated)	1.822 mg/m^3	
Absorption coefficient	5.969 mm^{-1}	
F(000)	1344	
Crystal size	0.22 x 0.2 x 0.18 mm^3	
Theta range for data collection	2.215 to 28.311°	
Index ranges	-15<=h<=15, -28<=k<=29, -13<=l<=13	
Reflections collected	64943	
Independent reflections	6163 [R(int) = 0.0488]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4920 and 0.2064	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6163 / 1 / 348	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0206, wR_2 = 0.0418	
R indices (all data)	R1 = 0.0219, wR_2 = 0.0423	
Absolute structure parameter	0.043(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.333 and -1.937 e.$Å^{-3}$	

*X-ray crystal structure has been already published (*Organometallics* **2005**, *24*, 486-493.) and it is also available at CCDC (264468).

8. Additional HPLC Chromatograms

8.1. Stability in Organic Solvents

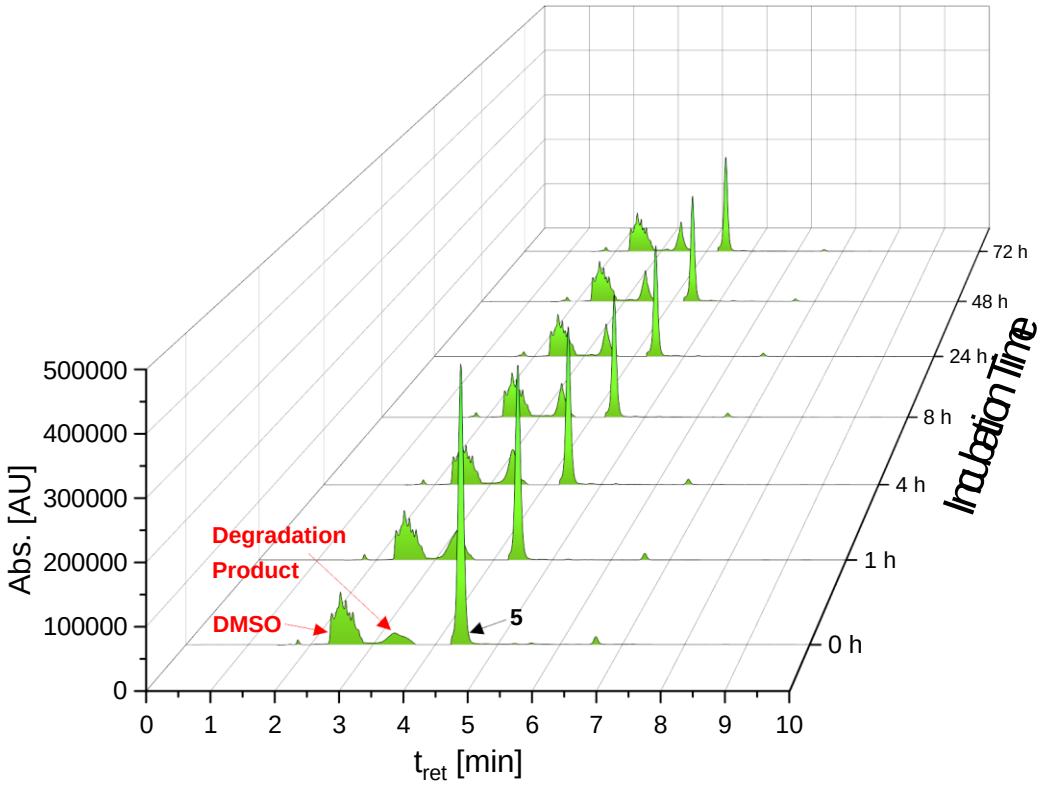


Figure S31. HPLC chromatograms of **5** incubated in DMSO up to 72 h. Complex concentration: 0.5 mM.

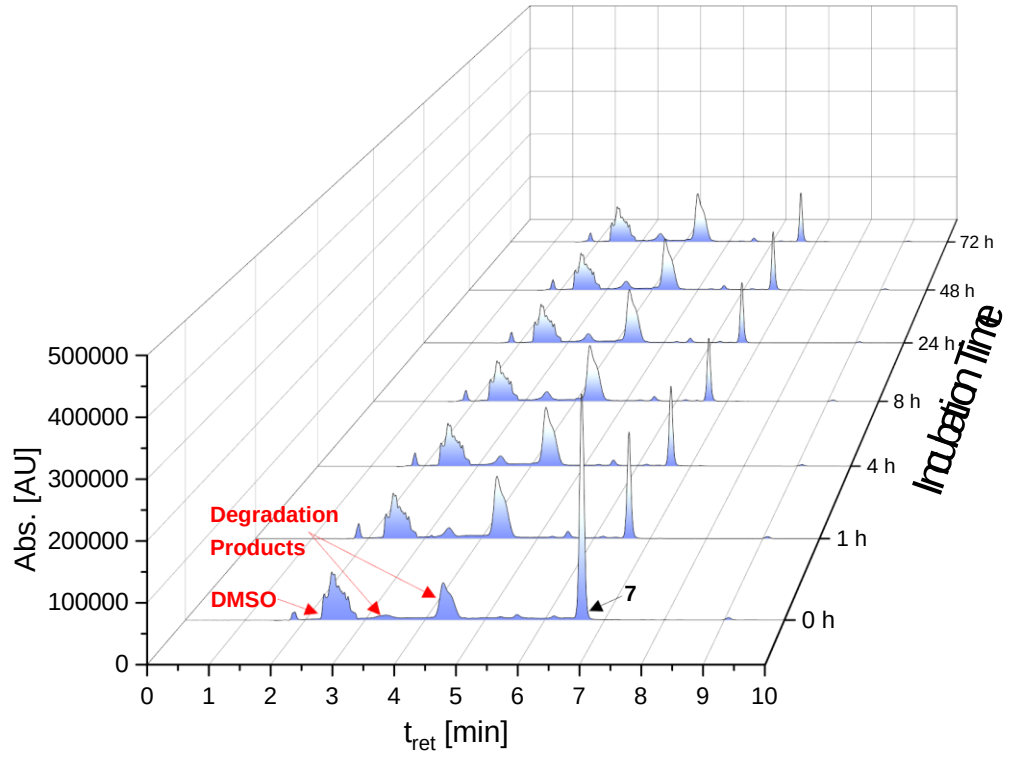


Figure S32. HPLC chromatograms of **7** incubated in DMSO up to 72 h. Complex concentration: 0.5 mM.

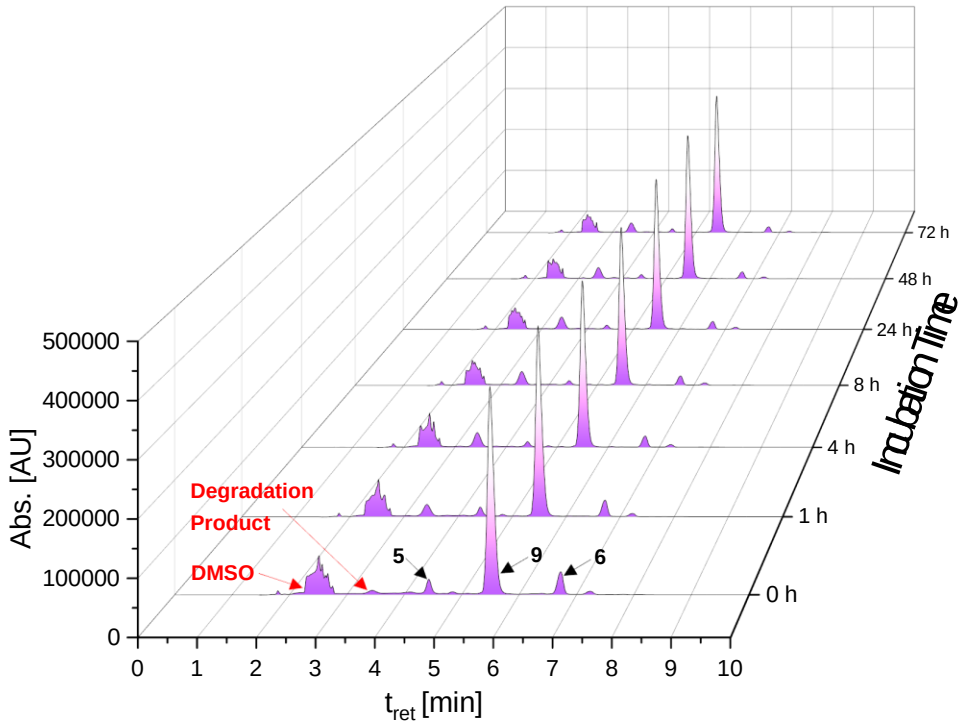


Figure S33. HPLC chromatograms of **9** incubated in DMSO up to 72 h. Complex concentration: 0.5 mM. Peaks **5** and **6** in the chromatograms of **9** come from synthesis (side products).

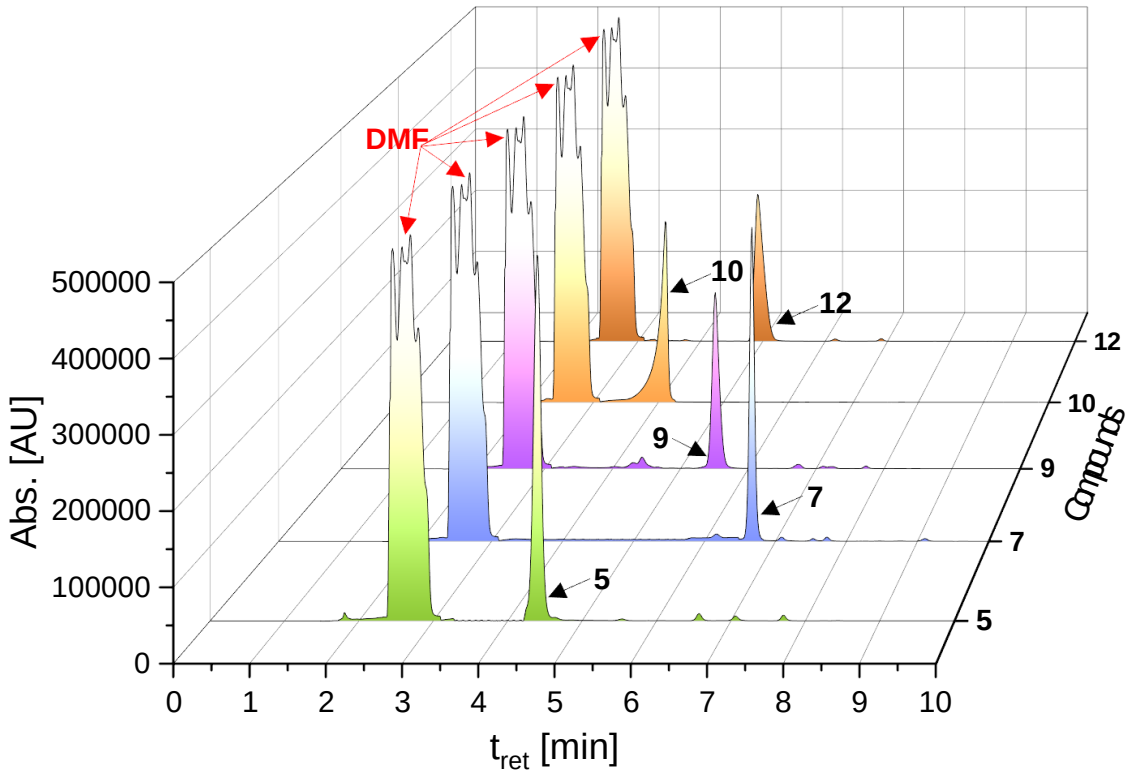


Figure S34. HPLC chromatograms of complexes **5**, **7**, **9**, **10**, and **12** in DMF at t = 72 h. Complex concentration: 0.5 mM.

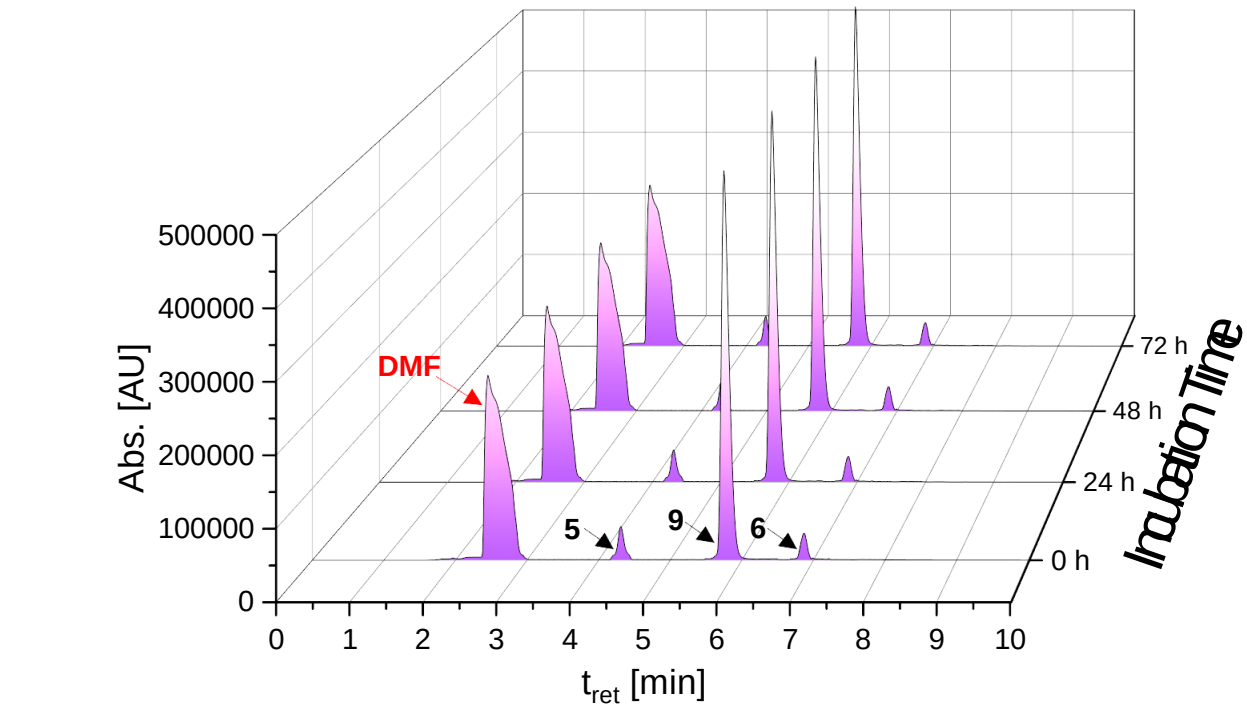


Figure S35. HPLC chromatograms of **9** incubated in DMF/water = 50:50 (v/v) up to 72 h. Complex concentration: 0.5 mM. Peaks **5** and **6** in the chromatograms of **9** come from synthesis (side products).

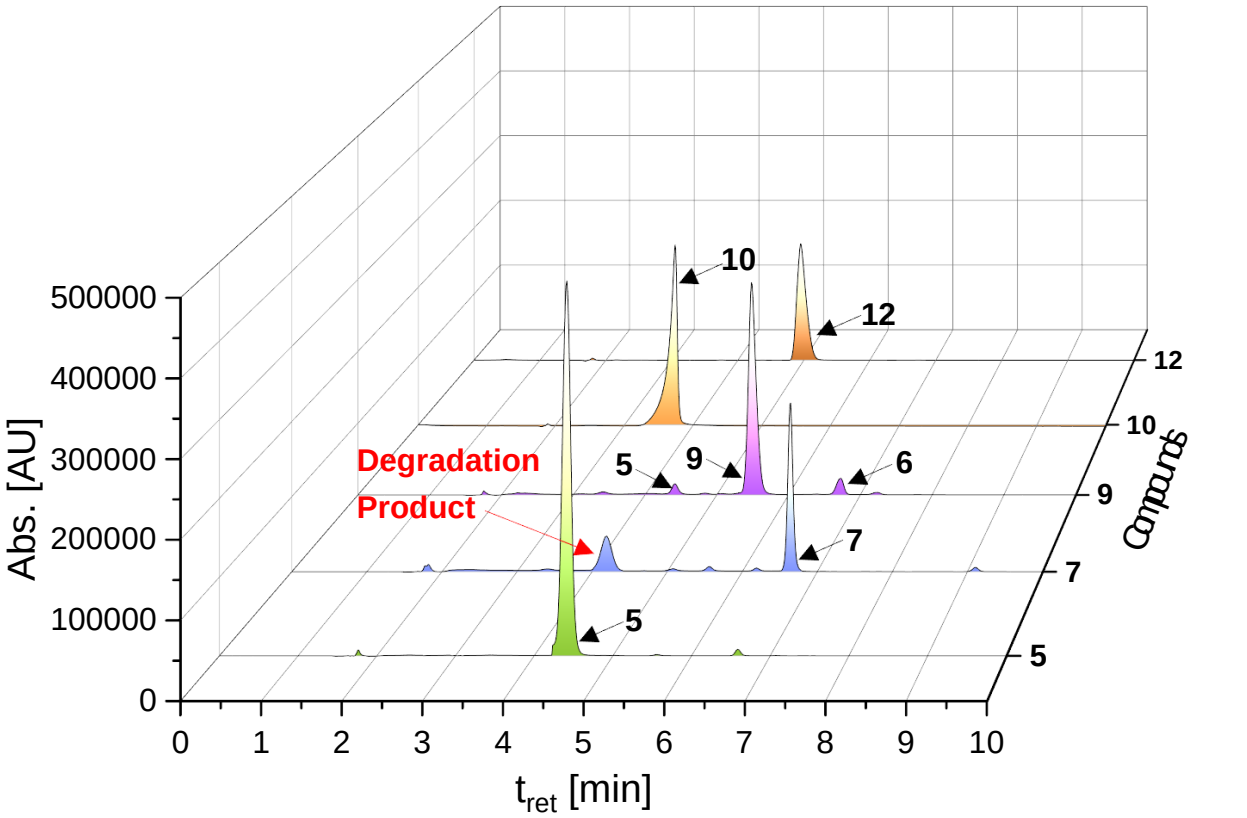


Figure S36. HPLC chromatograms of complexes **5**, **7**, **9**, **10**, and **12** in ACN at t = 72 h. Complex concentration: 0.5 mM. Peaks **5** and **6** in the chromatogram of **9** come from synthesis (side products).

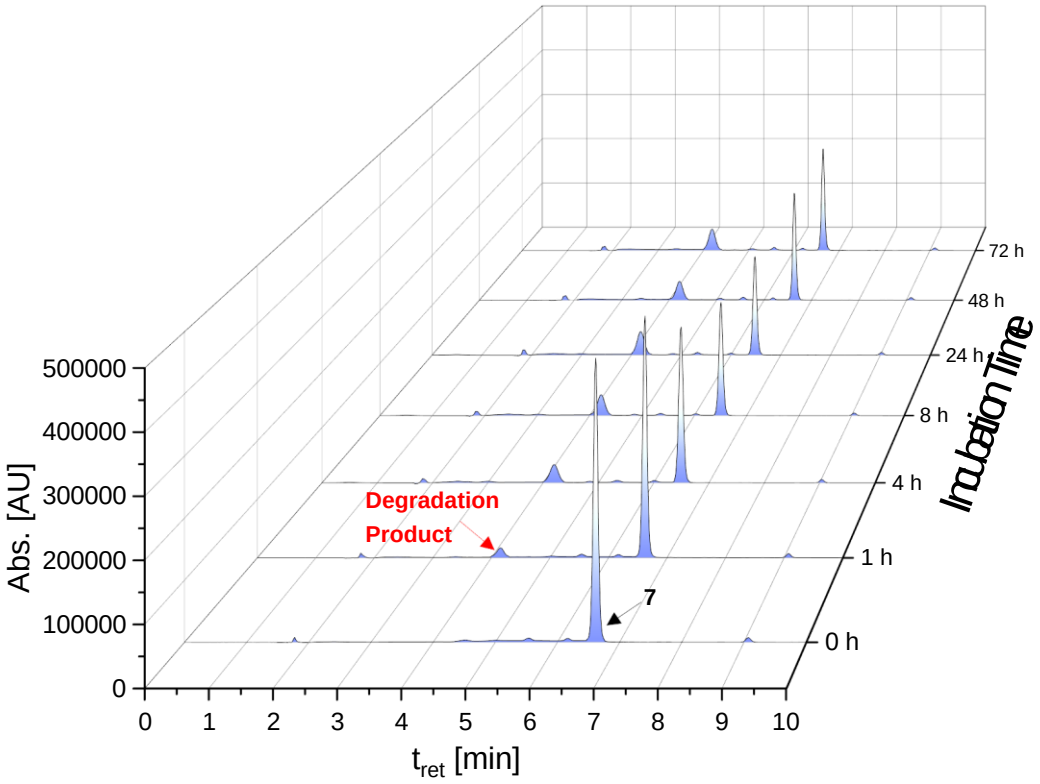


Figure S37. HPLC chromatograms of **7** incubated in ACN up to 72 h. Complex concentration: 0.5 mM.

8.2. Stability in RPMI 1640 cell culture medium (without FCS)

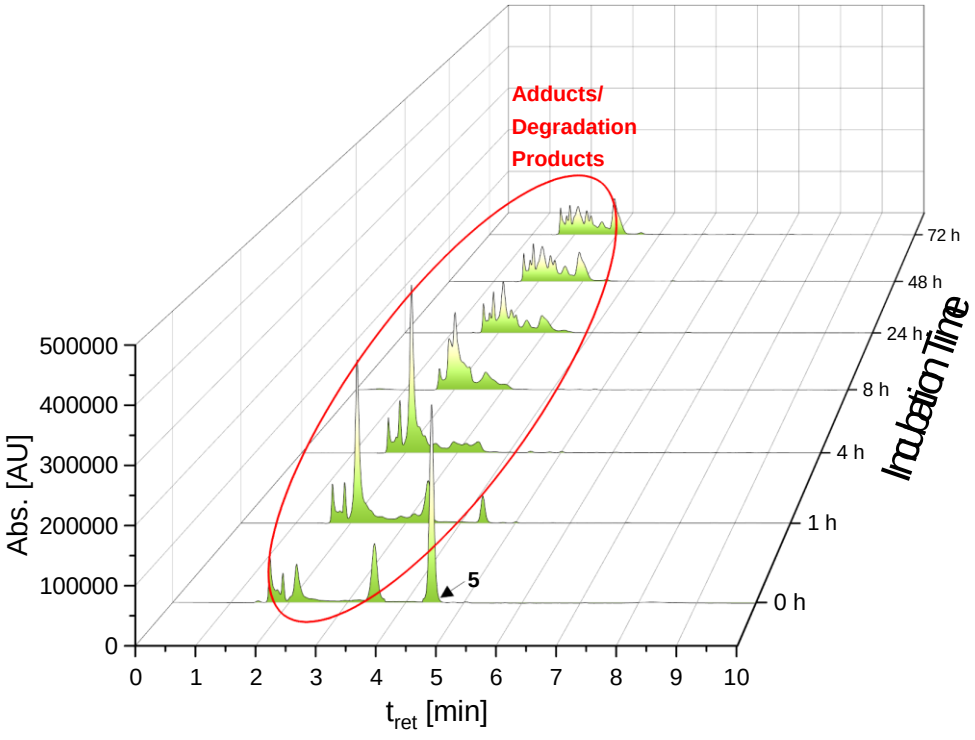


Figure S38. HPLC chromatograms of **5** over 72 h of incubation in ACN/RPMI 1640 (w/o FCS) = 50:50 (v/v). Complex concentration: 0.5 mM.

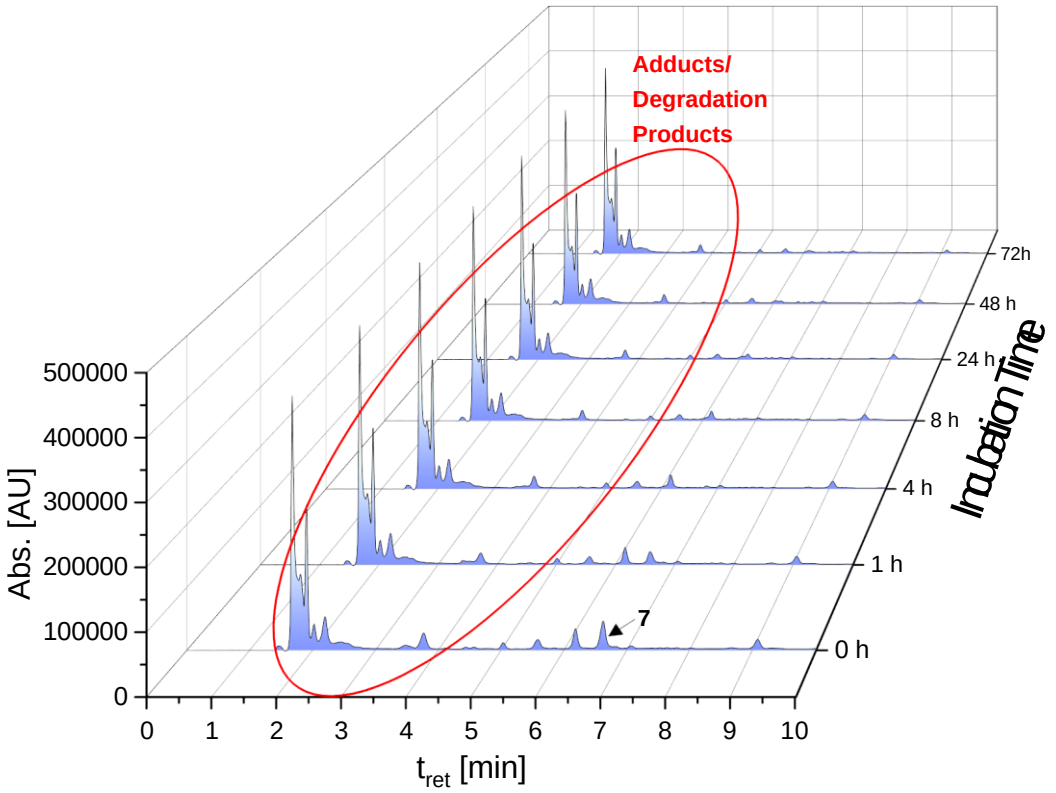


Figure S39. HPLC chromatograms of **7** over 72 h of incubation in ACN/RPMI 1640 (w/o FCS) = 50:50 (v/v). Complex concentration: 0.5 mM.

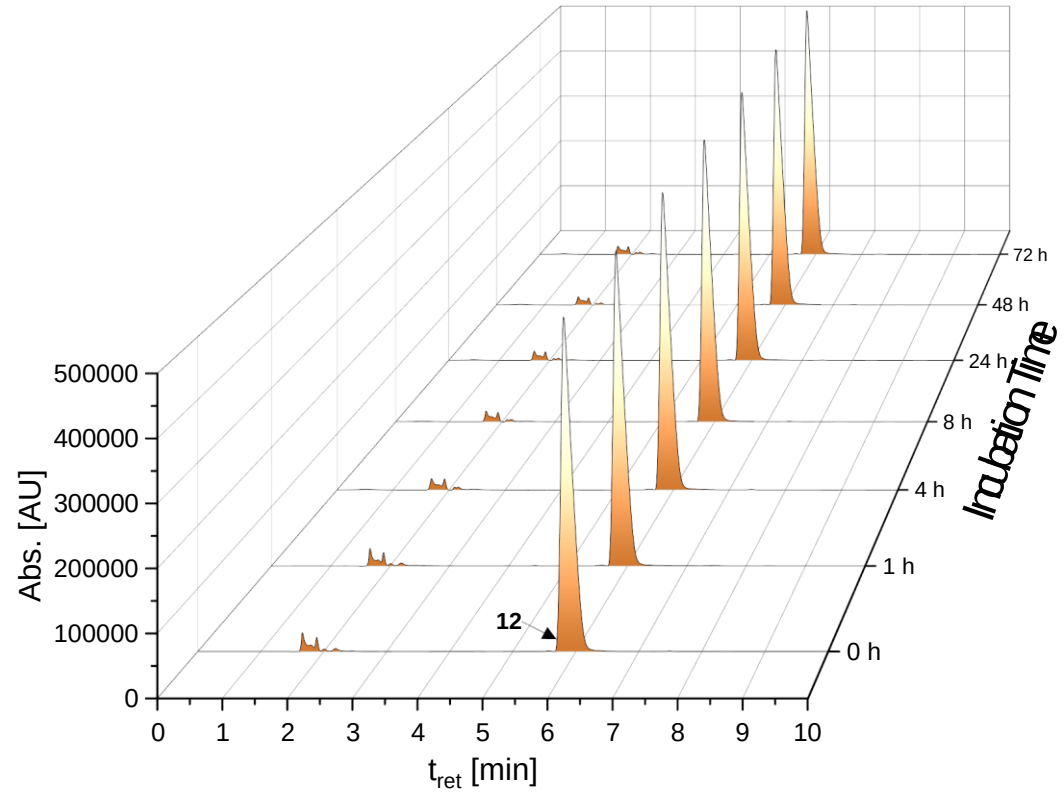


Figure S40. HPLC chromatograms of **12** over 72 h of incubation in ACN/RPMI 1640 (w/o FCS) = 50:50 (v/v). Complex concentration: 0.5 mM.

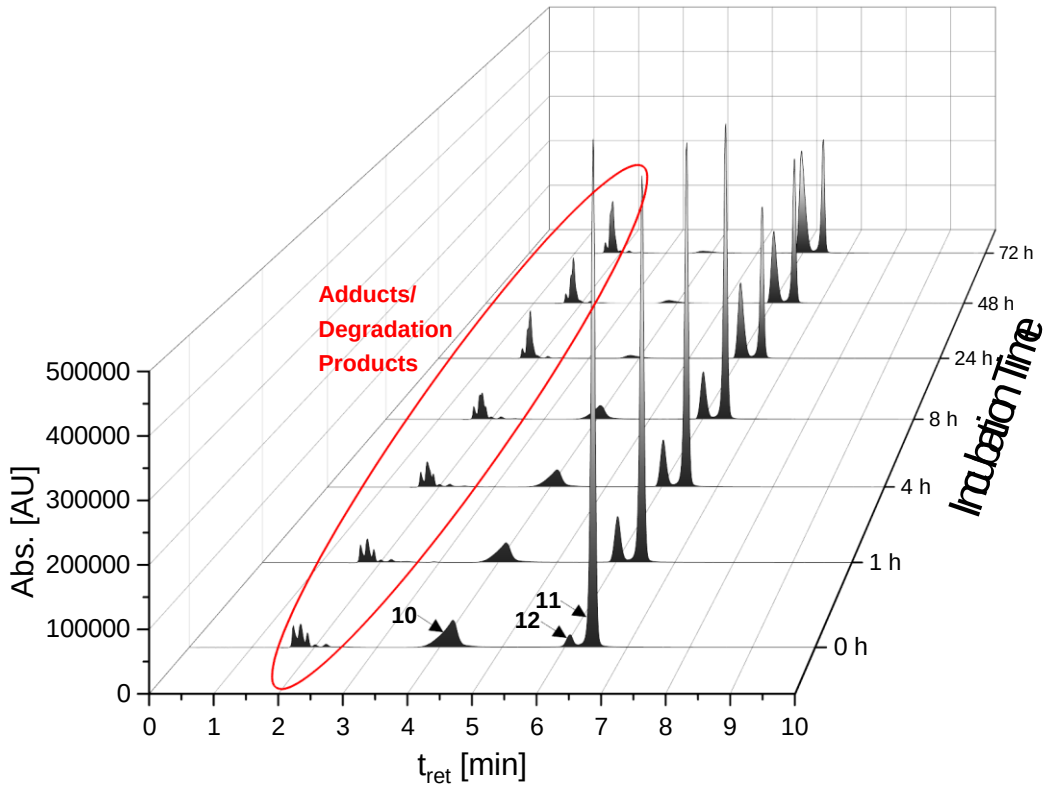


Figure S41. HPLC chromatograms of **11** over 72 h of incubation in ACN/RPMI 1640 (w/o FCS) = 50:50 (v/v). Complex concentration: 0.5 mM.

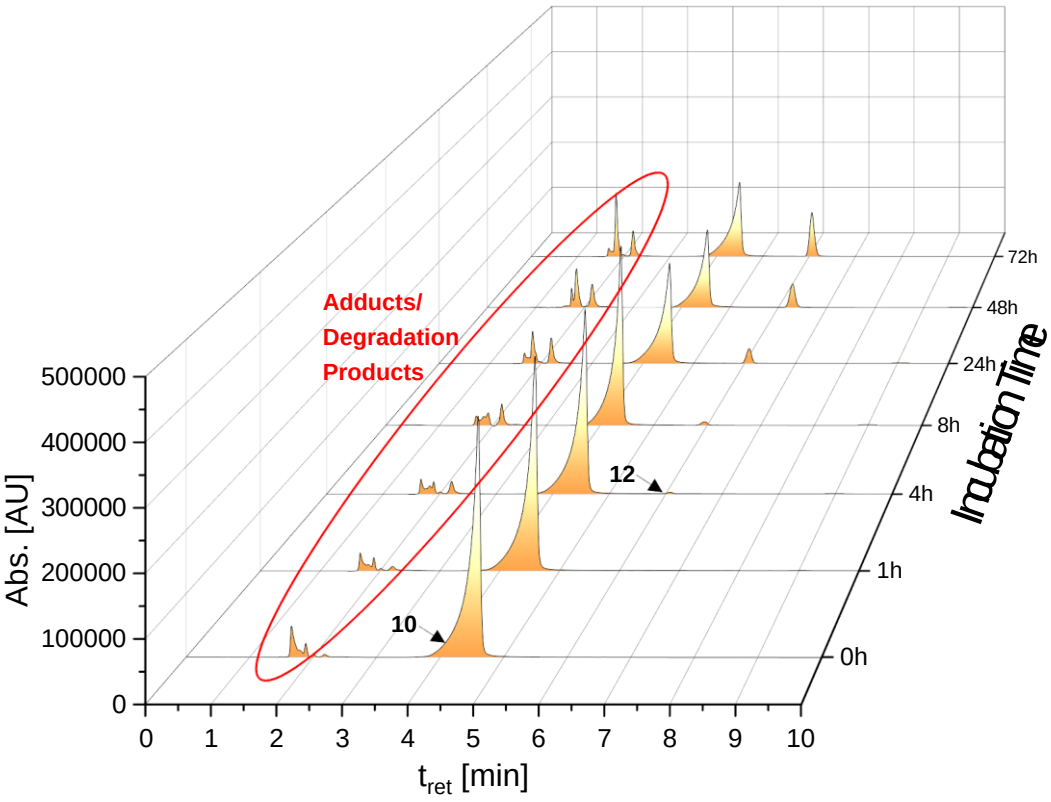


Figure S42. HPLC chromatograms of **10** over 72 h of incubation in ACN/RPMI 1640 (w/o FCS) = 50:50 (v/v). Complex concentration: 0.5 mM.

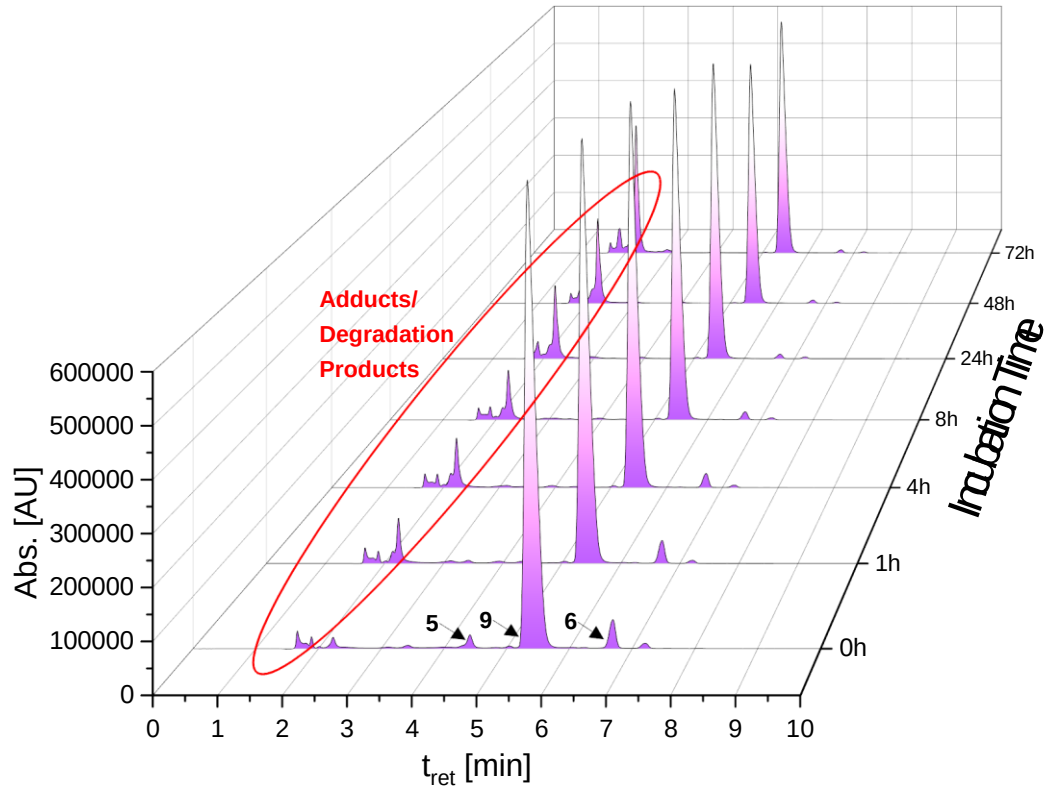


Figure S43. HPLC chromatograms of **9** over 72 h of incubation in ACN/RPMI 1640 (w/o FCS) = 50:50 (v/v). Complex concentration: 0.5 mM. Peaks **5** and **6** in the chromatograms of **9** come from synthesis (side products).

8.3. Interactions with Glutathione

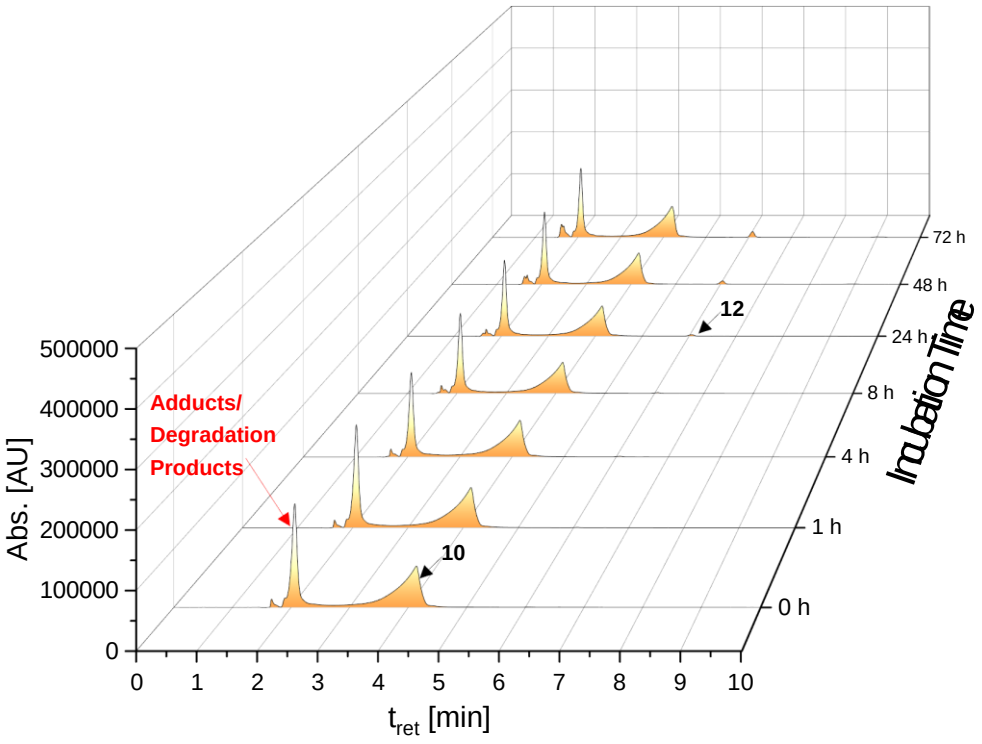


Figure S44. HPLC chromatograms up to 72 h of **10** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM.

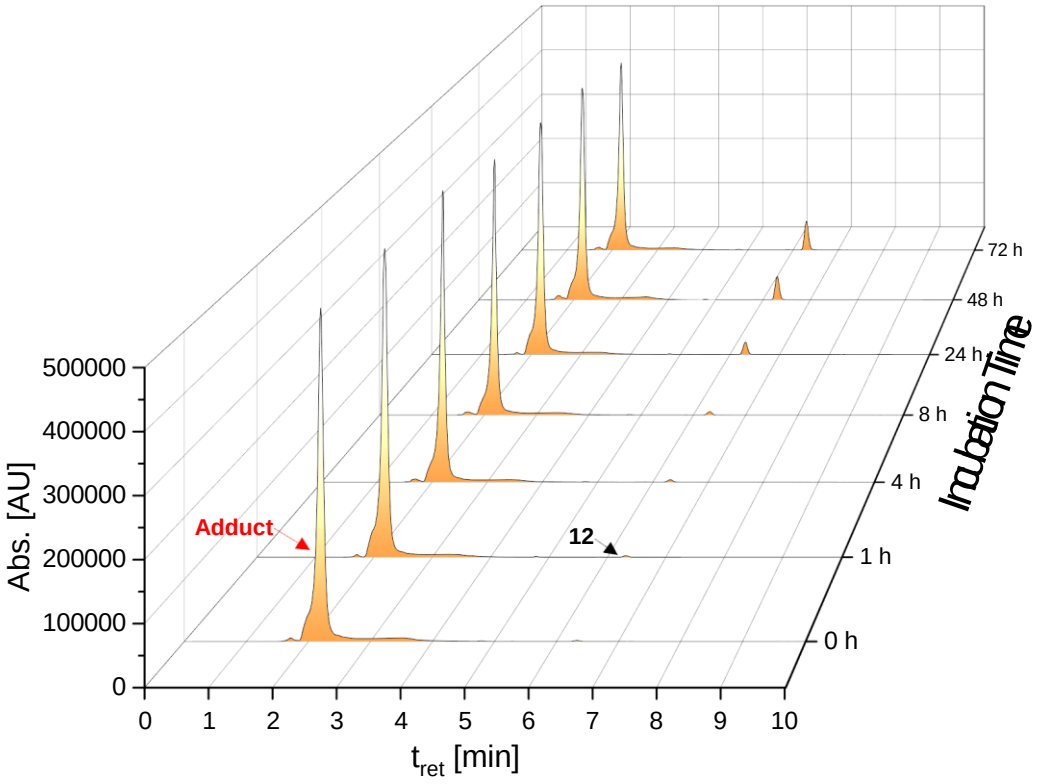


Figure S45. HPLC chromatograms up to 72 h of **10** dissolved in ACN/water = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM.

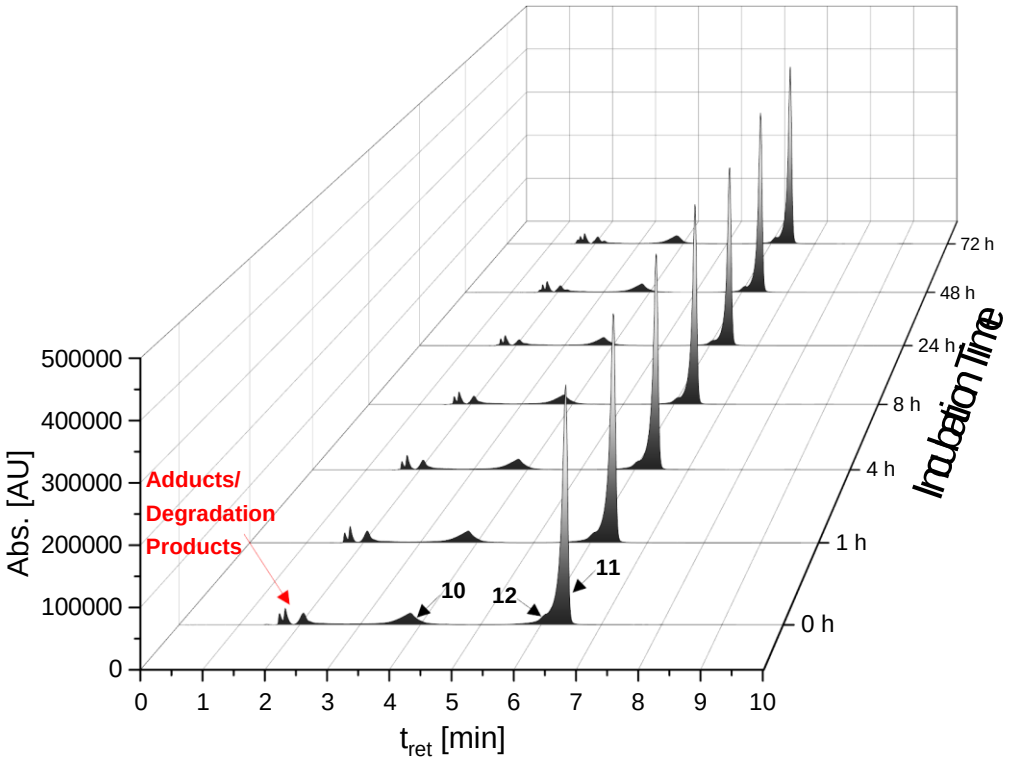


Figure S46. HPLC chromatograms up to 72 h of **11** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM.

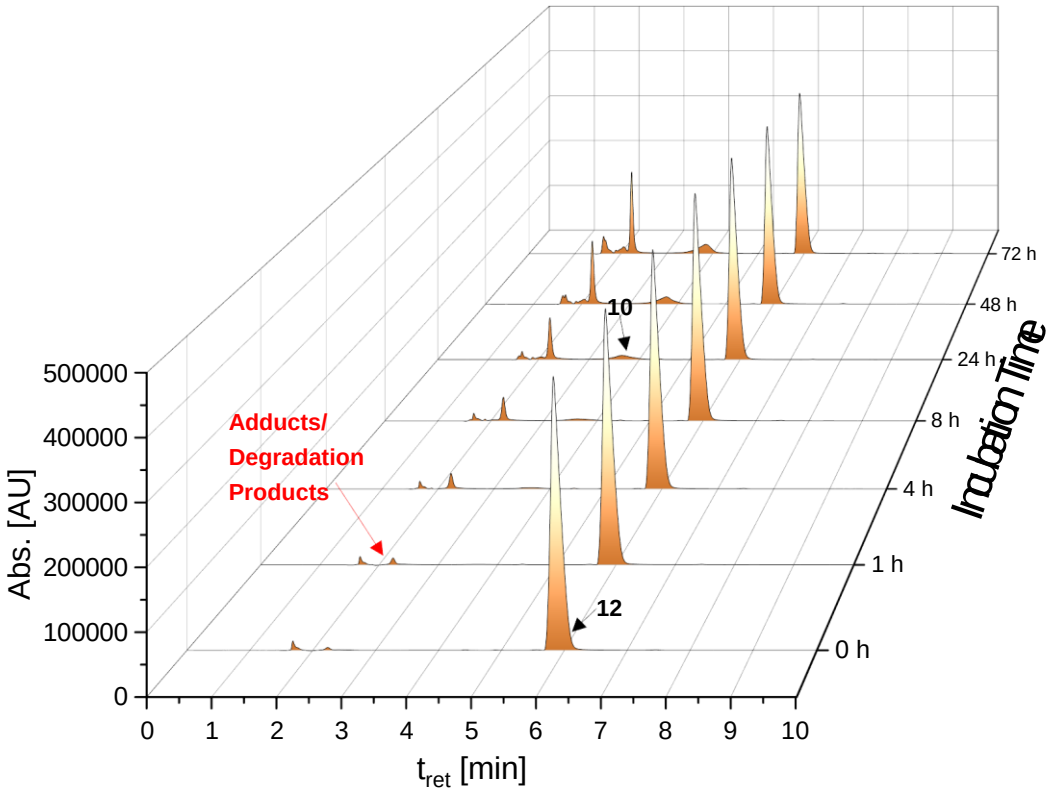


Figure S47. HPLC chromatograms up to 72 h of **12** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM.

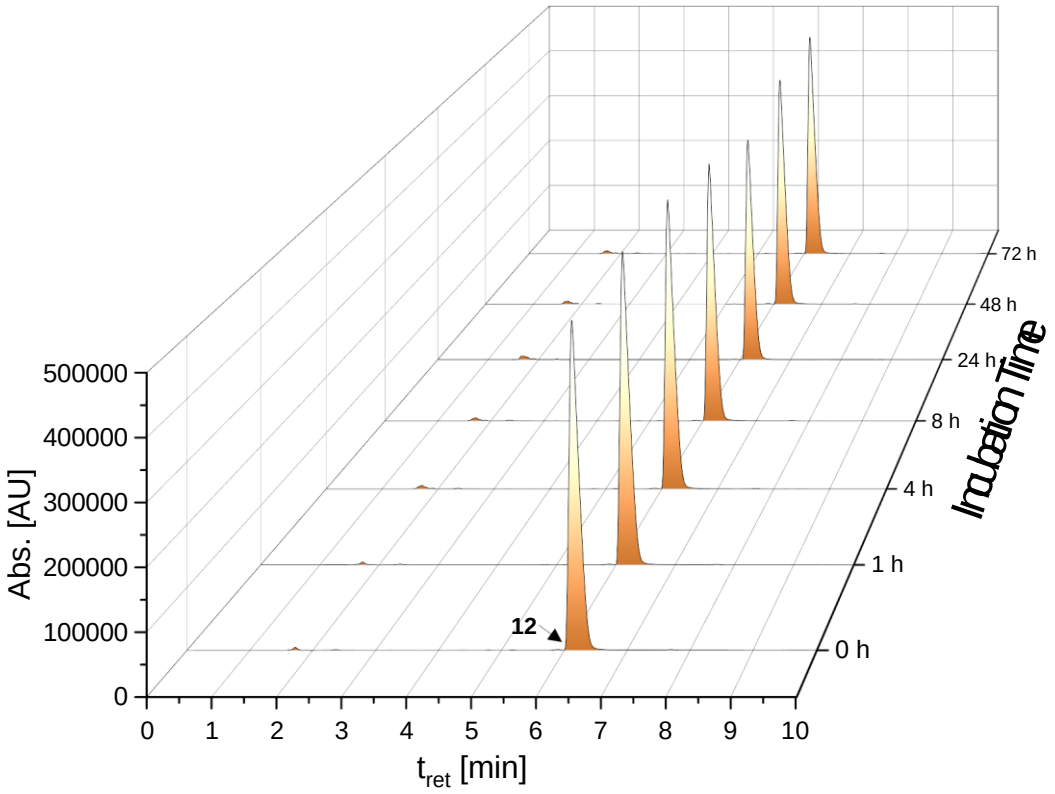


Figure S48. HPLC chromatograms up to 72 h of **12** dissolved in ACN/water = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM.

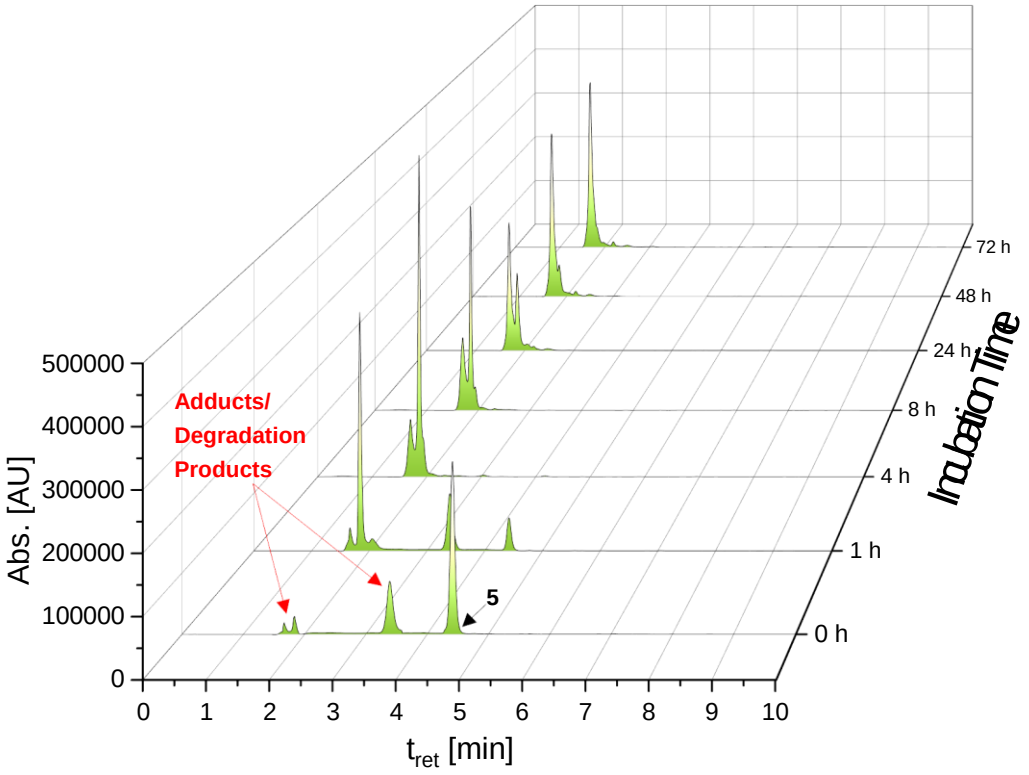


Figure S49. HPLC chromatograms up to 72 h of **5** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM.

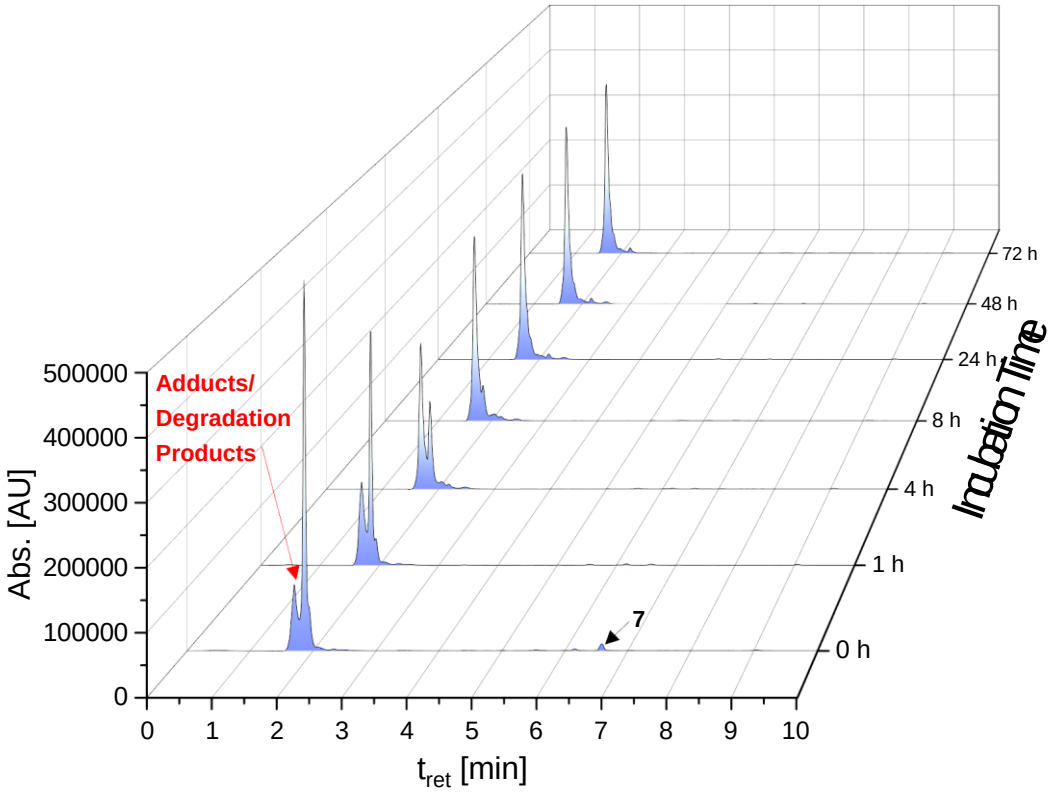


Figure S50. HPLC chromatograms up to 72 h of **7** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM.

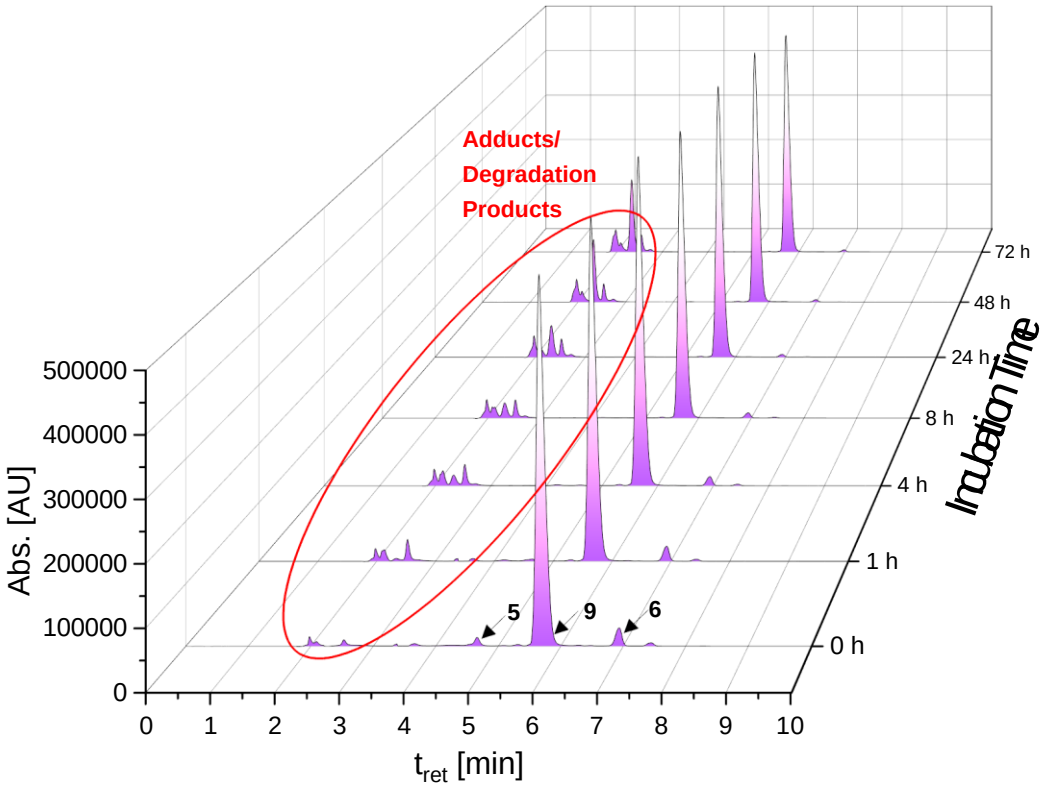


Figure S51. HPLC chromatograms up to 72 h of **9** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM. Peaks **5** and **6** in the chromatograms of **9** come from synthesis (side products).

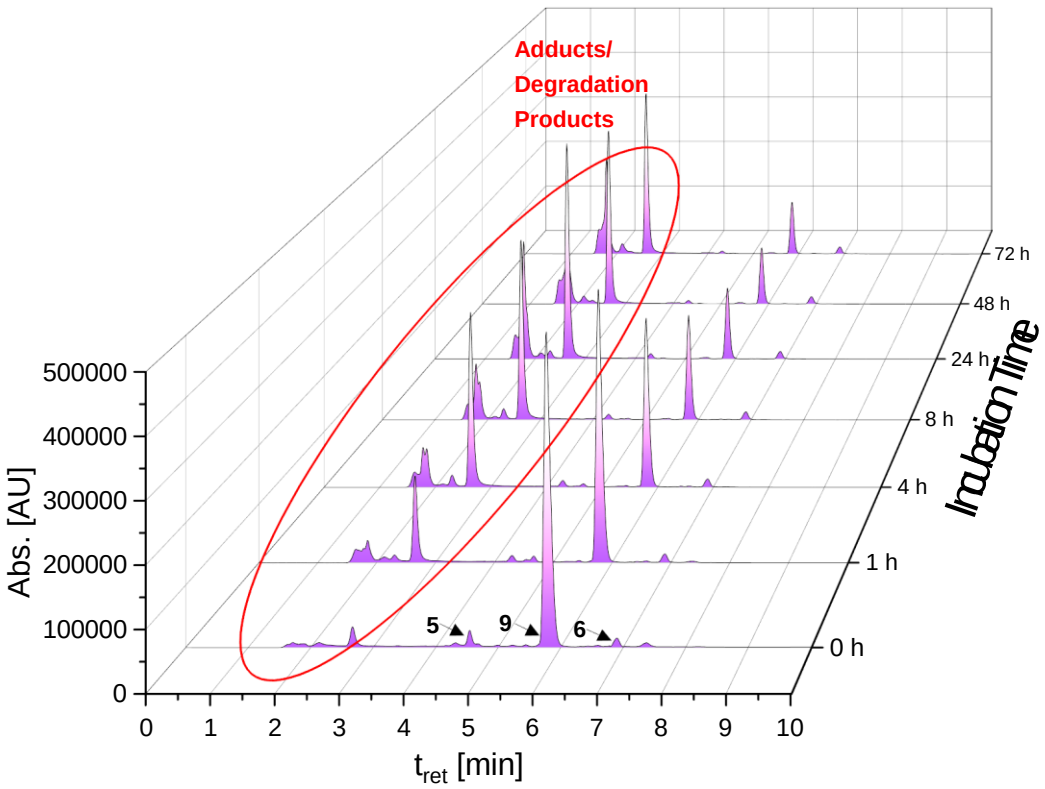


Figure S52. HPLC chromatograms up to 72 h of **9** dissolved in ACN/water = 50:50 (v/v) in presence of 5 equiv. GSH (red.). Complex concentration: 0.5 mM. Peaks **5** and **6** in the chromatograms of **9** come from synthesis (side products).

8.4. Interactions with 5`-GMP

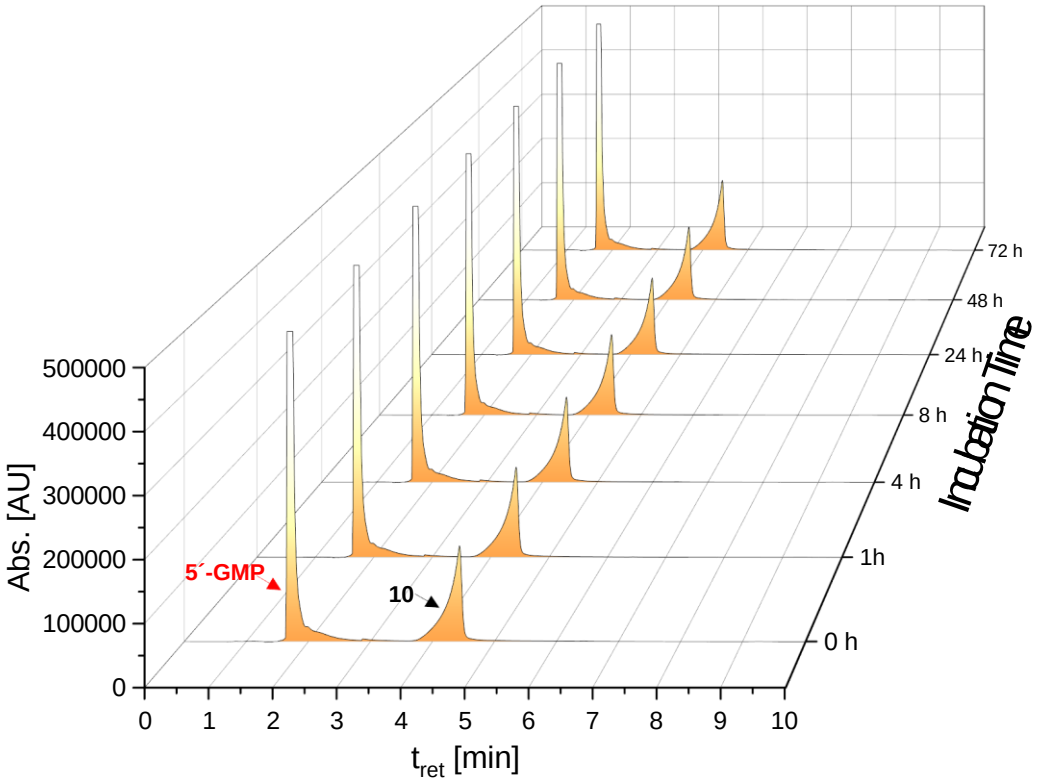


Figure S53. HPLC chromatograms up to 72 h of **10** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 500.000 AU.

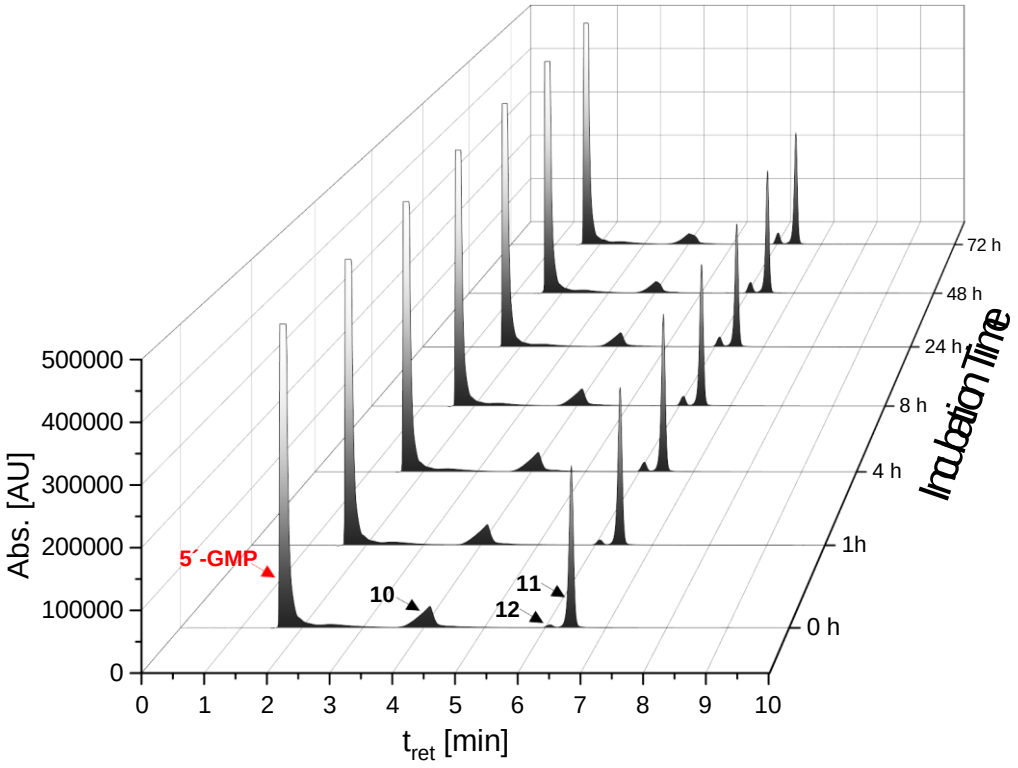


Figure S54. HPLC chromatograms up to 72 h of **11** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 500.000 AU.

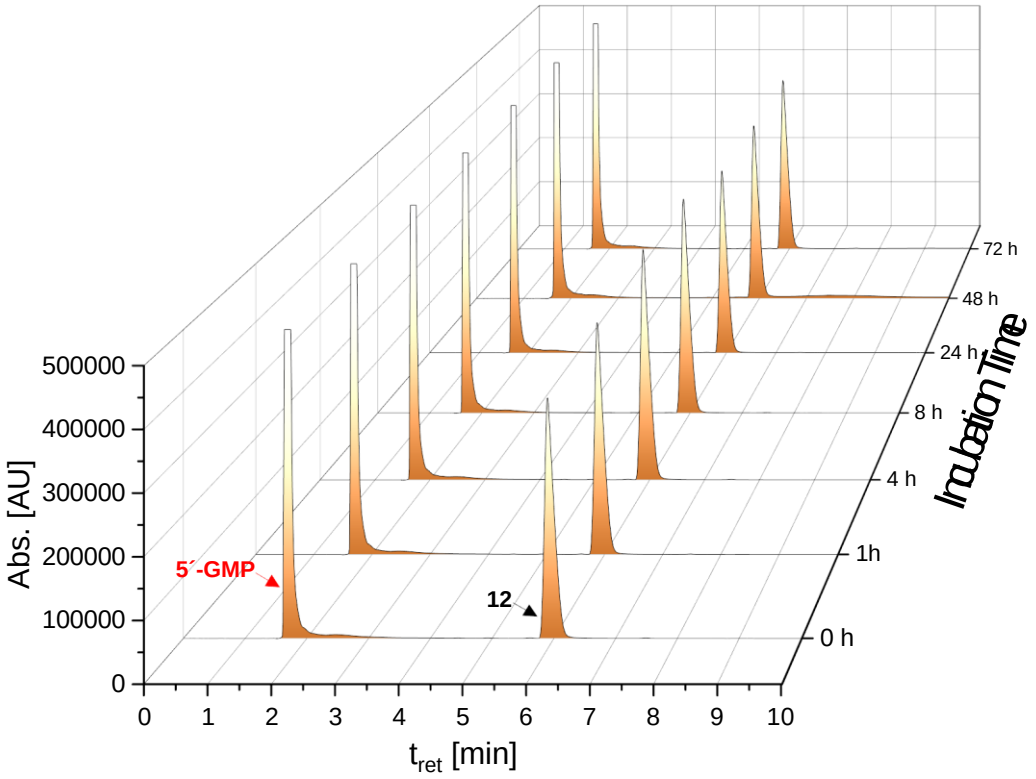


Figure S55. HPLC chromatograms up to 72 h of **12** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 500.000 AU.

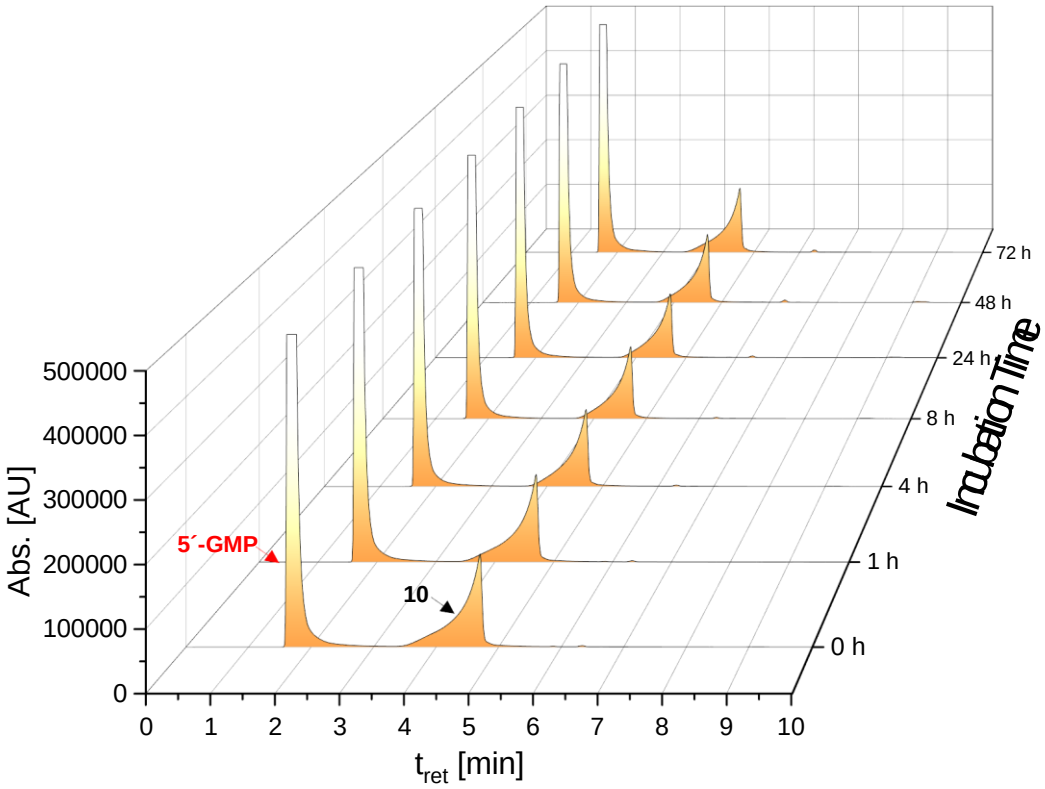


Figure S56. HPLC chromatograms up to 72 h of **10** dissolved in ACN/water = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 500.000 AU.

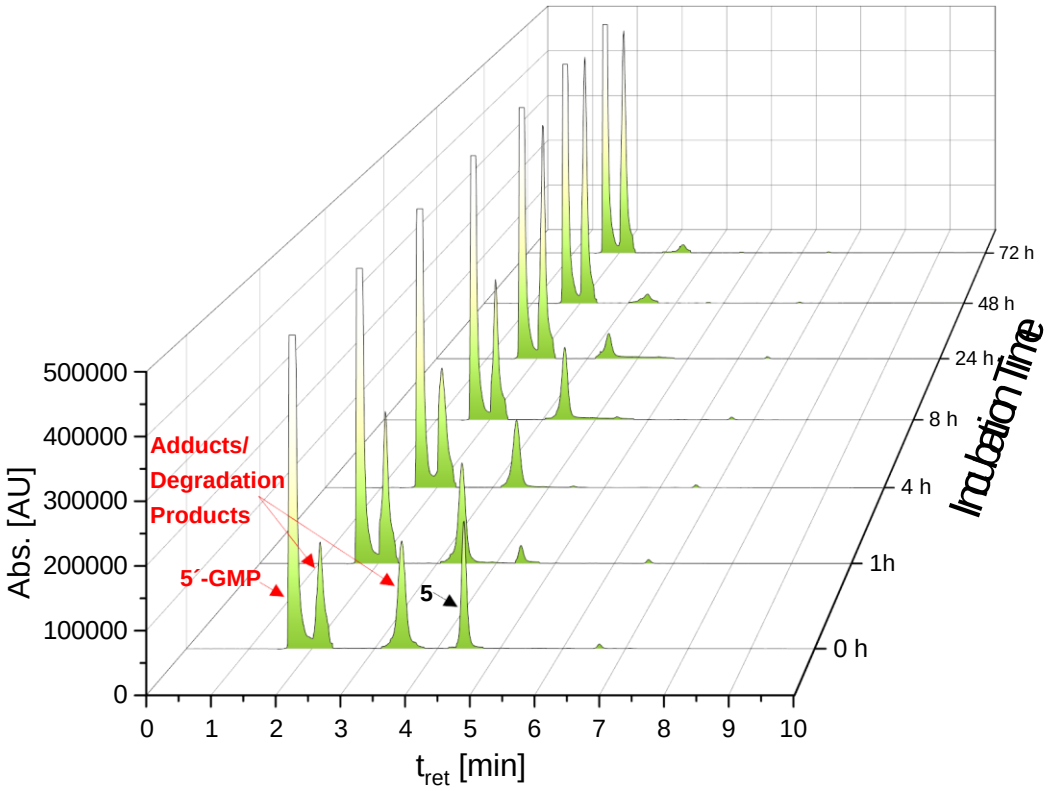


Figure S57. HPLC chromatograms up to 72 h of **5** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 500.000 AU.

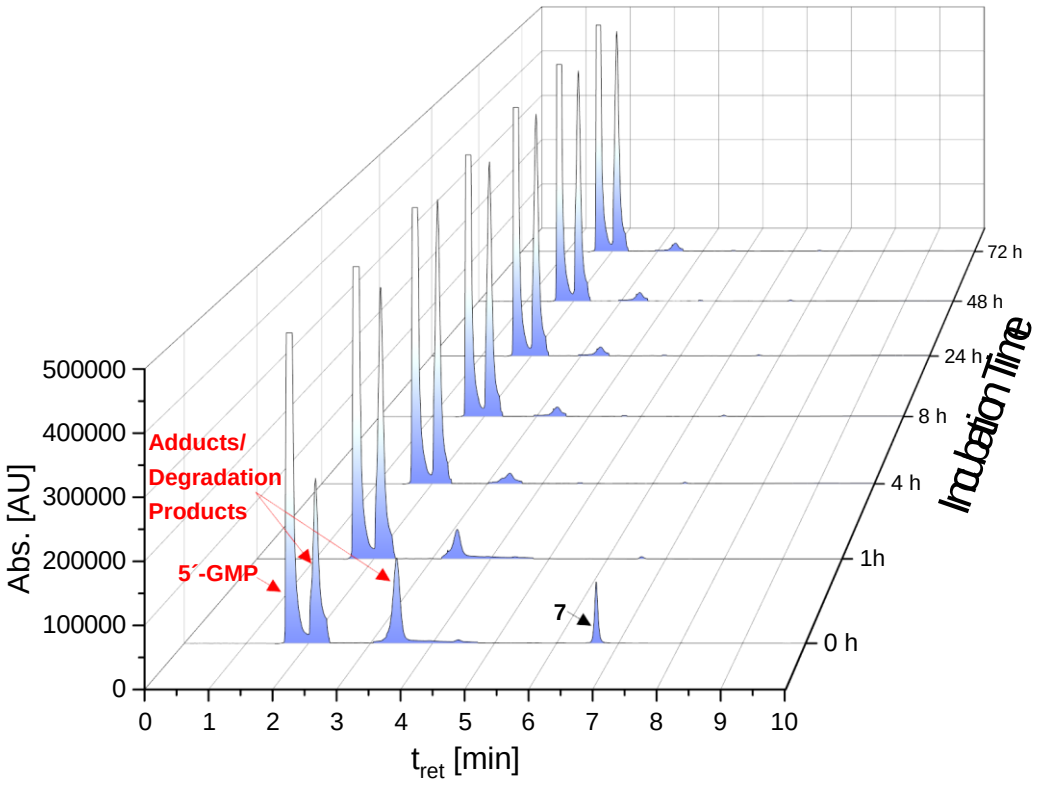


Figure S58. HPLC chromatograms up to 72 h of **7** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 500.000 AU.

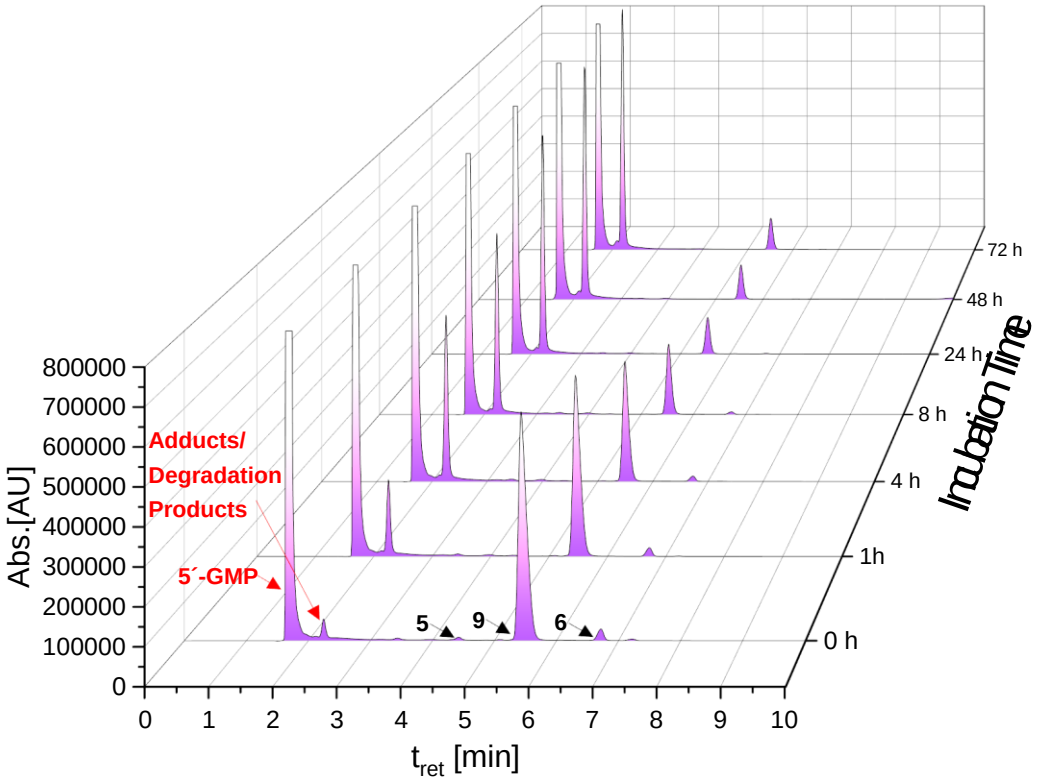


Figure S59. HPLC chromatograms up to 72 h of **9** dissolved in ACN/PBS = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 800.000 AU. Peaks **5** and **6** in the chromatograms of **9** come from synthesis (side products).

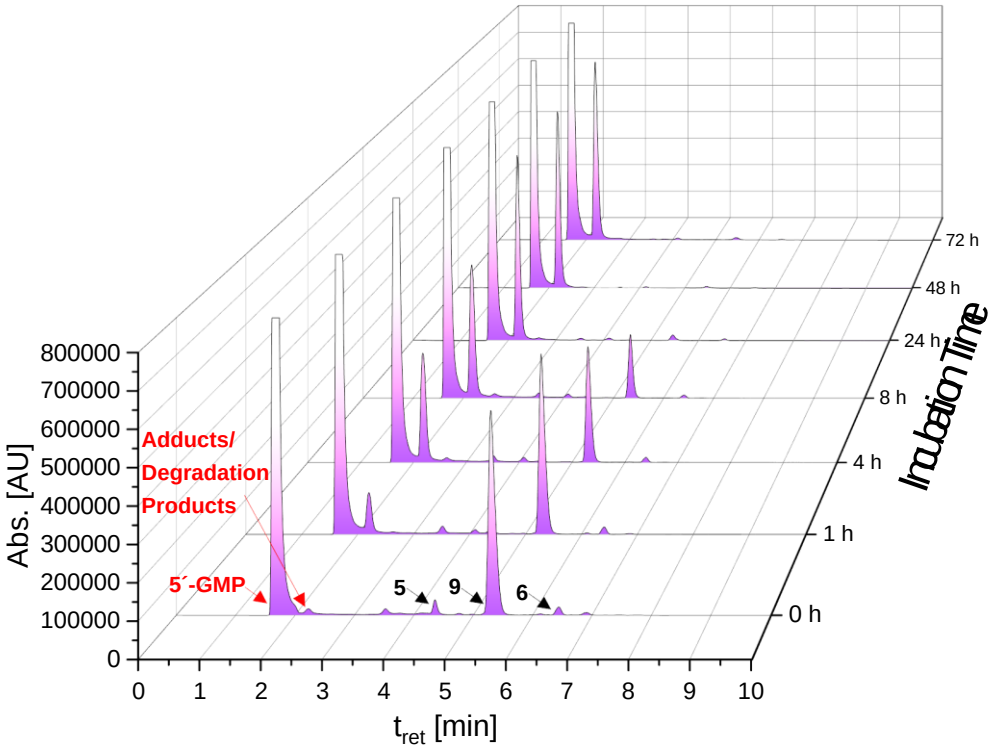


Figure S60. HPLC chromatograms up to 72 h of **9** dissolved in ACN/water = 50:50 (v/v) in presence of 5 equiv. 5´-GMP (at pH 7.4). Complex concentration: 0.5 mM. The 5´-GMP peak (t_{ret} = 1.82 min) was cut > 800.000 AU. Peaks **5** and **6** in the chromatograms of **9** come from synthesis (side products).

8.5. Interactions with 5´-GMP in the presence of GSH (competitive experiment)

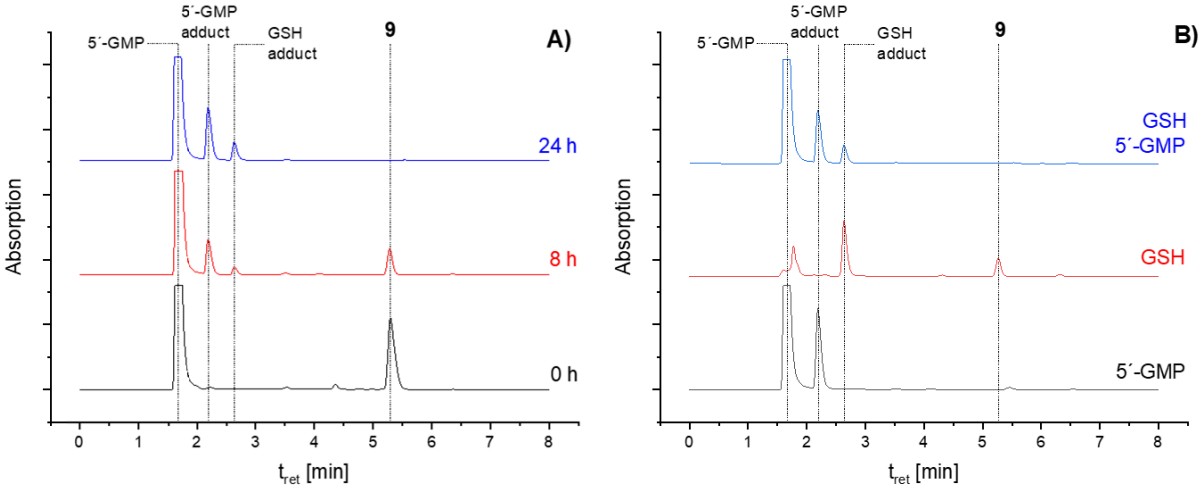


Figure S61. HPLC chromatograms of **9** in ACN/water = 50:50 (v/v) co-incubated with: A) 5´-GMP and GSH (both 5 equiv.) at 0, 8, and 24 h; B) 5´-GMP (5 equiv.), GSH (5 equiv.), or 5´-GMP and GSH (both 5 equiv.) at t = 24 h. After 24 h of co-incubation of **9** with 5´-GMP and GSH (both 5 equiv.), the entire amount of complex **9** was transformed into GMP- and GSH-adducts in a ratio of 64:36 according to the HPLC chromatogram recorded at 254 nm.

9. Concentration-Effect Curves of **5**, **7**, **9**, and **10**-**12**

The concentration-effect curves were displayed with GraphPad Prism 8.0 (GraphPad Software, Boston, MA, USA).

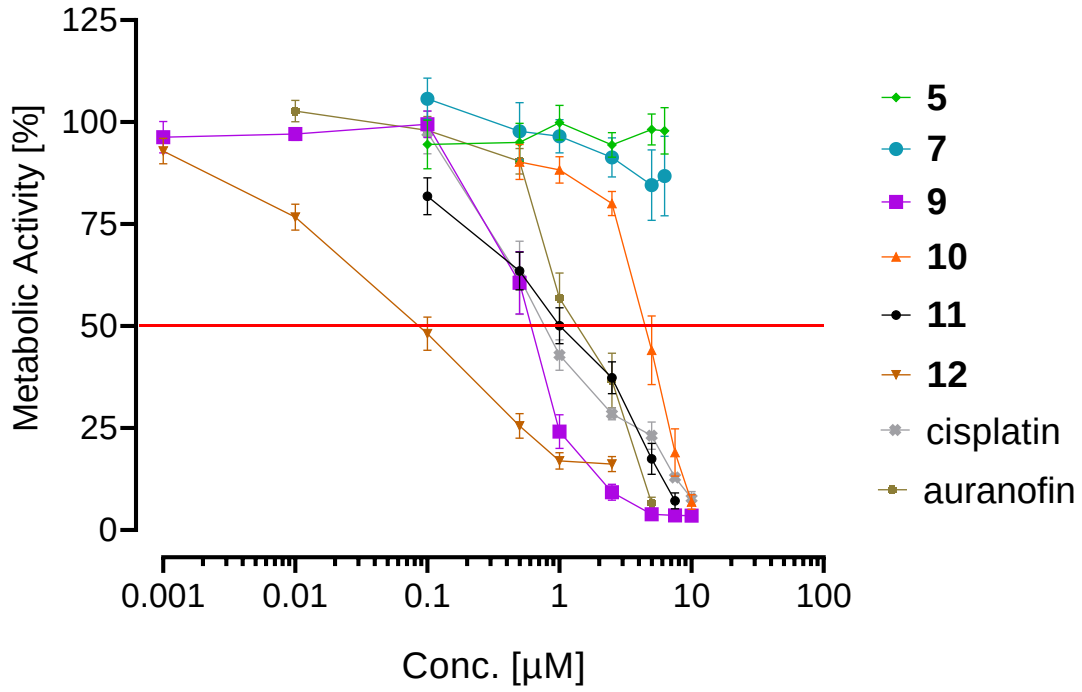


Figure S62. Concentration-effect curves of **5**, **7**, **9**-**12**, cisplatin, and auranofin in A2780wt cells. (exposure time: 72 h, n = 6 ± SEM)

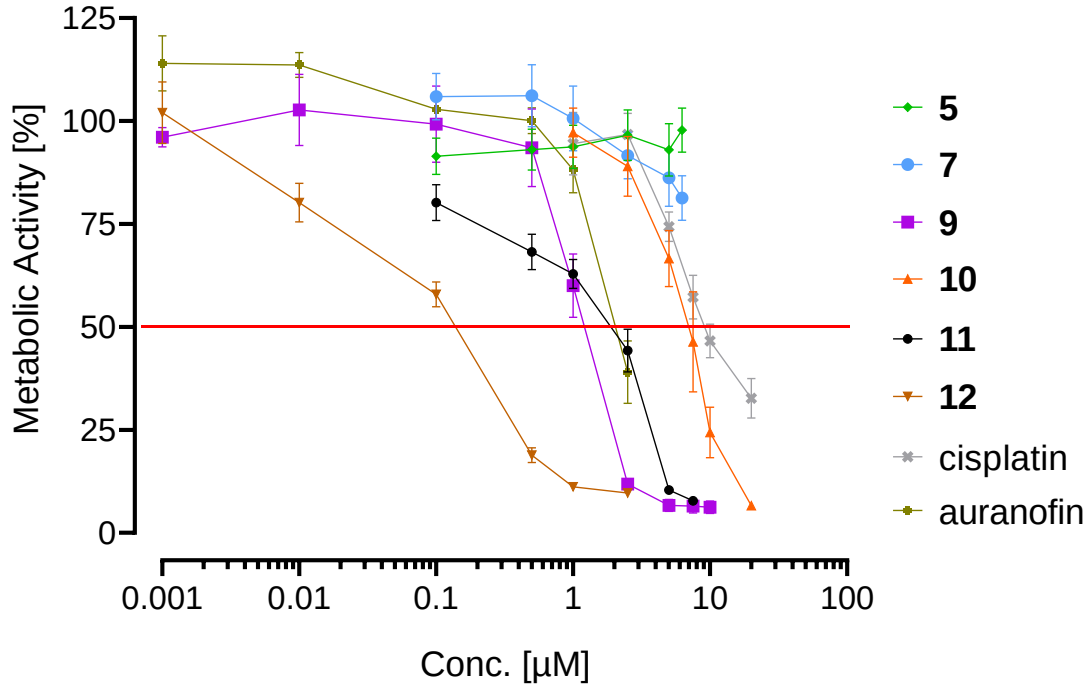


Figure S63. Concentration-effect curves of **5**, **7**, **9**-**12**, cisplatin, and auranofin in A2780cis cells (exposure time: 72 h, n = 6 ± SEM)