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Supplementary Information for

On the hydrolytic stability of unsymmetric platinum(IV) anticancer prodrugs containing axial halogens

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Experimental procedures

Reagents and instruments

Unless stated otherwise, all chemicals were bought from commercial suppliers and used as received without further purification and dilution. All reactions were carried out under atmospheric pressure with protection from light by aluminum foil. ^{1}H, ^{13}C, ^{19}F, and ^{195}Pt spectra were recorded using a Bruker AVANCE III 400 MHz spectrometer or a Bruker Ascend AVANCE III HD 600 MHz spectrometer at room temperature. Chemical shifts (δ) were reported in parts per million (ppm) and referenced as described below. ^{1}H and ^{13}C NMR spectra were referenced internally to residual solvent peaks, deuterated dimethyl sulfoxide (DMSO-d_6) or deuterated water (D_2O) were used as solvents. ^{19}F NMR spectra were referenced externally using C_6F_6 (δ = -164.9 ppm vs. $CFCl_3$) for organic solvent (DMSO-d_6) and aqueous F^- (KF, δ = -125.3 ppm vs. $CFCl_3$) for deuterated salt solution (D_2O + salt). ^{195}Pt NMR spectra were referenced externally using K_2PtCl_4 in D_2O (δ = -1628 ppm vs. Na_2PtCl_6). Electrospray ionization mass spectrometry (ESI-MS) was carried out on an Agilent API-2000 Triple-Q MS/MS spectrometer. Elemental analysis was performed using a Vario Micro elemental analyzer. RP-HPLC was carried out to analyze the hydrolysis and reduction of DCA-containing Pt(IV) compounds, using Shimadzu Prominence HPLC system with a Phenomenex C18 column (5 µm, 110 Å, 250 x 4.60 mm, 1 mL/min flow). The detectors were set at 254 nm and 365 nm. Phase A was 95% H_2O, 5% acetonitrile (ACN) and 0.1% formic acid. Phase B was 5% H_2O, 95% ACN, and 0.1% formic acid. Each time 40 µL sample was injected to the HPLC system. The HPLC program was set as follows: 0% to 100% phase B (linear increase from 0 to 9 min); 100% phase B to 0% B (linear decrease from 9 to 11 min); 0% phase B (from 11 to 12 min) and stopped at 12 min. All the results were calculated based on the HPLC chromatograms of 254 nm.

Synthesis of Pt(IV) complexes for hydrolytic stability investigation

The dihydroxylated Pt(IV) complexes **1**,[1] **5**,[2] and **9**[3] were obtained by oxidizing three FDA-approved Pt(II) complexes in H_2O by H_2O_2. Fluorinated Pt(IV) complexes **6** and **10**,[4] chlorinated Pt(IV) complexes **3**,[5] **7**,[6] and **11**,[7] and brominated Pt(IV) complexes **4**, **8**, and **12**[8] were prepared by following the methods described in the literature (Scheme S1). However, cisplatin-based unsymmetric fluorinated Pt(IV) complex (**2**) was unable to obtain by using *N*-fluorinating reagents.

The Pt(IV) complexes (0.28 mmol, that is 94 mg of **1**, 98 mg of **3**, 111 mg of **4**, 113 mg of **5**, 114 mg of **6**, 119 mg of **7**, 131 mg of **8**, 121 mg of **9**, 121 mg of **10**, 126 mg of **11**, or 138 mg of **12**) were suspended in 1.5 mL DMSO and succinic anhydride (0.34 mmol, 34 mg) was added to the solution. The mixture was stirred at room temperature overnight. After that, the solution was centrifuged to remove the unreacted Pt(IV) complexes. The desired compounds were precipitated by adding 50 mL dichloromethane and diethyl ether (1:10). The solid was collected by centrifugation and washed twice with 30 mL dichloromethane and diethyl ether (1:10) to remove the residual DMSO. After drying in vacuum, the final Pt(IV) complexes **1a**, **3a** to **12a** with axial succinato ligand were obtained (Scheme S2).

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(succinato)OH] (1a)**.[9]

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(succinato)Cl] (3a)**. Yield: 49%, 62 mg (0.14 mmol). Anal. Calcd for: $C_4H_{11}Cl_3N_2O_4Pt$ (452.58): C, 10.62; H, 2.45; N, 6.19. Found: C, 10.92; H, 2.55; N, 6.06. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.08 (s, 1H), 6.17 (m, 6H), 2.51 – 2.46 (m, 2H), 2.40 (t, J = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 179.8, 174.4, 31.6, 30.4. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 548.7. ESI-MS (positive ion mode): 453.1 *m/z* $[M+H]^+$; calcd for $C_4H_{12}Cl_3N_2O_4Pt$ *m/z* 453.0 $[M+H]^+$

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(succinato)Br] (4a)**. Yield: 52%, 73 mg (0.15 mmol). Anal. Calcd for: $C_4H_{11}BrClN_2O_4Pt$ (497.03): C, 9.67; H, 2.23; N, 5.64. Found: C, 9.32; H, 2.25; N, 5.25. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.07 (s, 1H), 6.73 – 5.90 (m, 6H), 2.49 (t, J = 7.1 Hz, 2H), 2.40 (t, J = 7.3 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 180.0, 174.4, 32.0, 30.4. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 277.1. ESI-MS (negative ion mode): 495.0 *m/z* $[M-H]^-$; calcd for $C_4H_{10}BrClN_2O_4Pt$ *m/z* 494.9 $[M-H]^-$

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)OH] (5a)**.[10]

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)F] (6a).** Yield: 41%, 58 mg (0.11 mmol). Anal. Calcd for: $C_{10}H_{17}FN_2O_8Pt$ (507.33): C, 23.67; H, 3.38; N, 5.52. Found: C, 23.69; H, 3.50; N, 5.43. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.08 (s, 1H), 6.56 – 5.94 (m, 6H), 2.53 – 2.46 (m, 6H), 2.36 (t, J = 7.0 Hz, 2H), 1.81 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 179.2, 176.7, 174.1, 56.1, 32.2, 31.7, 31.5, 30.6, 16.3. ^{19}F NMR (565 MHz, DMSO-d_6) δ -336.3 (s+d, J = 1310.8 Hz). ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 2383.8 (d, J = 1351.6 Hz). ESI-MS (positive ion mode): 530.1 *m/z* $[M+Na]^+$; calcd for $C_{10}H_{17}FN_2O_8PtNa$ *m/z* 530.1 $[M+Na]^+$

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)Cl] (7a).** Yield: 57%, 84 mg (0.16 mmol). Anal. Calcd for: $C_{10}H_{17}ClN_2O_8Pt$ (523.79): C, 22.93; H, 3.27; N, 5.35. Found: C, 22.69; H, 3.33; N, 5.46. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 6.13 (m, 6H), 2.51 (m, 6H), 2.38 (t, J = 7.1 Hz, 2H), 1.87 – 1.77 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.9, 176.8, 174.2, 56.2, 32.8, 31.3, 31.12, 30.3, 16.2. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1368.8. ESI-MS (positive ion mode): 525.1 *m/z* $[M+H]^+$; calcd for $C_{10}H_{18}ClN_2O_8Pt$ *m/z* 525.0 $[M+H]^+$

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)Br] (8a).** Yield: 50%, 80 mg (0.14 mmol). Anal. Calcd for: $C_{10}H_{17}BrN_2O_8Pt$ (568.24): C, 21.14; H, 3.02; N, 4.93. Found: C, 20.95; H, 3.26; N, 4.76. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.09 (s, 1H), 6.41 – 5.99 (m, 6H), 2.57 – 2.45 (m, 6H), 2.39 (t, J = 7.2 Hz, 2H), 1.86 – 1.78 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 179.1, 176.8, 174.2, 56.3, 33.4, 31.6, 30.8, 30.2, 16.1. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1149.3. ESI-MS (positive ion mode): 591.0 *m/z* $[M+Na]^+$; calcd for $C_{10}H_{17}BrN_2O_8PtNa$ *m/z* 591.0 $[M+Na]^+$

***trans*-[Pt(DACH)(ox)(succinato)OH] (9a)**, ***trans*-[Pt(DACH)(ox)(succinato)F] (10a)**, ***trans*-[Pt(DACH)(ox)(succinato)Cl] (11a)**, and ***trans*-[Pt(DACH)(ox)(succinato)Br] (12a)** were obtained by exactly following the reported method.[4,8]

Hydroxylated, chlorinated, and brominated Pt(IV) complexes which contain axial acetato ligand were synthesized by oxidizing the three FDA approved Pt(II) anticancer drugs with corresponding oxidizing regents in acetic acid (Scheme S3). Pt(II) anticancer drugs (0.28 mmol, which is 84 mg of cisplatin, 104 mg of carboplatin or 111 mg of oxaliplatin) were suspended in 3 mL acetic acid. Oxidizing regents (0.34 mmol, which is 12 mg of H_2O_2, 45 mg of NCS or 60 mg of NBS) were then added into the mixture. After stirring overnight at room temperature, the resulting solutions were separately added to 40 mL Et_2O. The precipitate was collected by centrifuge and then washed with 30 mL Et_2O for twice. After drying in vacuum, the final products were obtained.

Fluorinated Pt(IV) complexes **6b** and **10b** were synthesized by the reaction of acetic anhydride and fluorinated Pt(IV) complexes **6** and **10** (Scheme S3). Fluorinated Pt(IV) complexes **6** (0.28 mmol, 114 mg) and **10** (0.28 mmol, 121 mg) were suspended in a mixture of acetic anhydride and DMF (3 mL, v/v 2:1). The mixture was stirred overnight at 100 °C. After that, a clear solution formed, and most of the solvent was removed by rotary evaporator. The residual was washed by 30 mL Et_2O for twice and the final products **6b** and **10b** were obtained as white solid.

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(acetato)OH] (1b)**.[11]

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(acetato)Cl] (3b)**. Yield: 66%, 73 mg (0.18 mmol). Anal. Calcd for: $C_2H_9Cl_3N_2O_2Pt$ (394.55): C, 6.09; H, 2.30; N, 7.10. Found: C, 6.01; H, 2.56; N, 6.80. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.48 – 5.96 (m, 6H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.5, 24.0. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 553.2. ESI-MS (negative ion mode): 393.1 *m/z* [M-H]$^-$; calcd for $C_2H_8Cl_3N_2O_2Pt$ *m/z* 392.9 [M-H]$^-$

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(acetato)Br] (4b)**. Yield: 68%, 82 mg (0.19 mmol). Anal. Calcd for: $C_2H_9BrCl_2N_2O_2Pt$ (438.99): C, 5.47; H, 2.07; N, 6.38. Found: C, 5.87; H, 1.96; N, 6.16. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.51 – 5.93 (m, 6H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.8, 24.5. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 283.9. ESI-MS (negative ion mode): 437.0 *m/z* [M-H]$^-$; calcd for $C_2H_8BrCl_2N_2O_2Pt$ *m/z* 436.9 [M-H]$^-$

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)OH] (5b)**. Yield: 76%, 95 mg (0.21 mmol). Anal. Calcd for: $C_8H_{16}N_2O_7Pt$ (447.31): C, 21.48; H, 3.61; N, 6.26. Found: C, 21.16; H, 3.63; N, 6.21. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.09 – 5.69 (m, 6H), 2.54 (t, *J* = 8.0 Hz, 2H), 2.47(t, *J* = 9.0 Hz, 2H), 1.87 (s, 3H), 1.79 (p, *J* = 8.0 Hz, 2H), 1.74 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.3, 177.0, 56.2, 32.4, 31.6, 23.9, 16.3. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1757.9. ESI-MS (positive ion mode): 448.1 *m/z* [M+H]$^+$; calcd for $C_8H_{17}N_2O_7Pt$ *m/z* 448.1 [M+H]$^+$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)F] (6b).** Yield: 51%, 64 mg (0.14 mmol). Anal. Calcd for: $C_8H_{15}FN_2O_6Pt$ (449.30): C, 21.39; H, 3.37; N, 6.23. Found: C, 21.23; H, 3.61; N, 5.93. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.61 – 5.93 (m, 6H), 2.53 – 2.45 (m, 4H), 1.89 (s, 3H), 1.78 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 177.8, 176.6, 56.1, 32.5, 31.1, 22.0, 16.3. ^{19}F NMR (565 MHz, DMSO-d_6) δ -336.66 (s+d, *J* = 1305.2 Hz). ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 2377.2 (d, *J* = 1250.6 Hz). ESI-MS (positive ion mode): 450.1 *m/z* [M+H]$^+$; calcd for $C_8H_{16}FN_2O_6Pt$ *m/z* 450.1 [M+H]$^+$

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)Cl] (7b).** Yield: 80%, 105 mg (0.22 mmol). Anal. Calcd for: $C_8H_{15}ClN_2O_6Pt$ (465.75): C, 20.63; H, 3.25; N, 6.01. Found: C, 20.58; H, 3.47; N, 5.86. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.43 – 5.96 (m, 6H), 2.57 – 2.45 (m, 4H), 1.92 (s, 3H), 1.87 – 1.73 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 177.5, 176.8, 56.1, 32.4, 31.7, 23.5, 16.2. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1366.6. ESI-MS (positive ion mode): 467.2 *m/z* [M+H]$^+$; calcd for $C_8H_{16}ClN_2O_6Pt$ *m/z* 467.0 [M+H]$^+$

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)Br] (8b).** Yield: 69%, 99 mg (0.19 mmol). Anal. Calcd for: $C_8H_{15}BrN_2O_6Pt$ (510.20): C, 18.83; H, 2.96; N, 5.49. Found: C, 19.03; H, 3.13; N, 5.35. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.32 – 6.06 (m, 6H), 2.58 – 2.45 (m, 4H), 1.91 (s, 3H), 1.86 – 1.78 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 177.7, 176.8, 56.2, 33.1, 31.1, 23.9, 16.1. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1148.7. ESI-MS (negative ion mode): 509.2 *m/z* [M-H]$^-$; calcd for $C_8H_{14}BrN_2O_6Pt$ *m/z* 509.0 [M-H]$^-$

***trans*-[Pt(DACH)(ox)(acetato)OH] (9b)**.[4]

***trans*-[Pt(DACH)(ox)(acetato)F] (10b).** Yield: 64%, 85 mg (0.18 mmol). Anal. Calcd for: $C_{10}H_{17}FN_2O_6Pt$ (475.33): C, 25.27; H, 3.60; N, 5.89. Found: C, 25.06; H, 3.91; N, 5.62. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.26 (m, 4H), 2.54 (s, 2H), 2.07 (m, 2H), 1.94 (s, 3H), 1.48 (m, 4H), 1.12 (t, *J* = 9.7 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 179.0, 163.9, 61.7, 61.0, 30.8, 24.0, 22.8. ^{19}F NMR (565 MHz, DMSO-d_6) δ -328.7 (s+d, *J* = 1282.6 Hz). ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 2025.1 (d, *J* = 1215.8 Hz). ESI-MS (positive ion mode): 498.3 *m/z* [M+Na]$^+$; calcd for $C_{10}H_{17}FN_2O_6PtNa$ *m/z* 498.1 [M+Na]$^+$

***trans*-[Pt(DACH)(ox)(acetato)Cl] (11b).** Yield: 71%, 98 mg (0.20 mmol). Anal. Calcd for: $C_{10}H_{17}ClN_2O_6Pt$ (491.79): C, 24.42; H, 3.48; N, 5.70. Found: C, 24.54; H, 3.60; N, 5.68. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.98 – 7.41 (m, 4H), 2.58 (m, 2H), 2.06 (m, 2H), 1.98 (s, 3H), 1.61 – 1.31 (m, 4H), 1.13 (t, *J* = 11.3 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6 δ 179.0, 163.6, 62.0, 61.9, 31.3, 31.1, 24.2, 24.0, 21.5. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1007.8. ESI-MS (positive ion mode): 515.2 *m/z* [M+Na]$^+$; calcd for $C_{10}H_{17}ClN_2O_6PtNa$ *m/z* 515.0 [M+Na]$^+$

***trans*-[Pt(DACH)(ox)(acetato)Br] (12b)**.[8]

Pt(IV) complexes **1c**, **3c** to **12c** were synthesized by using the same method as the synthesis of Pt(IV) complexes **1a**, **3a** to **12a** (Scheme S2).

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(boc-β-alaninato)OH] (1c)**. Yield: 38%, 52 mg (0.10 mmol). Anal. Calcd for: $C_8H_{21}Cl_2N_3O_5Pt$ (505.26): C, 19.02; H,4.19; N, 8.32. Found: C, 19.38; H, 4.37; N, 7.88. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.62 (s, 1H), 6.19 – 5.67 (m, 6H), 3.11 (q, *J* = 6.8 Hz, 2H), 2.28 (t, *J* = 7.0 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 179.3, 155.9, 78.0, 37.6, 37.2, 28.7. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1044.7. ESI-MS (positive ion mode): 505.1 m/z [M+H]$^+$; calcd for $C_8H_{22}Cl_2N_3O_5Pt$ m/z 505.1 [M+H]$^+$.

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(boc-β-alaninato)Cl] (3c)**. Yield: 72%, 107 mg (0.20 mmol). Anal. Calcd for: $C_8H_{20}Cl_3N_3O_4Pt$ (523.70): C, 18.35; H, 3.85; N, 8.02. Found: C, 18.60; H, 3.69; N, 8.25. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.67 (t, *J* = 5.8 Hz, 1H), 6.21–6.05 (m, 6H), 3.12 (q, *J* = 6.6 Hz,

2H), 2.34 (td, *J* = 7.1, 2.3 Hz, 2H), 1.37 (d, *J* = 4.0 Hz, 9H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.6, 155.9, 78.1, 37.5, 36.9, 28.7. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 543.6. ESI-MS (negative ion mode): 522.3 m/z [M-H]$^-$; calcd for $C_8H_{19}Cl_3N_3O_4Pt$ m/z 522.7 [M-H]$^-$.

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(boc-β-alaninato)Br] (4c).** Yield: 60%, 96 mg (0.17 mmol). Anal. Calcd for: $C_8H_{20}BrCl_2N_3O_4Pt$ (568.13): C, 16.91; H, 3.55; N, 7.40. Found: C, 16.66; H, 3.57; N, 6.87. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.68 (s, 1H), 6.37 – 5.97 (m, 6H), 3.17 – 2.98 (m, 2H), 2.34 (t, *J* = 6.9 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.8, 155.9, 78.1, 37.5, 36.9, 28.7. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 274.0. ESI-MS (positive ion mode): 568.2 m/z [M+H]$^+$; calcd for $C_8H_{21}BrCl_2N_3O_4Pt$ m/z 568.0 [M+H]$^+$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)OH] (5c)**. Yield: 39%, 63 mg (0.11 mmol) Anal.Calcd for: $C_{14}H_{27}N_3O_9Pt$ (576.14) C, 29.17; H, 4.72; N, 7.29. Found: C, 29.06; H, 5.29; N, 7.08. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.64 (t, *J* = 5.6 Hz, 1H), 6.17 – 5.63 (m, 6H), 3.10 (q, *J* = 6.7 Hz, 2H), 2.54 (d, *J* = 7.9 Hz, 2H), 2.50 – 2.45 (m, 2H), 2.28 (t, *J* = 7.0 Hz, 2H), 1.79 (p, *J* = 8.0 Hz, 2H), 1.70 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.7, 177.0, 155.9, 78.0, 56.2, 37.5, 37.0, 32.6, 31.6, 28.7, 16.3. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1752.4. ESI-MS (positive ion mode): 599.1 m/z [M+Na]$^+$; calcd for $C_{14}H_{27}N_3O_9PtNa$ m/z 599.1 [M+Na]$^+$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)F] (6c)**. Yield: 59%, 97 mg (0.17 mmol) Anal.Calcd for: $C_{14}H_{26}FN_3O_8Pt$ (578.46) C, 29.07; H, 4.53; N, 7.26. Found: C, 28.90; H, 4.23; N, 7.13. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.67 (d, *J* = 6.7 Hz, 1H), 6.39–6.13 (m, 6H), 3.07 (t, *J* = 7.1 Hz, 2H), 2.53 (s, 4H), 2.32 (d, *J* = 7.6 Hz, 2H), 1.78 (t, *J* = 8.4 Hz, 2H), 1.37 (s, 9H).^{13}C NMR (151 MHz, DMSO-d_6) δ 178.4, 176.7, 155.9, 78.1, 56.2, 56.1, 37.3, 31.4, 28.7, 16.3. ^{19}F NMR (565 MHz, DMSO-d_6) δ -336.3 (s + d, *J* = 1304.0). ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 2370.0 (d, *J* = 1344.1 Hz). ESI-MS (negative ion mode): 577.5 m/z [M-H]$^-$; calcd for $C_{14}H_{25}FN_3O_8Pt$ m/z 577.5 [M-H]$^-$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)Cl] (7c)**. Yield: 56%, 95 mg (0.16 mmol). Anal. Calcd for: $C_{14}H_{26}ClN_3O_8Pt$ (594.91) C, 28.27; H, 4.41; N, 7.06. Found: C, 28.37; H, 4.48; N, 7.00. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.69 (t, *J* = 5.7 Hz, 1H), 6.25–6.00 (m, 6H), 3.09 (q, *J* = 6.6 Hz, 2H), 2.52 (d, *J* = 4.0 Hz, 4H), 2.33 (t, *J* = 6.9 Hz, 2H), 1.80 (h, *J* = 7.9, 7.1 Hz, 2H), 1.36 (s, 9H).^{13}C NMR (151 MHz, DMSO-d_6) δ 177.8, 176.8, 155.9, 78.1, 56.2, 37.3, 36.5, 32.7, 31.5, 28.7, 16.2. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1358.8. ESI-MS (negative ion mode): 593.3 m/z [M-H]$^-$; calcd for $C_{14}H_{25}ClN_3O_8Pt$ m/z 593.9 [M-H]$^-$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)Br] (8c)**. Yield: 52%, 94 mg (0.15 mmol). Anal.Calcd for: $C_{14}H_{26}BrN_3O_8Pt$ (639.36) C, 26.30; H, 4.10; N, 6.57. Found: C, 26.60; H, 3.98; N, 6.44. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.70 (d, *J* = 6.6 Hz, 1H), 6.27–6.02 (dd, *J* = 64.1, 37.4 Hz, 6H), 3.10 (q, *J* = 6.8 Hz, 2H), 2.56–2.54 (m, 4H), 2.33 (d, *J* = 7.1 Hz, 2H), 1.81 (t, *J* = 8.2 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 177.9, 176.8, 173.3, 155.9, 78.1, 56.3, 28.7, 16.1. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1142.9. ESI-MS (negative ion mode): 638.4 m/z [M-H]$^-$; calcd for $C_{14}H_{25}BrN_3O_8Pt$ m/z 638.4 [M-H]$^-$.

***trans*-[Pt(DACH)(ox)(boc-β-alaninato)OH] (9c)**. Yield: 35%, 59 mg (0.10 mmol). Anal. Calcd for: $C_{16}H_{29}N_3O_9Pt$ (602.16): C, 31.90; H, 4.85; N, 6.97. Found: C, 31.93; H, 5.05; N, 6.74. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.33 (s, 1H), 8.12 (s, 1H), 7.83 (s, 1H), 7.12 (s, 1H), 6.70 (t, *J* = 5.6 Hz, 1H), 3.07 (q, *J* = 7.1 Hz, 2H), 2.63 – 2.53 (m, 2H), 2.32 (t, *J* = 8.0 Hz, 2H), 2.07 (dd, *J* = 24.9, 12.6 Hz, 2H), 1.51 – 1.44 (m, 4H), 1.37 (s, 9H), 1.13 (t, *J* = 10.3 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 180.3, 164.3, 155.9, 78.1, 61.8, 60.6, 37.6, 37.4, 31.3, 31.2, 28.7, 24.2, 24.1. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1411.7. ESI-MS (positive ion mode): 625.3 m/z [M+Na]$^+$; calcd for $C_{16}H_{29}N_3O_9PtNa$ m/z 625.2 [M+Na]$^+$.

***trans*-[Pt(DACH)(ox)(boc-β-alaninato)F] (10c)**. Yield: 65%, 112 mg (0.18 mmol). Anal. Calcd for: $C_{16}H_{28}FN_3O_8Pt$ (604.50): C, 31.79; H, 4.67; N, 6.95. Found: C, 31.53; H, 4.71; N, 6.79. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (s, 1H), 8.27 (s, 1H), 7.96 (d, *J* = 46.5 Hz, 2H), 6.77 (s, 1H), 3.07 (s, 2H), 2.53 (s, 2H), 2.36 (d, *J* = 7.6 Hz, 2H), 2.06 (t, *J* = 15.7 Hz, 2H), 1.52–1.49 (m, 4H), 1.36 (t, *J* = 2.1 Hz, 9H), 1.13 (d, *J* = 10.8 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.8, 164.1, 156.0, 78.2, 61.5, 61.2, 37.1, 30.9, 30.8, 28.7, 24.1, 24.0. ^{19}F NMR (565 MHz, DMSO-d_6) -327.8 (s + d, *J* = 1278.0 Hz). ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 2026.8 (d, *J* = 1307.5 Hz). ESI-MS (negative ion mode): 603.4 m/z [M-H]$^-$; calcd for $C_{16}H_{27}FN_3O_8Pt$ m/z 603.5 [M-H]$^-$.

***trans*-[Pt(DACH)(ox)(boc-β-alaninato)Cl] (11c)**. Yield: 74%, 130 mg (0.21 mmol). Anal. Calcd for: $C_{16}H_{28}ClN_3O_8Pt$ (620.95): C, 30.95; H, 4.55; N, 6.77. Found: C, 31.14; H, 4.61; N, 6.72. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.33–8.16 (m, 3H), 7.63 (t, *J* = 10.4 Hz, 1H), 6.78 (t, *J* = 5.9 Hz, 1H), 3.08–3.10 (m, 2H), 2.54 (s, 2H), 2.40–2.37 (m, 2H), 2.11–2.08 (m, 1H), 2.02 (d, *J* = 12.5 Hz, 1H), 1.56–1.48 (m, 4H), 1.36 (s, 9H), 1.13 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.6, 163.8, 163.8, 156.0, 78.2, 62.1, 61.6, 37.7, 37.2, 31.3, 31.0, 28.7, 24.0, 24.0. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1013.7. ESI-MS (negative ion mode): 620.4 m/z [M-H]$^-$; calcd for $C_8H_{19}Cl_3N_3O_4Pt$ m/z 620.0 [M-H]$^-$.

***trans*-[Pt(DACH)(ox)(boc-β-alaninato)Br] (12c)**. Yield: 63%, 119 mg (0.18 mmol). Anal. Calcd for: $C_{16}H_{28}BrN_3O_8Pt$ (665.40): C, 28.88; H, 4.24; N, 6.32. Found: C, 28.86; H, 3.94; N, 6.02. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, *J* = 24.1 Hz, 3H), 7.59 (t, *J* = 10.1 Hz, 1H), 6.79 (d, *J* = 6.7 Hz, 1H), 3.09 (d, *J* = 7.0 Hz, 2H), 2.39–2.36 (m, 2H), 2.10 (d, *J* = 12.3 Hz, 1H), 2.02 (d, *J* = 12.4 Hz, 1H), 1.50–1.48 (m, 4H), 1.37 (s, 9H), 1.13 (m, 2H).^{13}C NMR (151 MHz, DMSO-d_6) δ 178.9, 163.7, 163.5, 156.0, 78.2, 63.2, 62.6, 61.7, 37.9, 37.2, 31.6, 28.7, 24.0. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 783.4. ESI-MS (negative ion mode): 664.3 m/z [M-H]$^-$; calcd for $C_{16}H_{27}BrN_3O_8Pt$ m/z 664.4 [M-H]$^-$.

DCA containing Pt(IV) complexes **14d** and **15d** were synthesized by using highly diluted DCA anhydride solution (**Scheme S4**). Pt(IV) complexes **5** (0.28 mmol, 113 mg) and **9** (0.28 mmol, 121 mg) were separately suspended in 10 mL DMF. DCA anhydride (0.22 mmol, 38 mg) was added into the mixture. The mixtures were stirred for 48 h at room temperature. After that, the unreacted Pt(IV) complexes were removed by centrifuge. The most of DMF was removed in vaccum and the residual was washed by 30 mL Et_2O for twice. After drying in vaccum, the Pt(IV) complexes **14d** and **15d** were obtained as white solid. A similar method has also been applied to the synthesis of cisplatin-based Pt(IV) complex **13d**, however, it could not be obtained.

DCA containing Pt(IV) complexes **13e**, **13g, 14e** to **14g**, and **15e** to **15g** were synthesized by the reaction between DCA anhydride and corresponding Pt(IV) complexes (**Scheme S4**). Pt(IV) complexes (0.28 mmol, which is 94 mg of **1**, 105 mg of **1b**, 113 mg of **5**, 125 mg of **5b**, 114 mg of **6**, 121 mg of **9**, 132 mg of **9b**, 121 mg of **10**) were separately added to 2 mL DCA anhydride. The mixtures were stirred overnight at

room temperature. After that, the mixtures were added to 30 mL Et_2O to induce precipitate. The precipitate was collected and washed with 30 Et_2O for twice. All the final products were obtained as white solid. Pt(IV) complex **13f** could not be obtained because we were unable to obtain cisplatin-based fluorinated Pt(IV) complex **2**.

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(DCA)(acetato)] (13e)**. Yield: 88%, 120 mg (0.25 mmol). Anal. Calcd for: $C_4H_{10}Cl_4N_2O_4Pt$ (487.02): C, 9.86; H, 2.07; N, 5.75. Found: C, 9.45; H, 1.91; N, 5.77. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.76 – 6.32 (m, 6H), 6.47 (s, 1H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.6, 171.0, 66.3, 23.0. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1226.8. ESI-MS (positive ion mode): 487.1 m/z $[M+H]^+$; calcd for $C_4H_{11}Cl_4N_2O_4Pt$ m/z 486.9 $[M+H]^+$.

***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(DCA)$_2$] (13g)**.[12]

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)OH] (14d)**. Yield: 28%, 40 mg (0.08 mmol). Anal. Calcd for: $C_8H_{14}Cl_2N_2O_7Pt$ (516.19): C, 18.61; H, 2.73; N, 5.43. Found: C, 18.21; H, 2.74; N, 4.94. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.40 (s, 1H), 6.22 – 5.69 (m, 5H), 2.61 – 2.52 (m, 4H), 2.18 (s, 0H), 1.79 (p, J = 8.0 Hz, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.9, 170.3, 67.8, 56.1, 32.6, 31.5, 16.3. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1768.8. ESI-MS (negative ion mode): 515.2 m/z $[M-H]^-$; calcd for $C_8H_{13}Cl_2N_2O_7Pt$ m/z 515.0 $[M-H]^-$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)(acetato)] (14e)**. Yield: 81%, 126 mg (0.22 mmol). Anal. Calcd for: $C_{10}H_{16}Cl_2N_2O_8Pt$ (558.23): C, 21.52; H, 2.89; N, 5.02. Found: C, 21.90; H, 3.12; N, 4.92. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.45 (s, 1H), 6.44 – 6.09 (m, 6H), 2.53 (d, J = 7.4 Hz, 2H), 2.48 (d, J = 8.2 Hz, 2H), 1.91 (s, 3H), 1.81 (p, J = 8.0 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 177.5, 176.7, 169.7, 66.3, 56.0, 49.1, 32.0, 31.2, 22.6, 16.2. ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 1966.2. ESI-MS (negative ion mode): 557.2 m/z $[M-H]^-$; calcd for $C_{10}H_{15}Cl_2N_2O_8Pt$ m/z 557.0 $[M-H]^-$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)F] (14f)**. Yield: 81%, 117 mg (0.22 mmol). Anal. Calcd for: $C_8H_{13}Cl_2FN_2O_6Pt$ (518.18): C, 18.54; H, 2.53; N, 5.41. Found: C, 18.17; H, 2.24; N, 5.13. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.49 (s, 1H), 6.48 – 6.19 (m, 6H), 2.55 (t, J = 8.0 Hz, 2H), 2.49 (d, J = 10.5 Hz, 2H), 1.94 – 1.72 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.5, 170.3, 65.1, 56.1, 32.4, 31.2, 16.3. ^{19}F NMR (565 MHz, DMSO-d_6) δ -342.4 (s+d, J = 1446.4 Hz). ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 2421.2 (d, J = 1669.8 Hz). ESI-MS (positive ion mode): 519.0 m/z $[M+H]^+$; calcd for $C_8H_{14}Cl_2FN_2O_6Pt$ m/z 519.0 $[M+H]^+$.

***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)$_2$] (14g)**.[31]

***trans*-[Pt(DACH)(ox)(DCA)OH] (15d)**, ***trans*-[Pt(DACH)(ox)(DCA)(acetato)] (15e)**, and ***trans*-[Pt(DACH)(ox)(DCA)$_2$] (15g)** were obtained by exactly following the reported method.[31]

***trans*-[Pt(DACH)(ox)(DCA)F] (15f).** Yield: 72%, 110 mg (0.20 mmol) Anal.Calcd for: $C_{10}H_{15}Cl_2FN_2O_6Pt$ (544.22) C, 22.07; H, 2.78; N, 5.15. Found: C, 22.26; H, 2.72; N, 4.96. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.65 – 7.77 (m, 4H), 6.53 (s, 1H), 2.57 (dd, J = 23.1, 12.8 Hz, 2H), 2.20 – 1.97 (m, 2H), 1.67 – 1.35 (m, 4H), 1.12 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 170.1, 163.8, 65.7, 61.5, 61.3, 30.8, 30.6, 24.1, 24.0. ^{19}F NMR (565 MHz, DMSO-d_6) δ -332.8 (s+d, J = 1418.2 Hz). ^{195}Pt NMR (129 MHz, DMSO-d_6) δ 2047.7 (d, J = 1343.9 Hz). ESI-MS (positive ion mode): 567.0 m/z $[M+Na]^+$; calcd for $C_{10}H_{15}Cl_2FN_2O_6PtNa$ m/z 567.0 $[M+Na]^+$.

Stability test.

The hydrolytic stability of Pt(IV) complexes which contain axial succinato (**a**), acetato (**b**) and boc-β-alaninato (**c**) ligand (R_1) was tested by ^{1}H NMR. Pt(IV) complexes (**1a-c**, **3a-c** to **12a-c**) were separately dissolved in phosphate buffer (50 mM, pH 7.4, D_2O) with a final concentration of 2±1 mM. The resulting solutions were transferred to NMR tubes, protected from light by aluminum foil, and incubated at 37 °C in water bath. At each time point of 0.08, 2, 4, 6, 8, 12, and 24 h, the ^{1}H NMR spectra of these Pt(IV) complexes were obtained. All the experiments were repeated once and the amount of remaining axial Pt-R_2 bond (%) was determined by the average integration ratio of the original carboxylato ligand and its resulting free carboxylate anion (the representative results are shown in Figures S1-S36). Under pseudo first-order reaction conditions where there is excess amount of phosphate to maintain the pH value, the half-lives ($t_{1/2}$) of axial Pt(IV)-R_2 bond in these Pt(IV) complexes, which are independent of the concentration of Pt(IV) complexes, were calculated and showed in Figure 2. Furthermore, from ^{1}H NMR, the hydrolysis of Pt(IV)-R_1 (R_1 = OH, F, Cl, Br) bond was only observed in the fluorinated and oxaliplatin-based Pt(IV) complexes **10a**-**10c**; we did not observe the hydrolysis of equatorial oxalato ligand for oxaliplatin-based Pt(IV) complexes **9a**, **9b**, and **9c** from our NMR tests (Figures S9, S21, and S33).

Due to the proton exchange reaction between axial DCA ligand(s) and D_2O which finally leads to the significantly decreased signal of DCA ligand in ^{1}H NMR, the hydrolytic stability of DCA-containing Pt(IV) complexes **13e**, **13g, 14d** to **14g**, and **15d** to **15g** were tested by RP-HPLC. All these DCA-containing Pt(IV) complexes were dissolved in phosphate buffer (50 mM, pH 7.4, H_2O) with a final concentration of 0.1 to 1.0 mM. The resulting solutions were protected from light by aluminum foil and incubated at 37 °C in water bath. At each time point of 0, 2, 4, 6, 8, 12 and 24 h, the samples were injected to RP-HPLC and HPLC chromatograms of these Pt(IV) complexes were obtained. All the experiments were repeated once and the decomposition of original Pt(IV) complexes was determined by the average change of peak area compared with the time 0 h (the representative results are shown in Figures S49-S59). Under pseudo first-order reaction conditions where there is excess amount of phosphate to maintain the pH value, the half-lives ($t_{1/2}$) of these DCA-containing Pt(IV) complexes, which are independent of the concentration of Pt(IV) complexes, were calculated and showed in Figure 4.

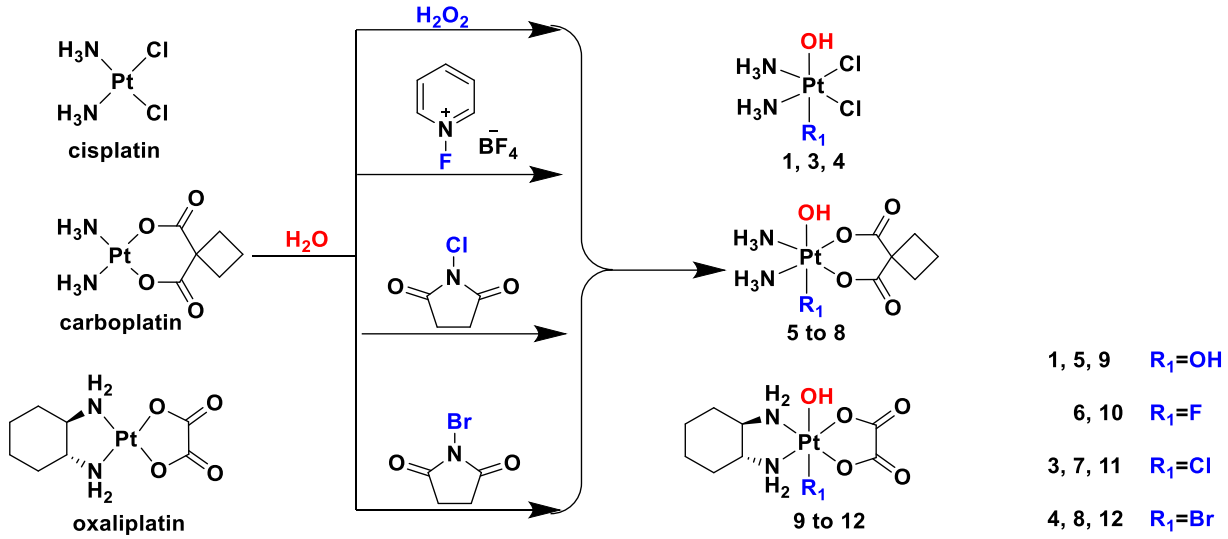
The stability of DCA-containing Pt(IV) complexes **13e** to **15e** in fetal bovine serum (FBS, pH 7.4) was tested by HPLC. Pt(IV) complexes **13e** to **15e** were separately dissolved in FBS with a final concentration of 0.1 to 1.0 mM. The resulting solutions were protected from light by aluminum foil and incubated at 37 °C in a water bath. At each time point of 0, 2, 4, 6, 8, 12, and 24 h, 100 µL FBS solution was taken and added to 400 µL MeOH to precipitate the proteins in FBS. After centrifuging and filtering, the clear supernatant was injected to RP-HPLC and HPLC chromatograms of these Pt(IV) complexes were obtained. All the experiments were repeated once and the decomposition of original Pt(IV) complexes was determined by the average change of peak area compared with the time 0 h. Under pseudo-first-order reaction

conditions where there is constant pH, the half-lives ($t_{1/2}$) of these DCA-containing Pt(IV) complexes, which are independent of the concentration of Pt(IV) complexes, were calculated (the representative results are shown in Figures S60-S63).

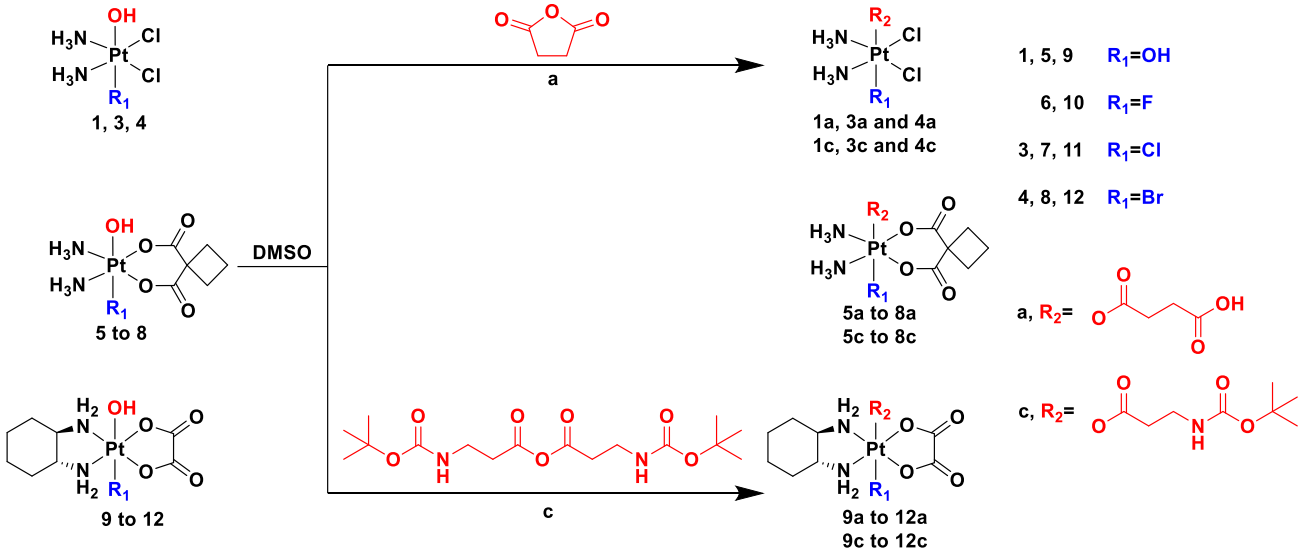
Computational Details

The Gibbs free energy barriers to hydrolyze the Pt(IV)-acetato bond (reaction pathway 1) for the carboplatin-based Pt(IV) complexes **6b-8b** and oxaliplatin-based Pt(IV) complexes **10b-12b** and the Pt(IV)-halide bond (reaction pathway 2) for the oxaliplatin-based Pt(IV) complexes **10b-12b** (Scheme S5) have been examined theoretically by using density functional theory at the M06-L/Aug-cc-pVTZ level of theory by using Gaussian 09 (Rev. D.01) package.[62]

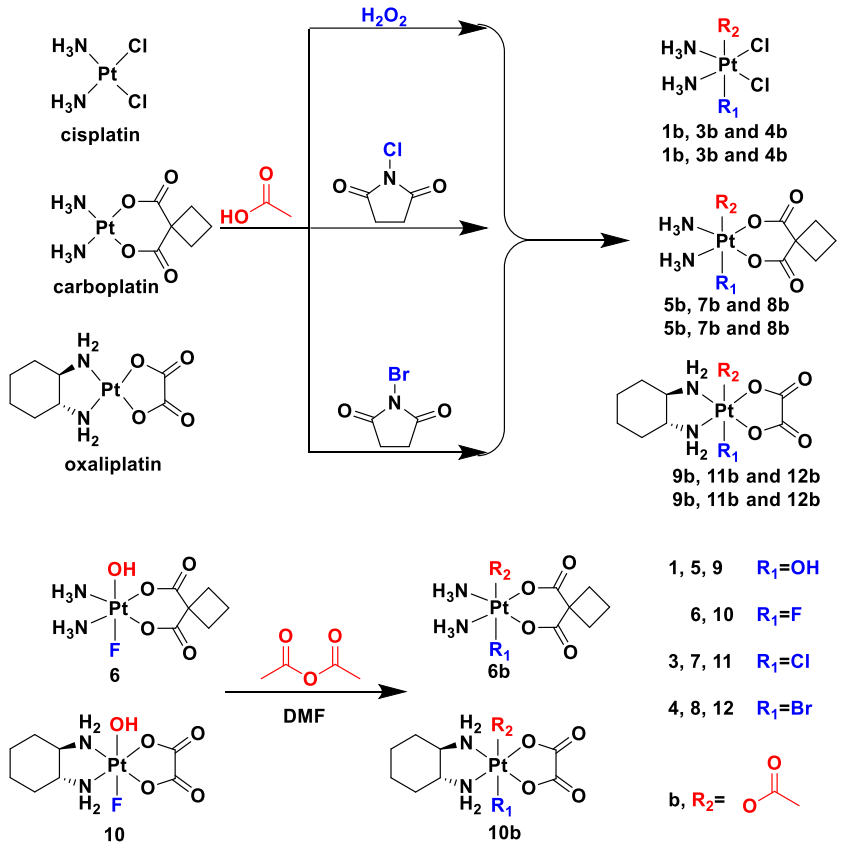
All geometries were optimized in an implicit aqueous environment described by the polarizable continuum model (PCM). Harmonic frequency analyses were performed for all optimized geometries to evaluate the zero-point corrections and thermal corrections to enthalpies and Gibbs free energies. No or one imaginary frequency was obtained, respectively, for all structures at local minima or for all transition structures located on a potential energy surface. The correct directions of the displacement vectors of the imaginary frequency for each transition structure pointing toward the associated reactant and product were confirmed with intrinsic reaction coordination (IRC) analyses. All Gibbs free energies at 298 K, $\Delta G°298$ (in kJ mol^{-1}), were reported relative to the sum of the corresponding free energies of a complex and a H_2O molecule (**R**). Charge densities were evaluated with Natural Bond Orbital (NBO) analyses.



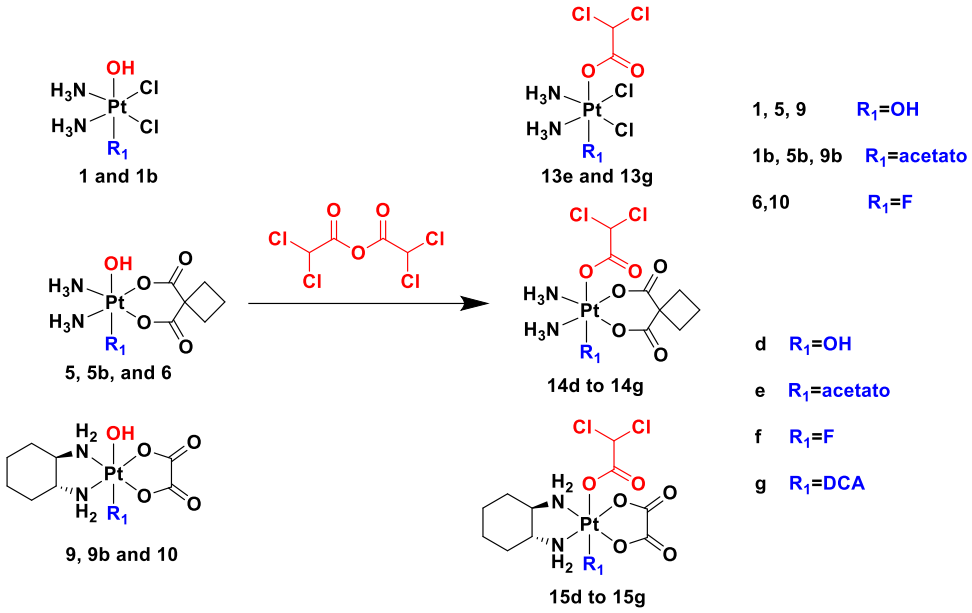
Scheme S1. Oxidation of three FDA approved Pt(II) drugs to their corresponding Pt(IV) complexes.



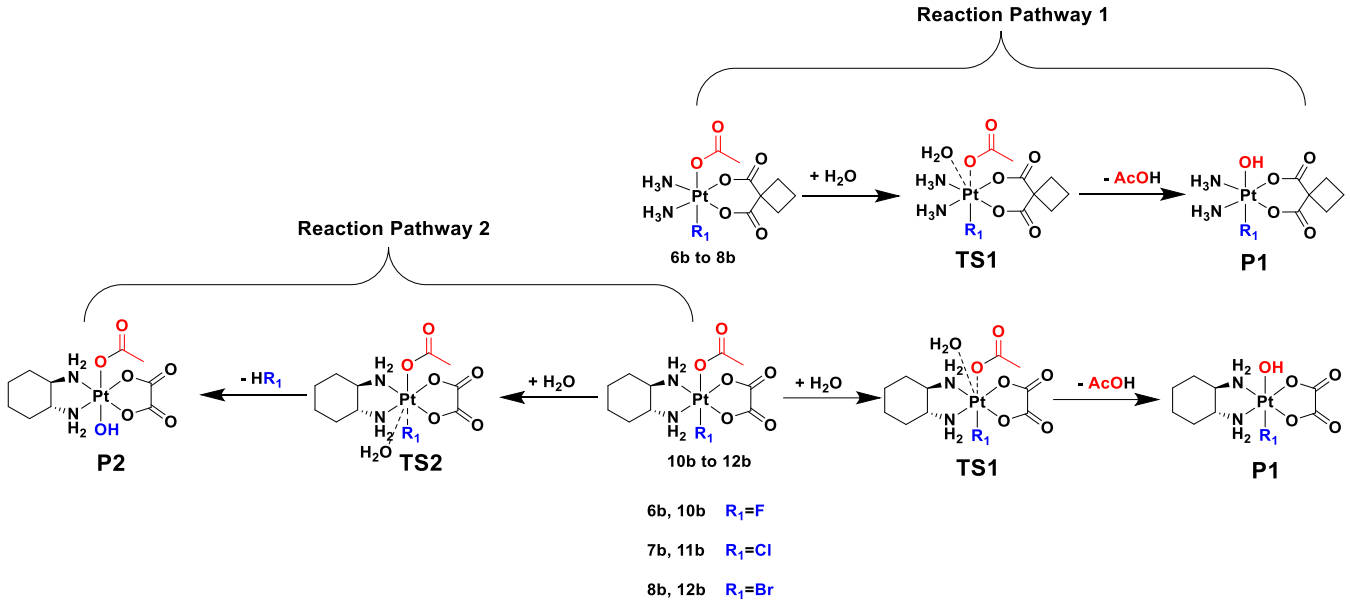
Scheme S2. Synthesis of Pt(IV) complexes **1a**, **3a** to **12a** and **1c**, **3c** to **12c** which contain axial succinato ligand (**a**) or boc-β-alaninato ligand (**c**) by the reaction between Pt(IV) complexes **1**, **3** to **12** and the corresponding anhydrides.



Scheme S3. Synthesis of Pt(IV) complexes **1b**, **3b** to **12b** which contain axial acetato ligand (**b**).



Scheme S4. Synthesis of Pt(IV) complexes **13e**, **13g**, **14d** to **14g**, and **15d** to **15g** which contain axial DCA ligand(s).



Scheme S5. Analyzed hydrolysis reaction steps by DFT calculation.

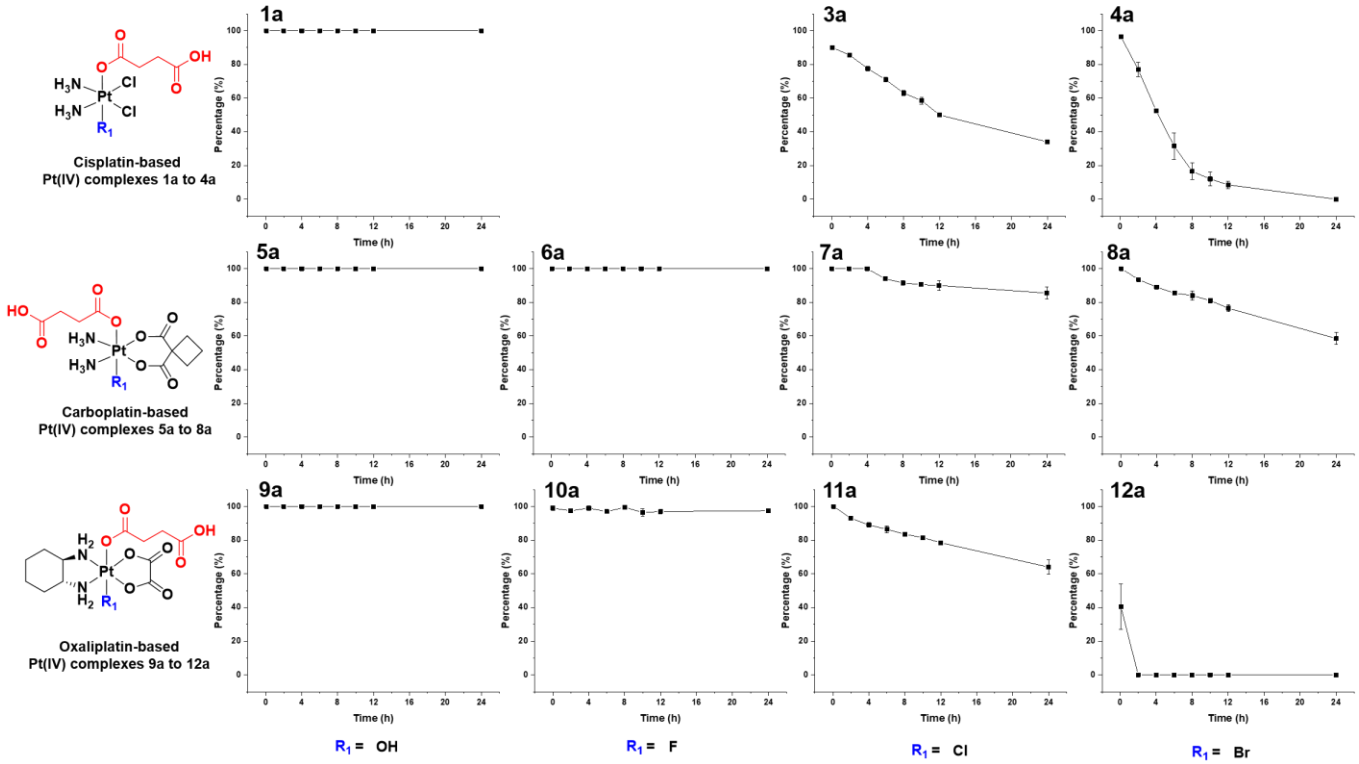


Figure S1. Hydrolytic stability of Pt(IV) complexes **1a**, **3a** to **12a** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h. All the results are calculated from two independent experiments.

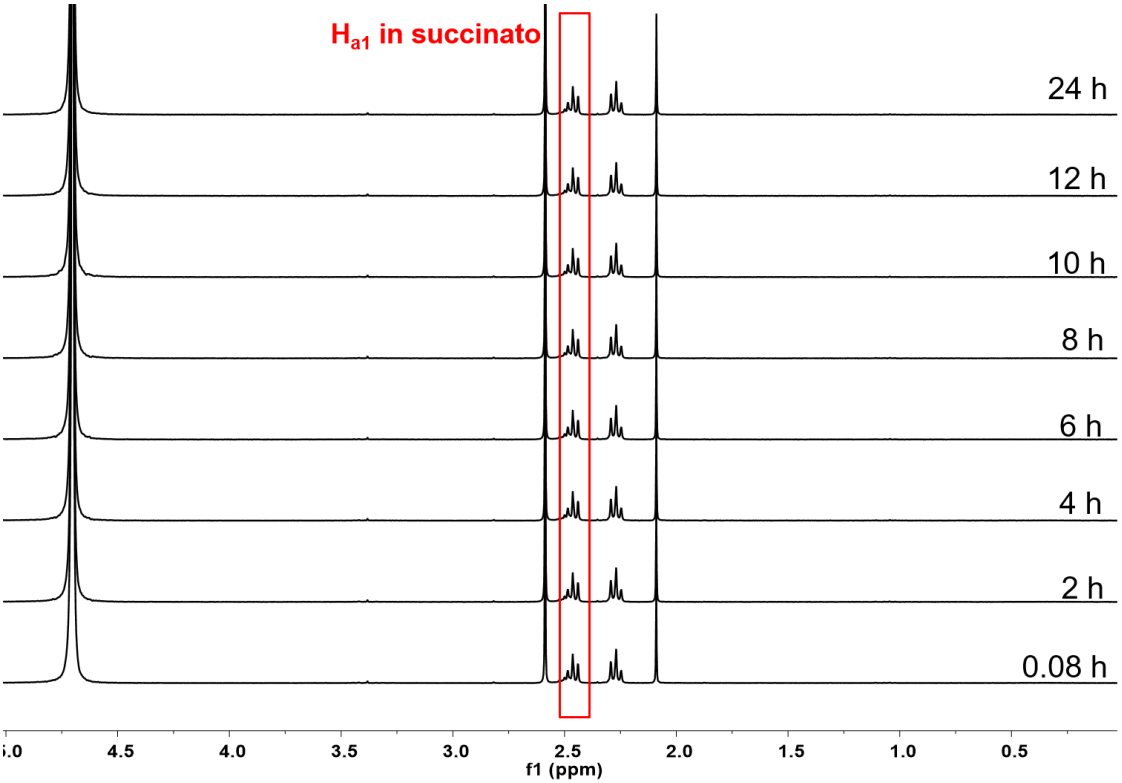


Figure S2. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(succinato)OH] (1a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

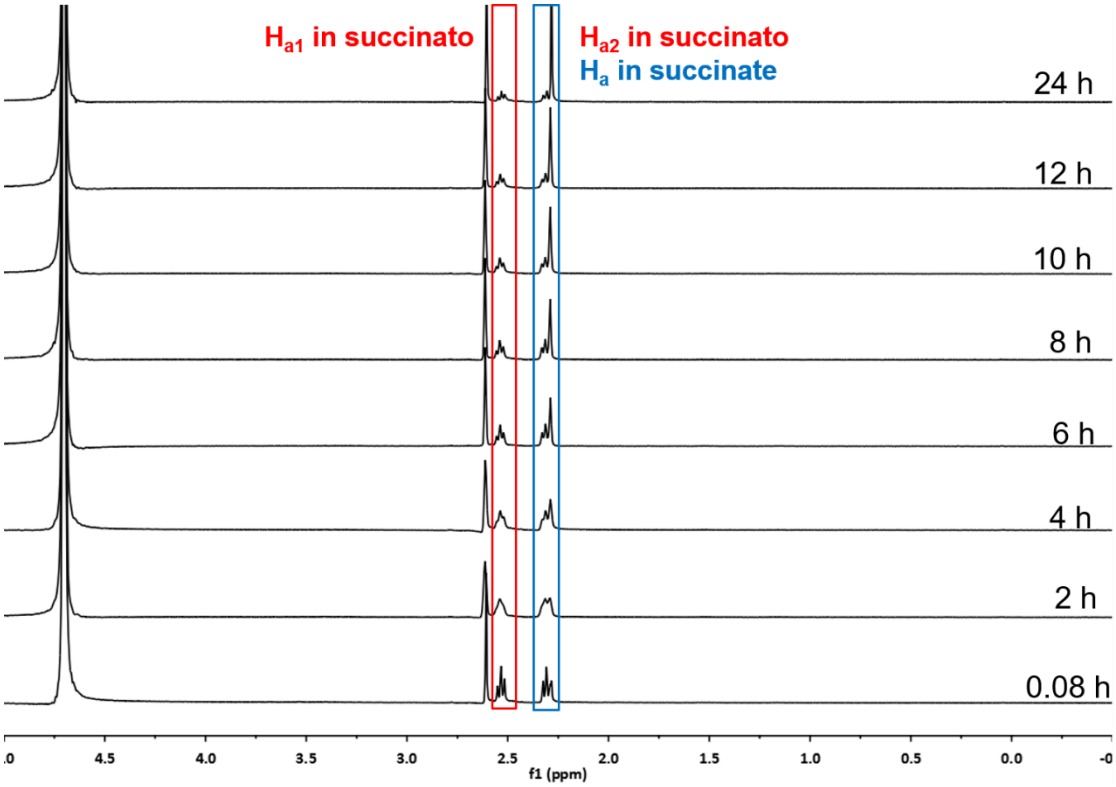


Figure S3. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(succinato)Cl] (3a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

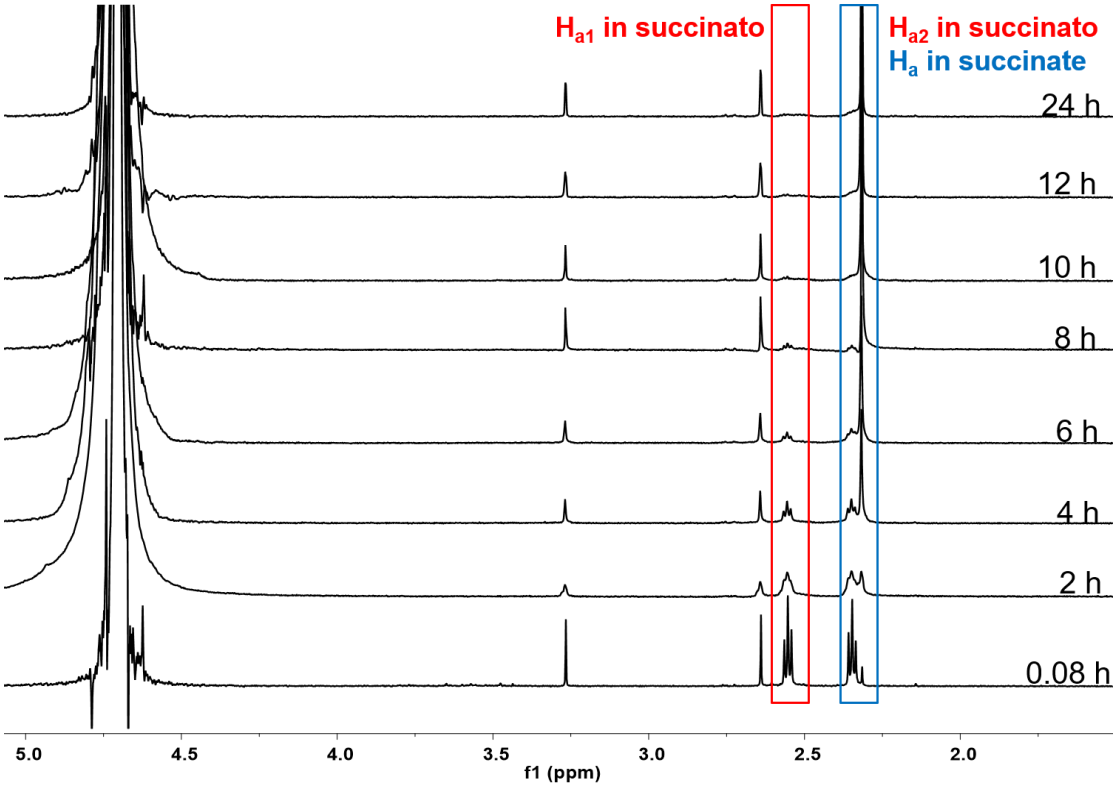


Figure S4. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(succinato)Br] (4a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

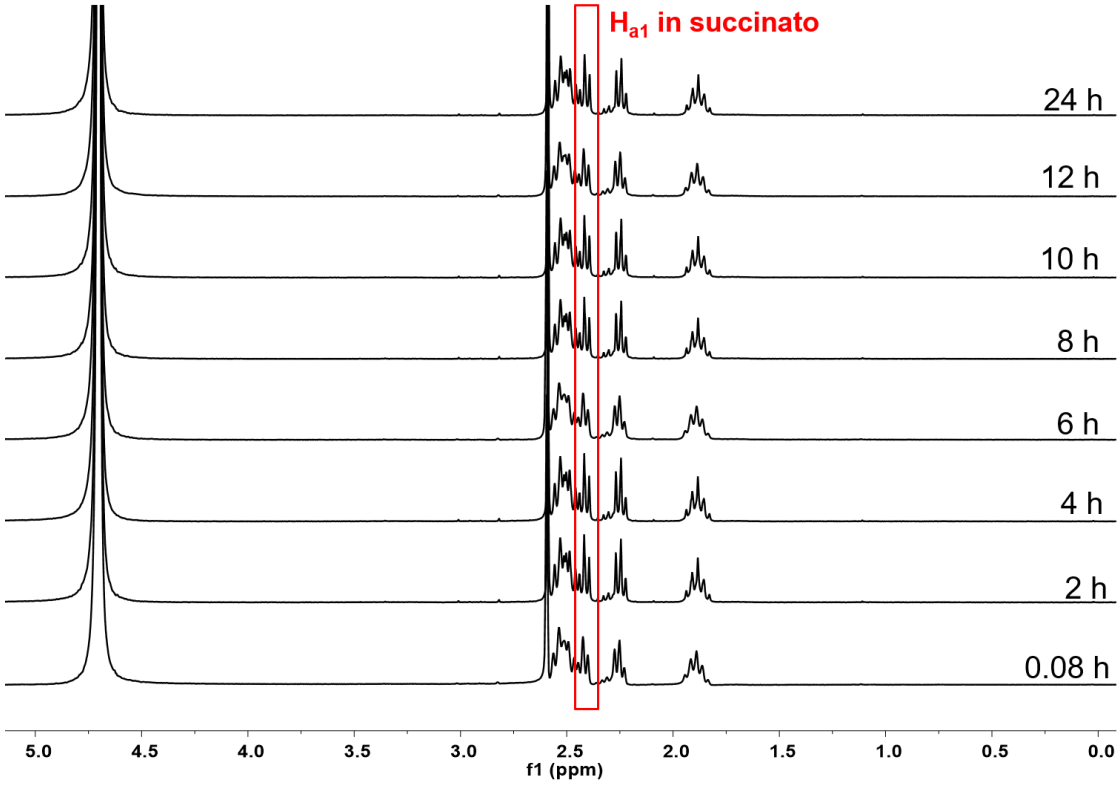


Figure S5. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)OH] (5a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

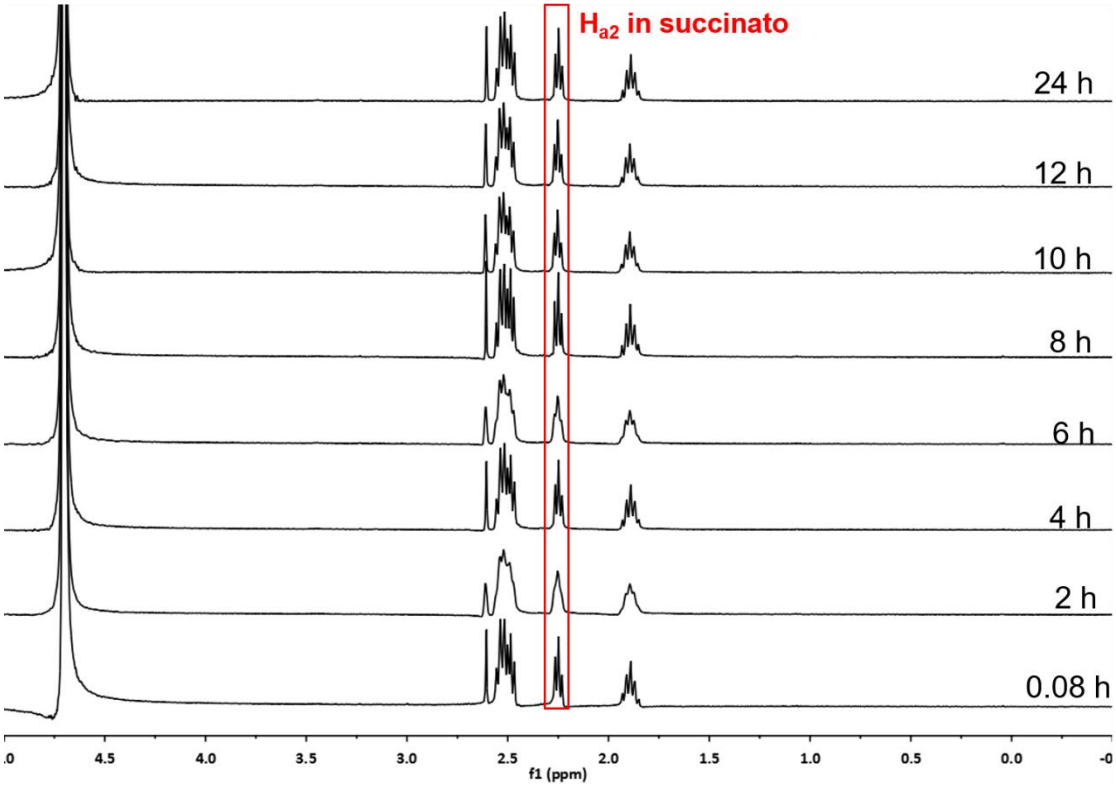


Figure S6. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)F] (6a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

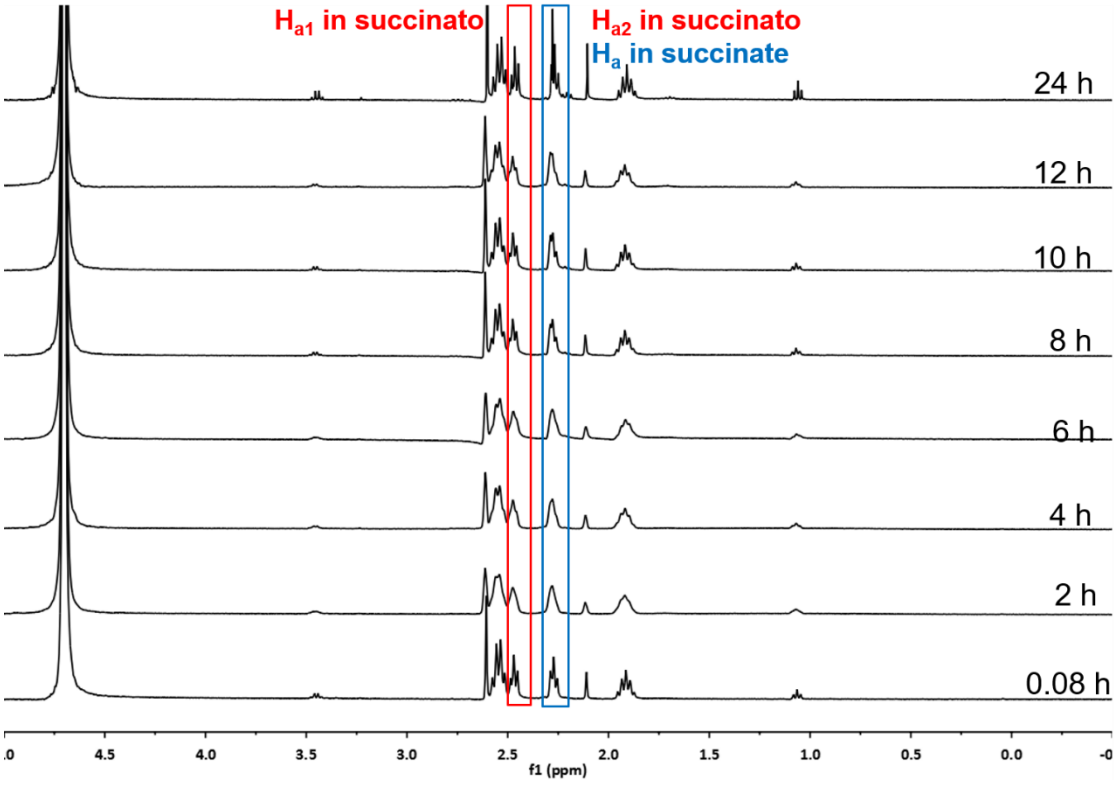


Figure S7. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)Cl] (7a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

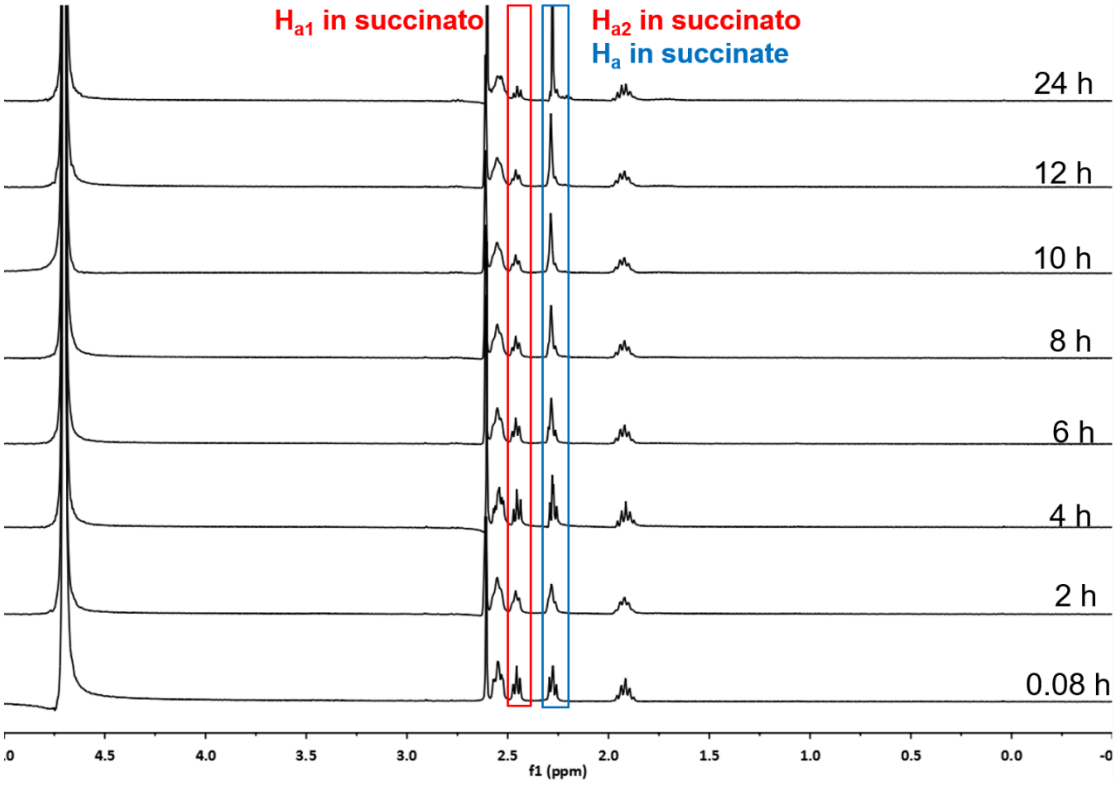


Figure S8. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)Br] (8a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

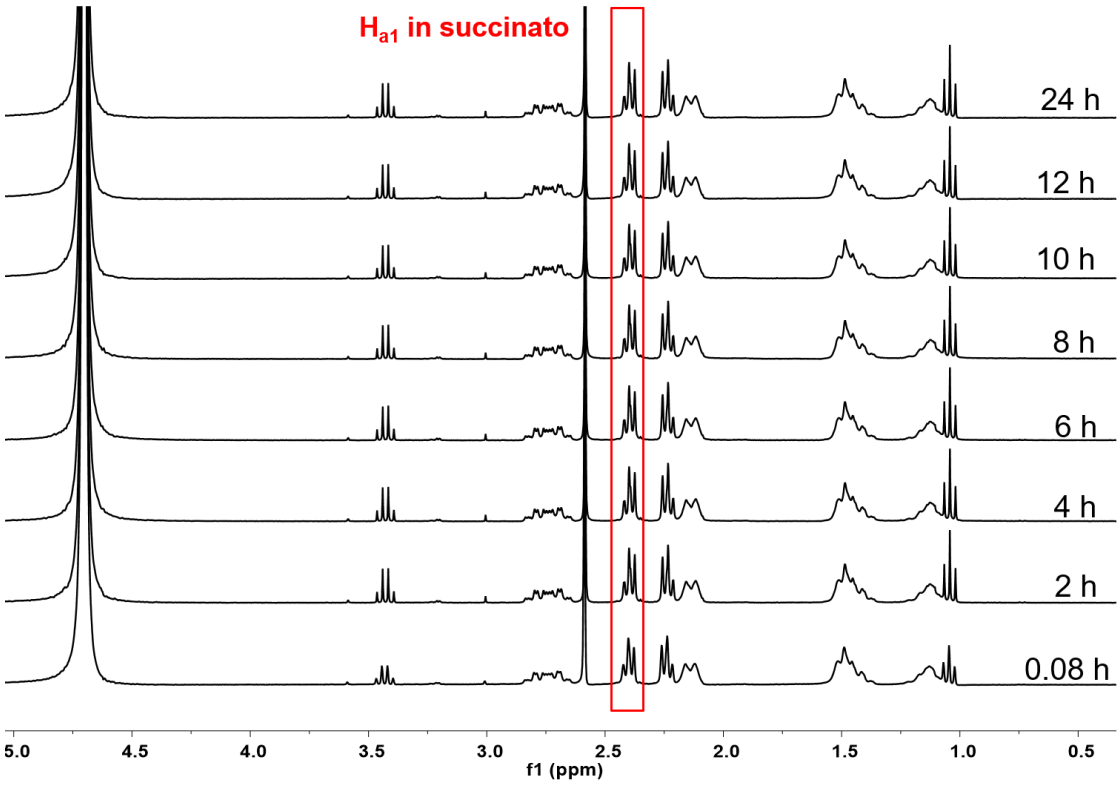


Figure S9. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(succinato)OH] (9a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

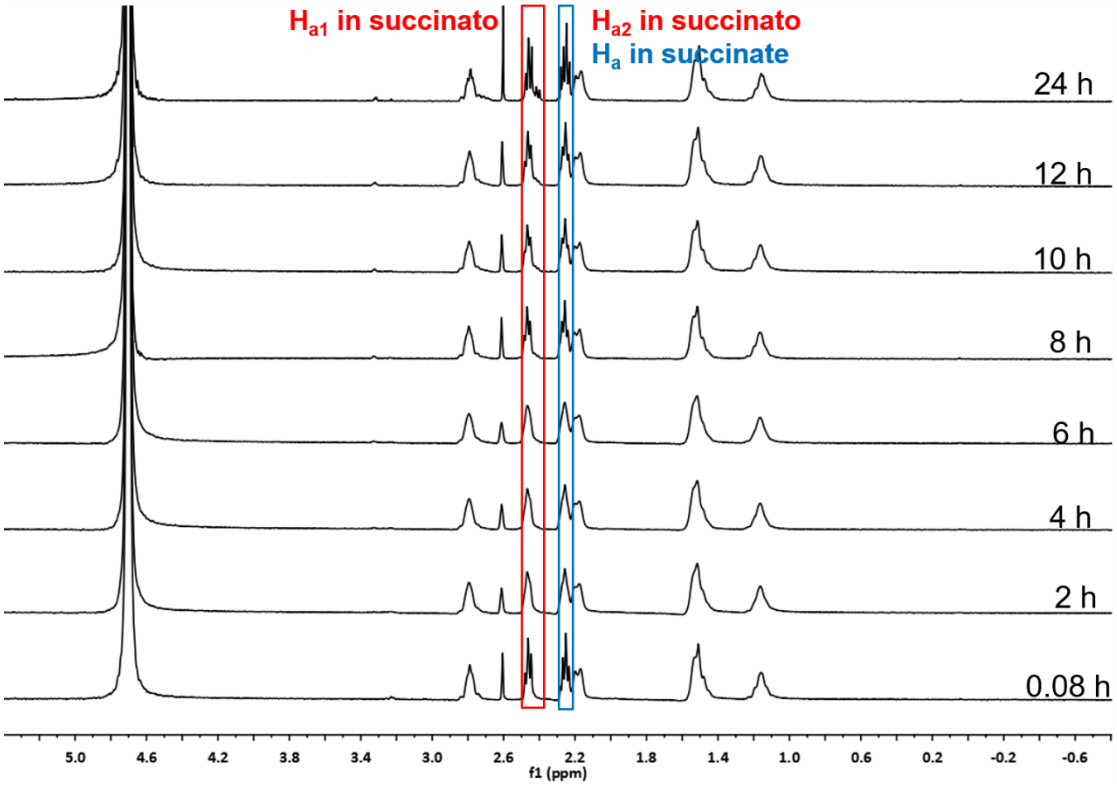


Figure S10. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(succinato)F] (10a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

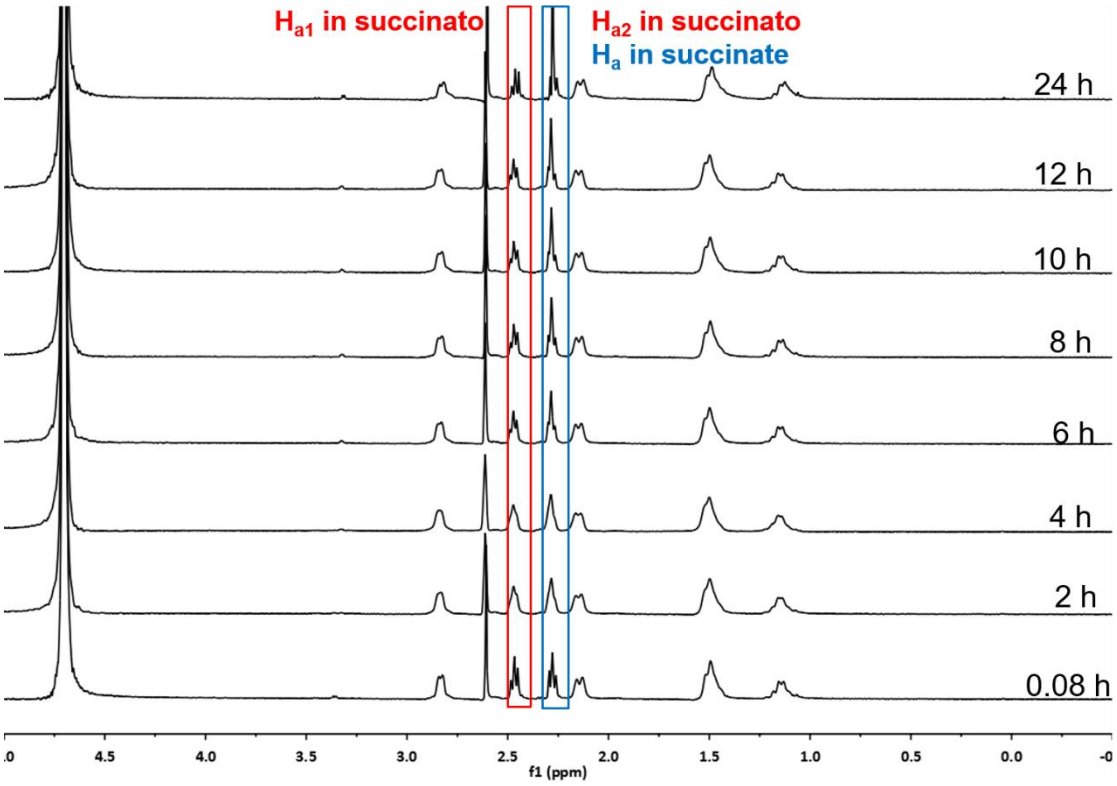


Figure S11. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(succinato)Cl] (11a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

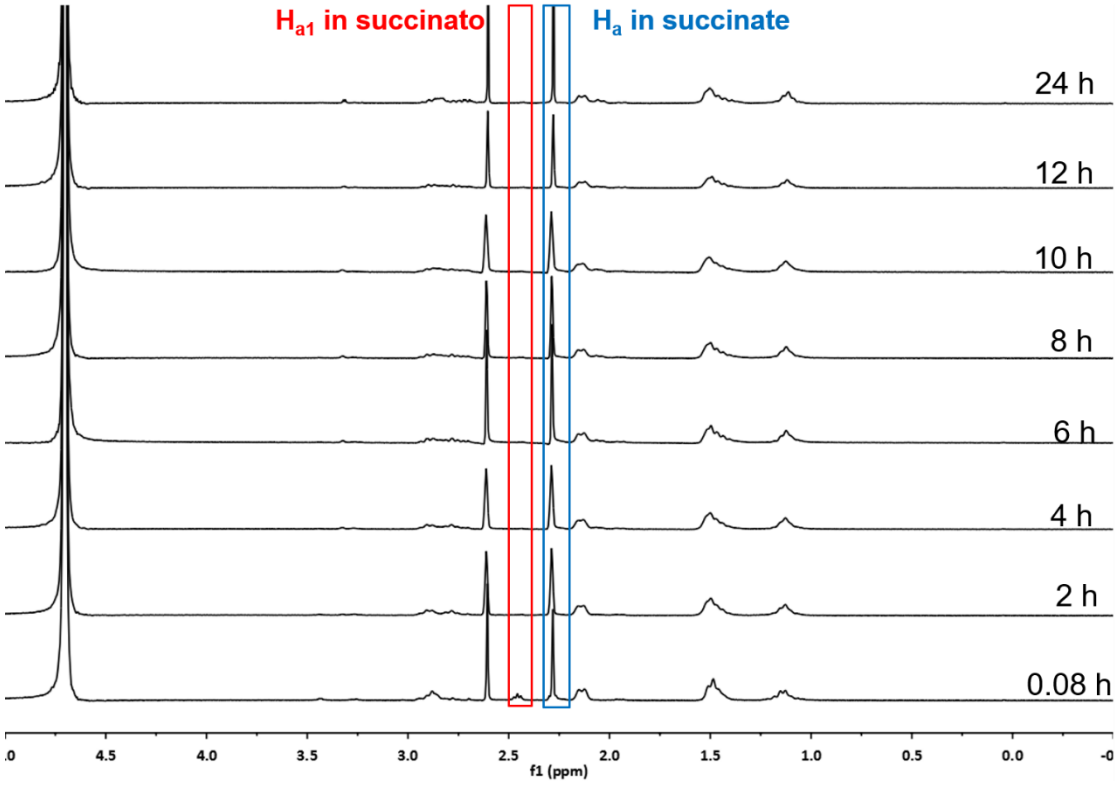


Figure S12. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(succinato)Br] (12a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

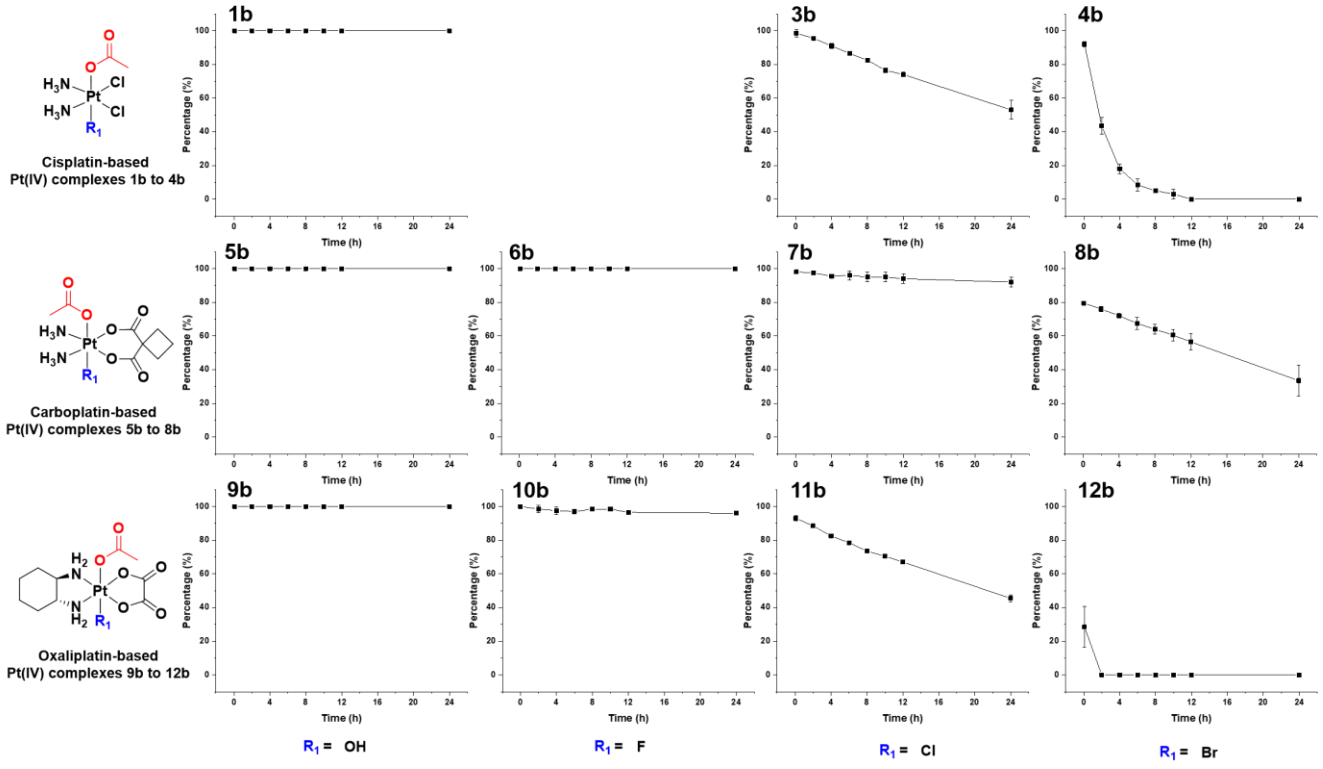


Figure S13. Hydrolytic stability of Pt(IV) complexes **1b**, **3b** to **12b** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h. All the results are calculated from two independent experiments.

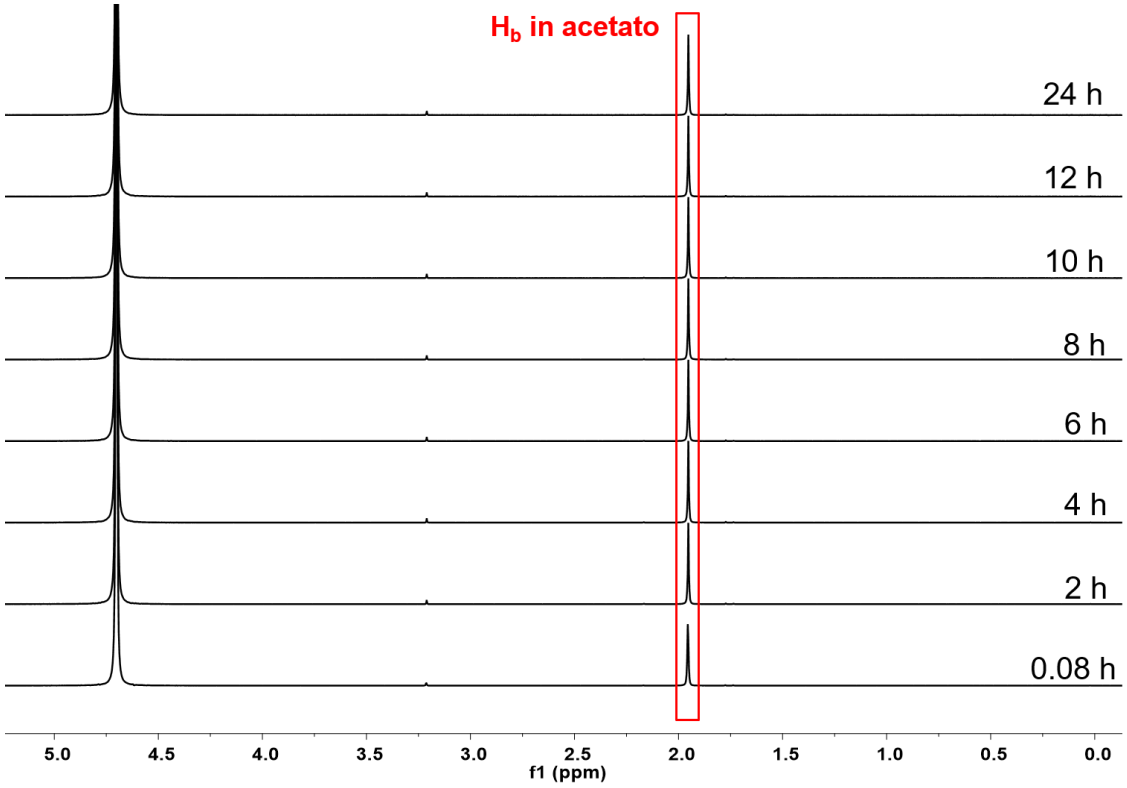


Figure S14. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(acetato)OH] (1b)** in phosphate buffer (50 mM, pH 7.4, D$_2$O) at 37 °C from 0.08 to 24 h.

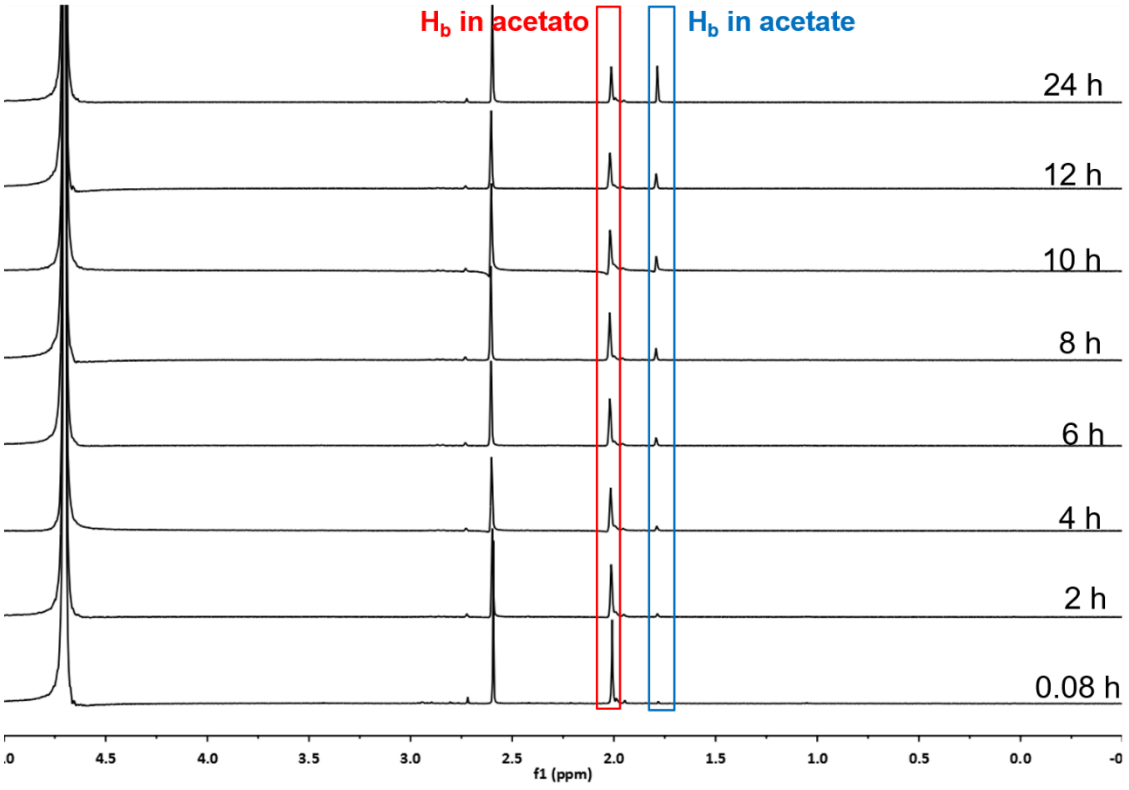


Figure S15. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(acetato)Cl] (3b)** in phosphate buffer (50 mM, pH 7.4, D$_2$O) at 37 °C from 0.08 to 24 h.

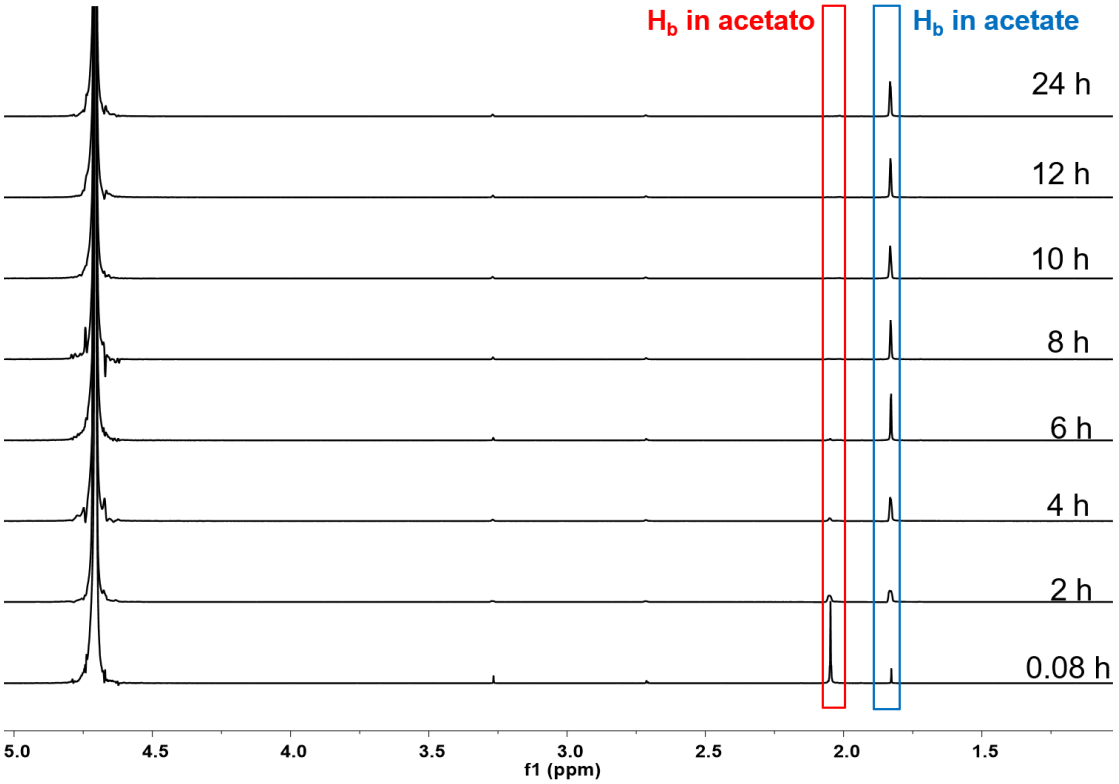


Figure S16. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(acetato)Br] (4b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

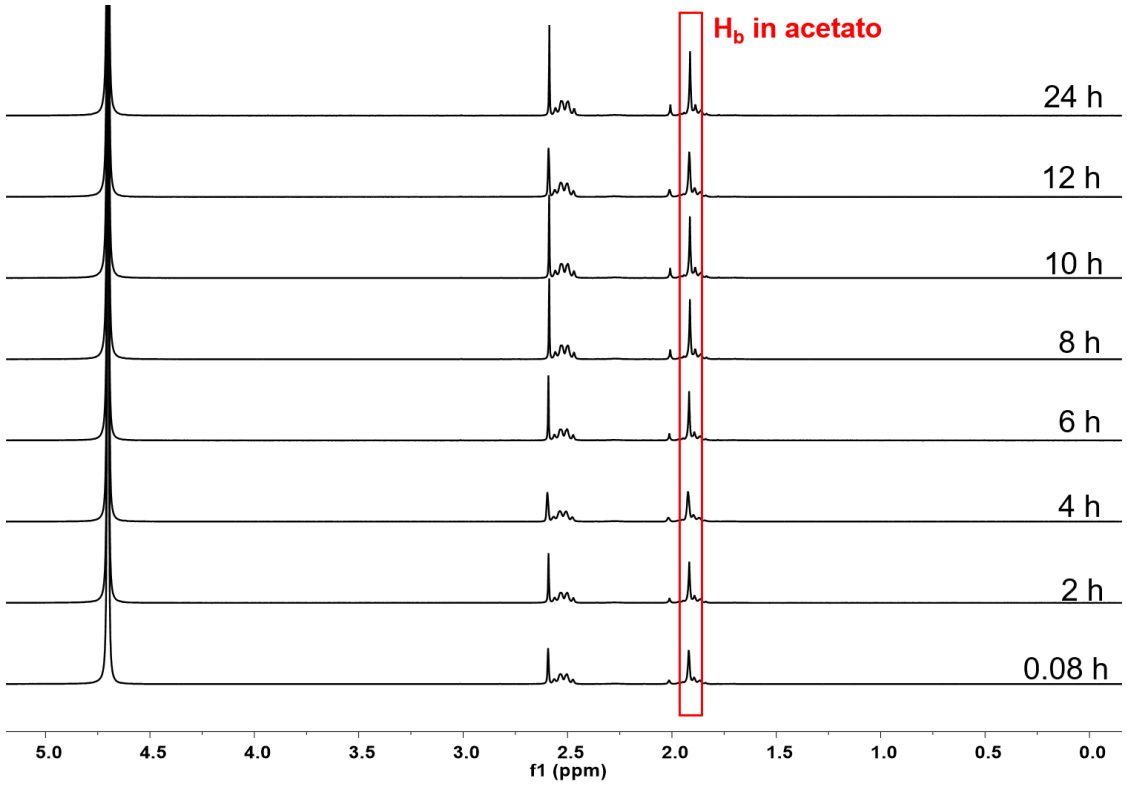


Figure S17. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)OH] (5b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

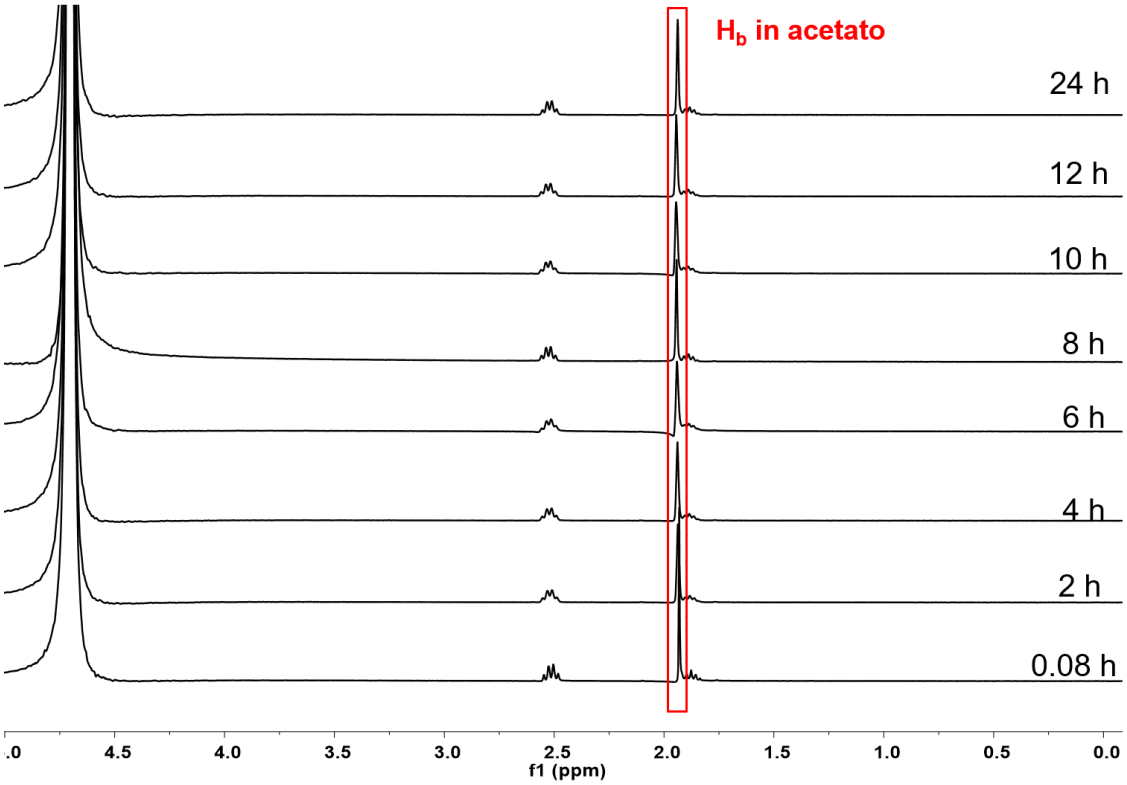


Figure S18. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)F] (6b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

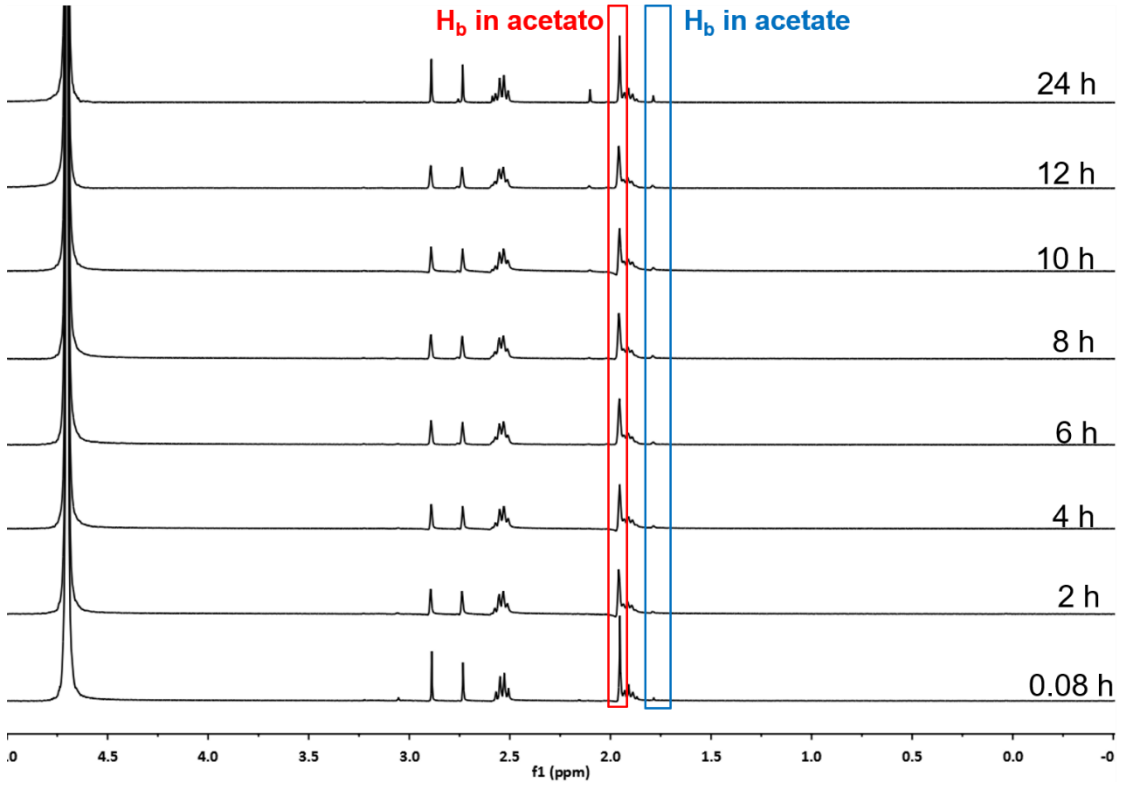


Figure S19. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)Cl] (7b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

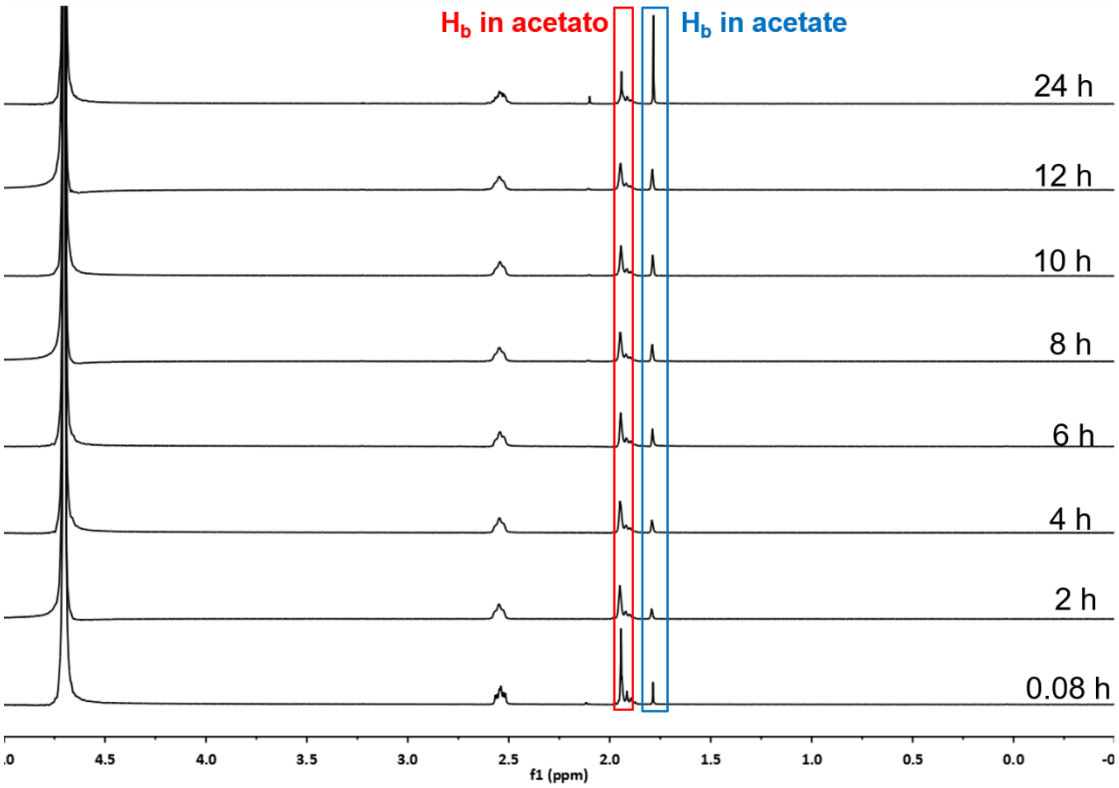


Figure S20. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)Br] (8b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

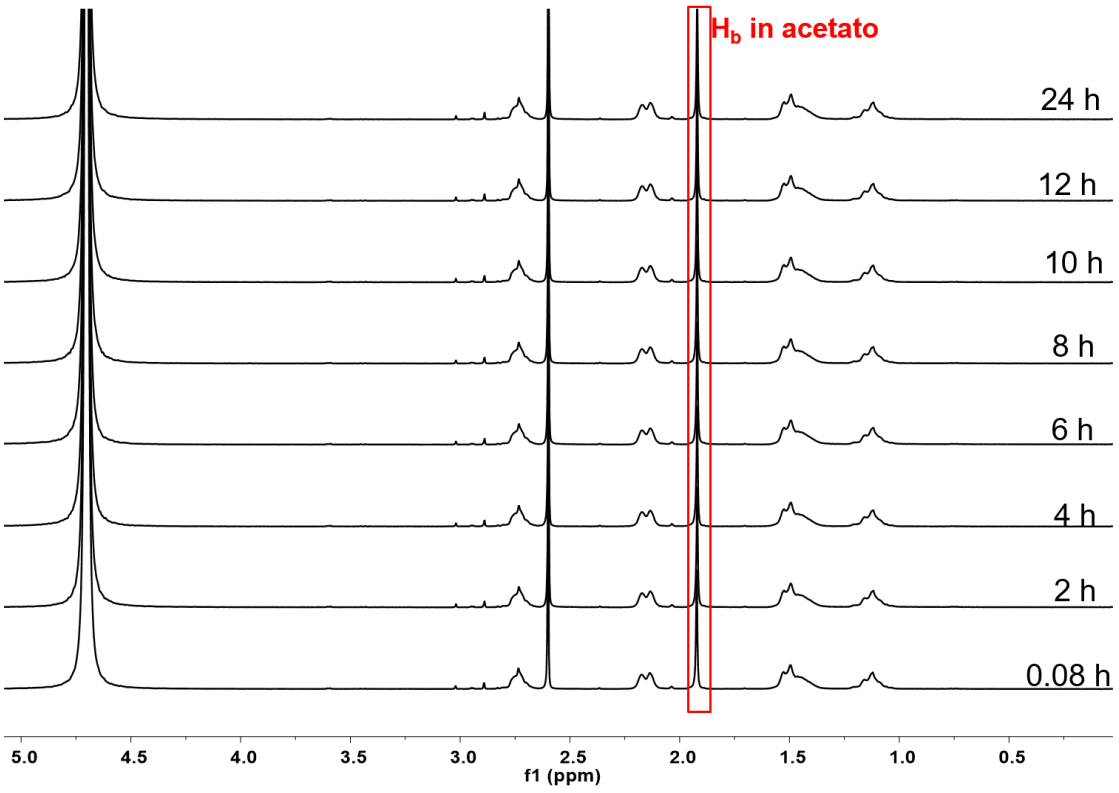


Figure S21. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(acetato)OH] (9b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

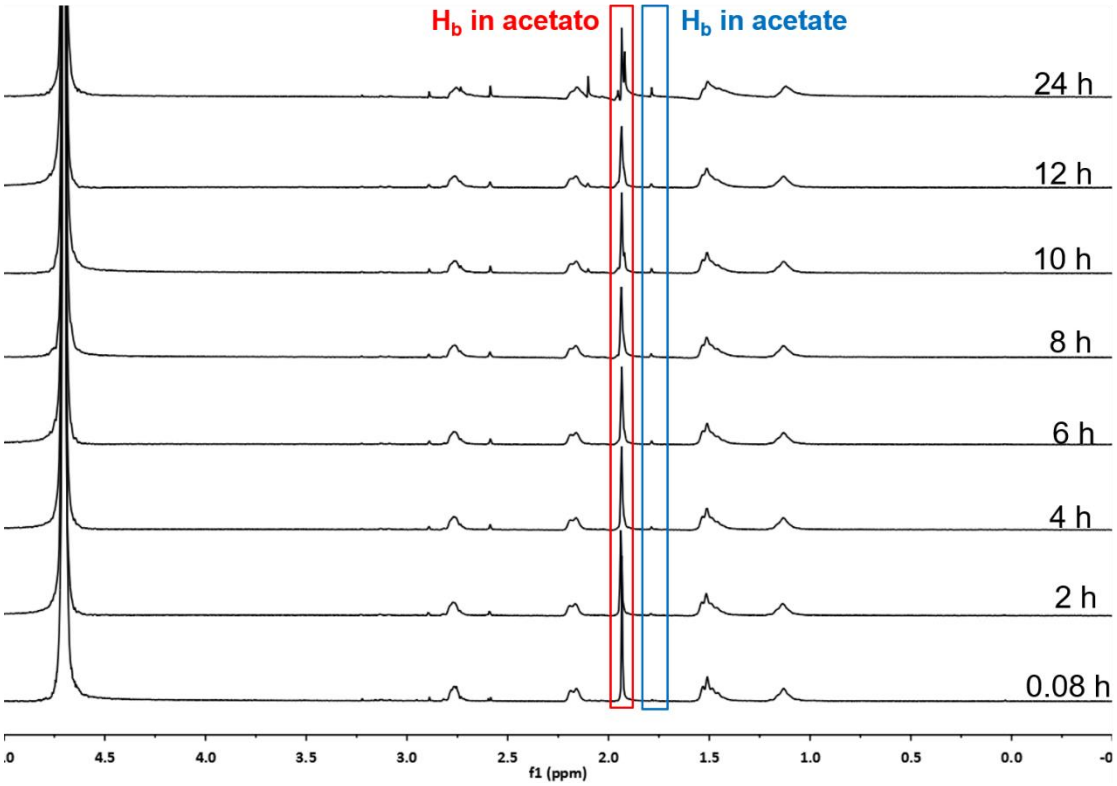


Figure S22. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(acetato)F] (10b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

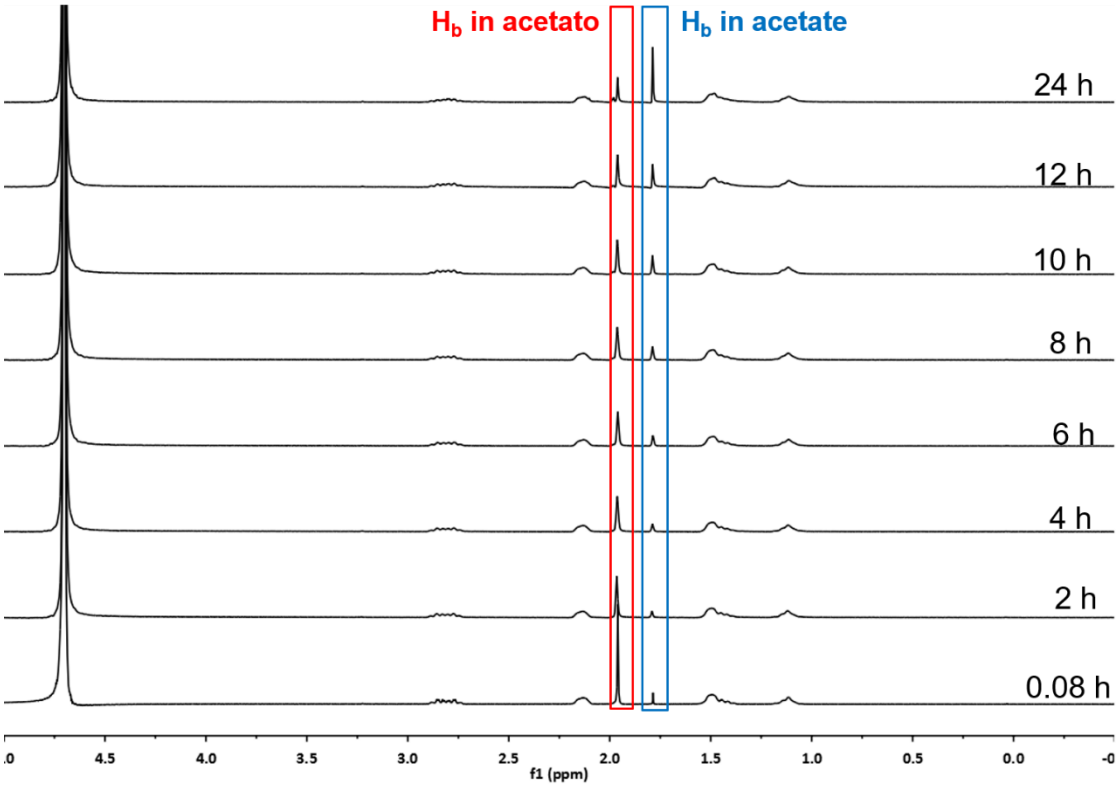


Figure S23. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(acetato)Cl] (11b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

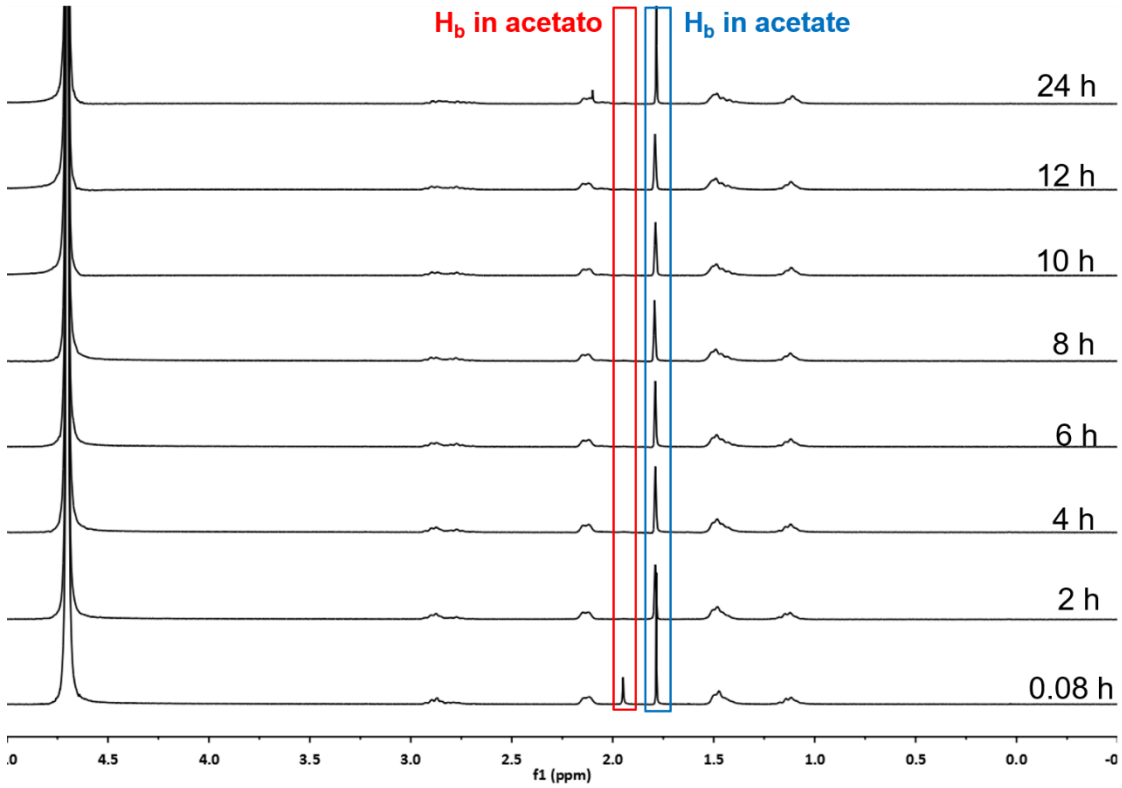


Figure S24. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(acetato)Br] (12b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

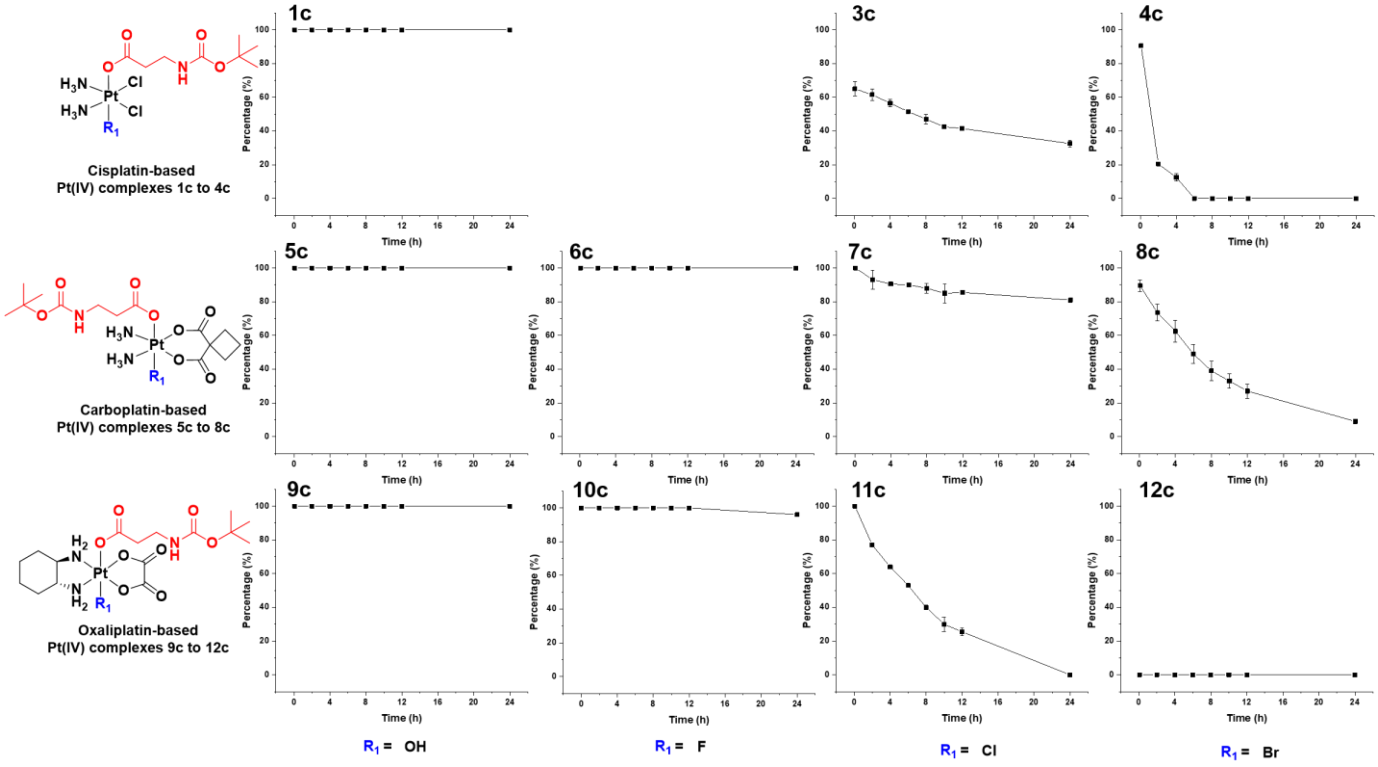


Figure S25. Hydrolytic stability of Pt(IV) complexes **1c**, **3c** to **12c** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h. All the results are calculated from two independent experiments.

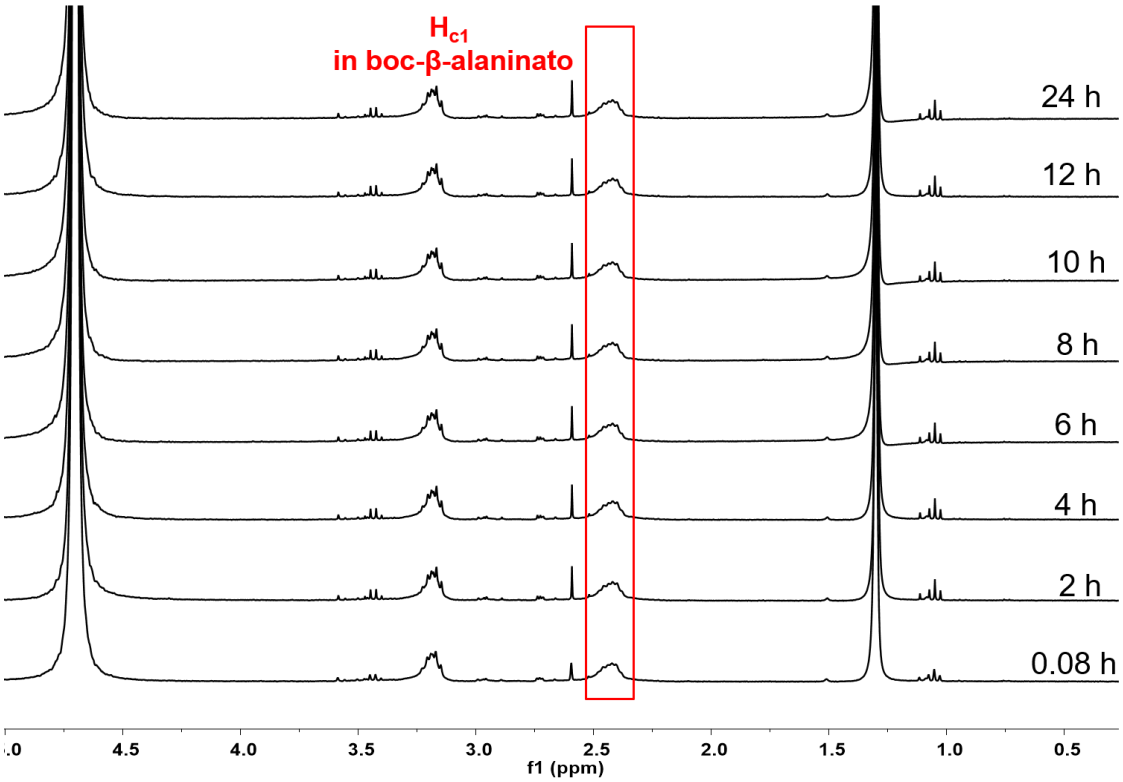


Figure S26. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(boc-β-alaninato)OH] (1c)** in phosphate buffer (50 mM, pH 7.4, D$_2$O) at 37 °C from 0.08 to 24 h.

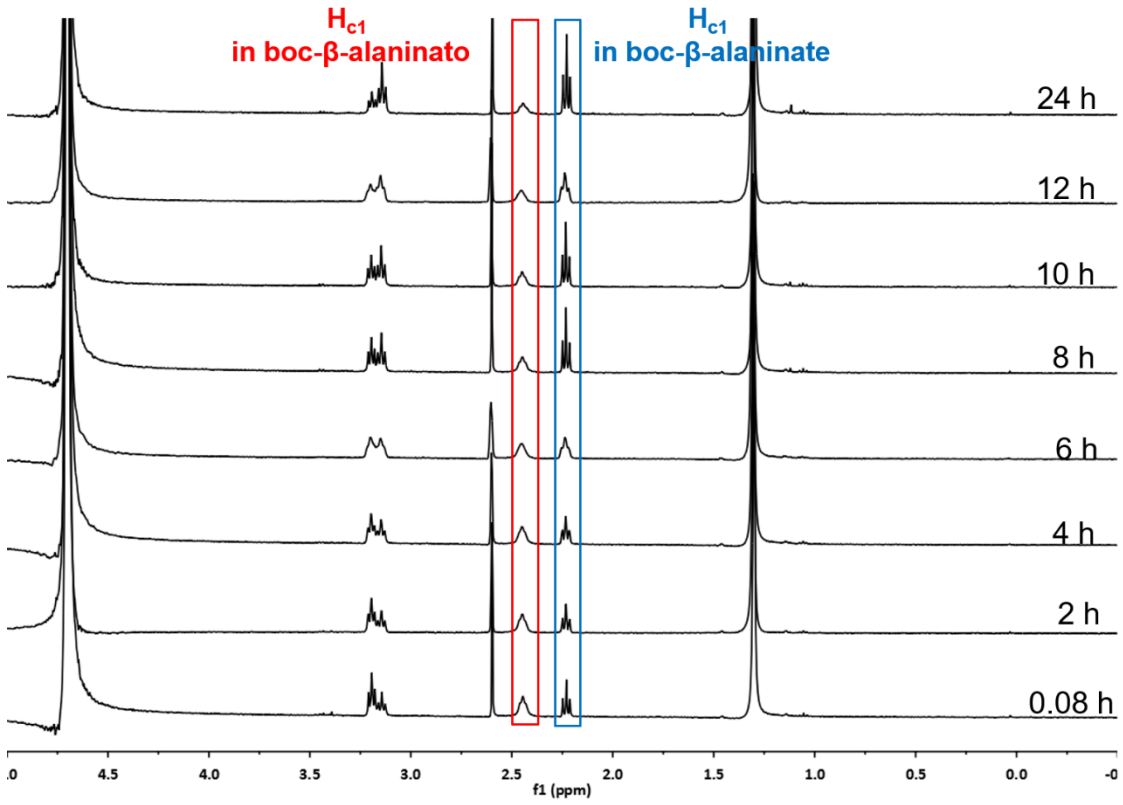


Figure S27. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(boc-β-alaninato)Cl] (3c)** in phosphate buffer (50 mM, pH 7.4, D$_2$O) at 37 °C from 0.08 to 24 h.

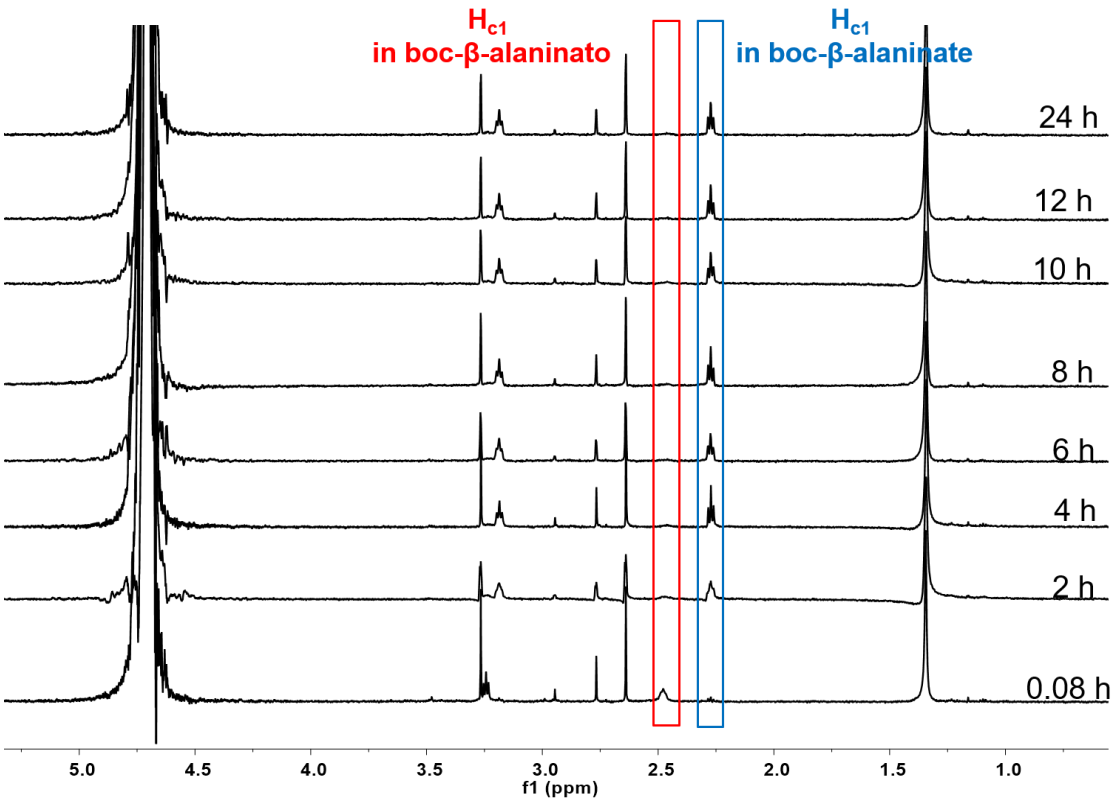


Figure S28. ^{1}H NMR of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(boc-β-alaninato)Br] (4c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

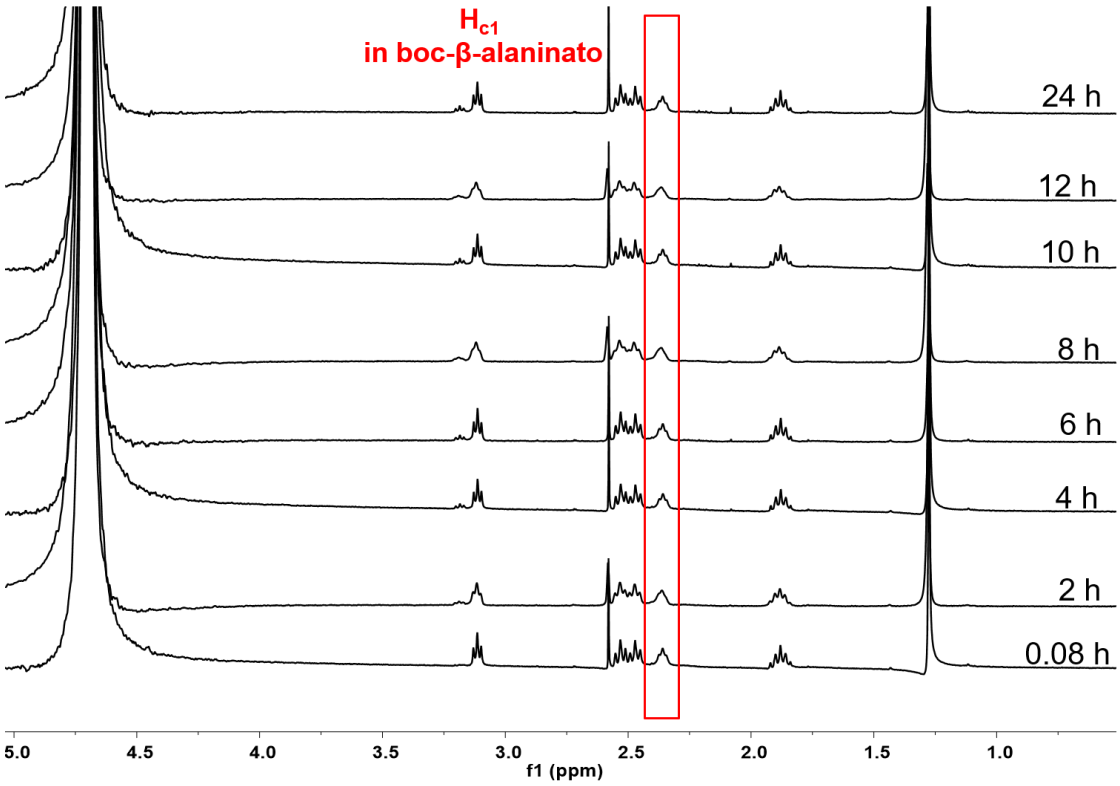


Figure S29. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)OH] (5c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

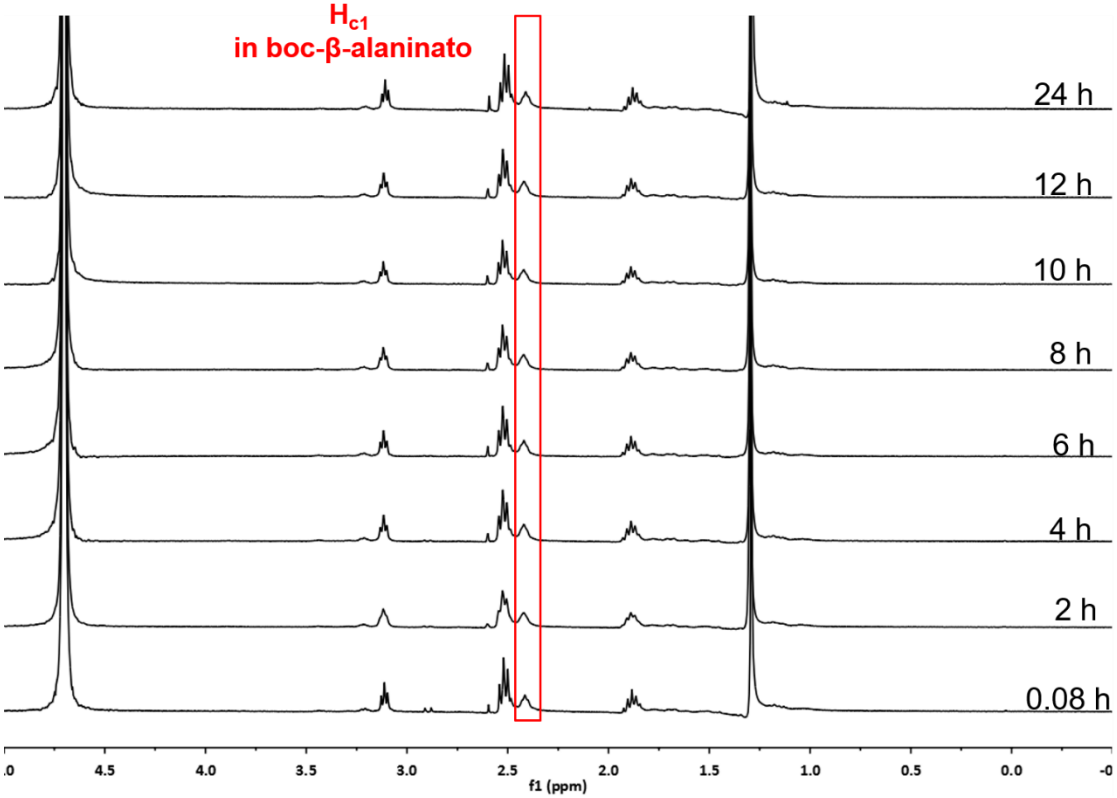


Figure S30. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)F] (6c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

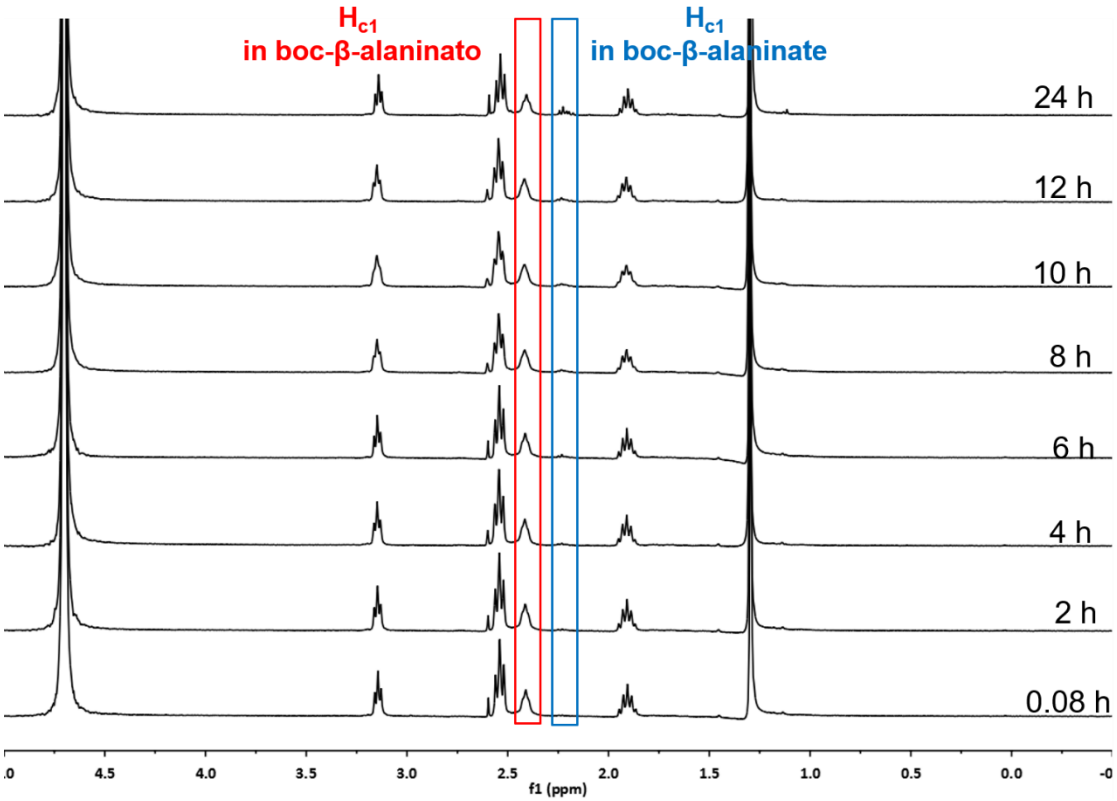


Figure S31. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)Cl] (7c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

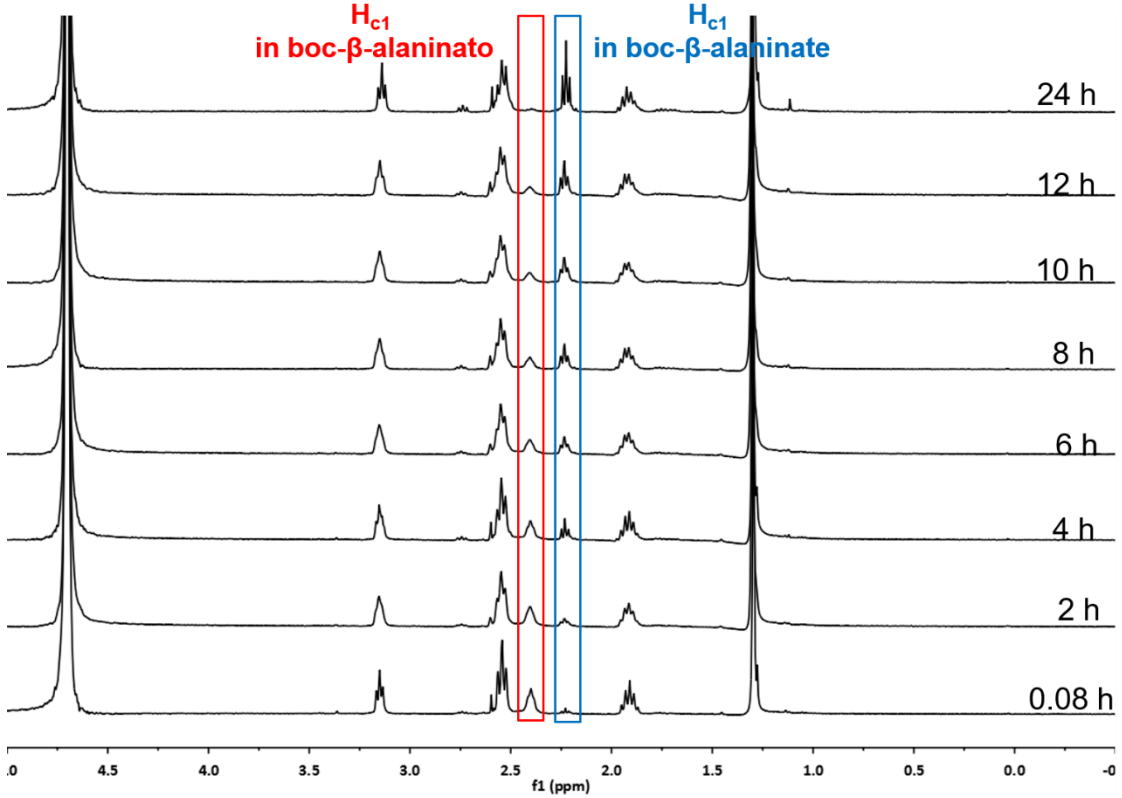


Figure S32. ^{1}H NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)Br] (8c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

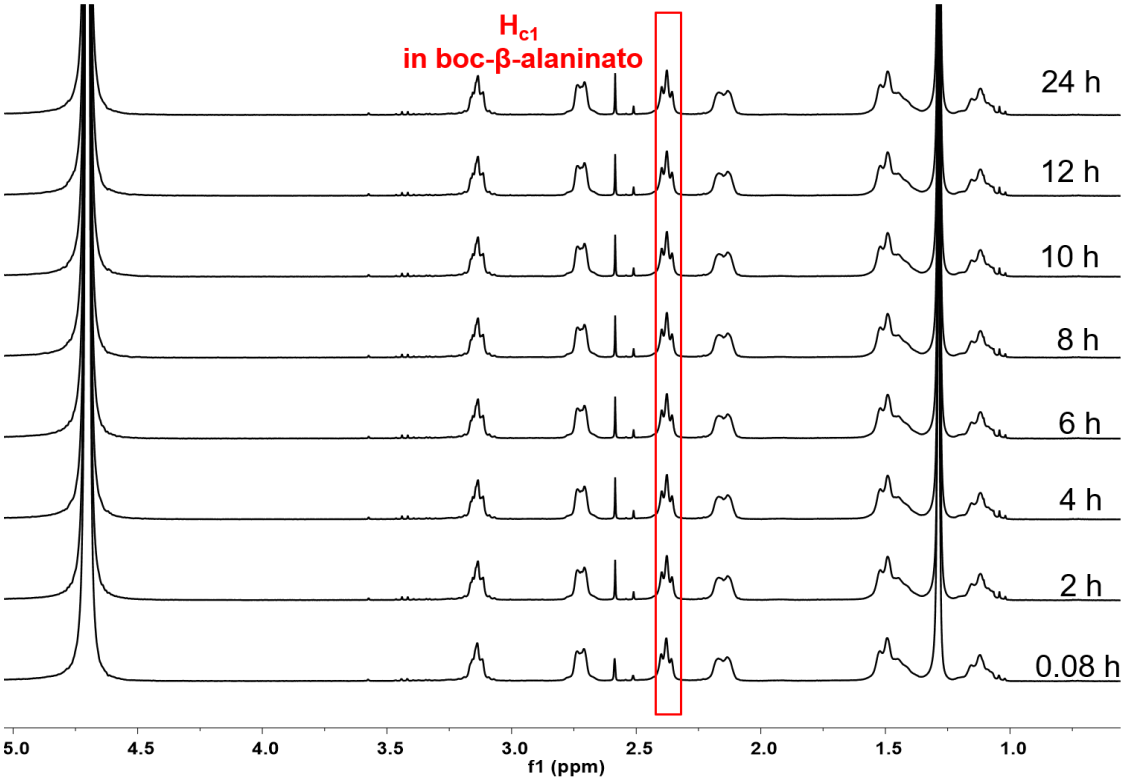


Figure S33. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)OH] (9c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

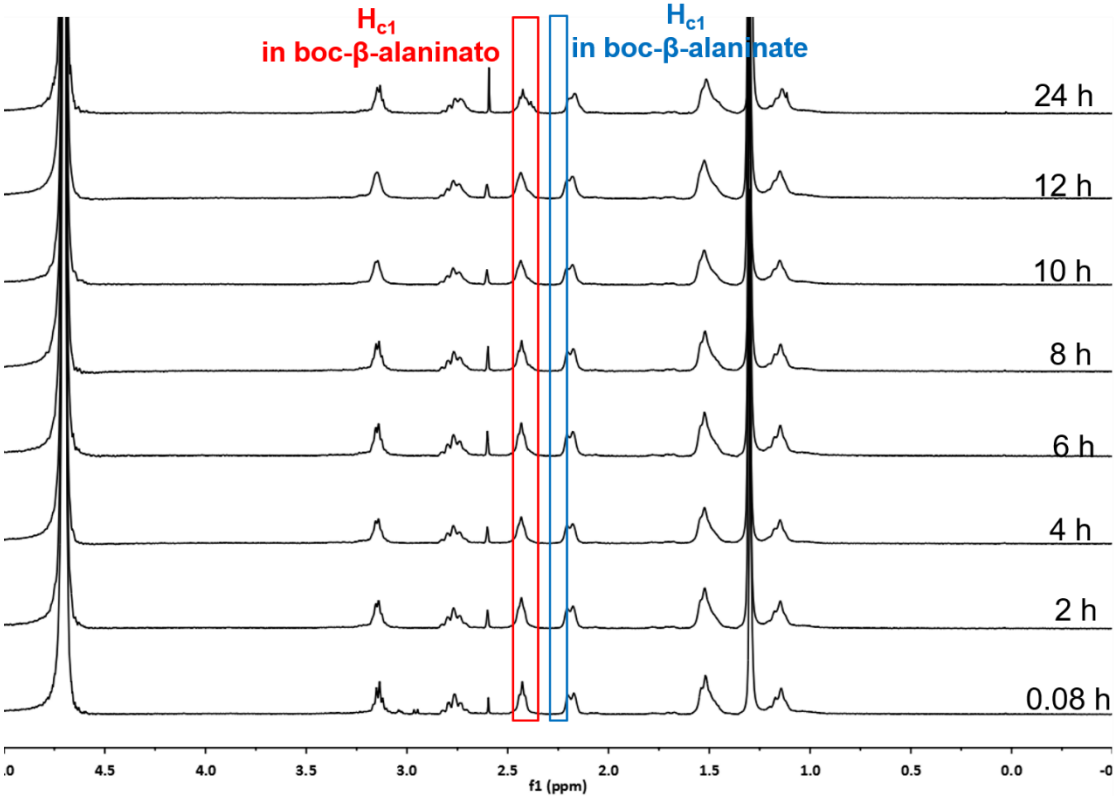


Figure S34. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)F] (10c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

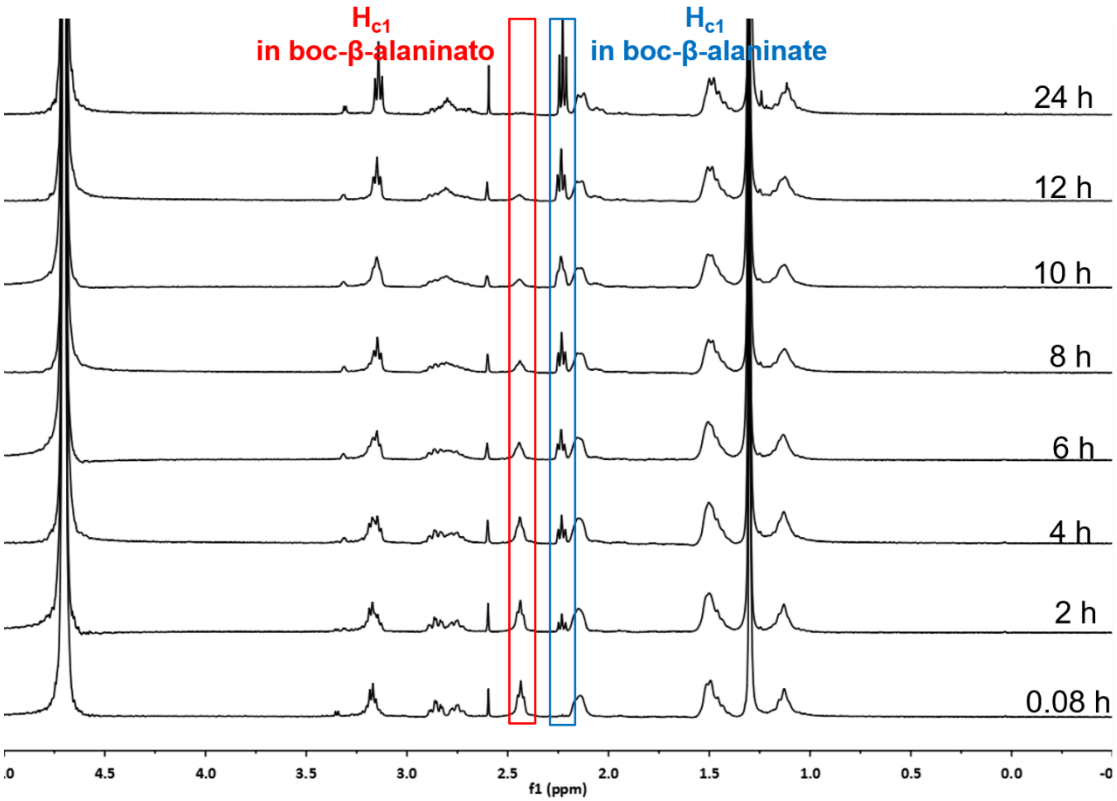


Figure S35. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)Cl] (11c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

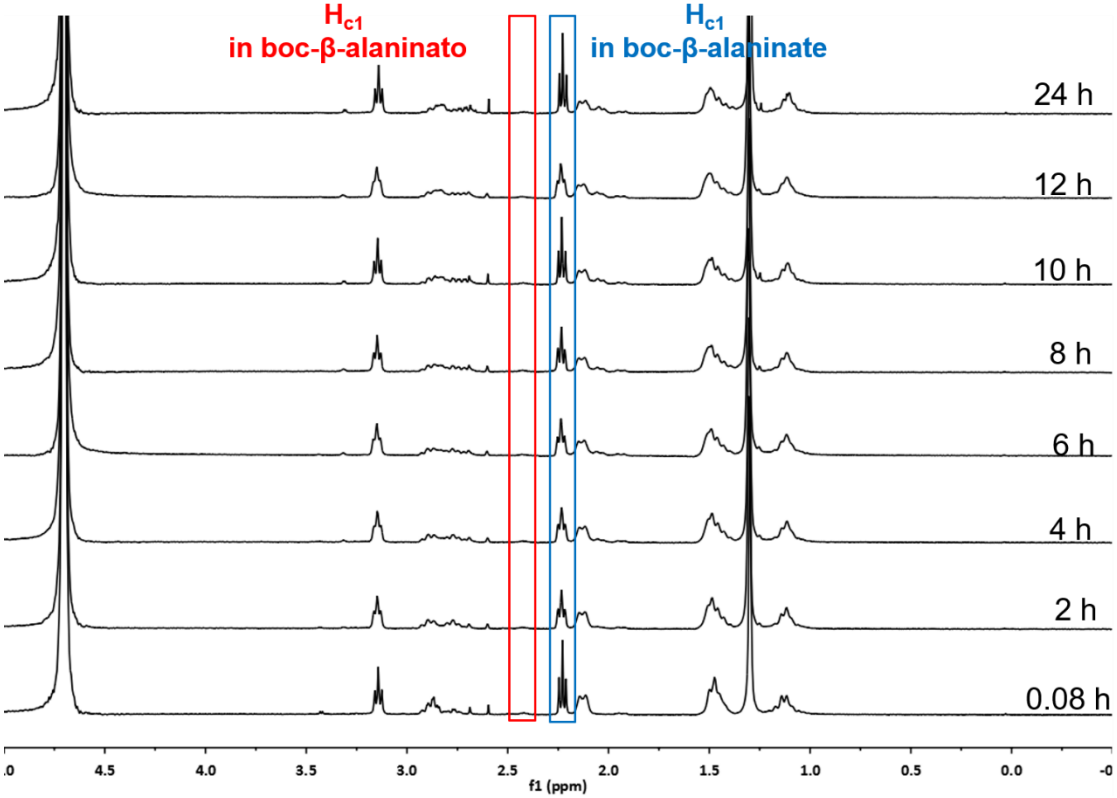


Figure S36. ^{1}H NMR of ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)Br] (12c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C from 0.08 to 24 h.

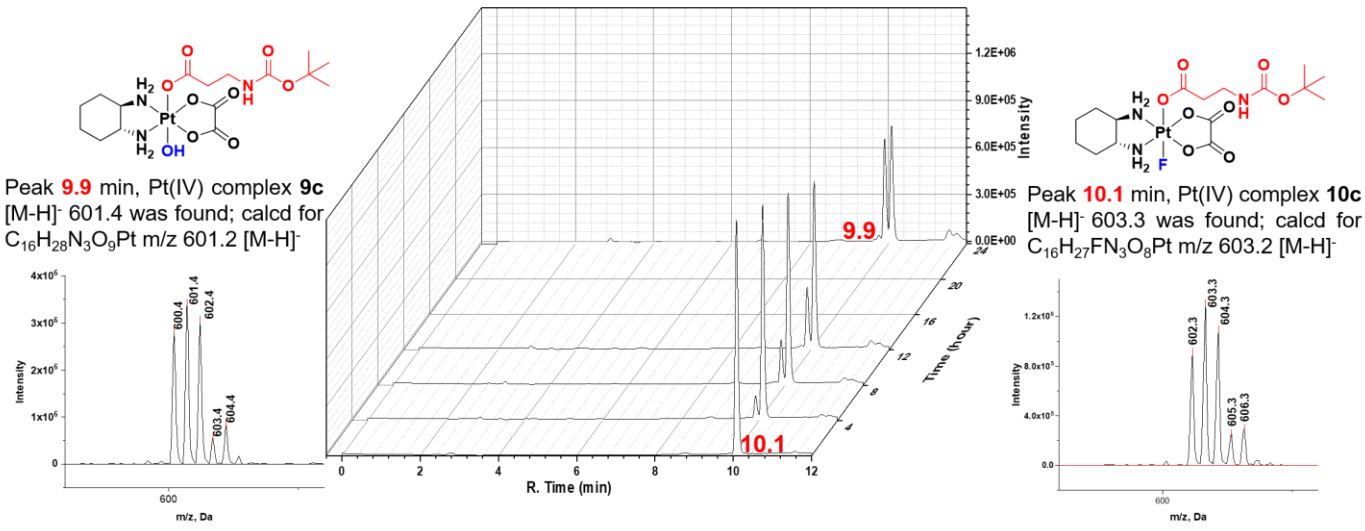


Figure S37. HPLC chromatograms and MS spectra of ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)F] (10c)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak at 10.1 min belongs to Pt(IV) complex **10c** and the appeared peak at 9.9 min belongs to Pt(IV) complex **9c**.

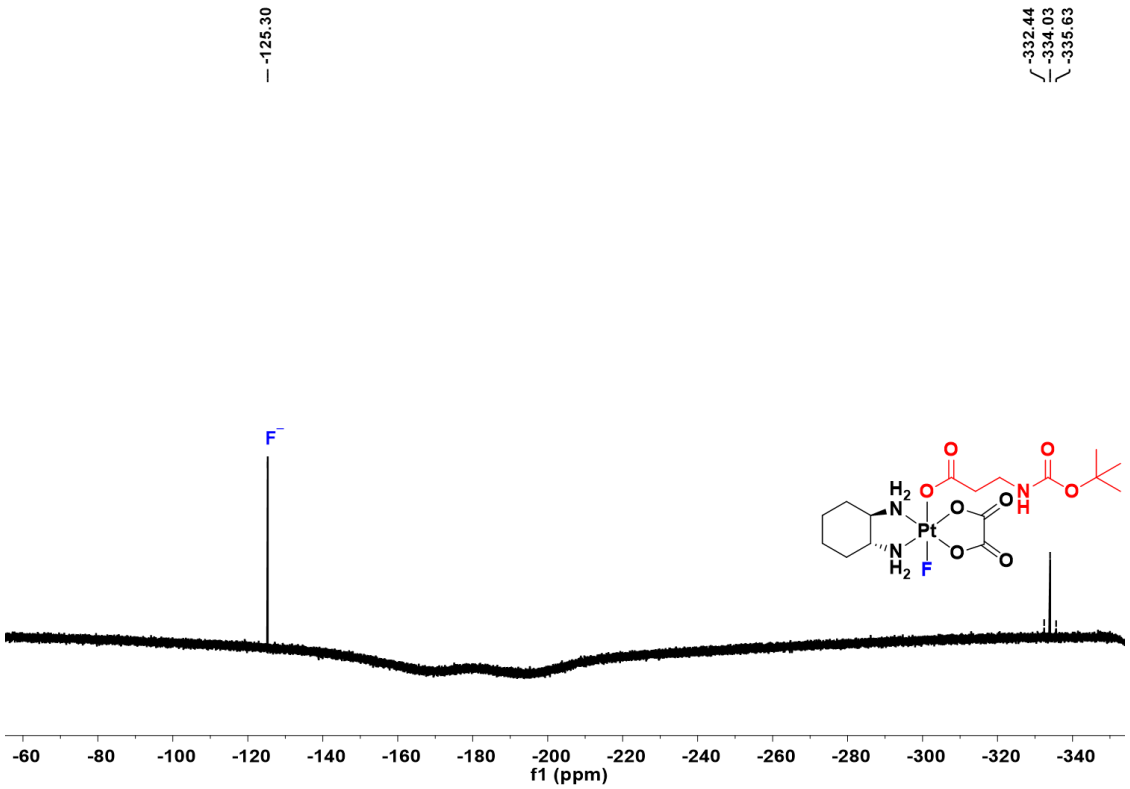


Figure S38. ^{19}F NMR of ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)F] (10c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C after 24 h. The F^- anion was detected in 125.3 ppm.

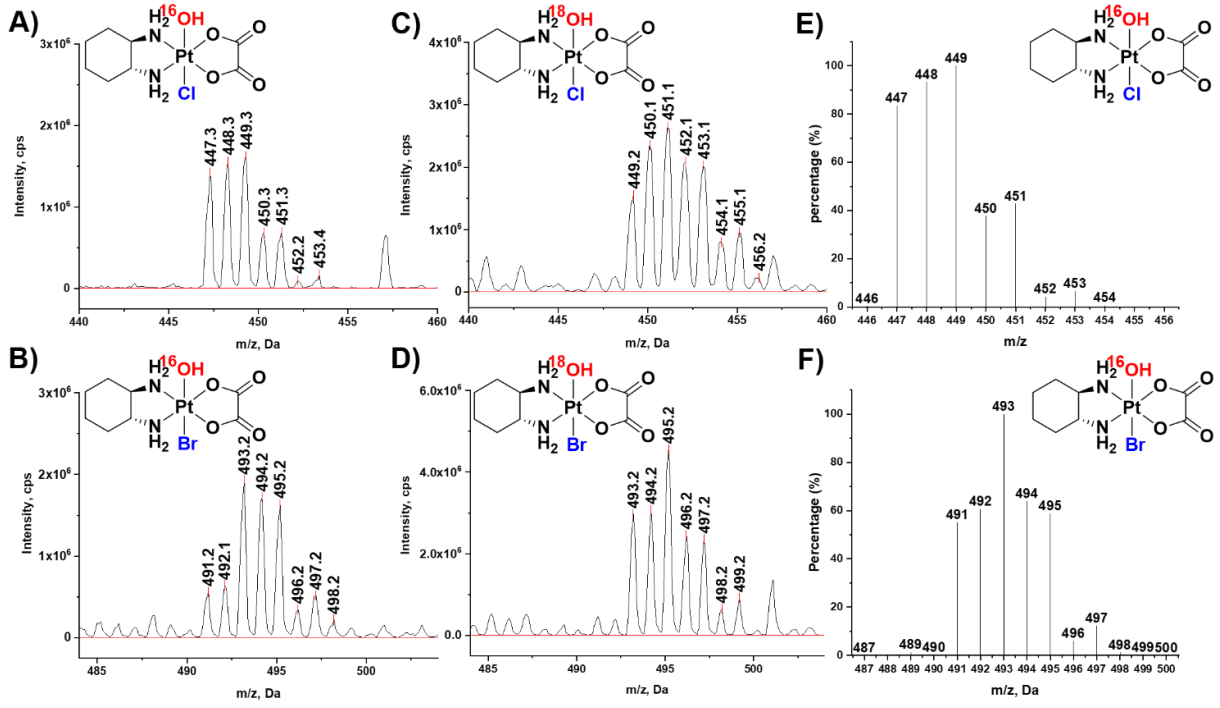


Figure S39. MS spectra [negative ion mode, $(M-H)^-$] of ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)Cl] (11c**, after 24 h**)** and ***trans*-[Pt(DACH)(ox)(boc-β-alaninato)Br] (12c**, after 5 min**)** in phosphate buffer (50 mM, pH 7.4, H_2O, **A** and **B**) or phosphate buffer (50 mM, pH 7.4, $H_2{}^{18}O$, **C** and **D**). The calculated MS spectra [negative ion mode, $(M-H)^-$] of Pt(IV) complexes **11** and **12** are shown in **E** and **F**. Since all the boc-β-alaninato ligand detached from Pt(IV) center in oxaliplatin-based Pt(IV) complexes **11c** and **12c** (**Figures S35** and **S36**), The formation of Pt(IV) complexes **11** and **12** during the hydrolysis proved that the Pt-R1 bonds (R_1 = Cl and Br) in Pt(IV) complexes **11c** and **12c** are more stable compared with their corresponding counter Pt-R_2 (R_2=boc-β-alaninato) bond**.**

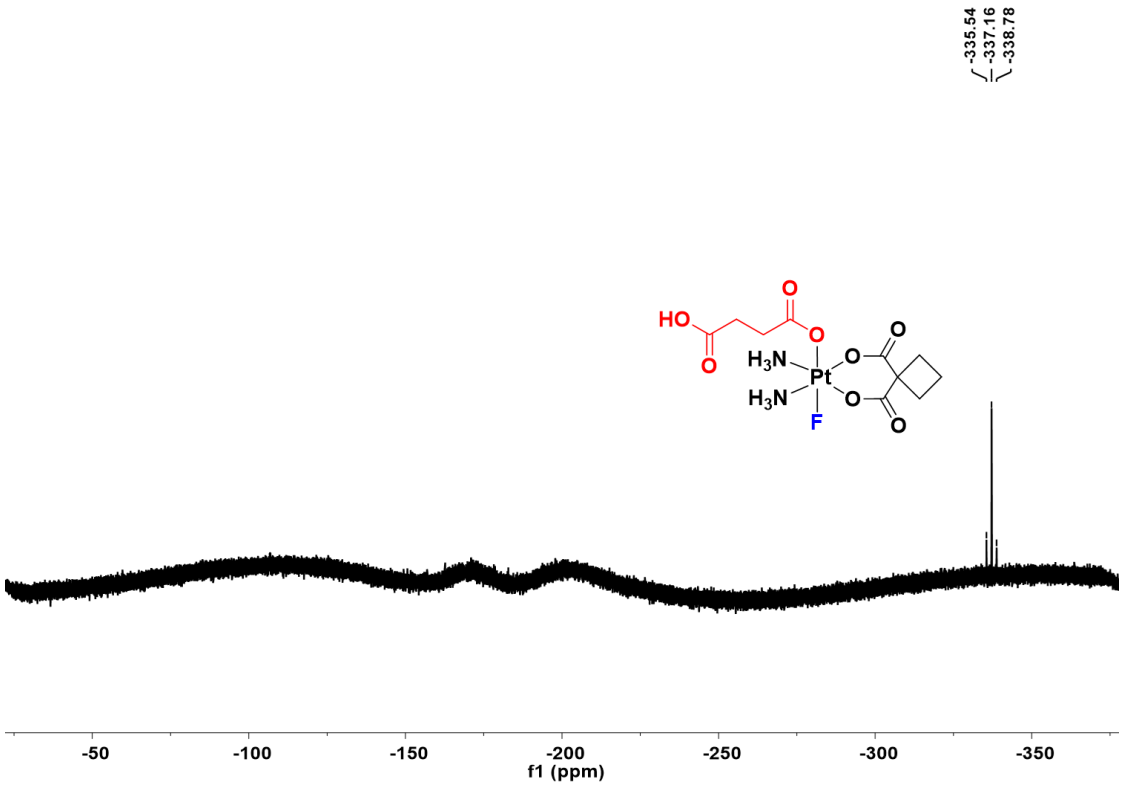


Figure S40. ^{19}F NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(succinato)F] (6a)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C after 24 h. No F^- anion could be detected in 125.3 ppm.

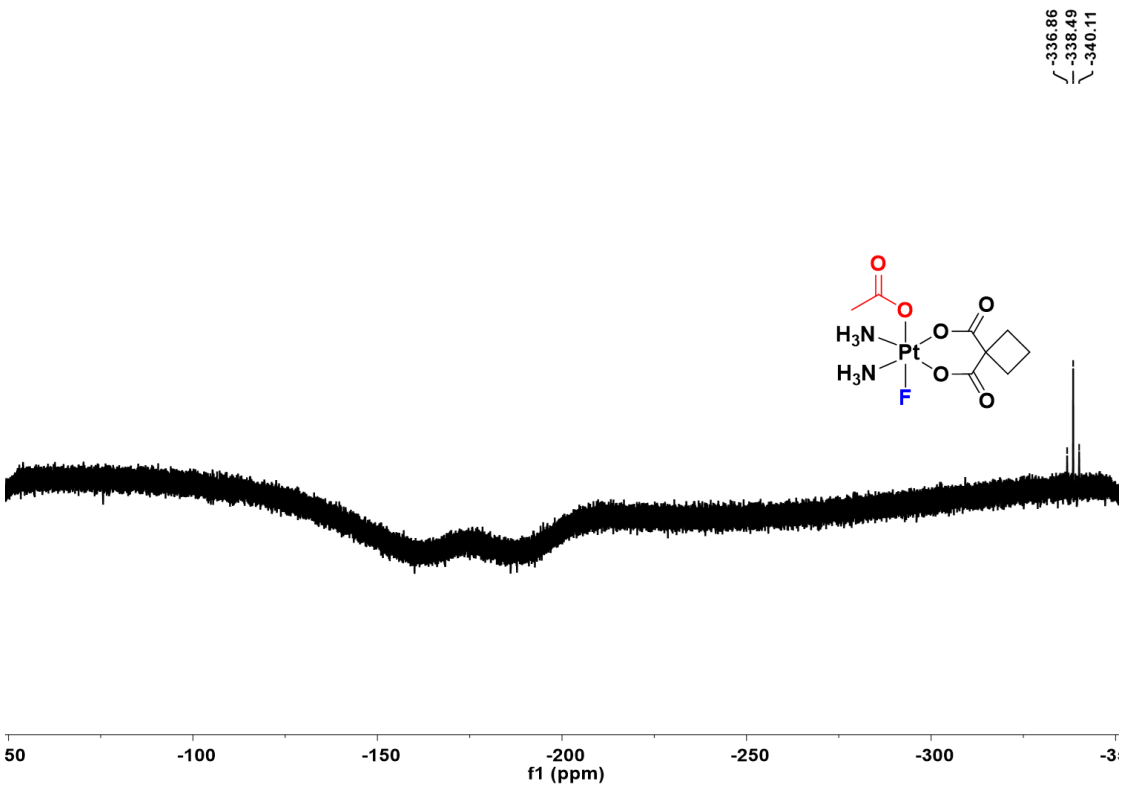


Figure S41. ^{19}F NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(acetato)F] (6b)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C after 24 h. No F^- anion could be detected in 125.3 ppm.

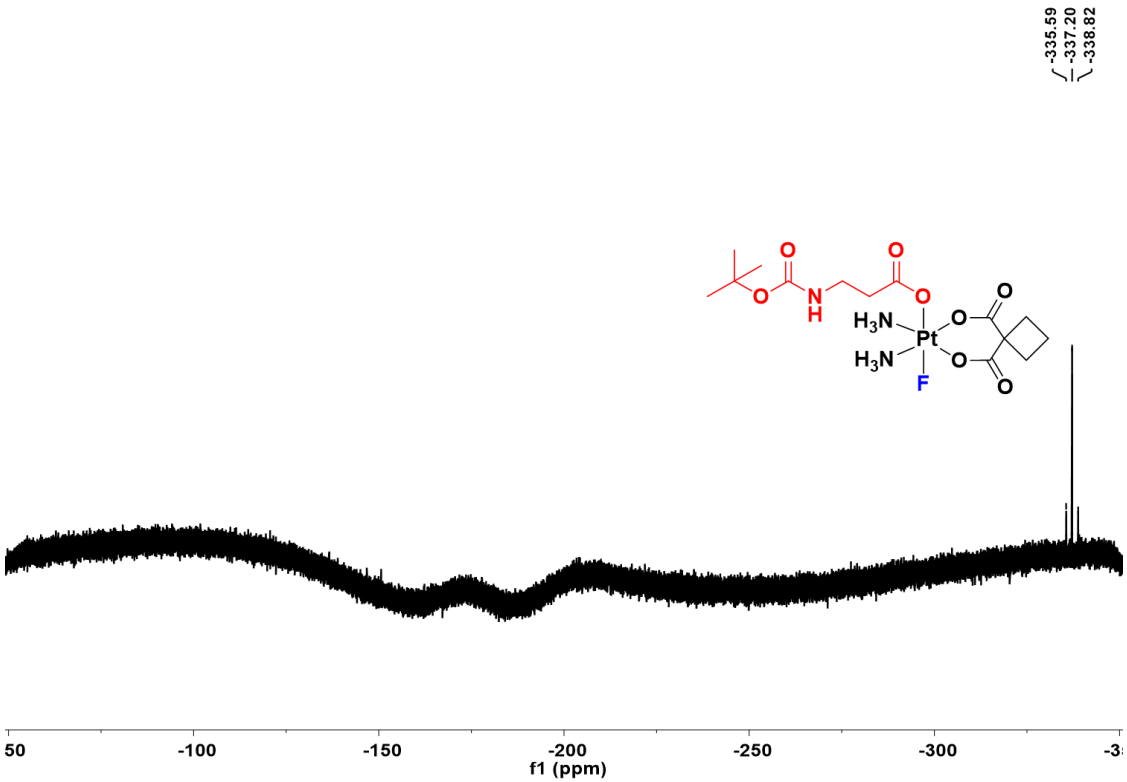
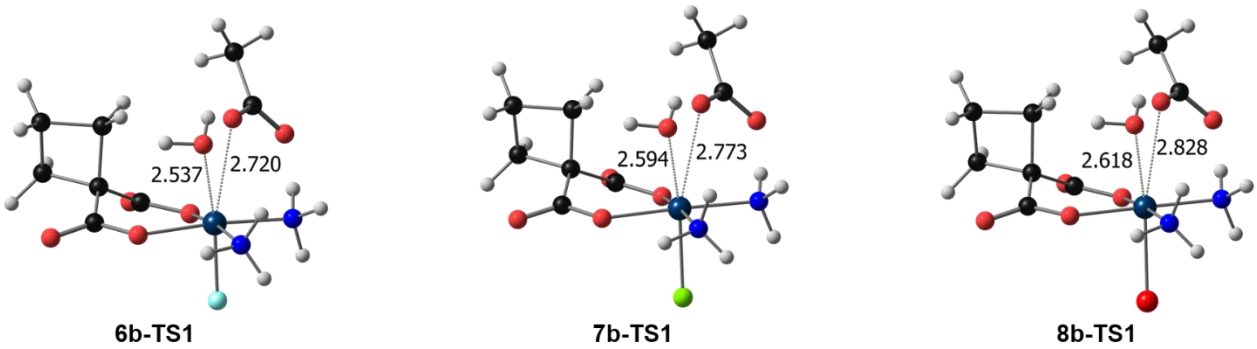


Figure S42. ^{19}F NMR of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(boc-β-alaninato)F] (6c)** in phosphate buffer (50 mM, pH 7.4, D_2O) at 37 °C after 24 h. No F^- anion could be detected in 125.3 ppm.

(A)



(B)

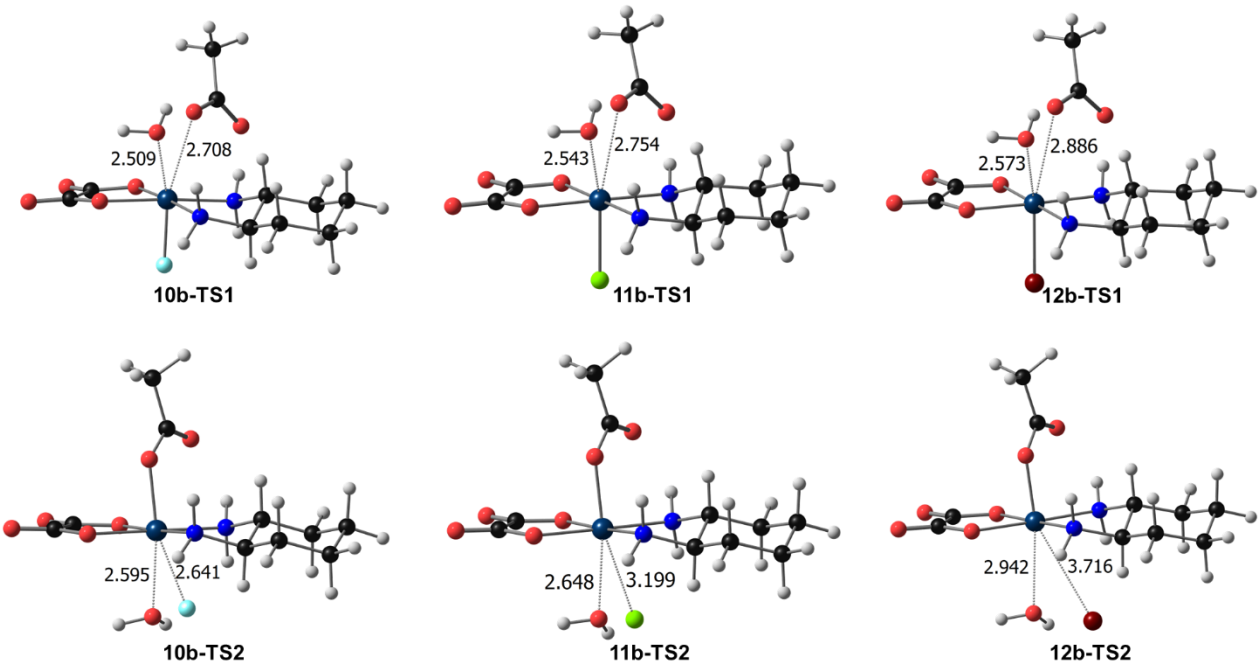


Figure S43. **(A)** Transition structures of hydrolysis of Pt(IV)-acetato bond (TS1) for the carboplatin-based Pt(IV) complexes **6b-8b** and **(B)** transition structures of hydrolysis of Pt(IV)-acetato bond (TS1) and Pt(IV)-halide bond (TS2) for oxaliplatin-based Pt(IV) complexes **10b-12b**, optimized at the M06-L/ Aug-cc-pVTZ level of theory. Interatomic distances along the reaction coordinates are given in Å.

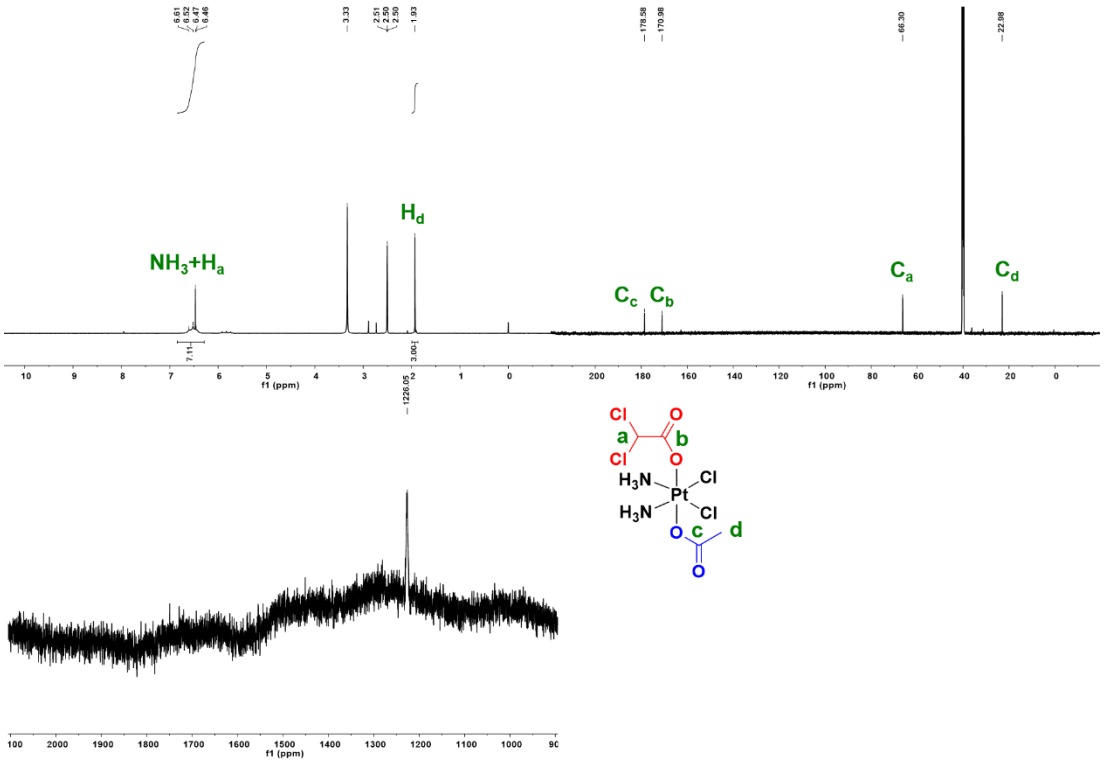


Figure S44. NMR spectra of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(DCA)(acetato)] (13e)** in DMSO-*d*$_6$.

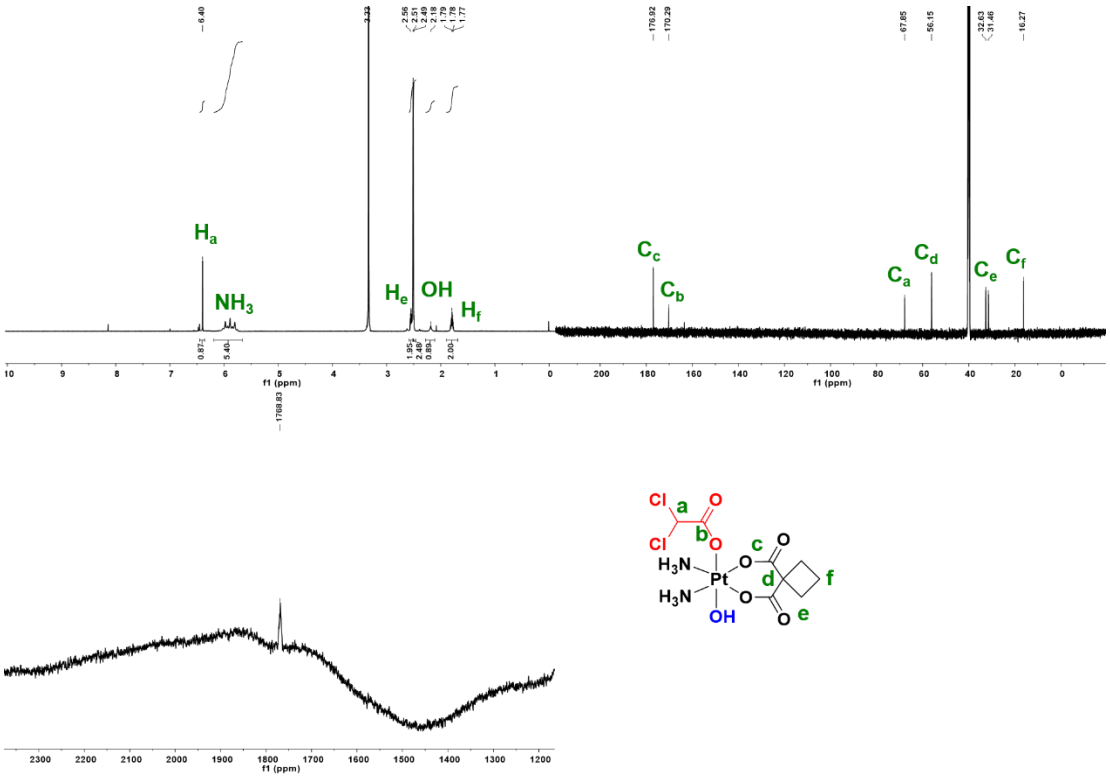


Figure S45. NMR spectra of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)OH] (14d)** in DMSO-*d*$_6$.

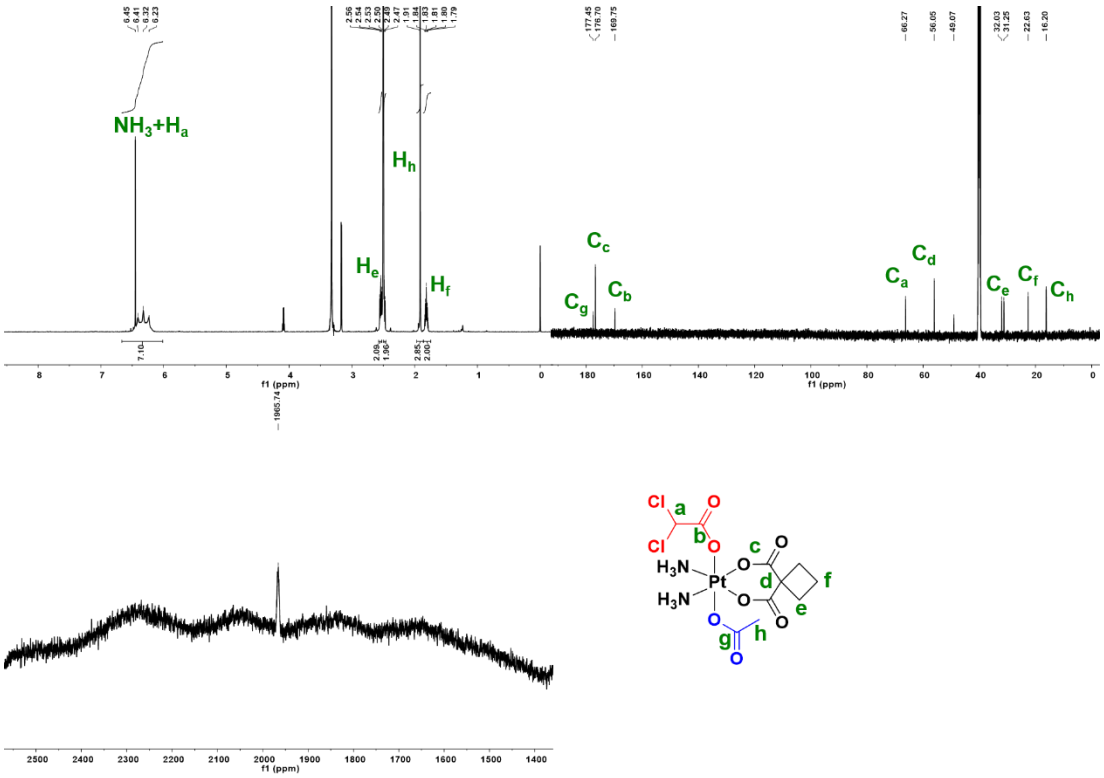


Figure S46. NMR spectra of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)(acetato)] (14e)** in DMSO-*d*$_6$.

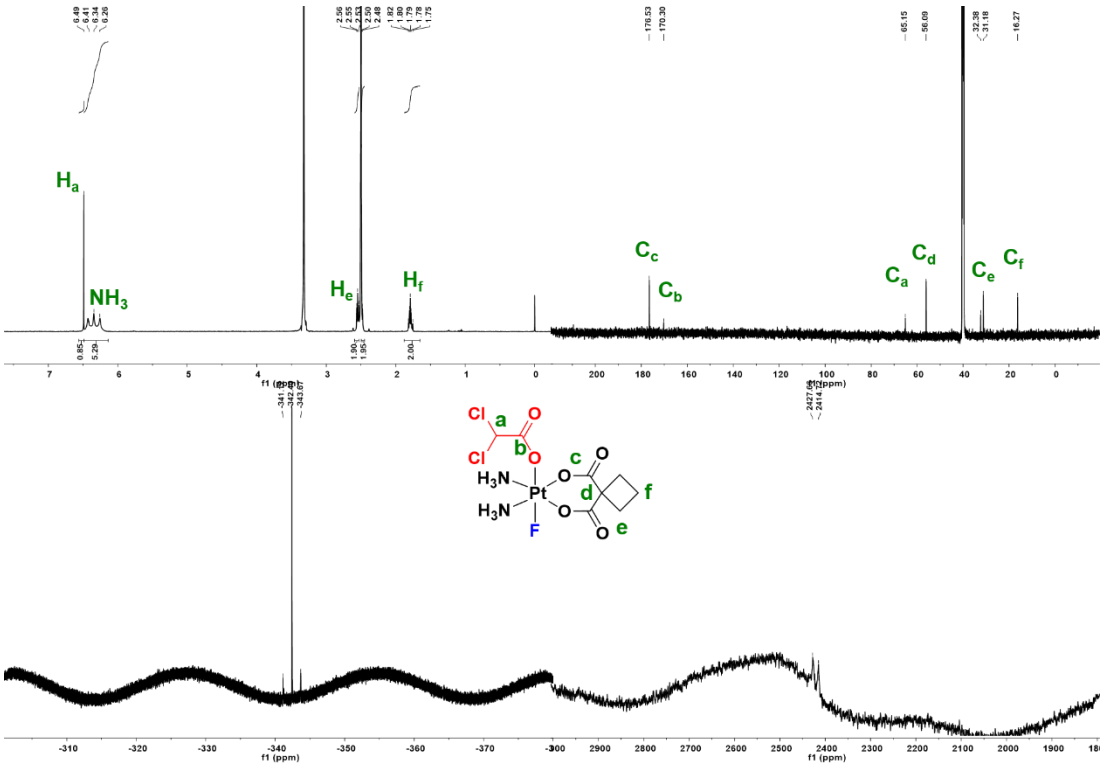


Figure S47. NMR spectra of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)F] (14f)** in DMSO-*d*$_6$.

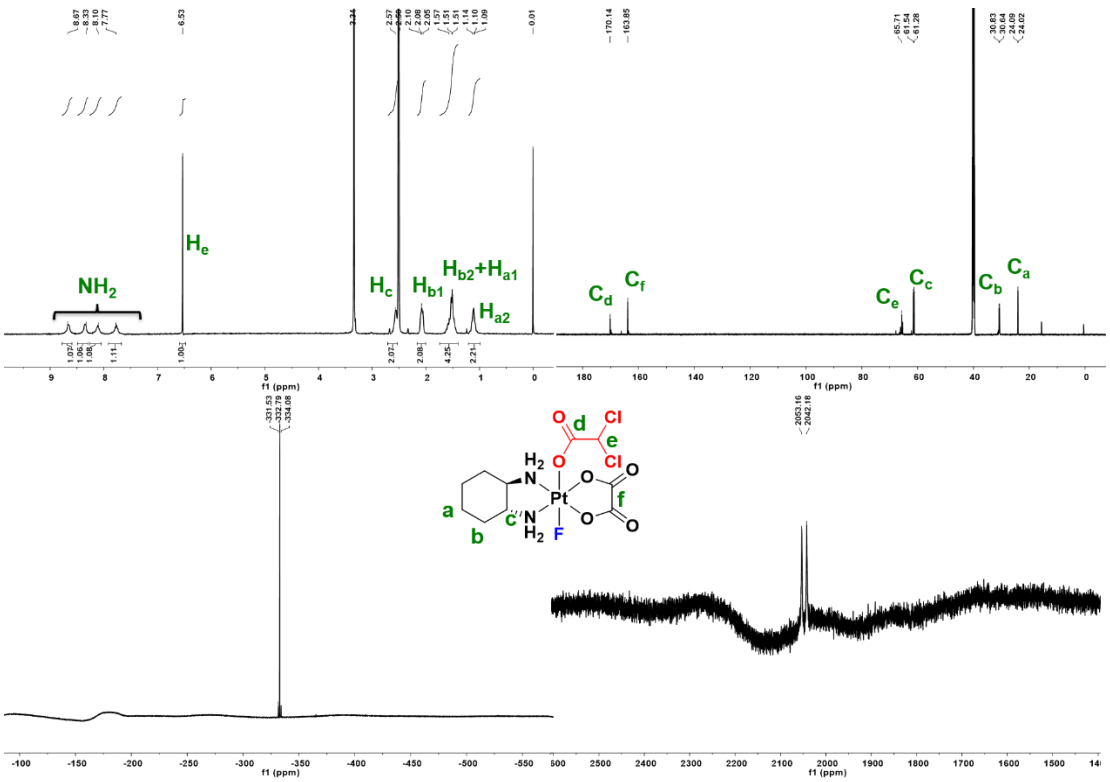


Figure S48. NMR spectra of ***trans*-[Pt(DACH)(ox)(DCA)F] (15f)** in DMSO-d_6.

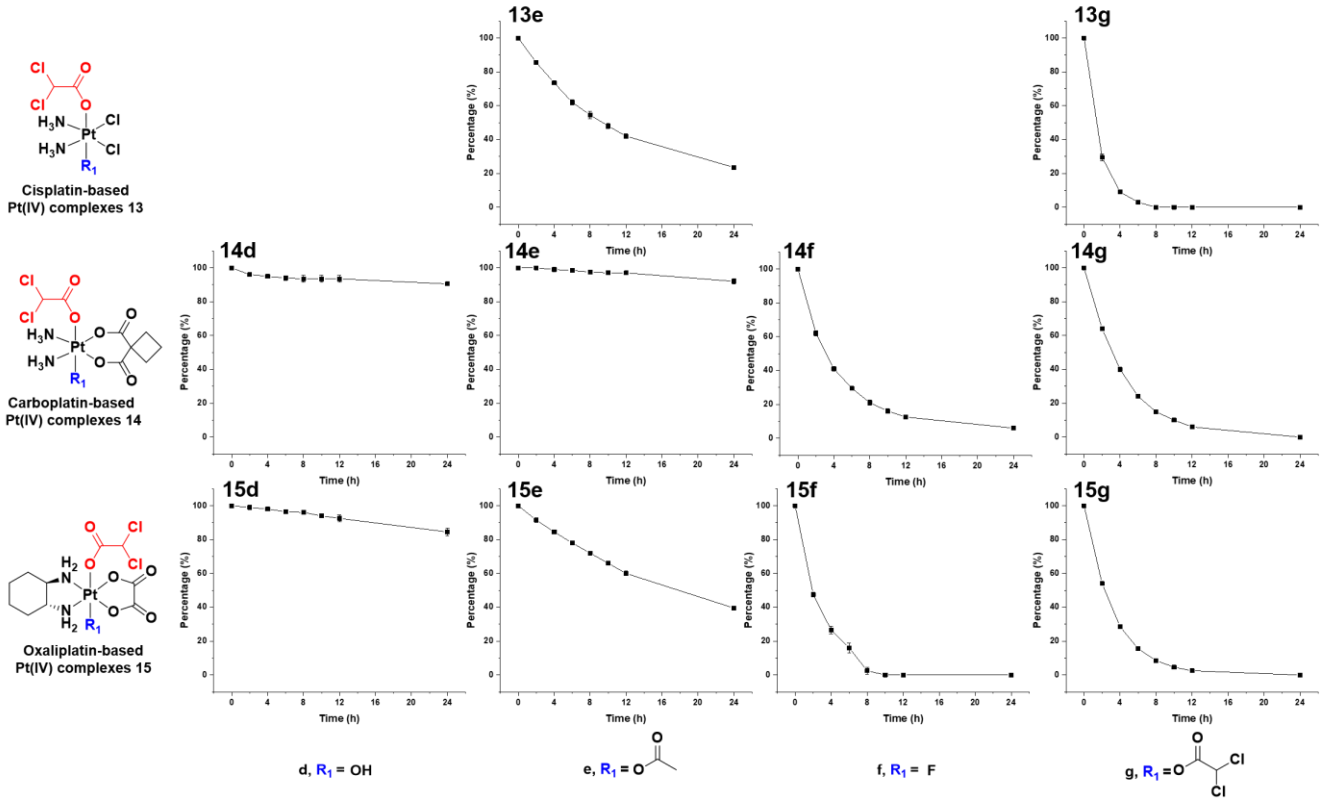


Figure S49. Hydrolytic stability of DCA-containing Pt(IV) complexes **13e**, **13g**, **14d** to **14g** and **15d** to **15g** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. All the results are calculated from two independent experiments.

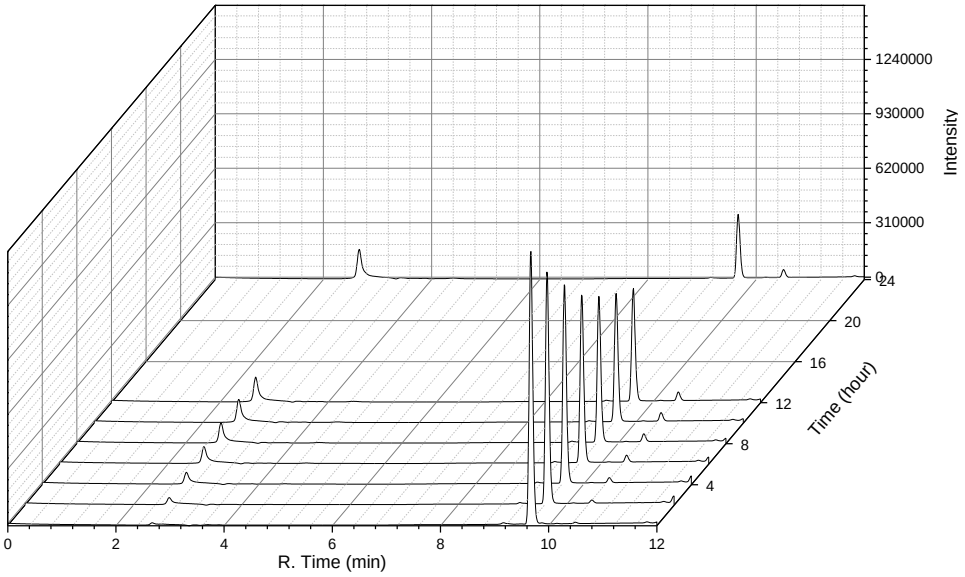


Figure S50. HPLC chromatograms of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(DCA)(acetato)] (13e)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 9.7 min belongs to complex **13e**.

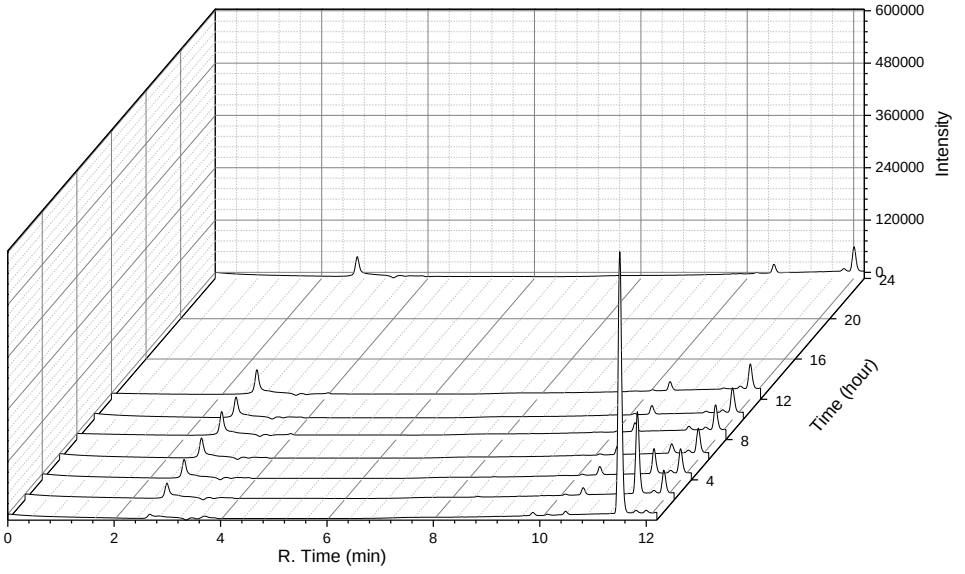


Figure S51. HPLC chromatograms of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(DCA)$_2$] (13g)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 11.5 min belongs to complex **13g**.

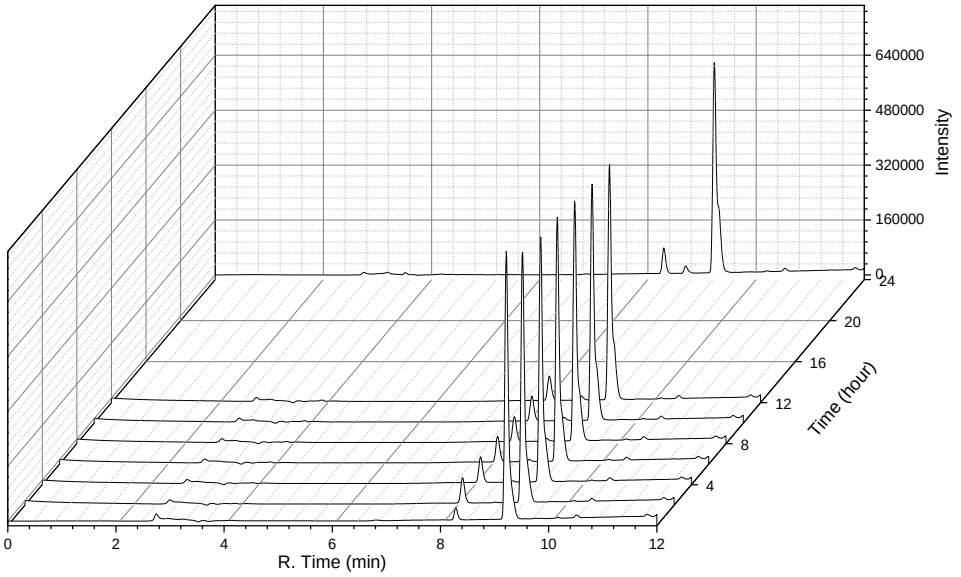


Figure S52. HPLC chromatograms of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)OH] (14d)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 9.2 min belongs to complex **14d**.

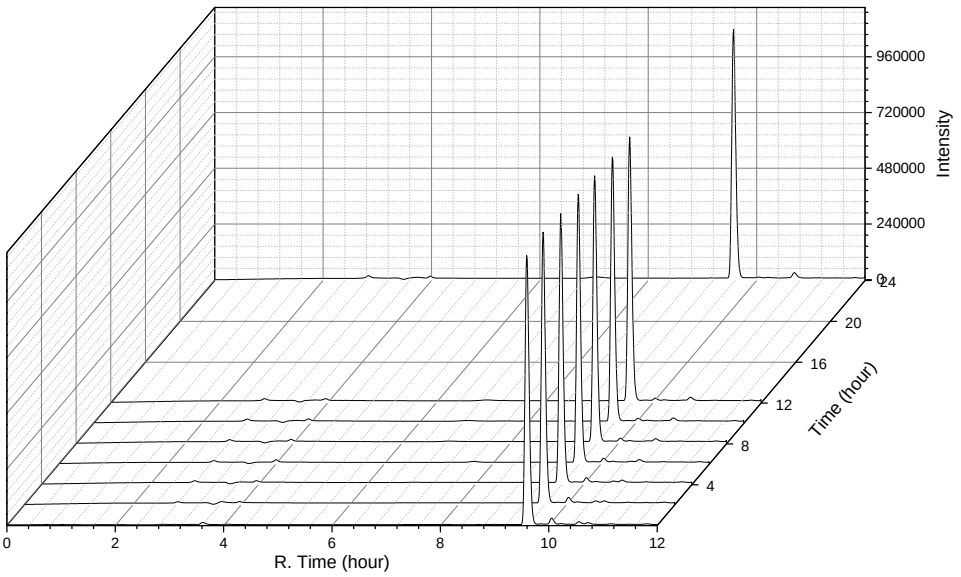


Figure S53. HPLC chromatograms of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)(acetato)] (14e)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 9.6 min belongs to complex **14e**.

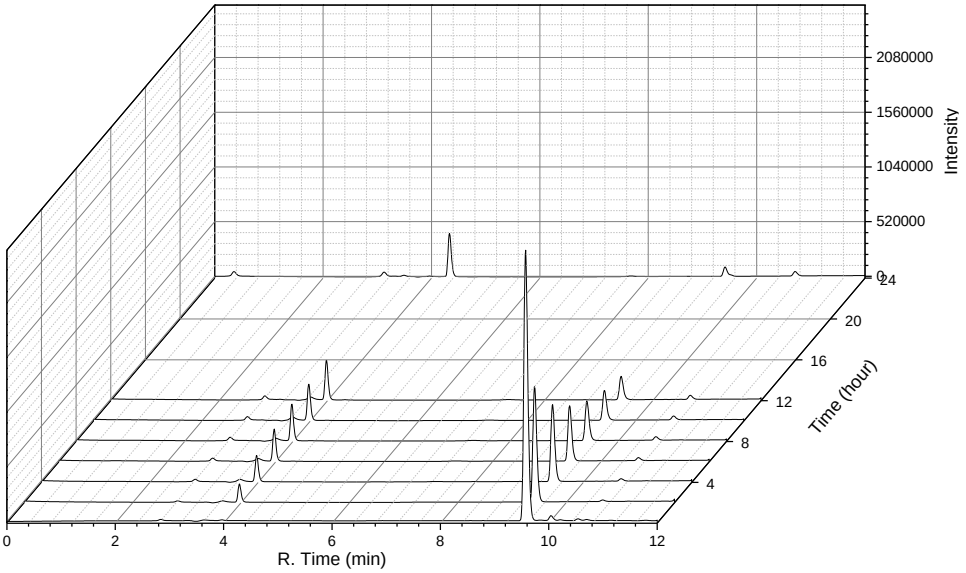


Figure S54. HPLC chromatograms of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)F] (14f)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 9.4 min belongs to complex **14f**.

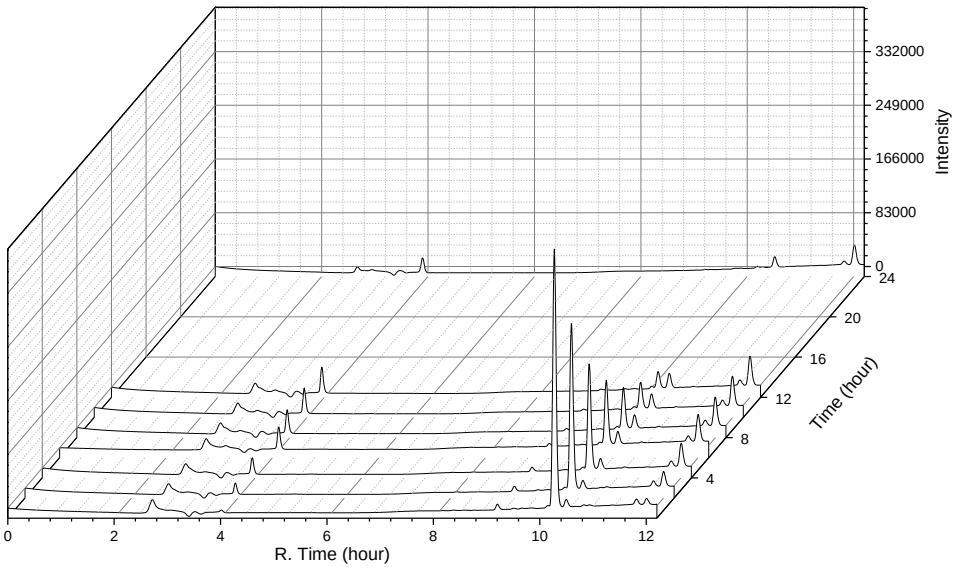


Figure S55. HPLC chromatograms of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)$_2$] (14g)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 10.3 min belongs to complex **14g**.

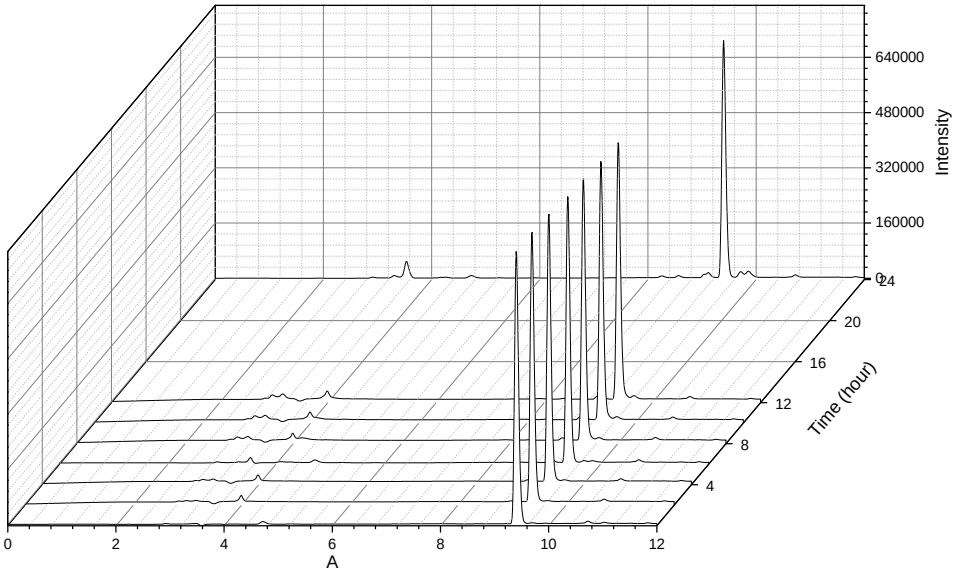


Figure S56. HPLC chromatograms of ***trans*-[Pt(DACH)(ox)(DCA)OH] (15d)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 9.4 min belongs to complex **15d**.

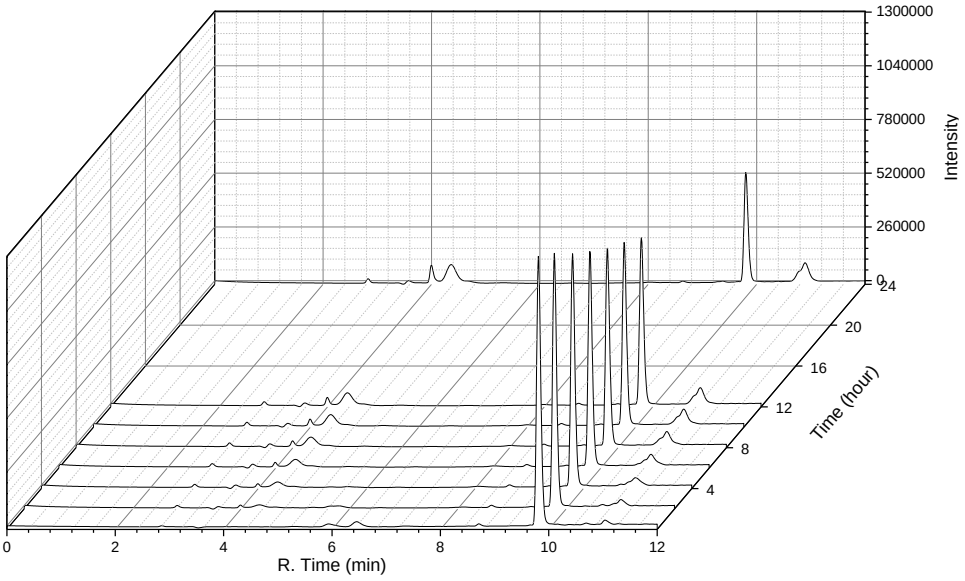


Figure S57. HPLC chromatograms of ***trans*-[Pt(DACH)(ox)(DCA)(acetato)] (15e)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 9.8 min belongs to complex **15e**.

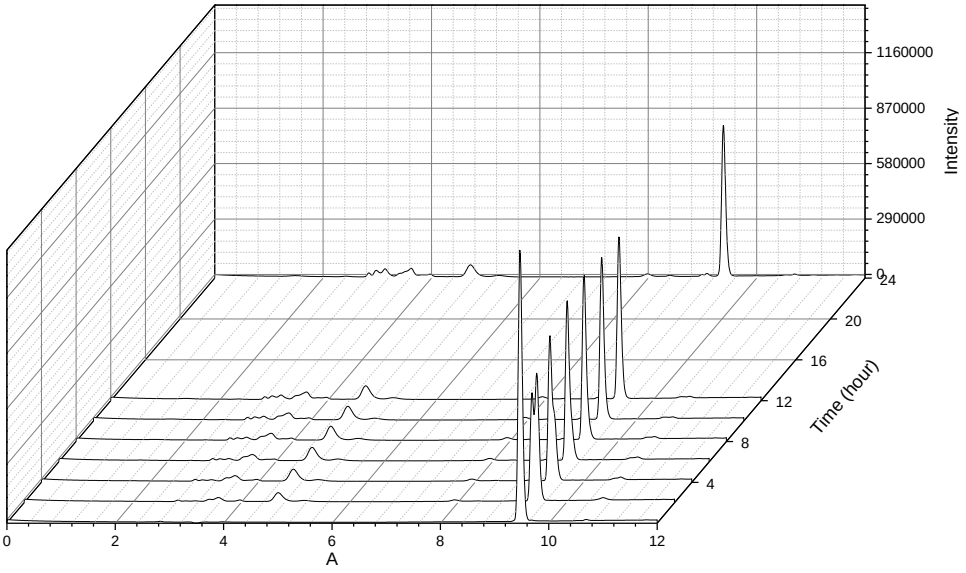


Figure S58. HPLC chromatograms of ***trans*-[Pt(DACH)(ox)(DCA)F] (15f)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 9.4 min belongs to complex **15f**.

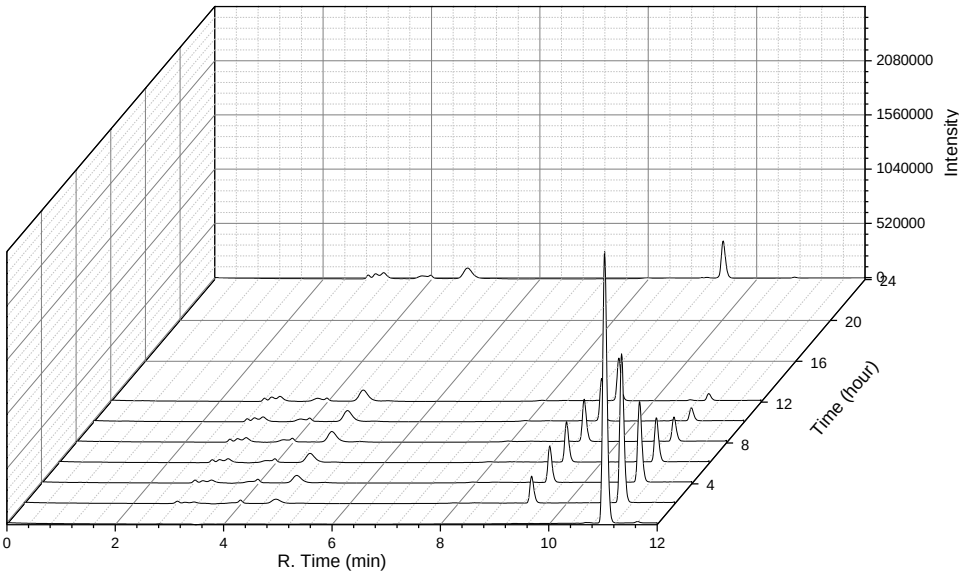


Figure S59. HPLC chromatograms of ***trans*-[Pt(DACH)(ox)(DCA)$_2$] (15g)** in phosphate buffer (50 mM, pH 7.4, H_2O) at 37 °C from 0 to 24 h. Chromatographic peak in 11.0 min belongs to complex **15g**.

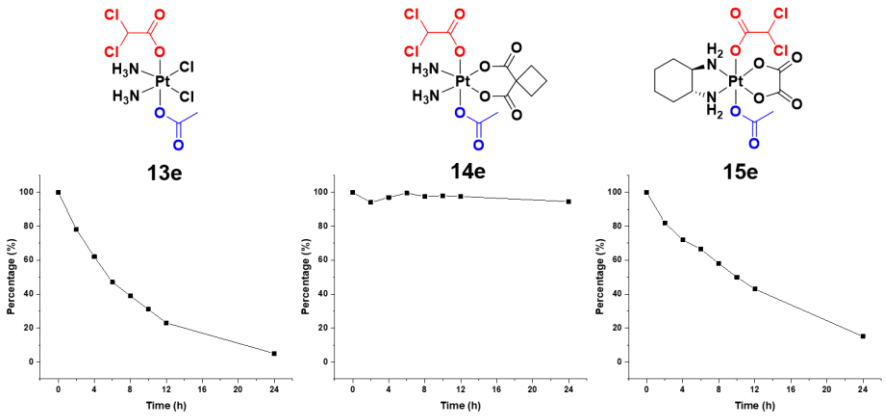


Figure S60. Stability of DCA-containing Pt(IV) complexes **13e**, **14e** and **15e** in FBS (pH 7.4) at 37 °C from 0 to 24 h. All the results are calculated from two independent experiments.

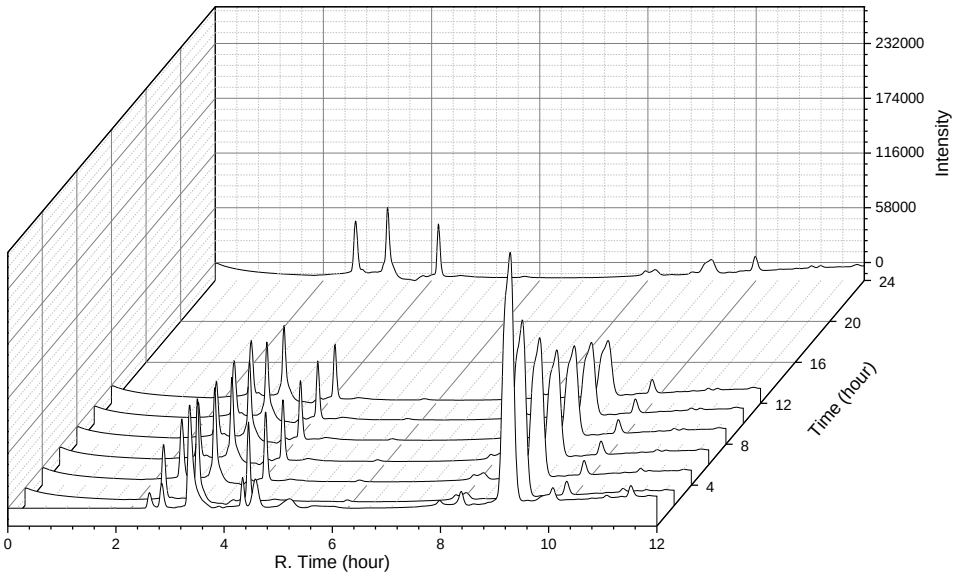


Figure S61. HPLC chromatograms of ***cis,cis,trans*-[Pt(NH$_3$)$_2$(Cl)$_2$(DCA)(acetato)] (13e)** in FBS (pH 7.4) at 37 °C from 0 to 24 h. Chromatographic peak in 9.3 min belongs to complex **13e**.

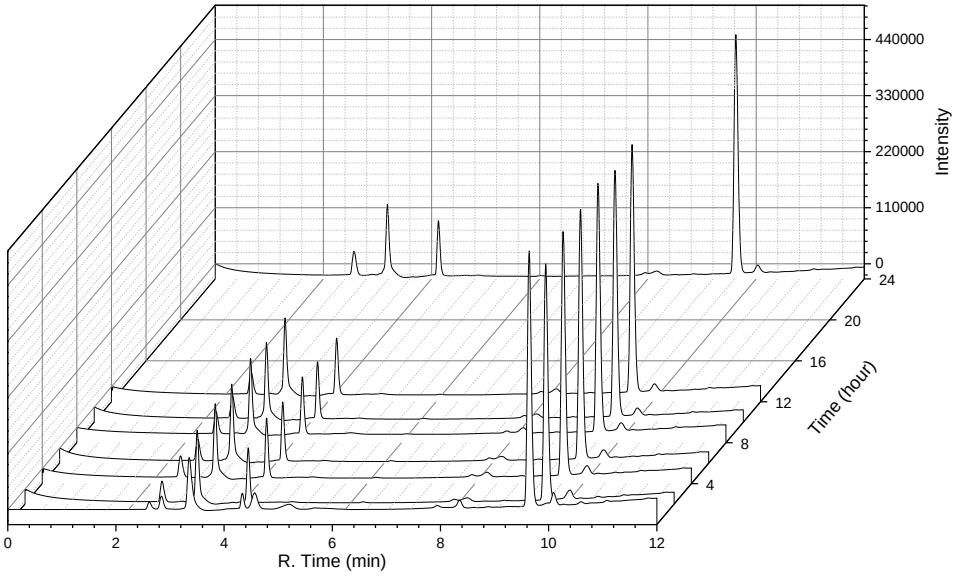


Figure S62. HPLC chromatograms of ***cis,trans*-[Pt(NH$_3$)$_2$(CBDCA)(DCA)(acetato)] (14e)** in FBS (pH 7.4) at 37 °C from 0 to 24 h. Chromatographic peak in 9.6 min belongs to complex **14e**.

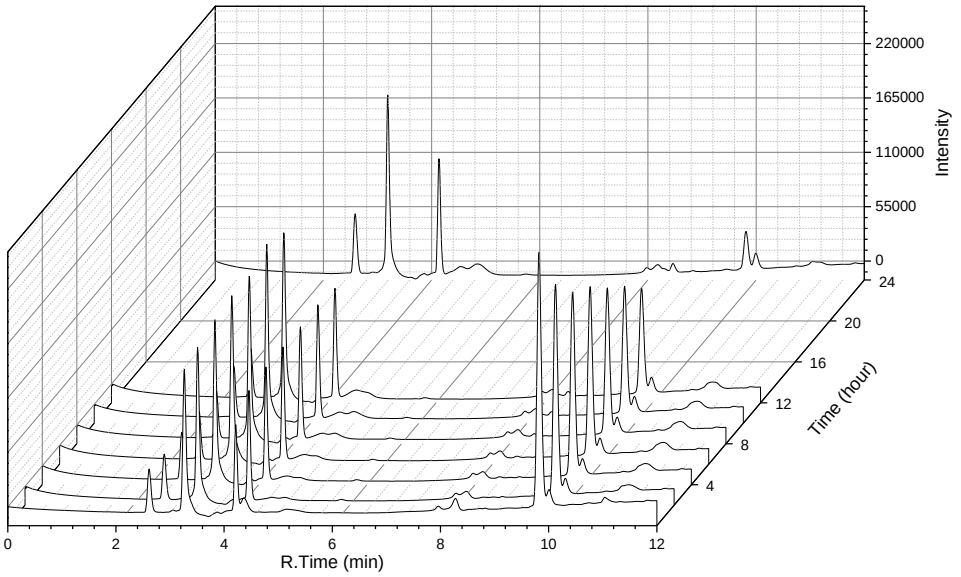


Figure S63. HPLC chromatograms of ***trans*-[Pt(DACH)(ox)(DCA)(acetato)] (15e)** in FBS (pH 7.4) at 37 °C from 0 to 24 h. Chromatographic peak in 9.8 min belongs to complex **15e**.

Table S1. Chemical shifts of succinato (**1a**, **3a** to **12a**), acetato (**1b**, **3b** to **12b**), and boc-β-alaninato (**1c**, **3c** to **12c**) ligands in phosphate buffer (50 mM, pH 7.4, D_2O).

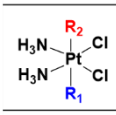
	Complex	R_1	Chemical shift of succinato (R_2, ppm)		Complex	Chemical shift of acetato (R_2, ppm)	Complex	Chemical shift of boc-β-alaninato (R_2, ppm)
			H_{a1}	H_{a2}		H_b		H_{c1}
	**1a**	OH	2.50	2.31	**1b**	1.97	**1c**	2.42
	3a	Cl	2.56	2.33	**3b**	2.02	**3c**	2.45
	4a	Br	2.54	2.33	**4b**	2.00	**4c**	2.44
	**5a**	OH	2.46	2.29	**5b**	1.93	**5c**	2.38
	6a	F	2.50	2.27	**6b**	1.94	**6c**	2.42
	7a	Cl	2.49	2.29	**7b**	1.96	**7c**	2.41
	8a	Br	2.48	2.30	**8b**	1.95	**8c**	2.40
	**9a**	OH	2.44	2.28	**9b**	1.92	**9c**	2.39
	10a	F	2.48	2.27	**10b**	1.94	**10c**	2.43
	11a	Cl	2.49	2.30	**11b**	1.96	**11c**	2.44
	12a	Br	2.48	2.30	**12b**	1.95	**12c**	2.42

Table S2. Hydrolysis free energy profiles ΔG°_{298} / kJ mol^{-1} of acetato in carboplatin-based Pt(IV) complexes (**6b**, **7b** and **8b**) and oxaliplatin-based Pt(IV) complexes (**10b**, **11b** and **12b**), evaluated at the M06-L/Aug-cc-pVTZ level of theory. The transition structures (TS1) for all Pt(IV) complexes **6b-8b** and **10b-12b** are available in Figure S43.

Pt(IV) complexes		R_1	Hydrolysis of acetato	
			TS1	**P1**
 Carboplatin-based	**6b**	F	170	39
	7b	Cl	156	38
	8b	Br	146	35
 Oxaliplatin-based	**10b**	F	158	35
	11b	Cl	140	34
	12b	Br	127	32

Table S3. Natural bond orbital (NBO) charge density on Pt center, halides (R_1) and acetato (AcO) ligands in Pt(IV) complexes **10b-12b** evaluated at the M06-L/Aug-cc-pVTZ level of theory.

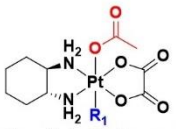
Pt(IV) complexes		R_1	NBO Charge Density (atomic unit)		
			Pt	R_1	AcO
 Oxaliplatin-based	**10b**	F	1.10	-0.55	-0.48
	11b	Cl	0.84	-0.33	-0.46
	12b	Br	0.76	-0.22	-0.48

Table S4. Cartesian coordinates of the optimized geometries as shown reported in Figure 3 and Table S2.

6b-R

N	-2.225424	-0.794786	-1.664599
N	-2.503770	0.187610	1.237690
Pt	-0.977562	-0.424355	-0.034329
C	-0.753489	2.511327	-0.148861
O	-1.145405	2.590683	1.007283
C	-0.345762	3.722593	-0.938717
H	-1.131771	4.470850	-0.878572
H	0.545121	4.148766	-0.480744
H	-0.133639	3.490632	-1.976525
O	-0.624084	1.405942	-0.840118
F	-1.329698	-2.276899	0.617096
H	-1.644247	-1.161640	-2.411066
H	-2.688474	0.037063	-2.010833
H	-2.223729	1.112727	1.569644
H	-2.551954	-0.470967	2.005899
C	2.263202	-0.237915	0.205830
C	3.795182	-0.288916	0.328791
H	4.264842	-1.223712	0.035894
H	4.086727	-0.033419	1.343406
C	3.910819	0.901050	-0.627614
H	4.633150	1.675562	-0.381137
H	4.075771	0.584313	-1.655250
C	2.437248	1.218865	-0.367730
H	1.806092	1.486149	-1.210922
H	2.298074	1.954656	0.423808
C	1.521193	-0.279948	1.531313
C	1.762402	-1.135322	-0.917300
O	2.129676	-0.317133	2.587602
O	0.213869	-0.180806	1.569849
O	2.539169	-1.771816	-1.608453
O	0.485667	-1.159266	-1.219046
H	-2.929269	-1.491212	-1.449001
H	-3.421146	0.251017	0.816323

6b-TS1

Pt	0.983852	-0.529493	-0.063190
O	0.490393	1.921684	1.008385
C	0.534484	2.991420	0.319949
O	1.272224	3.163677	-0.670788
C	-0.406533	4.096298	0.735998
H	-1.296093	4.041155	0.107377
H	0.047455	5.070324	0.574794
H	-0.720658	3.994913	1.770799
O	0.649673	-0.143248	2.421392
H	-0.138488	-0.628889	2.685779
H	0.381558	0.788069	2.290090
O	-0.485566	-1.865912	0.378213
O	-0.184292	0.494997	-1.359106
N	2.521795	0.726339	-0.655379
N	2.270759	-1.750409	1.045820
H	2.115729	1.683836	-0.774733
H	2.886289	0.377769	-1.535023
H	1.723832	-2.534714	1.384625
H	2.661808	-1.277779	1.851058
F	1.439021	-1.632745	-1.616365
C	-2.253855	-0.294683	-0.295342
C	-3.784569	-0.270693	-0.442386
H	-4.248441	-1.198814	-0.763829
H	-4.071831	0.536657	-1.110042
C	-3.911828	0.124966	1.031826
H	-4.654793	0.874281	1.293837
H	-4.047704	-0.743323	1.673303
C	-2.451574	0.576332	0.997305
H	-1.817357	0.357528	1.852314
H	-2.343471	1.631895	0.757355
C	-1.489446	0.423279	-1.392542
C	-1.755880	-1.679648	0.101484
O	-2.077981	1.005815	-2.289933
O	-2.528215	-2.611429	0.245770
H	3.020419	-2.119065	0.472108
H	3.287557	0.781526	0.004010

6b-P1

Pt	1.059723	-0.019842	0.030732
O	0.697877	-0.063580	1.997324
H	0.230789	-0.887271	2.171994
O	-0.309820	-1.421539	-0.435059
O	-0.172845	1.547280	-0.243507
N	2.487686	1.429162	0.456209
N	2.365351	-1.626845	0.226639
H	2.033597	2.333006	0.377427
H	3.265888	1.415070	-0.192001
H	1.836319	-2.478336	0.070075
H	2.782782	-1.683159	1.148138
F	1.550506	0.091504	-1.928035
C	-2.185821	0.135464	-0.119032
C	-3.706677	0.176472	-0.344899
H	-4.073177	-0.361634	-1.214537
H	-4.039693	1.209463	-0.383569
C	-3.927845	-0.454333	1.032624
H	-4.730956	-0.053612	1.646518
H	-4.039634	-1.534831	0.973082
C	-2.500373	-0.055750	1.411475
H	-1.891122	-0.777096	1.950452
H	-2.448530	0.898705	1.931950
C	-1.465923	1.440621	-0.423379
C	-1.581443	-1.162302	-0.639061
O	-2.093247	2.432093	-0.758394
O	-2.278615	-2.019310	-1.153642
H	3.105774	-1.593437	-0.464363
H	2.845438	1.340447	1.399939

7b-R

N	-2.198558	-0.217956	-1.785201
N	-2.421636	0.570160	1.190376
Pt	-0.966725	-0.192553	-0.096423
C	-0.322779	2.709923	0.009581
O	-0.755860	2.775675	1.152856
C	0.300066	3.895530	-0.673060
H	-0.350690	4.758324	-0.558801
H	1.238764	4.125370	-0.171678
H	0.497512	3.714553	-1.723840
O	-0.323317	1.646024	-0.751487
H	-1.648804	-0.600418	-2.547737
H	-2.503289	0.709730	-2.055351
H	-2.033487	1.456588	1.524861
H	-2.550410	-0.073895	1.961360
C	2.273410	-0.470042	0.199214
C	3.776701	-0.764798	0.339955
H	4.107653	-1.728235	-0.037570
H	4.074174	-0.654393	1.378580
C	4.099416	0.477806	-0.494631
H	4.919221	1.108518	-0.159228
H	4.251358	0.236666	-1.544398
C	2.681605	0.989420	-0.234432
H	2.123703	1.421348	-1.061010
H	2.626443	1.664972	0.618665
C	1.498074	-0.501078	1.505725
C	1.681872	-1.170838	-1.015521
O	2.068979	-0.697064	2.565640
O	0.219681	-0.208720	1.536031
O	2.385438	-1.825868	-1.765624
O	0.421987	-0.992765	-1.334191
H	-3.014610	-0.806488	-1.665859
H	-3.324327	0.735373	0.764378
Cl	-1.690162	-2.358124	0.465626

7b-TS1

N	2.437585	-1.061772	1.410456
N	2.270832	1.312928	-0.437293
Pt	1.015913	-0.259469	0.089064
C	-0.261525	3.118229	0.105686
O	0.501329	3.368751	-0.850723
C	-1.470547	3.993508	0.330439
H	-1.257173	5.025550	0.065463
H	-2.271324	3.645444	-0.323281
H	-1.827925	3.935526	1.354734
O	-0.110027	2.140209	0.903876
H	2.132085	-1.998303	1.652892
H	2.476112	-0.517543	2.264230
H	1.657290	2.113089	-0.720795
H	2.881493	1.040143	-1.198930
C	-2.190235	-0.741389	-0.309231
C	-3.673952	-1.067142	-0.550687
H	-3.896186	-2.089203	-0.844196
H	-4.081588	-0.375186	-1.282190
C	-3.994774	-0.645577	0.886397
H	-4.899494	-0.066255	1.053744
H	-3.989807	-1.493676	1.567705
C	-2.667941	0.113878	0.920384
H	-2.062459	0.066368	1.822322
H	-2.772096	1.157900	0.633253
C	-1.532012	0.090949	-1.392708
C	-1.430496	-1.955777	0.206004

O	-2.185644	0.537496	-2.323138
O	-0.267731	0.412838	-1.320137
O	-1.993139	-3.022576	0.384682
O	-0.172214	-1.841854	0.562687
O	0.465348	0.323376	2.555547
H	-0.213322	-0.275483	2.882137
H	0.009583	1.143601	2.277475
H	3.364934	-1.132969	1.009227
H	2.849835	1.626086	0.332370
Cl	1.948555	-1.535919	-1.575607

7b-P1

N	-2.254196	-1.698246	-0.327797
N	-2.368832	1.316767	-0.931703
Pt	-0.984389	-0.051076	-0.187444
H	-1.758334	-2.503870	0.039207
H	-2.495145	-1.890800	-1.293546
H	-1.948163	2.237983	-0.869578
H	-3.244781	1.339750	-0.423922
C	2.253329	0.156832	0.150711
C	3.752290	0.243830	0.485877
H	4.051908	-0.189601	1.435825
H	4.076742	1.278910	0.434490
C	4.083859	-0.534665	-0.790366
H	4.927648	-0.191074	-1.383945
H	4.201061	-1.599288	-0.600267
C	2.686495	-0.206965	-1.319259
H	2.126185	-0.997321	-1.812932
H	2.666411	0.678782	-1.951369
C	1.509554	1.481163	0.233321
C	1.618912	-1.082809	0.766912
O	2.110357	2.515948	0.472401
O	0.232771	1.551540	-0.049600
O	2.283870	-1.872623	1.414330
O	0.366686	-1.382178	0.504447
O	-0.483337	-0.336569	-2.115456
H	0.023305	-1.155533	-2.143167
H	-3.107903	-1.591604	0.206889
H	-2.560549	1.124554	-1.908488
Cl	-1.724956	0.350596	2.043283

8b-R

N	-1.868186	0.774801	-1.867754
N	-1.933854	1.434081	1.160653
Pt	-0.781990	0.286266	-0.148728
C	0.789663	2.822326	0.137545
O	0.349477	2.983145	1.270695
C	1.805876	3.760201	-0.453602
H	1.483983	4.786260	-0.297057
H	2.745715	3.627292	0.079935
H	1.973435	3.578931	-1.509607
O	0.470356	1.855626	-0.678461
H	-1.483452	0.221792	-2.626838
H	-1.762614	1.752723	-2.111768
H	-1.284495	2.147717	1.507915
H	-2.252090	0.852174	1.926094
C	2.167914	-1.071249	0.191704
C	3.482039	-1.856475	0.342922
H	3.488676	-2.856382	-0.081810
H	3.761318	-1.900204	1.391560
C	4.228284	-0.754321	-0.414039
H	5.199433	-0.450668	-0.030530
H	4.326627	-0.981785	-1.473248
C	3.053119	0.188021	-0.148327
H	2.699725	0.822552	-0.956754
H	3.195188	0.799457	0.742258
C	1.378690	-0.905406	1.479909
C	1.423777	-1.472571	-1.074223
O	1.815190	-1.329832	2.537033
O	0.268446	-0.207571	1.503472
O	1.896610	-2.289788	-1.846096
O	0.312305	-0.862582	-1.409570
H	-2.856611	0.563180	-1.801894
H	-2.743704	1.879500	0.749434
Br	-2.278769	-1.659675	0.275853

8b-TS1

Pt	0.843268	0.178862	0.317452
O	-1.121723	2.169622	0.731702
C	-1.449992	2.946429	-0.216452
O	-0.653864	3.371135	-1.082810
C	-2.905005	3.337239	-0.310423
H	-3.392621	2.671518	-1.023966
H	-3.012488	4.351547	-0.685572
H	-3.414857	3.235260	0.643581
O	-0.210821	0.762014	2.641615
H	-0.703632	-0.010549	2.934542
H	-0.852295	1.355016	2.201177
O	0.125776	-1.626053	0.923925
O	-0.396957	0.283481	-1.278772
N	1.599609	2.014468	-0.304575
N	2.238705	0.008008	1.877103
H	0.792698	2.566158	-0.686630
H	2.312029	1.894846	-1.015646
H	2.173207	-0.937415	2.239391
H	1.997552	0.641243	2.630696
C	-1.971977	-1.356443	-0.333413
C	-3.219366	-2.182982	-0.690227
H	-3.055691	-3.243456	-0.859610
H	-3.711110	-1.742072	-1.552563
C	-3.872846	-1.758393	0.628474
H	-4.929271	-1.501782	0.609559
H	-3.702762	-2.487220	1.417960
C	-2.878778	-0.599042	0.705425
H	-2.432298	-0.354567	1.666586
H	-3.264851	0.318470	0.266685
C	-1.468610	-0.447209	-1.439325
C	-0.955488	-2.190361	0.435805
O	-2.101283	-0.318672	-2.476415
O	-1.176061	-3.359147	0.703442
H	3.199119	0.164524	1.596301
H	2.010461	2.543218	0.455104
Br	2.398730	-0.980793	-1.159635

8b-P1

Pt	0.777134	-0.498087	0.005652
O	0.030924	-2.376799	0.152014
H	-0.559593	-2.492730	-0.600079
O	-0.506129	0.056370	-1.453893
O	-0.373233	0.145373	1.534837
N	2.078878	-1.112739	1.512833
N	1.959831	-1.192369	-1.564608
H	1.694243	-0.789030	2.394256
H	3.021894	-0.751882	1.434334
H	1.521808	-0.905249	-2.433631
H	1.989190	-2.206063	-1.546328
C	-2.379937	0.317568	0.116506
C	-3.817847	0.864035	0.119320
H	-3.996333	1.732391	-0.508492
H	-4.124261	1.077139	1.139096
C	-4.334363	-0.490966	-0.372804
H	-5.242651	-0.878447	0.082350
H	-4.447428	-0.516424	-1.454443
C	-3.013924	-1.123271	0.070633
H	-2.543982	-1.843318	-0.595472
H	-3.059401	-1.552389	1.069724
C	-1.601452	0.577941	1.397693
C	-1.696398	0.562095	-1.222452
O	-2.141681	1.110964	2.353265
O	-2.281699	1.121505	-2.133313
H	2.908701	-0.838645	-1.565645
H	2.116719	-2.125588	1.540061
Br	1.859193	1.782087	-0.094596

10b-R

C	3.641307	-0.827253	1.334078
C	2.397473	-0.834745	0.468139
C	2.372140	0.346488	-0.481943
C	3.604356	0.370445	-1.365914
C	4.862924	0.375926	-0.507536
C	4.885568	-0.801631	0.454854
H	2.344773	-1.755911	-0.117359
H	3.621490	0.059068	1.975191
H	3.642029	-1.695532	1.991642
H	3.594956	-0.516388	-2.006547
H	3.570988	1.238178	-2.023358
H	5.740916	0.359170	-1.150980
H	4.910427	1.310975	0.056652
H	4.946511	-1.735192	-0.110379
H	5.773224	-0.763336	1.083914
H	2.312679	1.270415	0.101403
N	1.132993	-0.790089	1.258301
N	1.104793	0.273164	-1.254446
Pt	-0.447492	-0.322522	-0.016856
C	-3.140945	-0.869818	0.601606
C	-3.145379	-0.239494	-0.809155
O	-1.969980	-0.998100	1.160895
O	-1.977427	0.103739	-1.283067
O	-4.172938	-1.217323	1.135321
O	-4.177598	-0.080107	-1.424195
C	-0.509522	2.585581	0.326870
O	-0.091913	2.709473	-0.815925
C	-0.894446	3.760366	1.177767
H	-0.239736	4.599088	0.962448
H	-1.910295	4.053278	0.916546
H	-0.872408	3.524787	2.236224
O	-0.693307	1.445252	0.950191
F	-0.236785	-2.120216	-0.853313
H	0.960558	-1.677946	1.718598
H	1.185339	-0.083594	1.988340
H	0.846800	1.185447	-1.631709
H	1.167094	-0.414061	-2.001389

10b-TS1

Pt	-0.485945	-0.445017	-0.064169
O	-0.221976	2.059668	0.931577
C	-0.012749	3.118659	0.257221
O	0.467080	3.128163	-0.895975
C	-0.401574	4.418513	0.914182
H	-0.245310	4.381294	1.988679
H	-1.464621	4.588492	0.745657
H	0.146697	5.251805	0.484840
O	-0.382982	0.048641	2.393183
H	-1.254991	-0.240854	2.684358
H	-0.434755	1.018989	2.269128
O	-2.062887	-1.436477	0.804931
O	-2.010895	0.573897	-0.956436
C	-3.189210	0.075364	-0.702754
C	-3.221338	-1.085205	0.316996
O	-4.207801	0.497628	-1.207068
O	-4.267551	-1.601610	0.645316
C	3.571665	0.677981	-1.047545
C	2.329056	0.246138	-0.291210
C	2.370848	-1.232556	0.040080
C	3.600062	-1.593229	0.850181
C	4.854336	-1.158867	0.101113
C	4.815882	0.322570	-0.243072
H	2.237482	0.822372	0.635920
H	3.593658	0.166926	-2.014460
H	3.523613	1.746744	-1.252906
H	3.549131	-1.083648	1.816757
H	3.613682	-2.663089	1.053602
H	5.732578	-1.387854	0.702388
H	4.946207	-1.745364	-0.816731
H	4.830151	0.912224	0.677356
H	5.704861	0.605439	-0.804361
H	2.357330	-1.797666	-0.895767
N	1.077861	0.489211	-1.038792
N	1.093562	-1.559604	0.735261
H	0.864970	1.513897	-1.120904

H	1.120842	0.069156	-1.964925
H	0.884536	-2.550583	0.673175
H	1.133153	-1.316471	1.722730
F	-0.549023	-1.664798	-1.594444

10b-P1

Pt	-0.505685	0.000726	0.034253
O	-0.379597	0.060308	2.027618
H	-1.143343	-0.423763	2.360713
O	-2.039629	-1.330594	0.108446
O	-2.036413	1.341029	-0.018694
C	-3.208810	0.775534	-0.091644
C	-3.212922	-0.767209	-0.012302
O	-4.243710	1.399763	-0.197034
O	-4.248167	-1.396830	-0.042478
C	3.564872	1.474127	-0.096591
C	2.334141	0.686581	0.308006
C	2.318684	-0.687391	-0.333128
C	3.564252	-1.476351	0.020878
C	4.807838	-0.694168	-0.382454
C	4.823510	0.688844	0.250132
H	2.299573	0.568844	1.394336
H	3.527951	1.659948	-1.174220
H	3.559437	2.446355	0.394444
H	3.573258	-1.658345	1.099741
H	3.536019	-2.450233	-0.465979
H	5.697087	-1.253932	-0.097769
H	4.836809	-0.599401	-1.471078
H	4.901008	0.593432	1.336228
H	5.700325	1.246841	-0.073843
H	2.238673	-0.572298	-1.417219
N	1.059441	1.361564	-0.065571
N	1.060380	-1.357644	0.097361
H	0.885815	2.166626	0.526737
H	1.093074	1.693975	-1.026915
H	0.869723	-2.177584	-0.468427
H	1.123208	-1.659794	1.068142
F	-0.495913	-0.028220	-1.986603

10b-TS2

Pt	0.434091	-0.253126	-0.031436
O	-0.046494	-2.789088	-0.300114
H	0.816426	-3.171515	-0.486238
H	-0.109006	-2.706712	0.696394
O	1.976130	-0.884363	-1.235454
O	1.980002	0.104456	1.251978
C	3.153075	-0.153992	0.741996
C	3.151664	-0.712666	-0.698858
O	4.188482	0.016686	1.349718
O	4.189204	-0.980967	-1.266866
F	-0.191917	-1.866596	1.963654
O	0.752573	1.537221	-0.873789
C	0.672861	2.650668	-0.159314
C	1.076753	3.830384	-0.998516
H	1.188876	3.583161	-2.047383
H	2.025605	4.201986	-0.616991
H	0.334152	4.613613	-0.874485
O	0.331895	2.735558	1.001226
C	-3.611162	0.502667	1.319163
C	-2.376904	0.521771	0.435460
C	-2.423008	-0.598302	-0.585598
C	-3.659344	-0.509482	-1.457731
C	-4.906876	-0.519001	-0.582563
C	-4.866474	0.587986	0.460013
H	-2.313231	1.479064	-0.091258
H	-3.613811	-0.426874	1.895927
H	-3.566800	1.321736	2.035638
H	-3.617846	0.417269	-2.037685
H	-3.672766	-1.332439	-2.171023
H	-5.790909	-0.419993	-1.210177
H	-4.988019	-1.488267	-0.083873
H	-4.896401	1.560714	-0.037975
H	-5.747364	0.541259	1.098143
H	-2.399601	-1.555560	-0.056447
N	-1.119811	0.370222	1.198131
N	-1.151492	-0.542408	-1.357139
H	-0.834766	1.235535	1.649953
H	-1.130647	-0.419495	1.860859
H	-0.991414	-1.414430	-1.851188
H	-1.163061	0.213251	-2.037897

10b-P2

Pt	-0.444207	-0.358853	-0.028857
O	-0.167933	-2.180934	-0.828242
H	-0.920426	-2.335949	-1.409521
O	-1.975231	-1.006936	1.162144
O	-1.979512	0.041745	-1.300571
C	-3.155610	-0.197618	-0.781727
C	-3.150876	-0.800376	0.641772
O	-4.191691	0.017718	-1.373128
O	-4.189535	-1.069758	1.209273
O	-0.688513	1.460416	0.938655
C	-0.497175	2.586937	0.309607
C	-0.878157	3.784637	1.133196
H	-0.747535	3.602547	2.195146
H	-1.931798	4.001150	0.961475
H	-0.302125	4.651138	0.824501
O	-0.072438	2.697691	-0.837364
C	3.601352	0.395957	-1.350921
C	2.361894	0.348811	-0.478376
C	2.404626	-0.826514	0.478473
C	3.640811	-0.787969	1.354436
C	4.891959	-0.738702	0.486116
C	4.851695	0.434074	-0.481577
H	2.276227	1.273852	0.100341
H	3.617557	-0.494353	-1.986645
H	3.554488	1.259102	-2.013694
H	3.596596	0.100721	1.991146
H	3.655342	-1.652784	2.016470
H	5.773369	-0.678567	1.122282
H	4.978153	-1.672890	-0.074866
H	4.872476	1.372222	0.079291
H	5.736126	0.434849	-1.116433
H	2.375761	-1.751634	-0.102561
N	1.104139	0.244684	-1.260937
N	1.132603	-0.802515	1.256766
H	0.834569	1.151159	-1.645101
H	1.181006	-0.455725	-1.994635
H	0.971289	-1.692448	1.716729
H	1.165596	-0.092007	1.984006

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C	3.659101	-0.589590	1.453072
C	2.425444	-0.719405	0.576628
C	2.386213	0.359499	-0.493611
C	3.630690	0.317817	-1.365303
C	4.879897	0.443020	-0.496921
C	4.915994	-0.626731	0.587195
H	2.405354	-1.702062	0.088454
H	3.610666	0.361191	2.000128
H	3.671258	-1.387446	2.200085
H	3.648830	-0.634379	-1.911724
H	3.586571	1.114249	-2.112711
H	5.768979	0.377184	-1.128669
H	4.901991	1.437757	-0.034649
H	5.007635	-1.617002	0.124279
H	5.796952	-0.500032	1.220971
H	2.303340	1.340462	-0.006658
N	1.148589	-0.629835	1.347472
N	1.127687	0.188824	-1.270483
Pt	-0.447103	-0.272353	0.028335
C	-3.177955	-0.549076	0.759956
C	-3.177916	-0.065564	-0.710017
O	-2.003908	-0.721574	1.306114
O	-2.002962	0.132899	-1.250863
O	-4.219859	-0.749312	1.352064
O	-4.216774	0.117827	-1.311732
C	-0.386938	2.695796	0.082168
O	-0.015668	2.686248	-1.085721
C	-0.701812	3.965823	0.823058
H	-0.053635	4.767399	0.471741
H	-1.734972	4.243636	0.600390
H	-0.609211	3.846658	1.900794
O	-0.575251	1.632099	0.830788
H	0.991357	-1.478879	1.889783
H	1.173828	0.147559	2.011194
H	0.858106	1.067259	-1.726792
H	1.211823	-0.556852	-1.963451
Cl	-0.355277	-2.510068	-0.729105

11b-TS1

Pt	-0.463722	-0.417610	0.001453
O	-0.204434	2.208273	0.789785
C	-0.006023	3.197240	0.016954
O	0.488226	3.094247	-1.127700
C	-0.424288	4.551721	0.527590
H	0.085595	5.347048	-0.008053
H	-0.242064	4.643760	1.594952
H	-1.496414	4.667921	0.371203
O	-0.281550	0.322204	2.427424
H	-1.140096	0.069228	2.783604
H	-0.344520	1.271556	2.192553
O	-2.042532	-1.297190	0.992649
O	-1.993601	0.600678	-0.884269
C	-3.179907	0.202221	-0.515758
C	-3.209817	-0.901767	0.563126
O	-4.202171	0.675054	-0.964760
O	-4.258382	-1.338540	0.986857
Cl	-0.598921	-1.995340	-1.654763
C	3.596057	0.687957	-1.011432
C	2.347290	0.292470	-0.244948
C	2.409851	-1.156948	0.196156
C	3.628649	-1.429155	1.055070
C	4.889674	-1.030168	0.297553
C	4.832118	0.418977	-0.162197
H	2.229631	0.934261	0.634669
H	3.643862	0.103537	-1.934995
H	3.532945	1.736367	-1.300437
H	3.548686	-0.846453	1.977539
H	3.657824	-2.479373	1.342374
H	5.760009	-1.194883	0.930505
H	5.009580	-1.684308	-0.569957
H	4.821181	1.079042	0.709076
H	5.725527	0.672942	-0.730296
H	2.427436	-1.789451	-0.695709
N	1.107972	0.458543	-1.032365
N	1.125924	-1.460662	0.888486
H	0.880162	1.473761	-1.187708
H	1.188096	-0.012089	-1.931021
H	0.941816	-2.458202	0.899513
H	1.139411	-1.138566	1.854408

11b-P1

Pt	0.484237	0.017816	-0.085722
O	0.289706	0.462287	-2.037702
H	1.052588	0.068453	-2.476113
O	2.020121	-1.257503	-0.490816
O	2.018219	1.344985	0.129313
C	3.194465	0.795982	0.007427
C	3.197327	-0.706452	-0.350714
O	4.231520	1.410275	0.143928
O	4.233013	-1.315811	-0.508330
Cl	0.551769	-0.489811	2.236615
C	-3.591518	1.460370	0.238496
C	-2.351353	0.749191	-0.265603
C	-2.354455	-0.715168	0.127323
C	-3.591504	-1.423239	-0.389120
C	-4.844779	-0.715602	0.110227
C	-4.841078	0.755816	-0.274369

H	-2.285031	0.821418	-1.354252
H	-3.584431	1.450661	1.332464
H	-3.571183	2.504321	-0.071392
H	-3.572789	-1.414149	-1.482932
H	-3.577059	-2.467127	-0.078689
H	-5.726226	-1.212845	-0.290939
H	-4.903667	-0.809708	1.197608
H	-4.887896	0.850087	-1.362348
H	-5.725706	1.255011	0.117238
H	-2.298482	-0.789551	1.217007
N	-1.087177	1.342412	0.254949
N	-1.088196	-1.309215	-0.385023
H	-0.893677	2.234055	-0.188629
H	-1.149495	1.509827	1.256700
H	-0.908400	-2.212650	0.039325
H	-1.134734	-1.442270	-1.393822

11b-TS2

Pt	0.433190	-0.143334	-0.157787
O	-0.007878	-2.568906	-1.124176
H	0.865954	-2.787391	-1.467190
H	-0.035852	-2.952871	-0.223911
O	1.965265	-0.499184	-1.473881
O	1.984426	-0.065715	1.163656
C	3.155463	-0.207151	0.605139
C	3.146677	-0.446057	-0.919759
O	4.193363	-0.167851	1.230091
O	4.177113	-0.589450	-1.540656
O	0.734101	1.798829	-0.568995
C	0.690272	2.719474	0.384291
C	1.108062	4.051129	-0.173679
H	1.167772	4.055711	-1.255367
H	2.087718	4.288069	0.236761
H	0.404878	4.804692	0.169220
O	0.370641	2.542863	1.540056
C	-3.621141	0.330493	1.310315
C	-2.386777	0.535670	0.451907
C	-2.427405	-0.347803	-0.779389
C	-3.662246	-0.079392	-1.616231
C	-4.911077	-0.275521	-0.765311
C	-4.875796	0.589459	0.485520
H	-2.324469	1.580612	0.133377
H	-3.621994	-0.699346	1.680205
H	-3.579511	0.982359	2.181631
H	-3.621133	0.948956	-1.986880
H	-3.671731	-0.733239	-2.487062
H	-5.794258	-0.049596	-1.360350
H	-4.989892	-1.327851	-0.480641
H	-4.908269	1.644571	0.201544
H	-5.756894	0.407672	1.098568
H	-2.403571	-1.395243	-0.463040
N	-1.128296	0.234569	1.175182
N	-1.154699	-0.125404	-1.517186
H	-0.827578	1.008643	1.765564
H	-1.194719	-0.622514	1.732928
H	-1.001462	-0.858110	-2.202375
H	-1.162104	0.767222	-2.004658
Cl	-0.121952	-2.557232	1.866326

12b-R

C	3.667283	-0.335130	1.530218
C	2.434429	-0.532571	0.671449
C	2.407524	0.436339	-0.494527
C	3.648925	0.298726	-1.354349
C	4.897204	0.492492	-0.502873
C	4.921492	-0.469076	0.675259
H	2.402398	-1.553216	0.280500
H	3.629870	0.661126	1.980724
H	3.669609	-1.054699	2.347827
H	3.656761	-0.698443	-1.804498
H	3.612964	1.017494	-2.171913
H	5.782923	0.359475	-1.121702
H	4.927198	1.521778	-0.136056
H	4.998742	-1.495680	0.308077
H	5.801274	-0.294711	1.292239
H	2.333745	1.456744	-0.105749
N	1.160256	-0.352477	1.426913
N	1.149209	0.205085	-1.250895
Pt	-0.421883	-0.075845	0.088230
C	-3.134624	-0.125851	0.868608
C	-3.130876	0.215420	-0.637231
O	-1.963654	-0.316897	1.409291
O	-1.956247	0.274969	-1.204603
O	-4.172914	-0.206605	1.490368
O	-4.163413	0.414123	-1.240861
C	-0.247478	2.880092	-0.152214
O	0.103855	2.743556	-1.317584
C	-0.507269	4.228922	0.455603
H	0.111637	4.978104	-0.027646
H	-1.551060	4.487009	0.282081
H	-0.338111	4.230577	1.527316
O	-0.458551	1.906371	0.696539
H	0.989828	-1.141168	2.042348
H	1.202309	0.478321	2.013474
H	0.895424	1.035955	-1.788776
H	1.225710	-0.601069	-1.865134
Br	-0.441797	-2.500007	-0.462628

12b-TS1

Pt	-0.448783	-0.246554	0.175407
O	0.011508	2.583677	0.503676
C	0.312024	3.386667	-0.429011
O	0.782194	3.019325	-1.531966
C	0.056091	4.851700	-0.183197
H	0.571110	5.473182	-0.909669
H	0.355592	5.133194	0.823419
H	-1.013676	5.042283	-0.262756
O	-0.040808	0.936789	2.423439
H	-0.887340	0.855011	2.875343
H	-0.044112	1.818374	1.989569
O	-2.043638	-0.820963	1.338497
O	-1.942827	0.699104	-0.860589
C	-3.134282	0.486750	-0.373539
C	-3.193494	-0.386150	0.898556
O	-4.140815	0.949794	-0.866306
O	-4.248077	-0.623783	1.447004
C	3.643069	0.465115	-1.038767
C	2.390652	0.258810	-0.207176
C	2.380823	-1.111613	0.442516
C	3.602905	-1.328732	1.312203
C	4.866489	-1.119783	0.486078
C	4.880506	0.249409	-0.176837
H	2.327443	1.027695	0.570689
H	3.637431	-0.248616	-1.868015
H	3.632224	1.462483	-1.476628
H	3.578245	-0.614949	2.140872
H	3.579121	-2.325849	1.749739
H	5.740611	-1.244318	1.122986
H	4.928154	-1.897571	-0.279601
H	4.924997	1.026666	0.590578
H	5.774240	0.367244	-0.787380
H	2.337645	-1.869463	-0.345254
N	1.146565	0.382580	-0.996968
N	1.100535	-1.227591	1.196062
H	0.982143	1.381295	-1.291901
H	1.197080	-0.201436	-1.828672
H	0.868067	-2.197480	1.380981
H	1.158552	-0.747109	2.091886
Br	-0.749176	-2.158827	-1.296475

12b-P1

Pt	0.429538	-0.281766	0.015840
O	0.155622	-2.286516	0.111724
H	0.918374	-2.635905	0.586219
O	1.961095	-0.384102	1.357216
O	1.961393	-0.495565	-1.316477
C	3.135164	-0.533740	-0.750430
C	3.137287	-0.456276	0.791877
O	4.170532	-0.638744	-1.374023
O	4.171886	-0.481323	1.422981
C	-3.646846	-0.275789	-1.463976
C	-2.412725	-0.594517	-0.643227
C	-2.404222	0.173632	0.663841
C	-3.646108	-0.117515	1.483116
C	-4.893662	0.199036	0.668101
C	-4.902730	-0.559892	-0.649791
H	-2.364995	-1.663935	-0.422934
H	-3.619031	0.780647	-1.747548
H	-3.636714	-0.853497	-2.387174
H	-3.643698	-1.174995	1.763746
H	-3.622826	0.457379	2.407803
H	-5.780065	-0.040855	1.252821
H	-4.933012	1.273799	0.472283
H	-4.969838	-1.633132	-0.453623
H	-5.782130	-0.297560	-1.235443
H	-2.333852	1.242965	0.445631
N	-1.142918	-0.271791	-1.353864
N	-1.143379	-0.180200	1.372958
H	-0.959630	-0.942651	-2.092827
H	-1.195214	0.647336	-1.787329
H	-0.957322	0.461664	2.136092
H	-1.203071	-1.119909	1.762329
Br	0.600628	2.226307	-0.122218

12b-TS2

Pt	-0.585886	0.054566	0.199680
O	0.240295	-2.119034	2.002107
H	-0.635076	-2.484912	2.160066
H	0.572556	-2.585167	1.212784
O	-2.121292	-0.293066	1.509708
O	-2.029844	-0.427962	-1.164974
C	-3.194815	-0.667297	-0.622963
C	-3.250571	-0.574316	0.918326
O	-4.176646	-0.957384	-1.270375
O	-4.283137	-0.770959	1.520947
O	-1.211681	1.956463	0.242586
C	-1.273706	2.671079	-0.875153
C	-1.896191	4.008590	-0.586380
H	-1.267218	4.778290	-1.025081
H	-2.033576	4.193991	0.471835
H	-2.863426	4.035295	-1.083990
O	-0.897274	2.324026	-1.972273
C	3.415531	0.957881	-1.194184
C	2.108283	1.097549	-0.436164
C	2.215186	0.465026	0.938559
C	3.328765	1.087652	1.755801
C	4.647075	0.960136	1.002284
C	4.555293	1.568891	-0.388786
H	1.845777	2.153989	-0.323739
H	3.602983	-0.107574	-1.361400
H	3.329345	1.424591	-2.174288
H	3.097279	2.142783	1.928392
H	3.385163	0.609413	2.732769
H	5.440845	1.436209	1.575422
H	4.913069	-0.097152	0.922304
H	4.400112	2.647843	-0.306375
H	5.492452	1.432067	-0.925804
H	2.386887	-0.608917	0.810765
N	0.972233	0.448550	-1.139224
N	0.878995	0.577043	1.582559
H	0.594567	1.025186	-1.888047
H	1.250721	-0.469767	-1.500055
H	0.796008	-0.069808	2.362782
H	0.705092	1.520646	1.919730
Br	1.418127	-2.844575	-0.97703

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