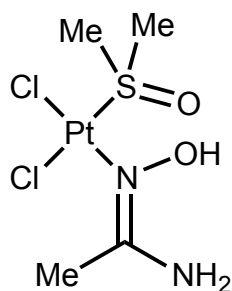


## Electronic Supporting Information

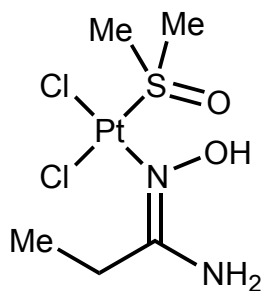
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### Characterization of 3a–b and 3d–f

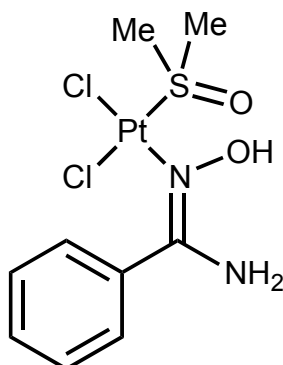


**3a.** Yield: 96% (80.3 mg). Mp: 142 °C (dec). Anal. Calcd for C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>PtS: C, 11.49; H, 2.89; N, 6.70. Found: C, 11.68; H, 2.74; N, 6.88. HRESI<sup>+</sup>-MS (MeOH, *m/z*): 346.0153 ([M – 2Cl – H]<sup>+</sup>, calcd 346.0183), 382.9909 ([M – Cl]<sup>+</sup>, calcd 382.9937), 440.9490 ([M + Na]<sup>+</sup>, calcd 440.9515), 800.9536 ([2M – Cl]<sup>+</sup>, calcd 800.9561), 858.9113 ([2M + Na]<sup>+</sup>, calcd 858.9142). IR (KBr, selected bonds, cm<sup>-1</sup>): 3480(m-s), 3366(s), 3215(s) ν(O–H) and ν(N–H); 2998(m), 2926(w-m), 2785(w) ν(C–H); 1663(vs) ν(C=N); 1105(vs) ν(S=O). <sup>1</sup>H NMR (CD<sub>3</sub>OD, δ): 3.45 (s, br, 6H, S(CH<sub>3</sub>)<sub>2</sub>), 2.36 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, δ): 158.29 (C(NH<sub>2</sub>)=NOH), 43.20 (s, CH<sub>3</sub>), 42.96 (s, CH<sub>3</sub>), 17.64 (CH<sub>3</sub>). Crystals of **3a** suitable for X-ray diffraction were obtained by the slow evaporation of MeOH solution at RT in air.

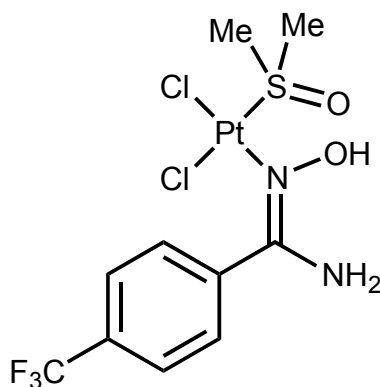


**3b.** Yield: 83% (71.8 mg). Mp: 160 °C (dec). Anal. Calcd for C<sub>5</sub>H<sub>14</sub>N<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>PtS: C, 13.89; H, 3.26; N, 6.48. Found: C, 13.89; H, 3.12; N, 6.54. HRESI<sup>+</sup>-MS (MeOH, *m/z*): 360.0320 ([M – 2Cl – H]<sup>+</sup>, calcd 360.0340), 418.9885 ([M – Cl – H + Na]<sup>+</sup>, calcd 418.9913), 454.9648 ([M + Na]<sup>+</sup>, calcd 454.9672), 812.9913 ([2M – 2Cl – 2H + Na]<sup>+</sup>, calcd 812.9937), 886.9433 ([2M + Na]<sup>+</sup>, calcd 886.9456), 1245.9653 ([3M – 2Cl – 2H + Na]<sup>+</sup>, calcd 1245.9721). IR (KBr, selected bonds, cm<sup>-1</sup>): 3462(s), 3378(vs), 3233(s) ν(O–H) and ν(N–H); 3009(w-m), 2914(w-m), 2803(w) ν(C–H); 1659(vs) ν(C=N); 1117(s) ν(S=O). <sup>1</sup>H NMR (CD<sub>3</sub>OD, δ): 3.46 (s, 3H, CH<sub>3</sub>), 3.44 (s, 3H, CH<sub>3</sub>),

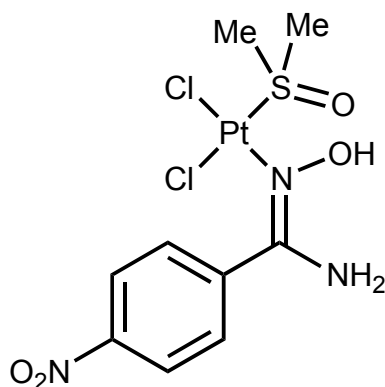
2.92–2.76 (m, 2H,  $CH_2$ ), 1.32 (t, 3H,  $CH_3$ ).  $^{13}C\{^1H\}$  NMR ( $CD_3OD$ ,  $\delta$ ): 162.29 ( $C(NH_2)=NOH$ ), 43.31 (s,  $CH_3$ ), 42.98 (s,  $CH_3$ ), 26.08 ( $CH_2$ ), 10.17 ( $CH_3$ ). Crystals of **3b** suitable for X-ray diffraction were obtained by the slow evaporation of MeOH solution at RT in air.



**3d**. Yield: 92% (88.4 mg). Mp: 149 °C (dec). Anal. Calcd for  $C_9H_{14}N_2Cl_2O_2PtS$ : C, 22.51; H, 2.94; N, 5.83. Found: C, 22.58; H, 2.88; N, 5.84. HRESI<sup>+</sup>-MS (MeOH,  $m/z$ ): 408.0325 ( $[M - 2Cl - H]^+$ , calcd 408.0341), 445.0087 ( $[M - Cl]^+$ , calcd 445.0095), 502.9661 ( $[M + Na]^+$ , calcd 502.9674), 518.9390 ( $[M + K]^+$ , calcd 518.9412), 924.9872 ( $[2M - Cl]^+$ , calcd 924.9878), 982.9455 ( $[2M + Na]^+$ , calcd 982.9459), 998.9189 ( $[2M + K]^+$ , calcd 998.9198). IR (KBr, selected bonds,  $cm^{-1}$ ): 3451(s), 3320(s)  $\nu(O-H)$  and  $\nu(N-H)$ ; 3187(m), 3005(w-m), 2924(w)  $\nu(C-H)$ ; 1655(vs)  $\nu(C=N)$ ; 1138(m)  $\nu(S=O)$ .  $^1H$  NMR ( $CD_3OD$ ,  $\delta$ ): 8.02 (d, 2H,  $CH$ ), 7.63 (t, 1H,  $CH$ ), 7.57 (t, 2H,  $CH$ ), 3.37 (s, 3H,  $CH_3$ ), 2.59 (s, 3H,  $CH_3$ ).  $^{13}C\{^1H\}$  NMR ( $CD_3OD$ ,  $\delta$ ): 159.05 ( $C(NH_2)=NOH$ ), 132.46 ( $C-C(NH_2)=NOH$ ), 130.74 ( $p-C$ ), 129.60, 127.83 ( $o-$  and  $m-C$ ), 42.95 ( $CH_3$ ), 42.48 ( $CH_3$ ). Crystals of **3d**•MeOH suitable for X-ray diffraction were obtained by the slow evaporation of MeOH solution at RT in air.

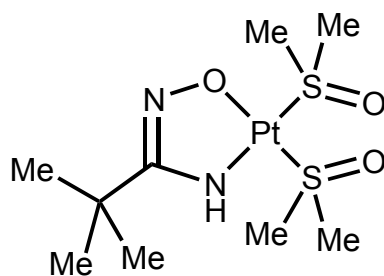


**3e**·½H<sub>2</sub>O. Yield: 97% (108.1 mg). Mp: 185 °C (dec). Anal. Calcd for C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>Cl<sub>2</sub>F<sub>3</sub>O<sub>2</sub>PtS·½H<sub>2</sub>O: C, 21.55; H, 2.53; N, 5.03. Found: C, 21.48; H, 2.70; N, 5.01. HRESI<sup>+</sup>-MS (MeOH, *m/z*): 476.0230 ([M – 2Cl – H]<sup>+</sup>, calcd 476.0215), 512.9982 ([M – Cl]<sup>+</sup>, calcd 512.9970), 570.9570 ([M + Na]<sup>+</sup>, calcd 570.9548), 1060.9621 ([2M – Cl]<sup>+</sup>, calcd 1060.9627), 1118.9207 ([2M + Na]<sup>+</sup>, calcd 1118.9208), 1134.8940 ([2M + K]<sup>+</sup>, calcd 1134.8946). IR (KBr, selected bonds, cm<sup>-1</sup>): 3451(s), 3342(s) ν(O–H) and ν(N–H); 3185(w-m), 3027(w), 3002(w), 2920(w-m) ν(C–H); 1661(vs) ν(C=N); 1138(s) ν(S=O). <sup>1</sup>H NMR (CD<sub>3</sub>OD, δ): 8.17 (d, 2H, CH), 7.90 (d, 2H, CH), 3.41 (s, 3H, CH<sub>3</sub>), 2.73 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>OD, δ): 157.89 (s, C(NH<sub>2</sub>)=NOH), 136.24 (s, C–C(NH<sub>2</sub>)=NOH), 132.30 (q, *J*<sub>CF</sub> = 32 Hz, C–CF<sub>3</sub>), 130.44 (s, C–C–C–CF<sub>3</sub>), 124.71 (q, *J*<sub>CF</sub> = 4 Hz, C–C–CF<sub>3</sub>), 123.88 (q *J*<sub>CF</sub> = 272 Hz, CF<sub>3</sub>), 43.11 (s, CH<sub>3</sub>), 42.55 (s, CH<sub>3</sub>). Crystals of **3e** suitable for X-ray diffraction were obtained by the slow evaporation of MeOH solution at RT in air.

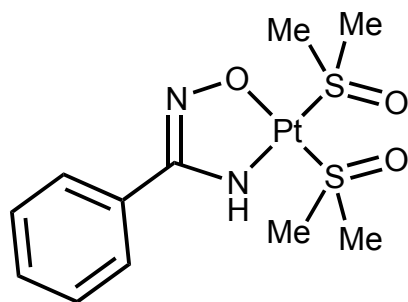


**3f**. Yield: 98% (102.9 mg). Mp: 183 °C (dec). Anal. Calcd for C<sub>9</sub>H<sub>13</sub>N<sub>3</sub>Cl<sub>2</sub>O<sub>4</sub>PtS: C, 21.65; H, 3.52; N, 6.39. Found: C, 21.73; H, 3.41; N, 6.48. HRESI<sup>+</sup>-MS (MeOH, *m/z*): 453.0172 ([M – 2Cl – H]<sup>+</sup>, calcd 453.0191), 489.9923 ([M – Cl]<sup>+</sup>, calcd 489.9946), 547.9517 ([M + Na]<sup>+</sup>, calcd 547.9524), 1014.9577 ([2M – Cl]<sup>+</sup>, calcd 1014.9580), 1072.9157 ([2M + Na]<sup>+</sup>, calcd 1072.9161). IR (KBr, selected bonds, cm<sup>-1</sup>): 3439(s), 3335(s) ν(O–H) and ν(N–H); 3185(m), 3107(w), 3079(w), 3001(w-m), 2918(w-m) ν(C–H); 1661(vs) ν(C=N); 1520(vs) ν(N=O)<sub>as</sub>; 1346(vs) ν(N=O)<sub>s</sub>; 1136(s) ν(S=O). <sup>1</sup>H NMR (CD<sub>3</sub>OD, δ): 8.43 (d, 2H, CH), 8.19 (d, 2H, CH), 3.42 (s, 3H, CH<sub>3</sub>), 2.83 (s, 3H, CH<sub>3</sub>). CP-MAS TOSS <sup>13</sup>C{<sup>1</sup>H} NMR (δ): 155.19 (C(NH<sub>2</sub>)=NOH), 149.60, 148.08, 146.40, 138.11, 133.02, 129.73, 123.36, 122.12 (Ar), 46.59, 44.17, 42.66, 40.18 (s, CH<sub>3</sub>). Crystals of **3f** suitable for X-ray diffraction were obtained by the slow evaporation of MeNO<sub>2</sub> solution at RT in air.

### Characterization of 4c–g

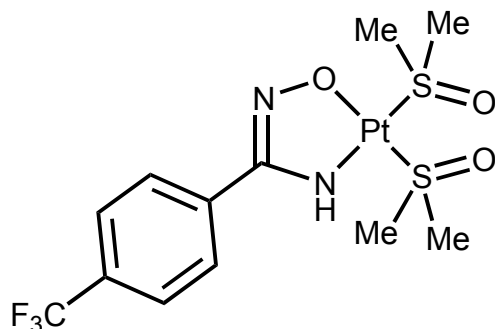


**4c.** Yield: 86% (80.1 mg). Mp: 189 °C (dec). Anal. Calcd for C<sub>9</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>PtS<sub>2</sub>: C, 23.22; H, 4.76; N, 6.02. Found: C, 23.04; H, 4.71; N, 6.09. HRESI<sup>+</sup>-MS (MeOH, *m/z*): 466.0783 ([M + H]<sup>+</sup>, calcd 466.0793). IR (KBr, selected bonds, cm<sup>-1</sup>): 3420(w-m), 3360(m), 3295(m) ν(N–H); 3003(m), 2969(m), 2913(m), 2870(w) ν(C–H); 1630(w) ν(C=N); 1126(vs) ν(S=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 4.85 (s+d, *J*<sub>PtH</sub> = 112 Hz, br, 1H, NH), 3.51 (s+d, *J*<sub>PtH</sub> = 17 Hz, 6H, S(CH<sub>3</sub>)<sub>2</sub>), 3.48 (s+d, *J*<sub>PtH</sub> = 15 Hz, 6H, S(CH<sub>3</sub>)<sub>2</sub>), 1.31 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): 168.94 (s, C(NH)=NO), 47.02 (s+d, *J*<sub>PtC</sub> = 36 Hz, S(CH<sub>3</sub>)<sub>2</sub>), 46.32 (s+d, *J*<sub>PtC</sub> = 34 Hz, S(CH<sub>3</sub>)<sub>2</sub>), 32.26 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.88 (s, C(CH<sub>3</sub>)<sub>3</sub>). Crystals of **4c** suitable for X-ray diffraction were obtained by the slow evaporation of MeNO<sub>2</sub> solution at RT in air.

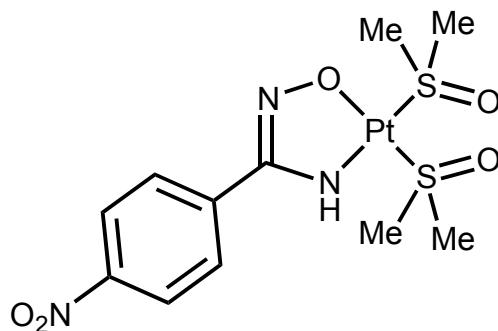


**4d**•H<sub>2</sub>O. Yield: 74% (74.5 mg). Mp: 190 °C (dec). Anal. Calcd for C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>PtS<sub>2</sub>•H<sub>2</sub>O: C, 26.24; H, 4.00; N, 5.56. Found: C, 26.03; H, 3.94; N, 5.60. HRESI<sup>+</sup>-MS (*m/z*): 486.0399 ([M + H]<sup>+</sup>, calcd 486.0480). IR (KBr, selected bonds, cm<sup>-1</sup>): 3337(m) ν(N–H); 2986(m), 2909(w-m) ν(C–H); 1638(w) ν(C=N); 1126(vs) ν(S=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.77–7.73 (m, 2H, *o*-CH), 7.36–7.32 (m, 3H, *m*-, *p*-CH), 5.52 (s+d, *J*<sub>PtH</sub> = 112 Hz, br, 1H, NH), 3.56 (s+d, *J*<sub>PtH</sub> = 24 Hz, 6H, S(CH<sub>3</sub>)<sub>2</sub>), 3.54 (s+d, *J*<sub>PtH</sub> = 24 Hz, 6H, S(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): 161.46 (s, C(NH)=NO), 130.50 (s, C–

C(NH)=NO), 128.45 (s, *p*-CH), 128.29, 126.74 (2s, *o*-, *m*-CH), 47.01 (s+d,  $J_{\text{PtC}} = 38$  Hz, S(CH<sub>3</sub>)<sub>2</sub>), 46.23 (s+d,  $J_{\text{PtC}} = 34$  Hz, S(CH<sub>3</sub>)<sub>2</sub>).

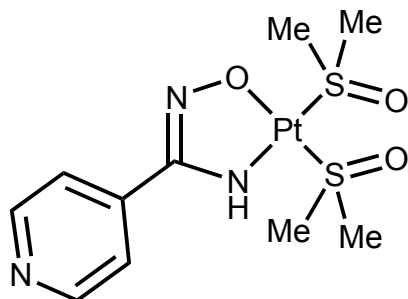


**4e**•H<sub>2</sub>O. Yield: 78% (89.2 mg). Mp: 213 °C (dec). Anal. Calcd for C<sub>12</sub>H<sub>17</sub>N<sub>2</sub>F<sub>3</sub>O<sub>3</sub>PtS<sub>2</sub>•H<sub>2</sub>O: C, 25.22; H, 3.35; N, 4.90. Found: C, 25.13; H, 3.51; N, 4.98. HRESI<sup>+</sup>-MS (*m/z*): 476.0206 ([M – Me<sub>2</sub>SO + H]<sup>+</sup>, calcd 476.0215), 554.0364 ([M + H]<sup>+</sup>, calcd 554.0354). IR (KBr, selected bonds, cm<sup>-1</sup>): 3337(m) ν(N–H); 3013(w-m), 2990(m), 2911(m) ν(C–H); 1618(m) ν(C=N); 1123(vs) ν(S=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.86 (d, 2H, CH), 7.59 (d, 2H, CH), 5.26 (s+d,  $J_{\text{PtH}} = 108$  Hz, br, 1H, NH), 3.57 (s+d,  $J_{\text{PtH}} = 20$  Hz, 6H, S(CH<sub>3</sub>)<sub>2</sub>), 3.54 (s+d,  $J_{\text{PtH}} = 20$  Hz, 6H, S(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, δ): 160.26 (s, C(NH)=NO), 133.90 (s, C–C(NH)=NO), 130.21 (q,  $J_{\text{CF}} = 32$  Hz, C–CF<sub>3</sub>), 126.82 (s, C–C–C–CF<sub>3</sub>), 125.30 (q,  $J_{\text{CF}} = 4$  Hz, C–C–CF<sub>3</sub>), 124.18 (q  $J_{\text{CF}} = 272$  Hz, CF<sub>3</sub>), 46.97 (s+d,  $J_{\text{PtC}} = 39$  Hz, S(CH<sub>3</sub>)<sub>2</sub>), 46.33 (s+d,  $J_{\text{PtC}} = 32$  Hz, S(CH<sub>3</sub>)<sub>2</sub>).



**4f**•H<sub>2</sub>O. Yield: 95% (104.1 mg). Mp: 210 °C (dec). Anal. Calcd for C<sub>11</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>PtS<sub>2</sub>•H<sub>2</sub>O: C, 24.09; H, 3.49; N, 7.66. Found: C, 23.99; H, 3.54; N, 7.65. HRESI<sup>+</sup>-MS (*m/z*): 531.0306 ([M + H]<sup>+</sup>, calcd 531.0331), 553.0104 ([M + Na]<sup>+</sup>, calcd 553.0150). IR (KBr, selected bonds, cm<sup>-1</sup>): 3414(m), 3335(m) ν(N–H); 2990(m), 2913(m) ν(C–H); 1597(m) ν(C=N); 1516(m-s) ν(N=O)<sub>as</sub>; 1341(s) ν(N=O)<sub>s</sub>; 1130(vs) ν(S=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 8.20 (d, 2H, CH), 7.92 (d, 2H, CH), 5.27 (s+d,

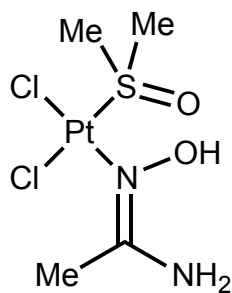
$J_{\text{PtH}} = 108 \text{ Hz}$ , br, 1H, *NH*), 3.58 (s+d,  $J_{\text{PtH}} = 20 \text{ Hz}$ , 6H,  $\text{S}(\text{CH}_3)_2$ ), 3.55 (s+d,  $J_{\text{PtH}} = 20 \text{ Hz}$ , 6H,  $\text{S}(\text{CH}_3)_2$ ). CP-MAS TOSS  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 161.75 ( $\text{C}(\text{NH})=\text{NO}$ ), 148.61, 145.56, 135.64, 123.33 (Ar), 45.47 ( $\text{S}(\text{CH}_3)_2$ ), 41.01 ( $\text{S}(\text{CH}_3)_2$ ). Crystals of **4f** suitable for X-ray diffraction were obtained by the slow evaporation of MeOH solution at RT in air.



**4g**· $\text{H}_2\text{O}$ . Yield: 91% (91.7 mg). Mp: 218 °C (dec). Anal. Calcd for  $\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}_3\text{PtS}_2\cdot\text{H}_2\text{O}$ : C, 23.81; H, 3.80; N, 8.33. Found: C, 23.76; H, 3.84; N, 8.30. HRESI<sup>+</sup>-MS ( $m/z$ ): 487.0412 ( $[\text{M} + \text{H}]^+$ , calcd 487.0432), 509.0210 ( $[\text{M} + \text{Na}]^+$ , calcd 509.0252). IR (KBr, selected bonds,  $\text{cm}^{-1}$ ): 3422(m)  $\nu(\text{N}-\text{H})$ ; 2994(w-m), 2913(w-m)  $\nu(\text{C}-\text{H})$ ; 1597(m)  $\nu(\text{C}=\text{N})$ ; 1130(s)  $\nu(\text{S}=\text{O})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 8.59 (d, 2H, *CH*), 7.62 (d, 2H, *CH*), 5.28 (s+d,  $J_{\text{PtH}} = 88 \text{ Hz}$ , br, 1H, *NH*), 3.58 (s+d,  $J_{\text{PtH}} = 12 \text{ Hz}$ , 6H,  $\text{S}(\text{CH}_3)_2$ ), 3.54 (s+d,  $J_{\text{PtH}} = 12 \text{ Hz}$ , 6H,  $\text{S}(\text{CH}_3)_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 159.19 ( $\text{C}(\text{NH})=\text{NO}$ ), 150.04 (*CH*), 137.71 ( $\text{C}-\text{C}(\text{NH})=\text{NO}$ ), 120.76 (*CH*), 46.96 ( $\text{S}(\text{CH}_3)_2$ ), 46.39 ( $\text{S}(\text{CH}_3)_2$ ).

## Spectra of 3a–b and 3d–f

3a



### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

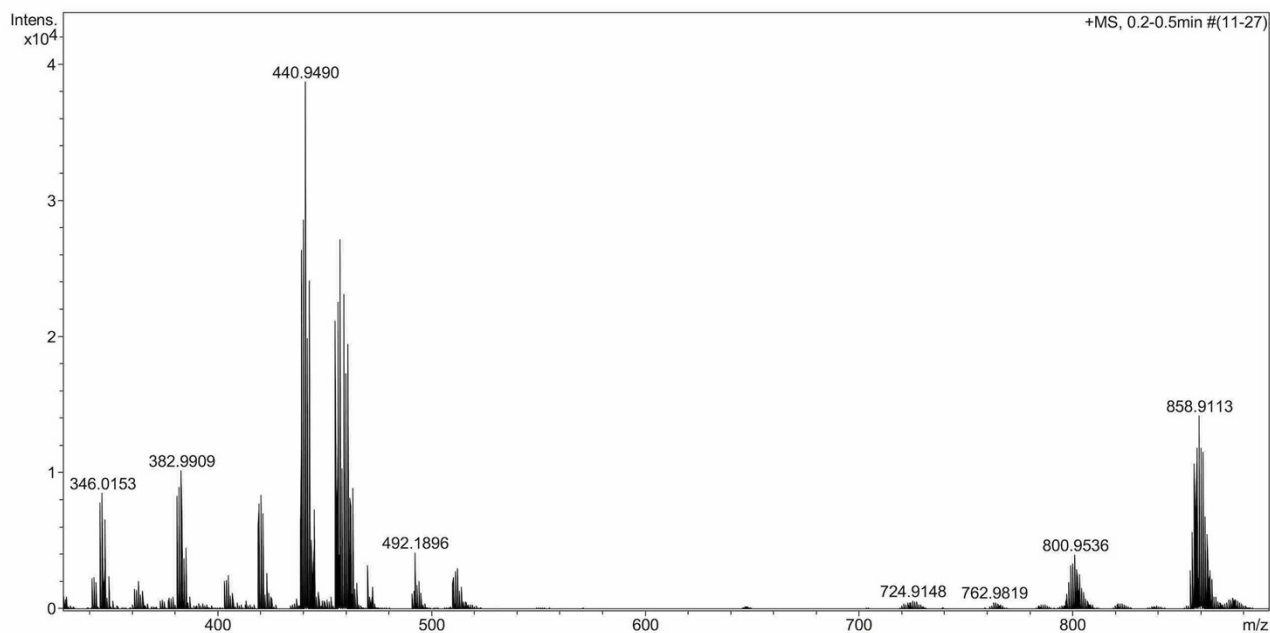
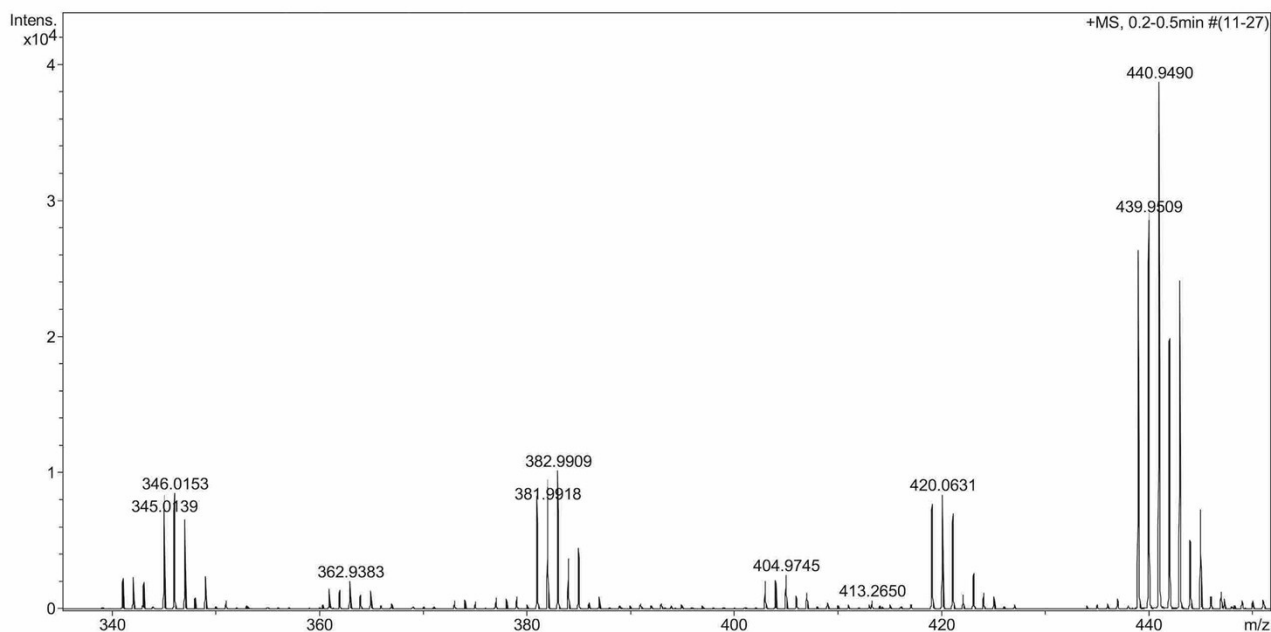


Figure S1. HR ESI<sup>+</sup>-MS spectrum of 3a.

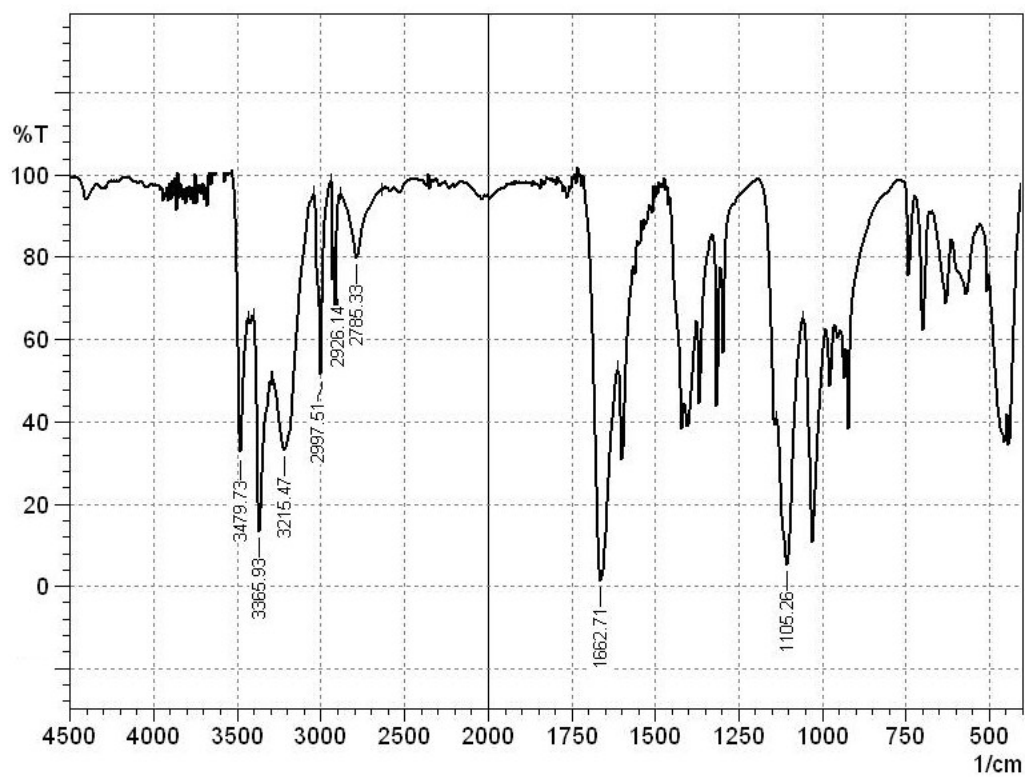


**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



**Figure S2.** HR ESI<sup>+</sup>-MS spectrum of **3a** (low region).



**Figure S3.** IR spectrum of **3a**.

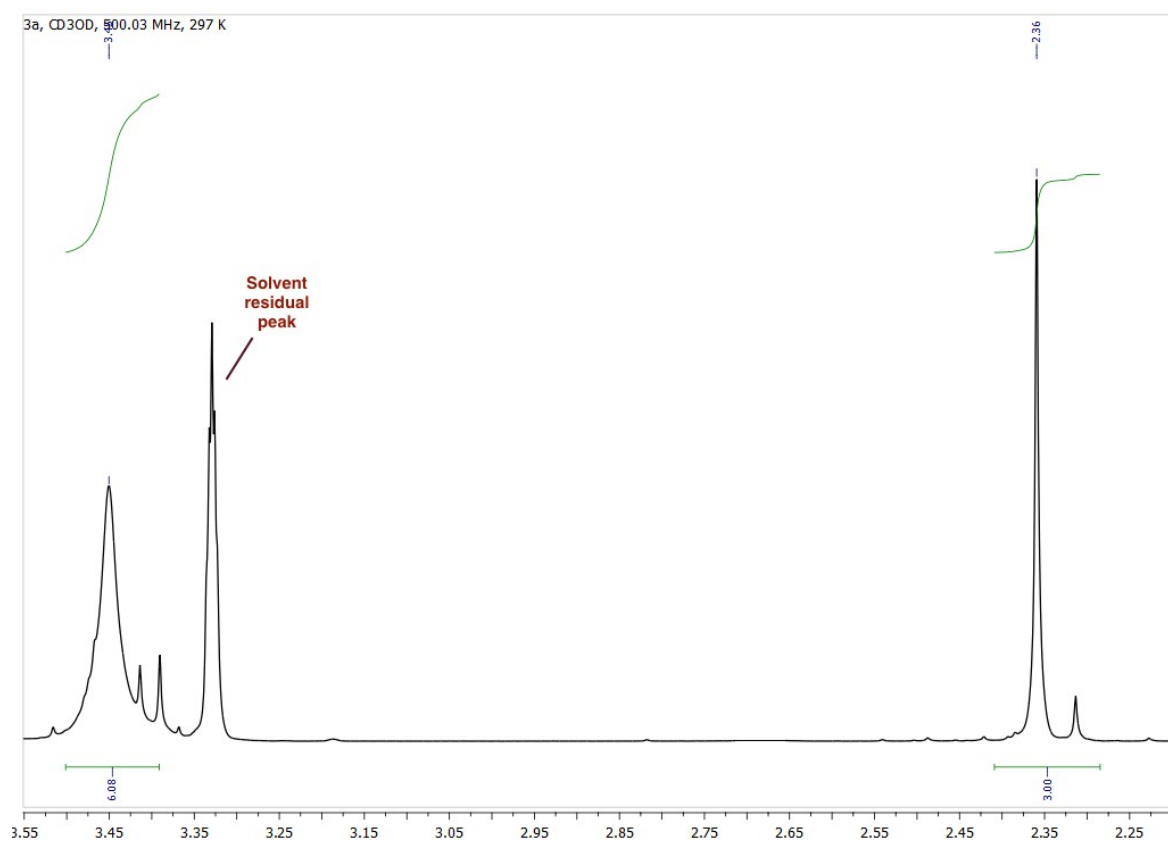


Figure S4.  $^1\text{H}$  NMR spectrum of **3a**.

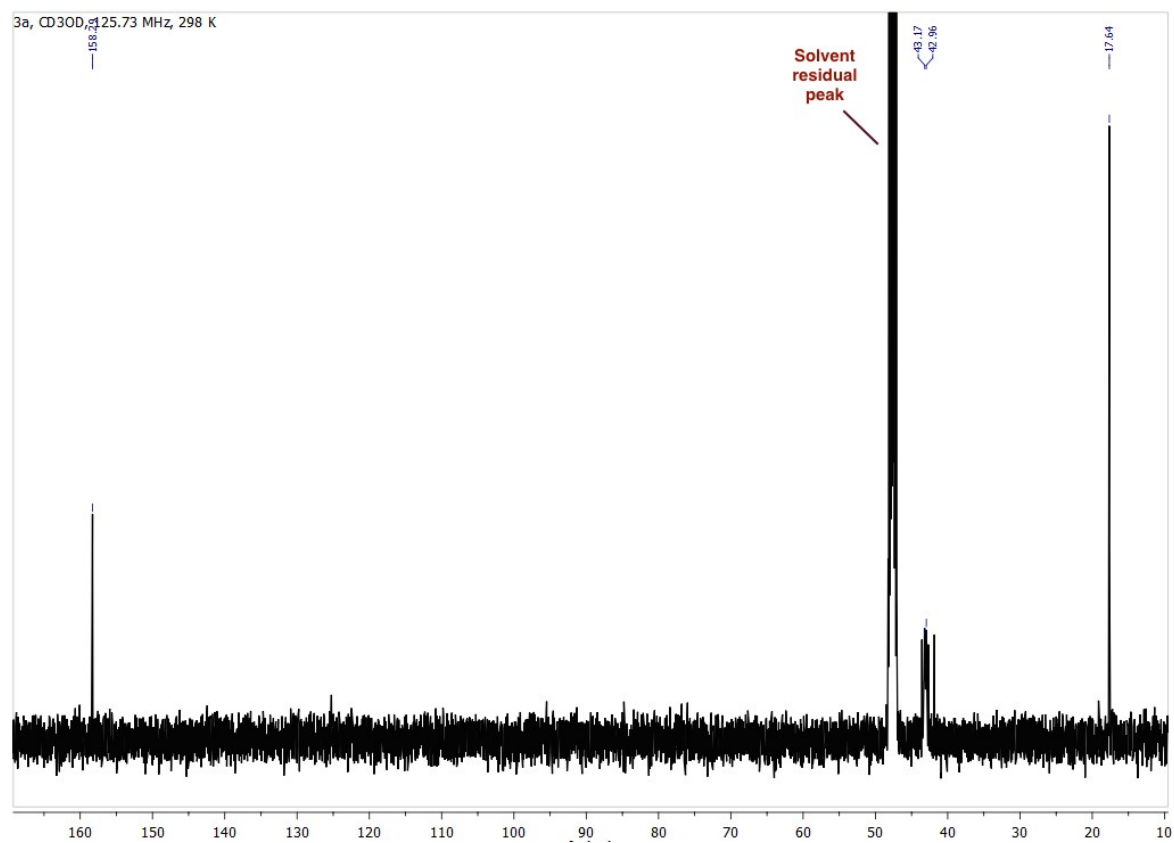
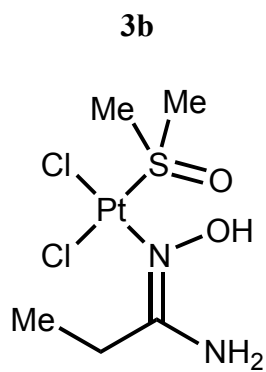
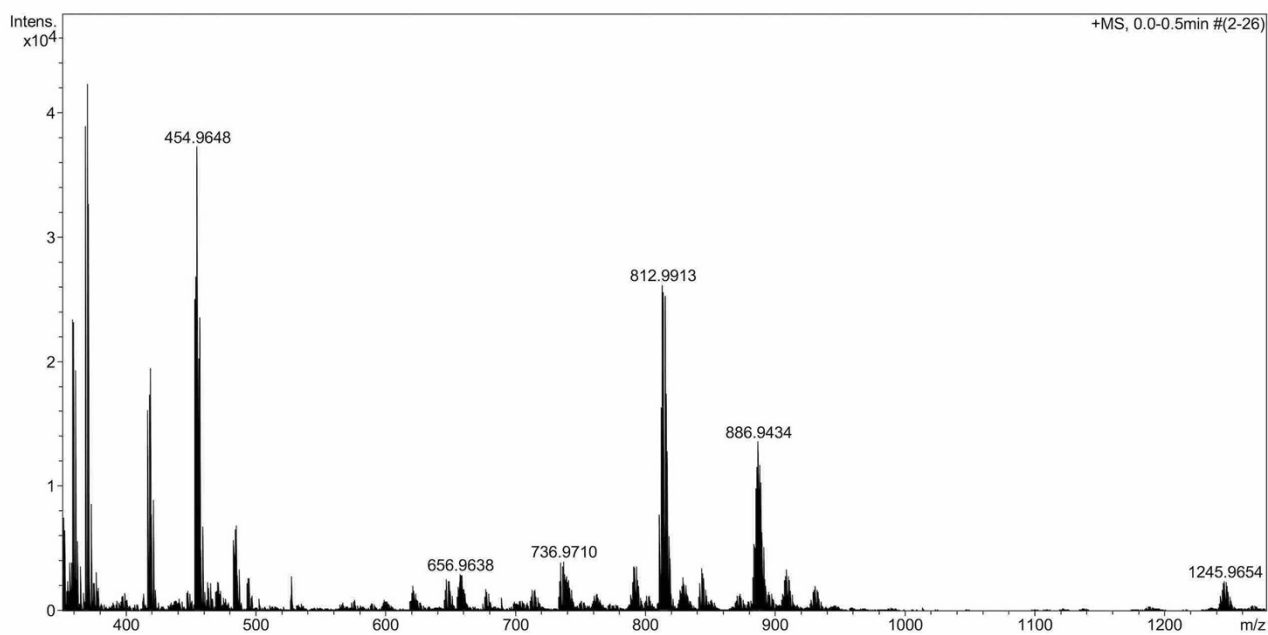


Figure S5.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3a**.



**Acquisition Parameter**

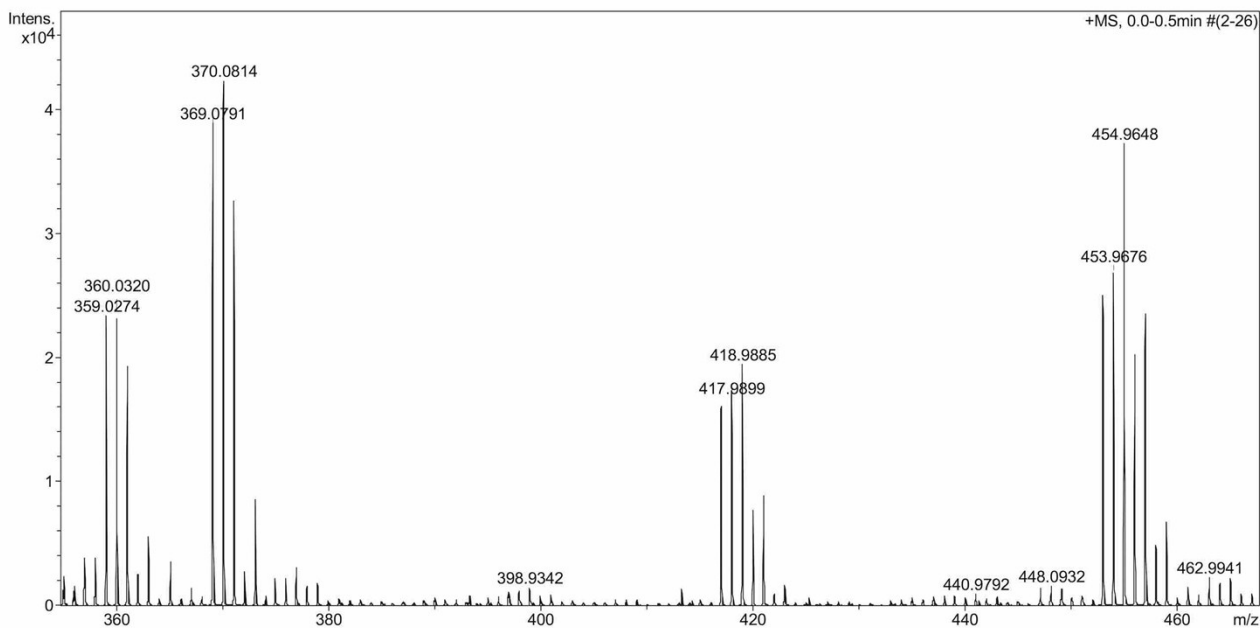
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source



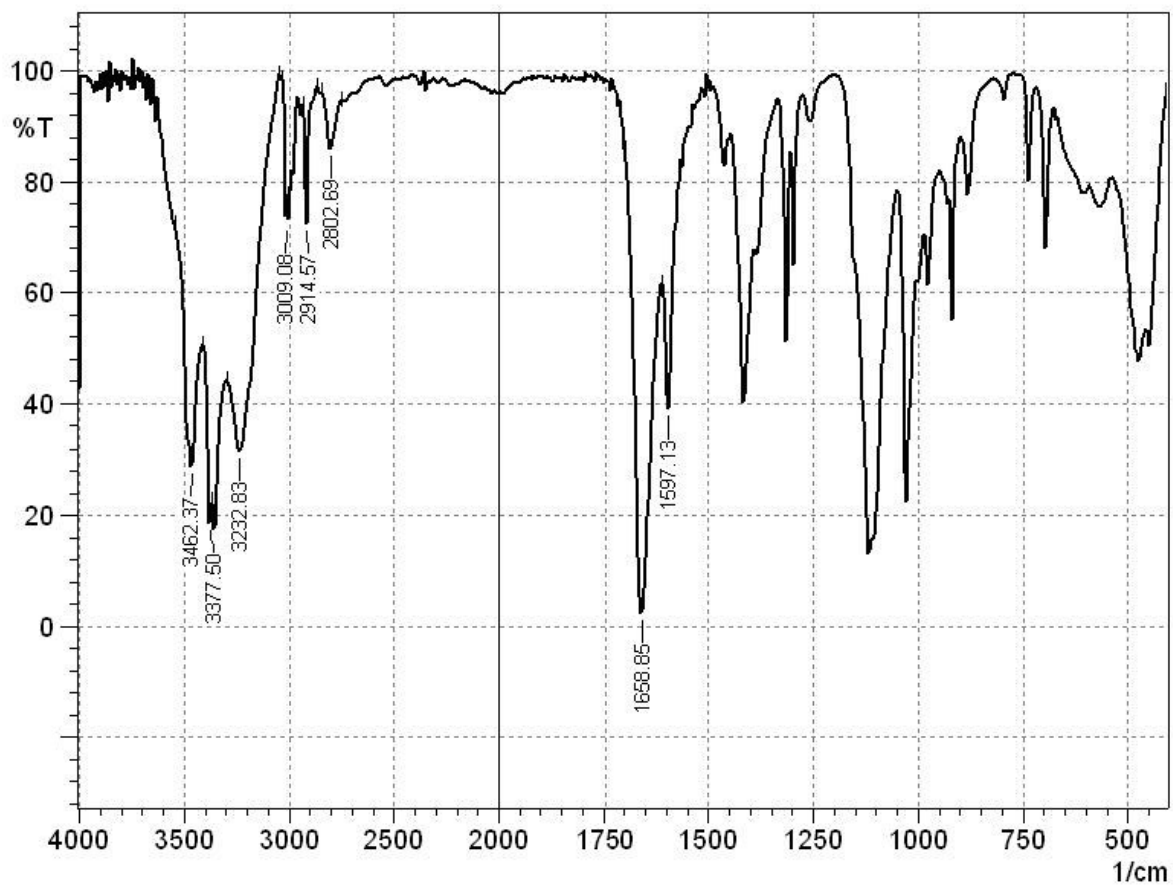
**Figure S6.** HR ESI<sup>+</sup>-MS spectrum of **3b**.

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



**Figure S7.** HR ESI<sup>+</sup>-MS spectrum of **3b** (low region).



**Figure S8.** IR spectrum of **3b**.

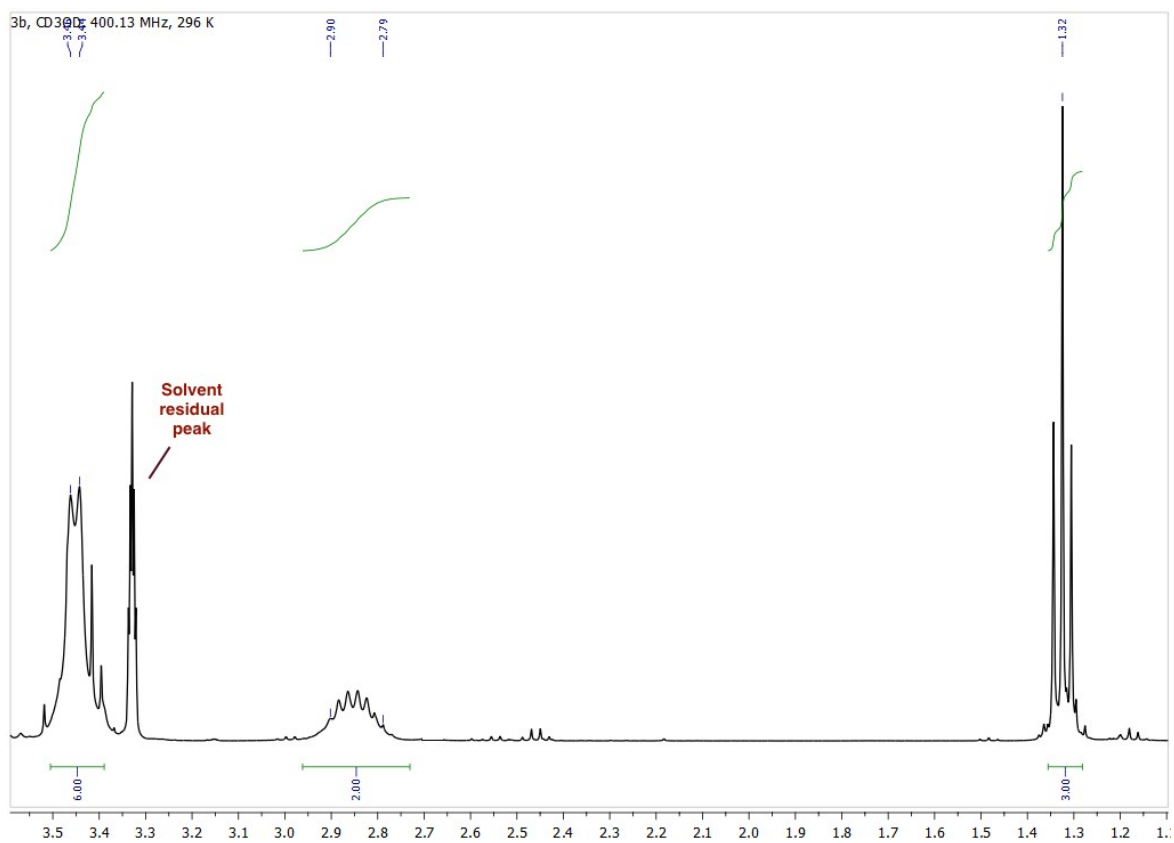


Figure S9.  $^1\text{H}$  NMR spectrum of **3b**.

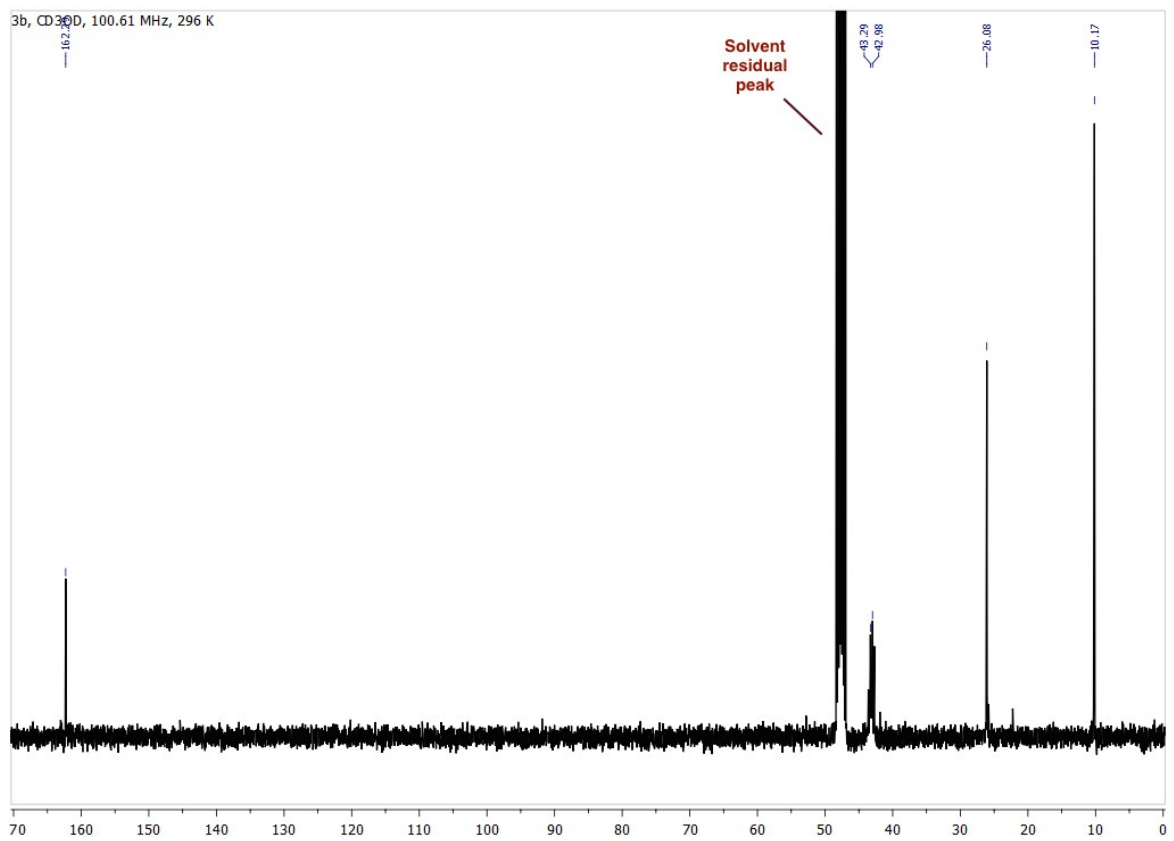
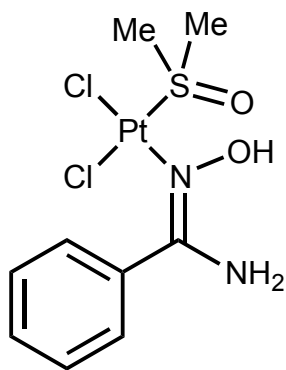


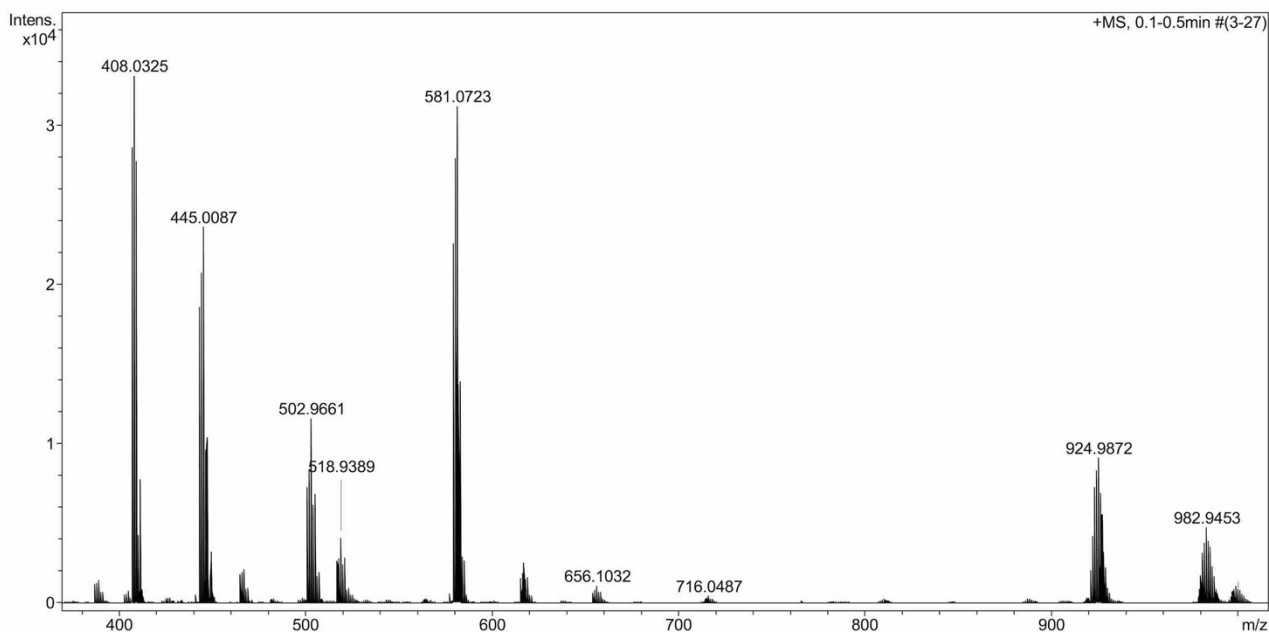
Figure S10.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3b**.

**3d**



**Acquisition Parameter**

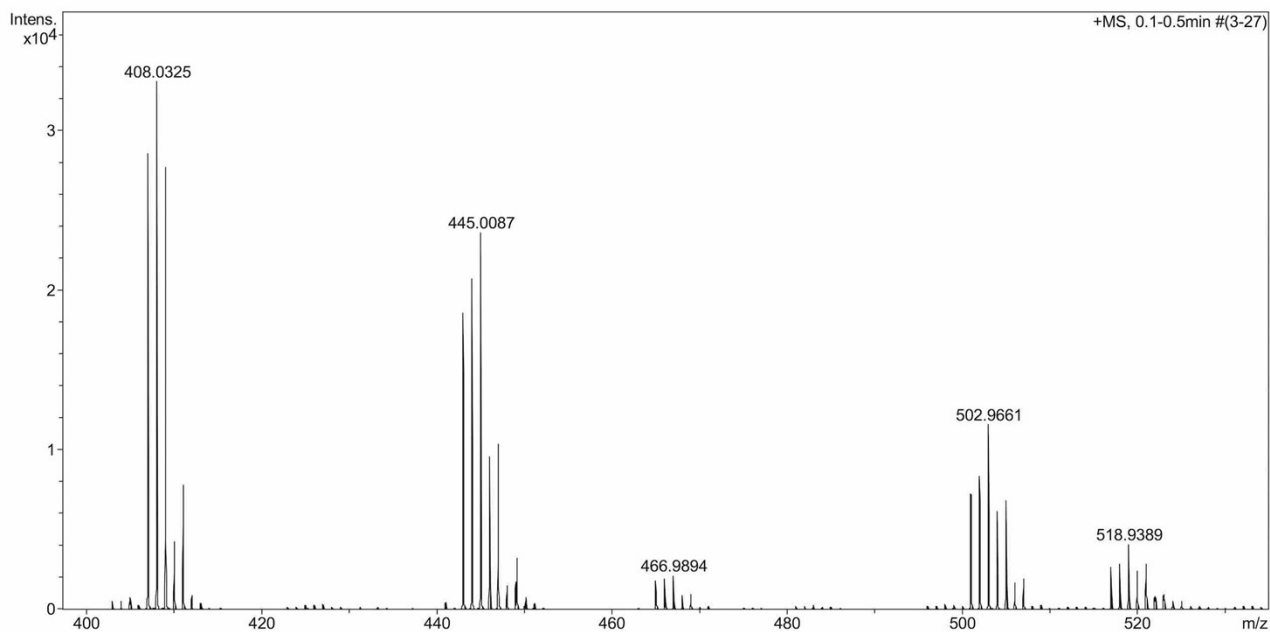
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



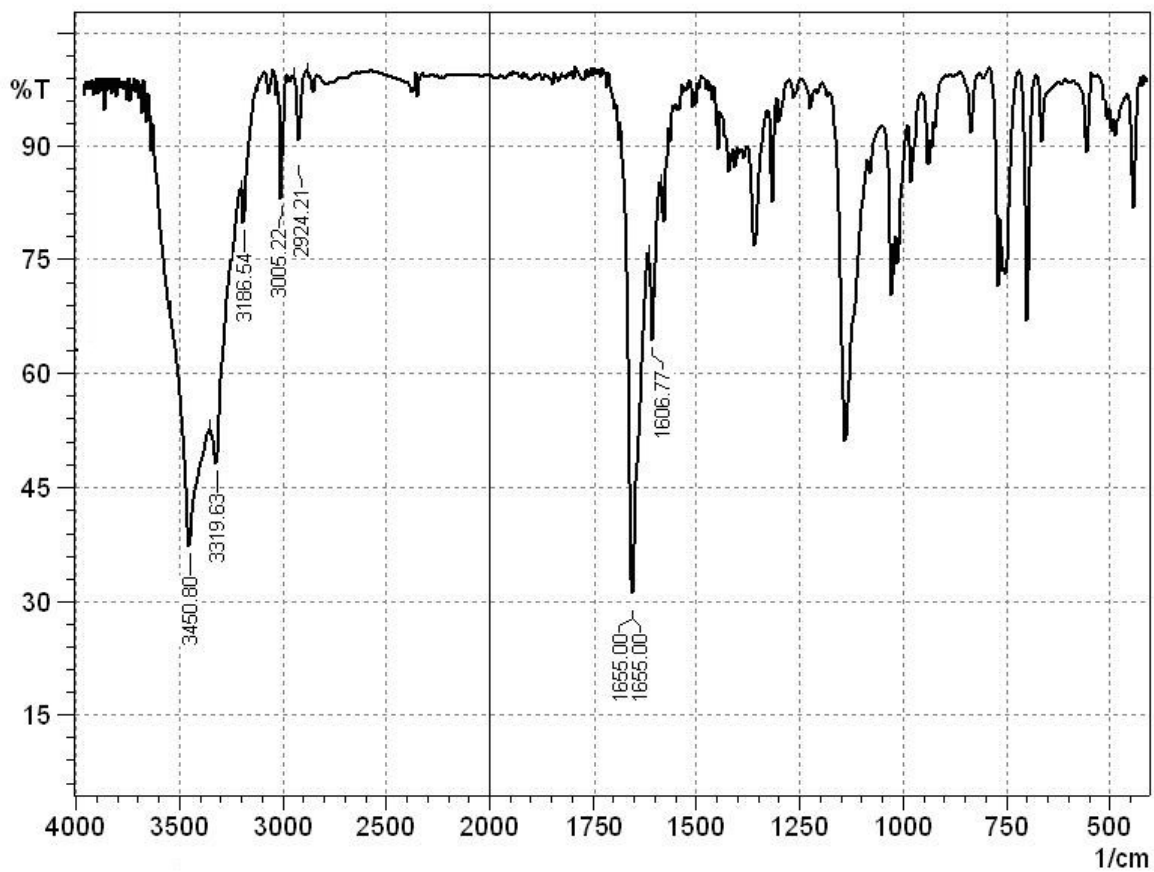
**Figure S11.** HR ESI<sup>+</sup>-MS spectrum of **3d**.

**Acquisition Parameter**

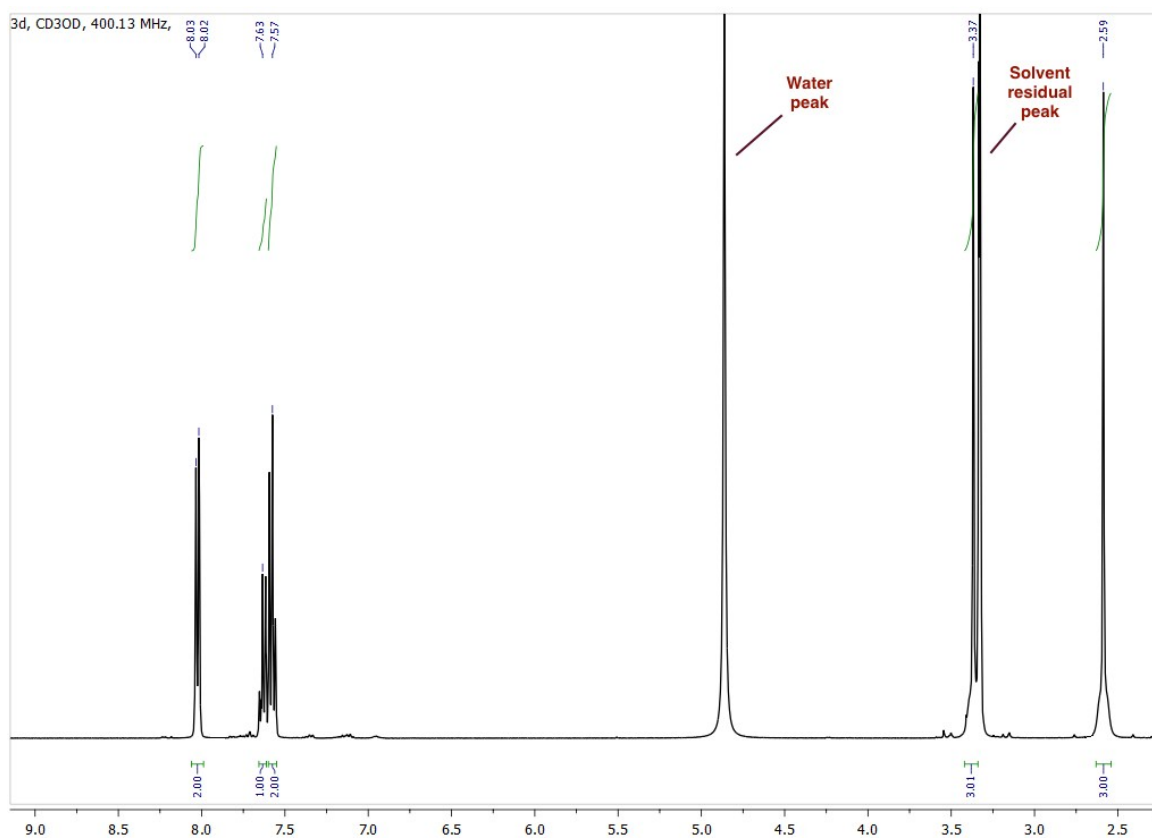
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



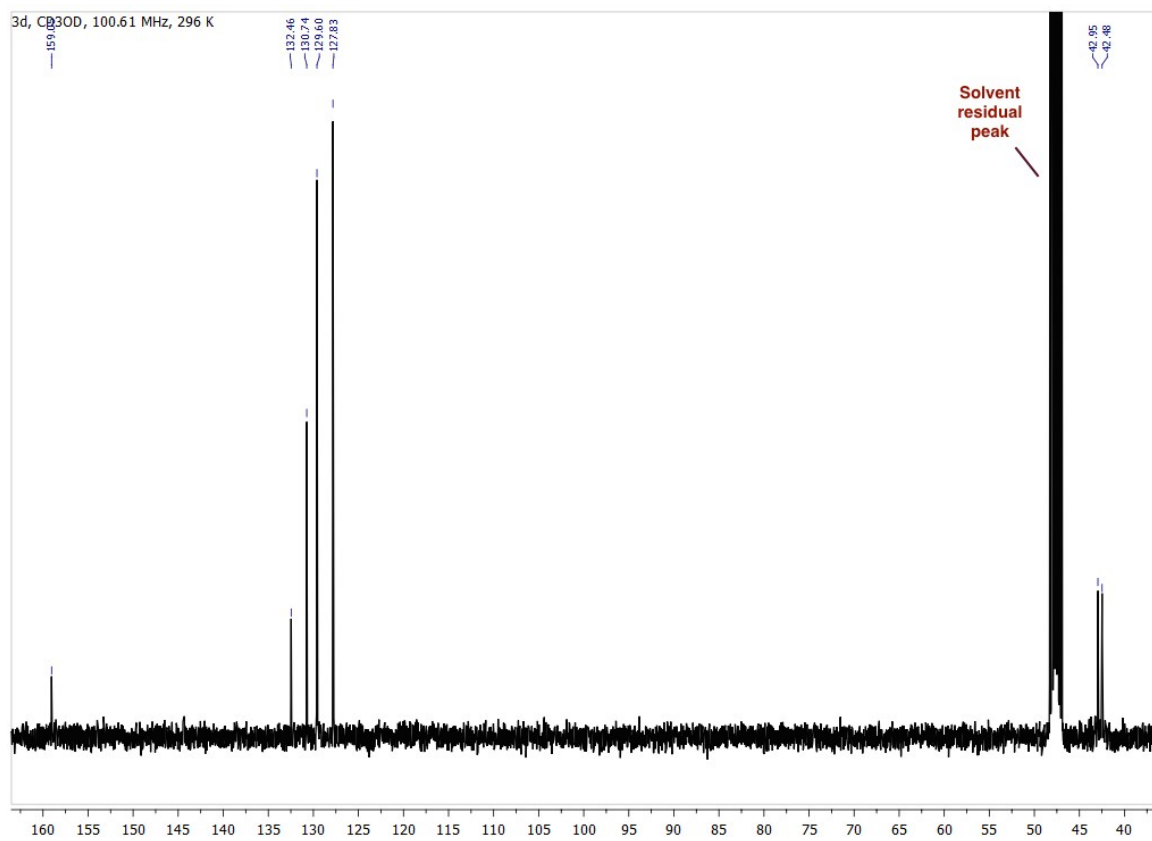
**Figure S12.** HR ESI<sup>+</sup>-MS spectrum of **3d** (low region).



**Figure S13.** IR spectrum of **3d**.

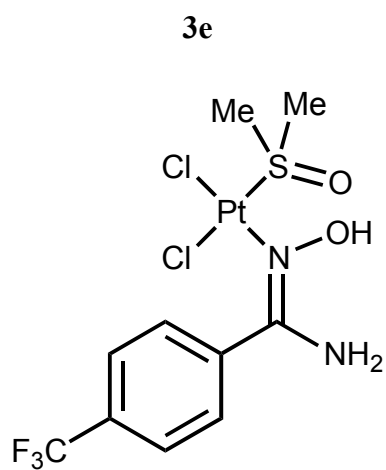


**Figure S14.**  $^1\text{H}$  NMR spectrum of **3d**.



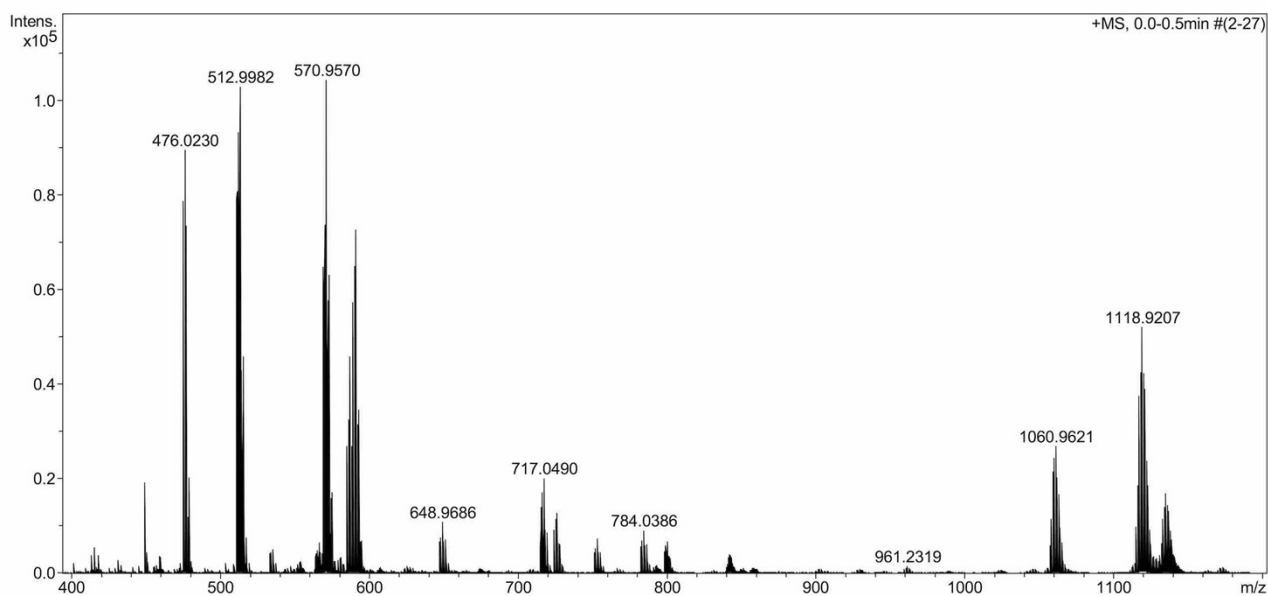
**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3d**.





**Acquisition Parameter**

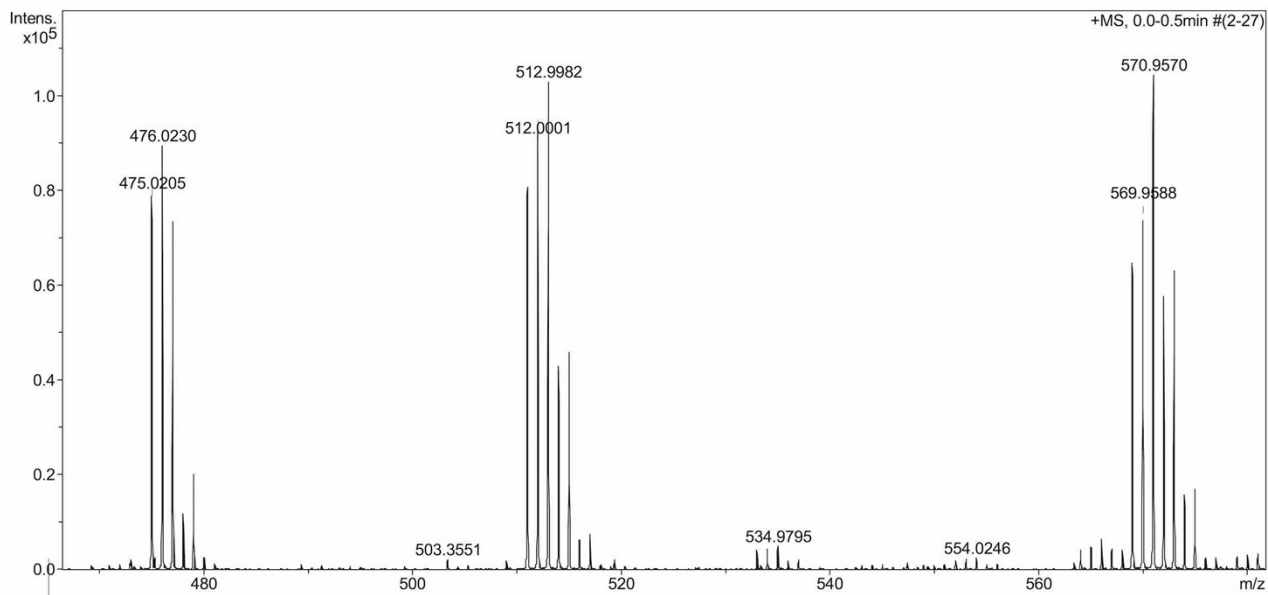
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source



**Figure S16.** HR ESI<sup>+</sup>-MS spectrum of **3e**.

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



**Figure S17.** HR ESI<sup>+</sup>-MS spectrum of **3e** (low region).

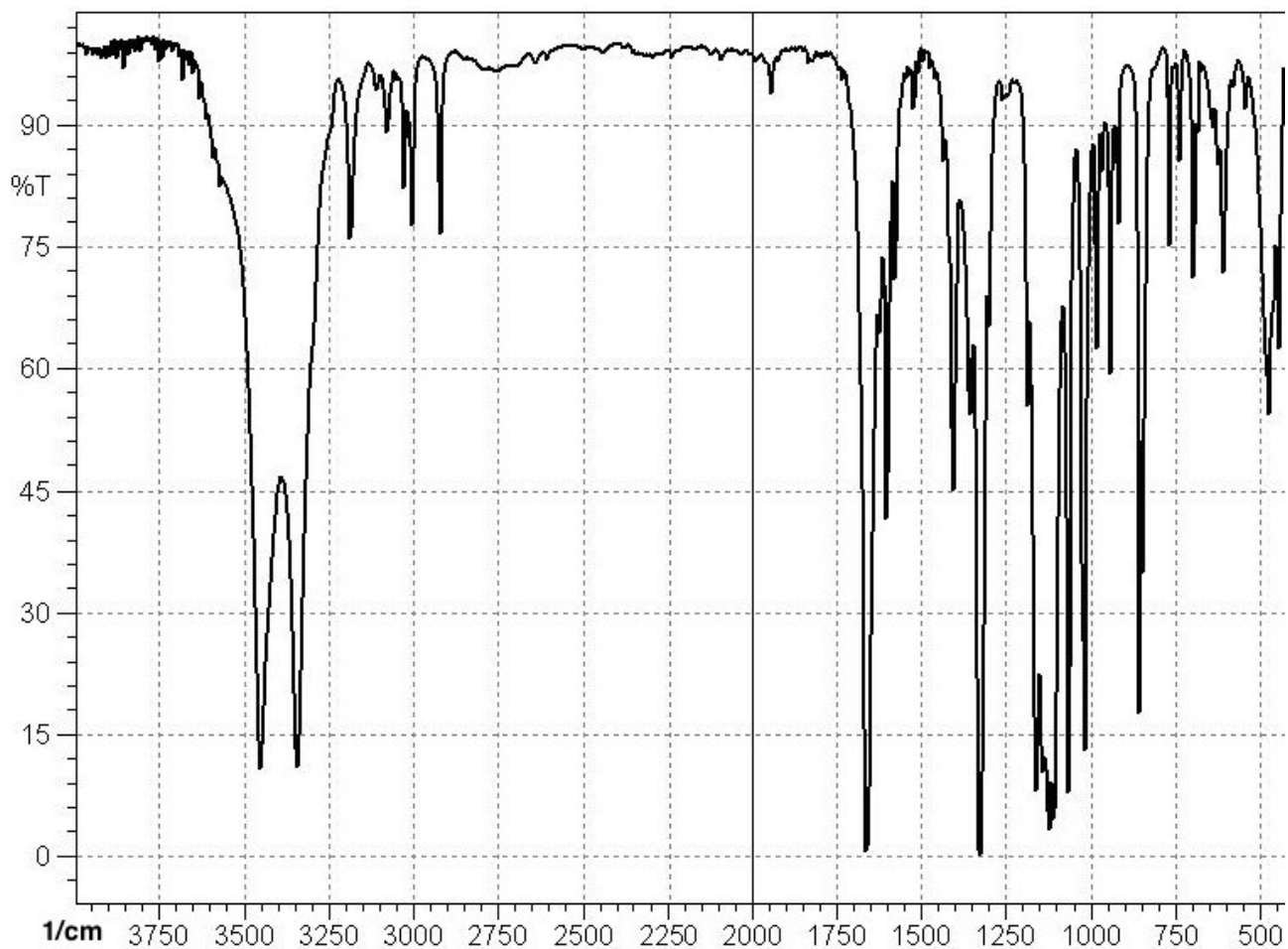


Figure S18. IR spectrum of **3e**.

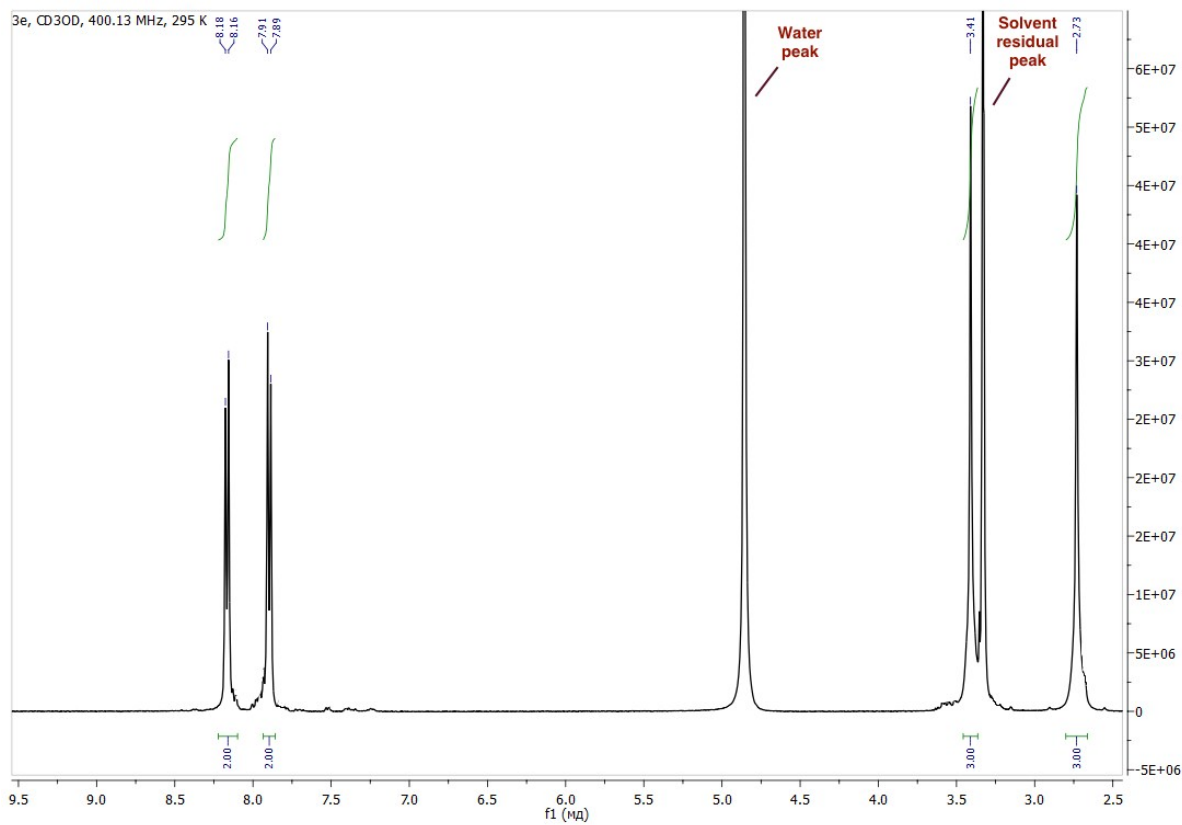
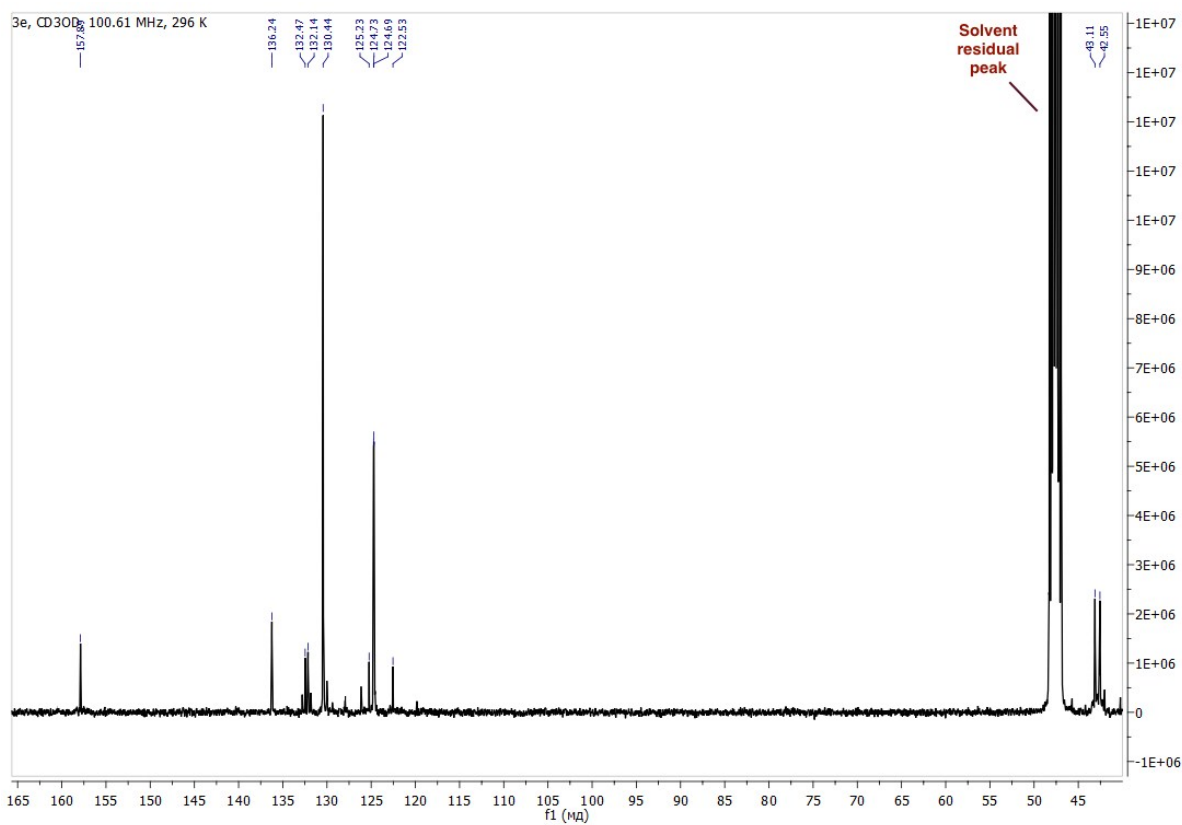
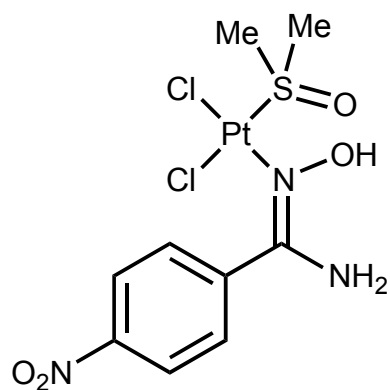


Figure S19.  $^1\text{H}$  NMR spectrum of **3e**.



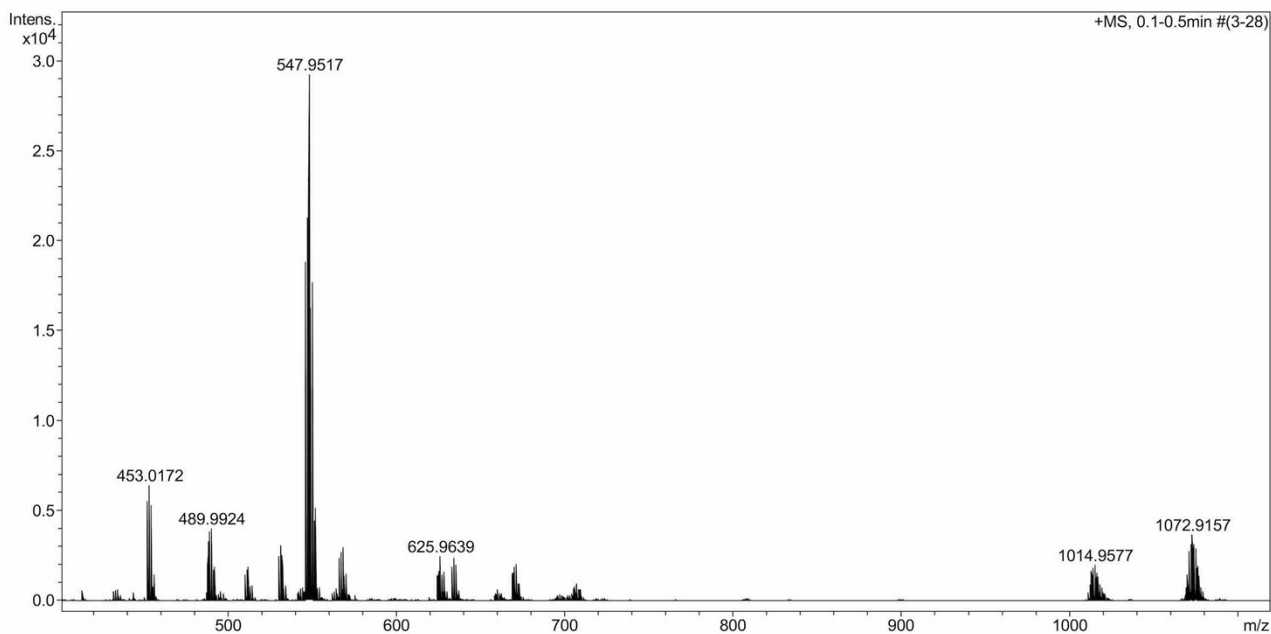
**Figure S20.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3e**.

**3f**



**Acquisition Parameter**

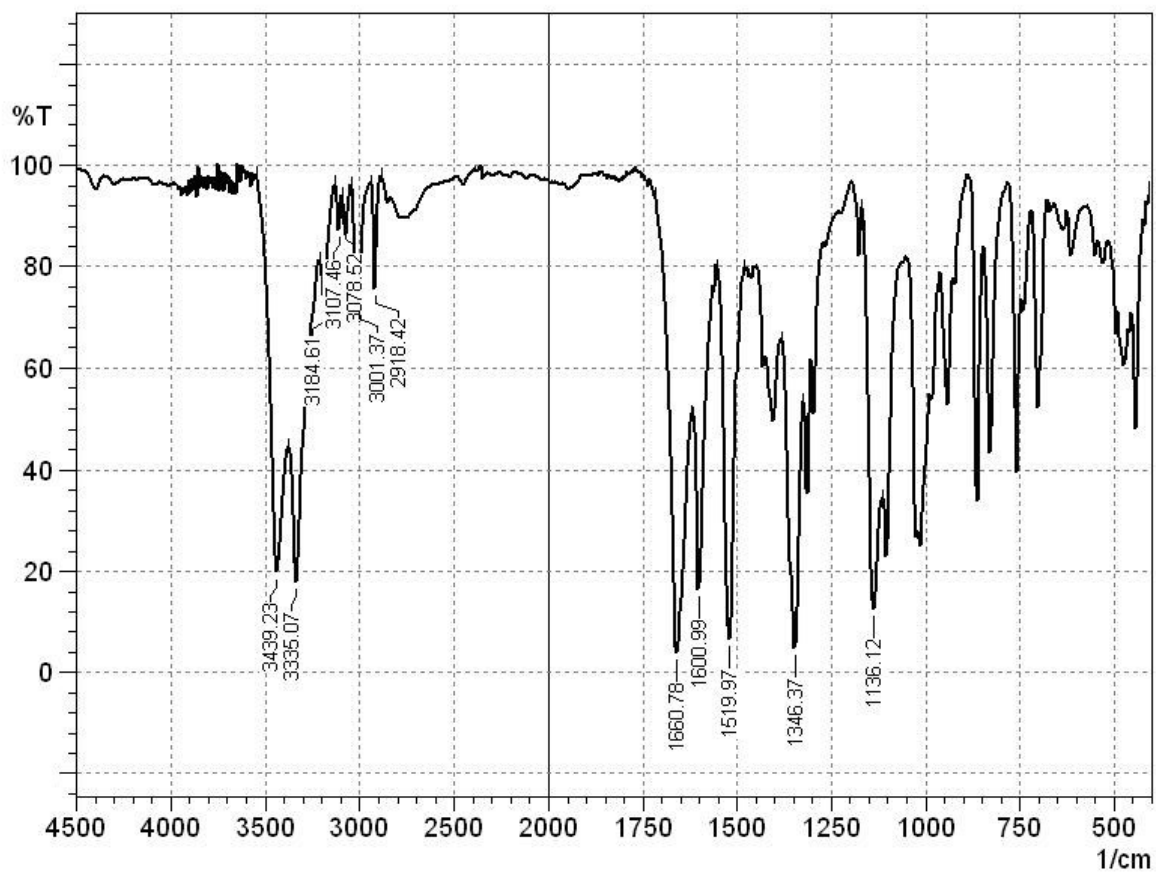
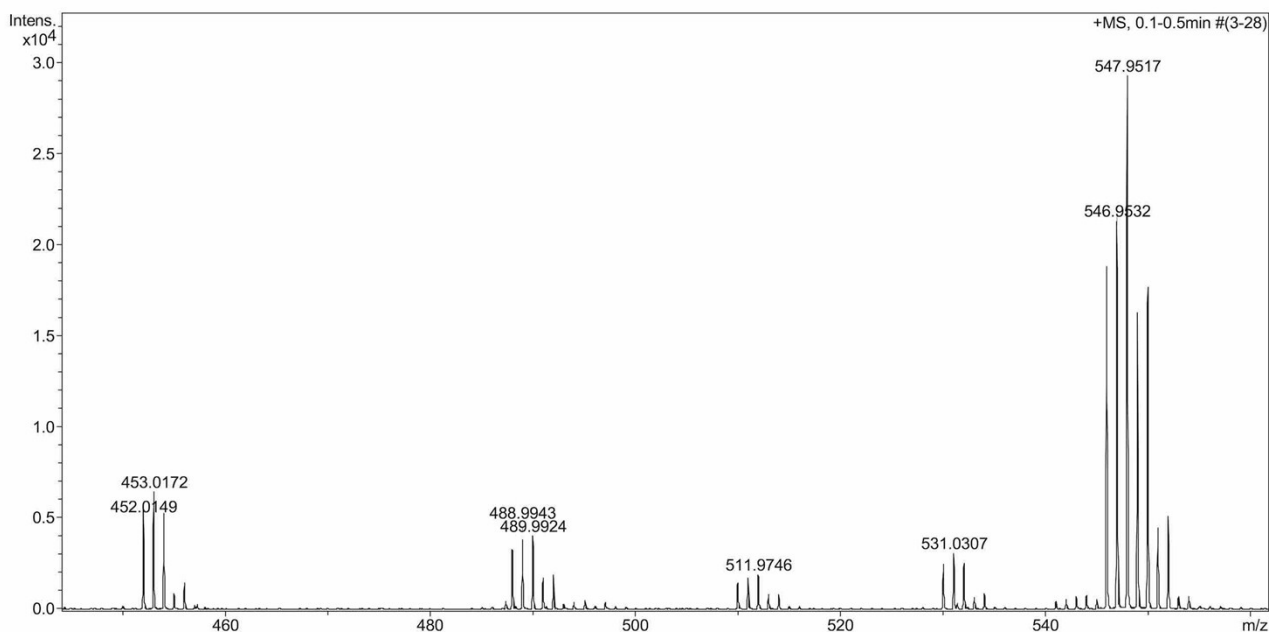
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source



**Figure S21.** HR ESI<sup>+</sup>-MS spectrum of **3f**.

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



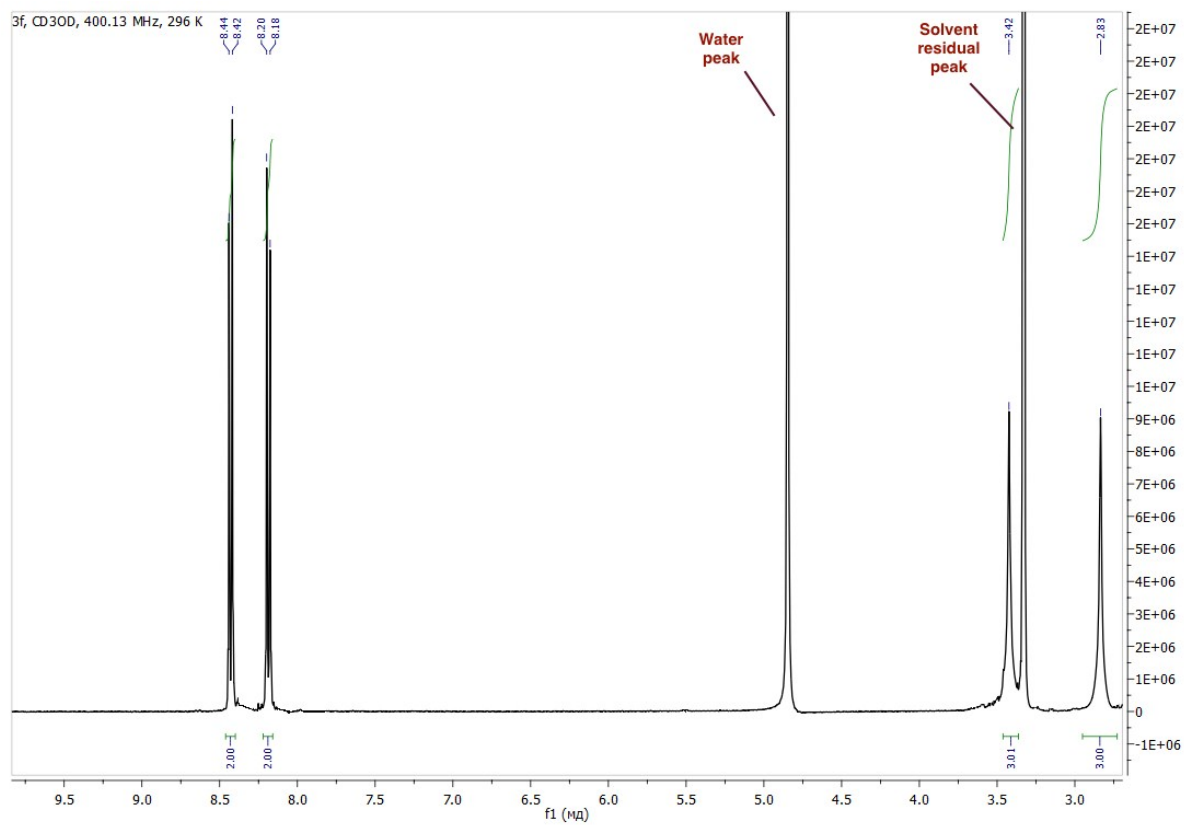


Figure S24.  $^1\text{H}$  NMR spectrum of **3f**.

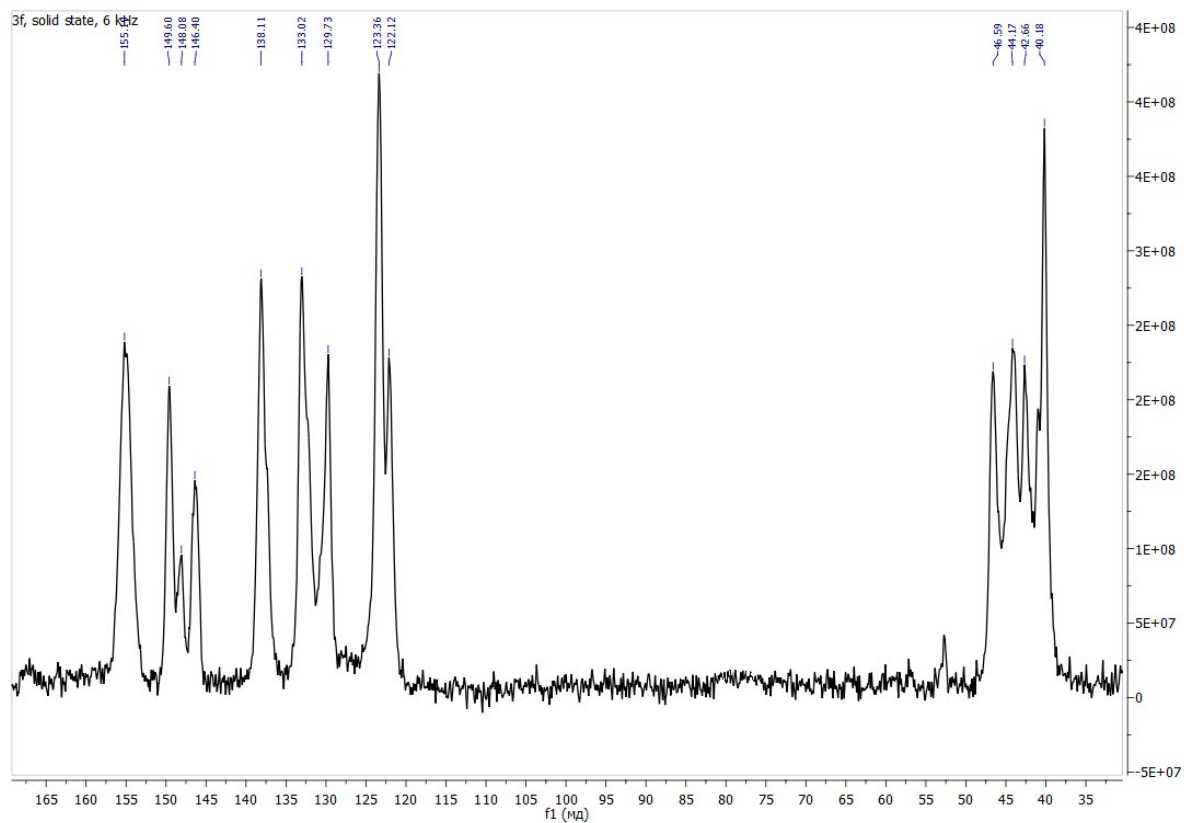


Figure S25. CP-MAS TOSS  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3f**.

## Spectra of 4a-g

### 4a

#### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

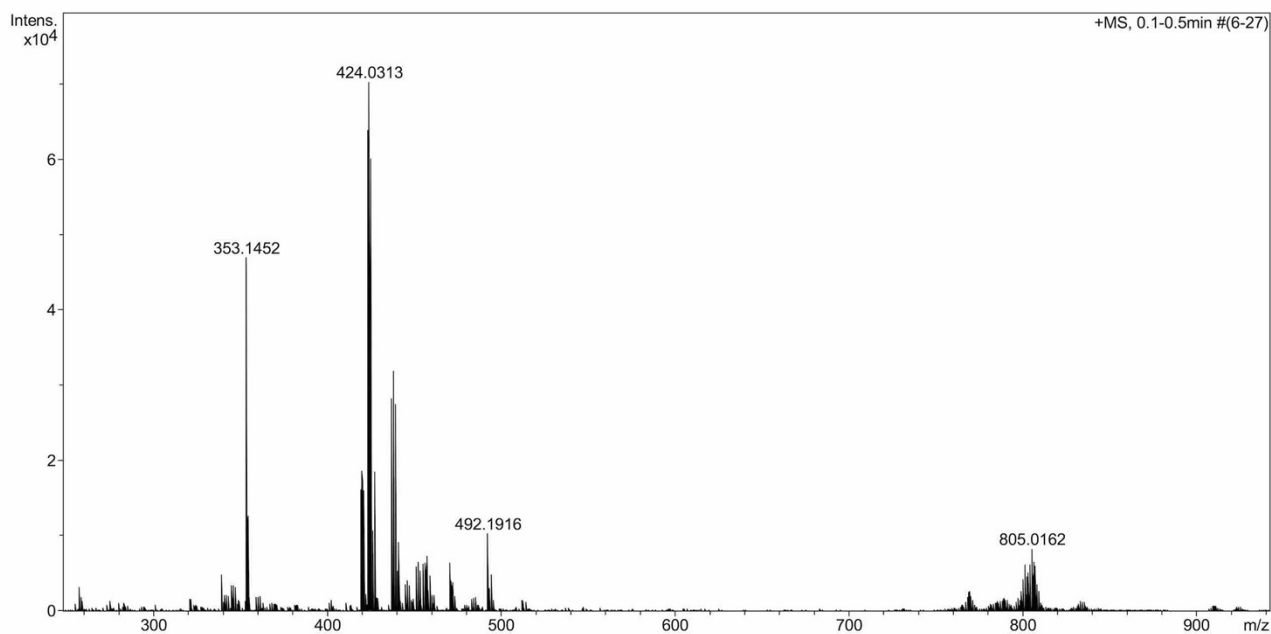


Figure S26. HR ESI+-MS spectrum of 4a reaction mixture.

#### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

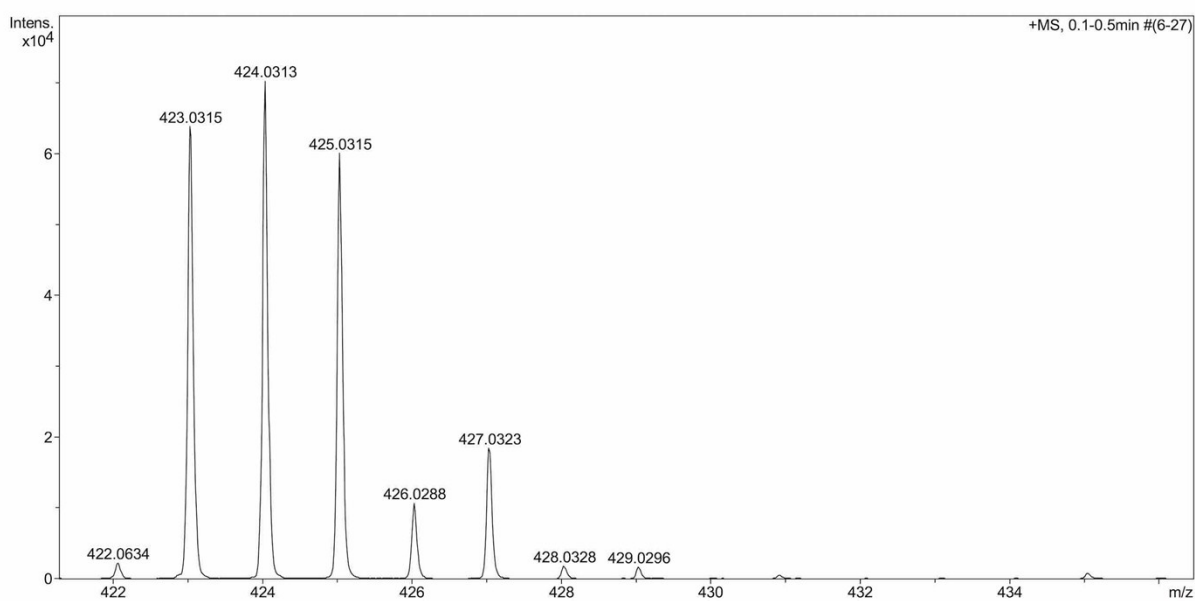


Figure S27. HR ESI+-MS spectrum of 4a reaction mixture.



## 4b

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

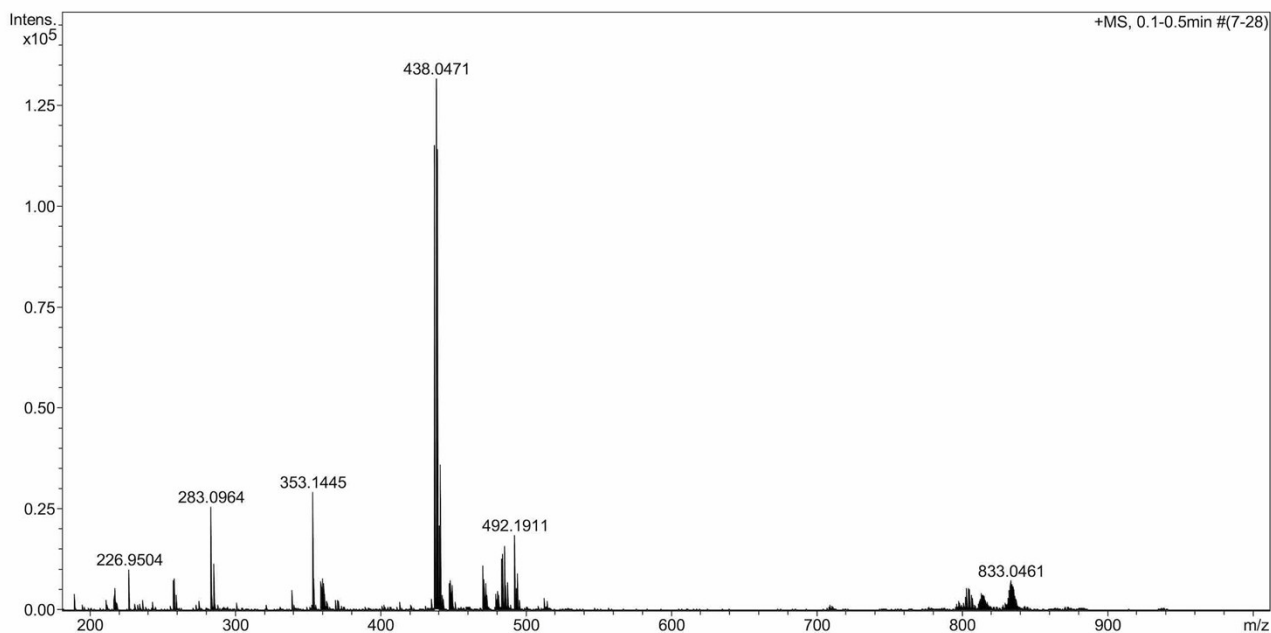


Figure S28. HR ESI<sup>+</sup>-MS spectrum of **4b** reaction mixture.

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

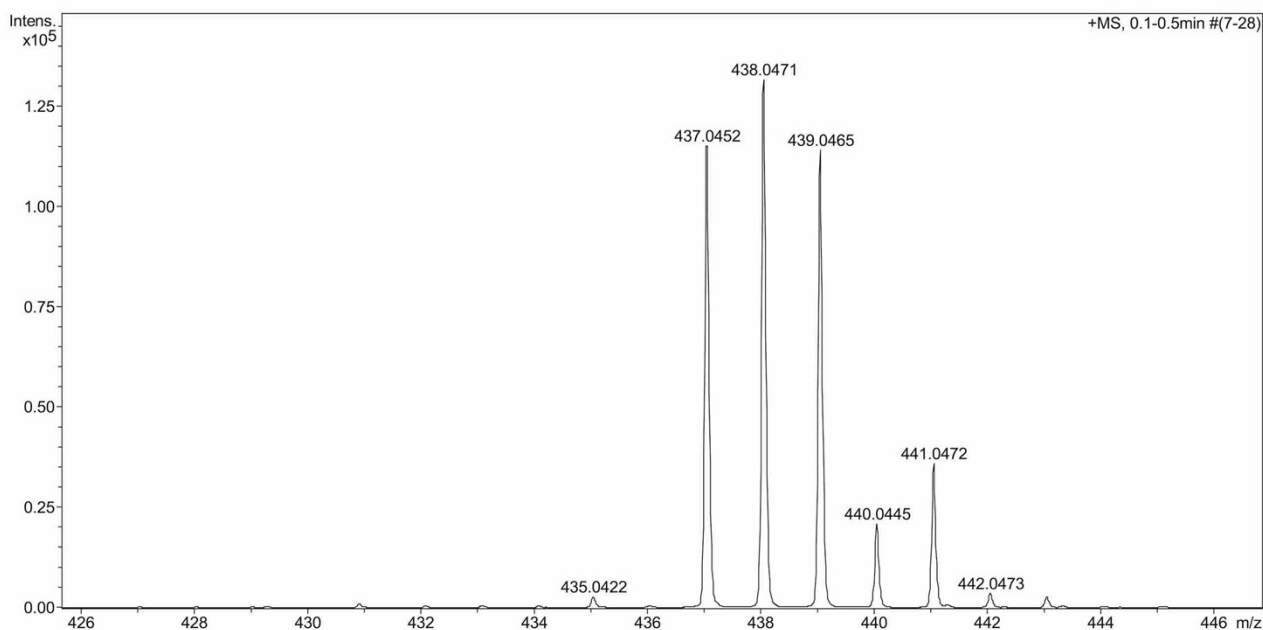
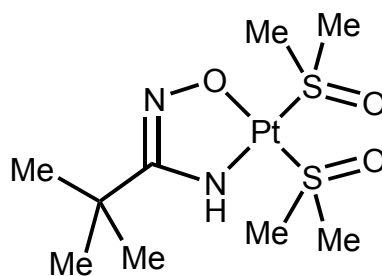


Figure S29. HR ESI<sup>+</sup>-MS spectrum of **4b** reaction mixture.

4c



Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source

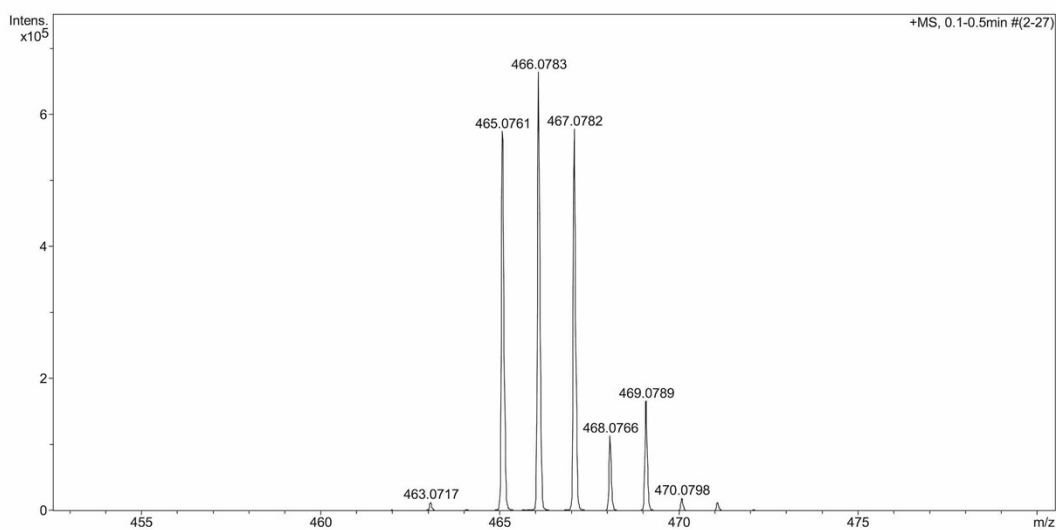


Figure S30. HR ESI<sup>+</sup>-MS spectrum of 4c.

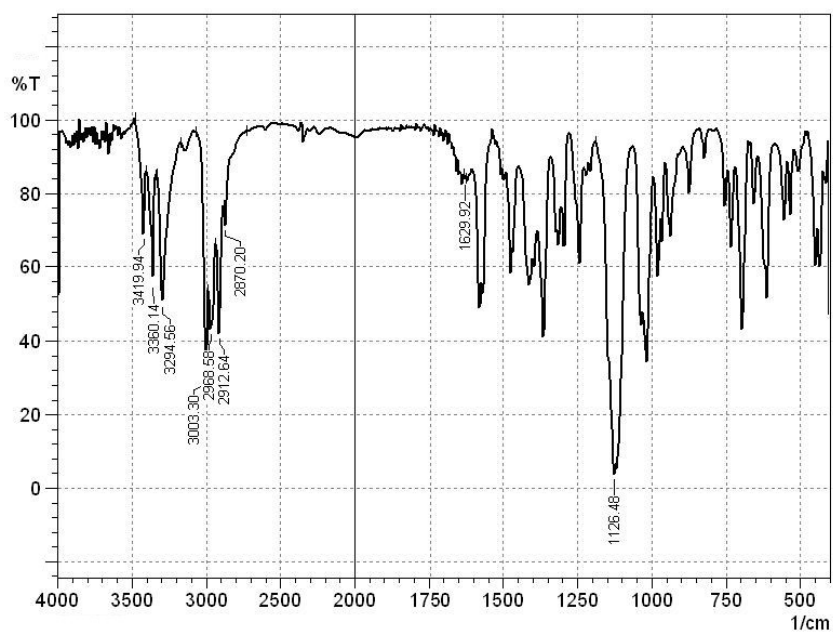


Figure S31. IR spectrum of 4c.

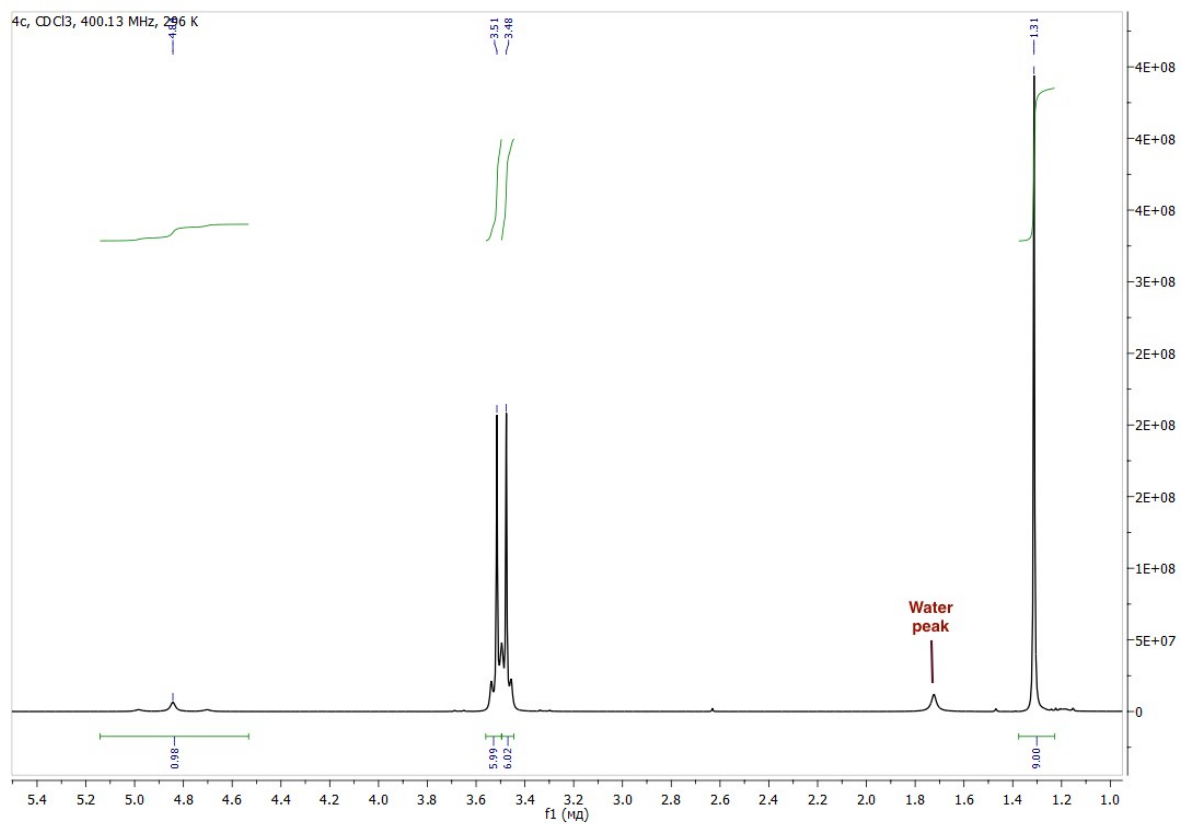


Figure S32. <sup>1</sup>H NMR spectrum of **4c**.

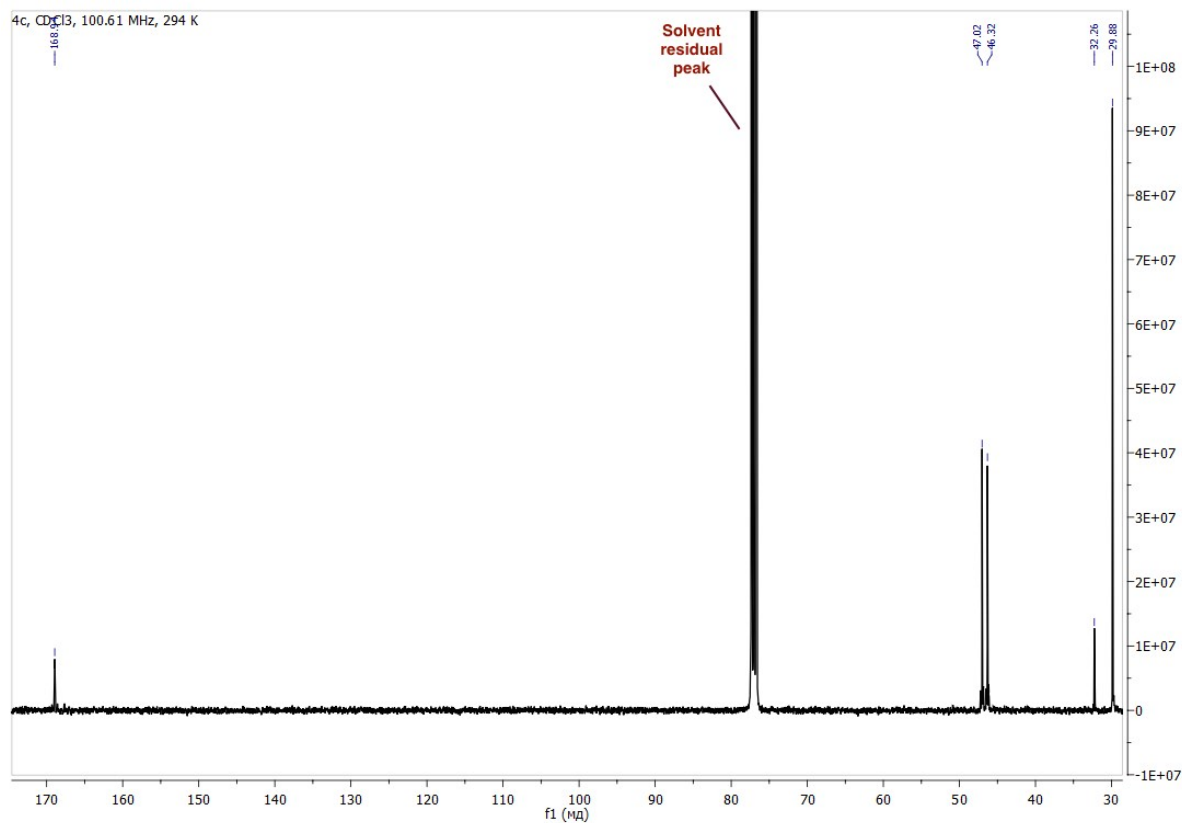
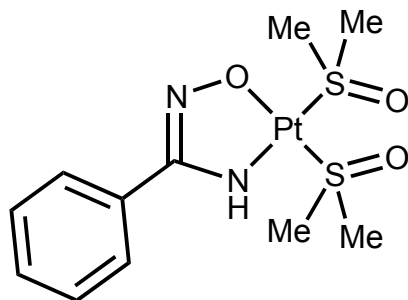


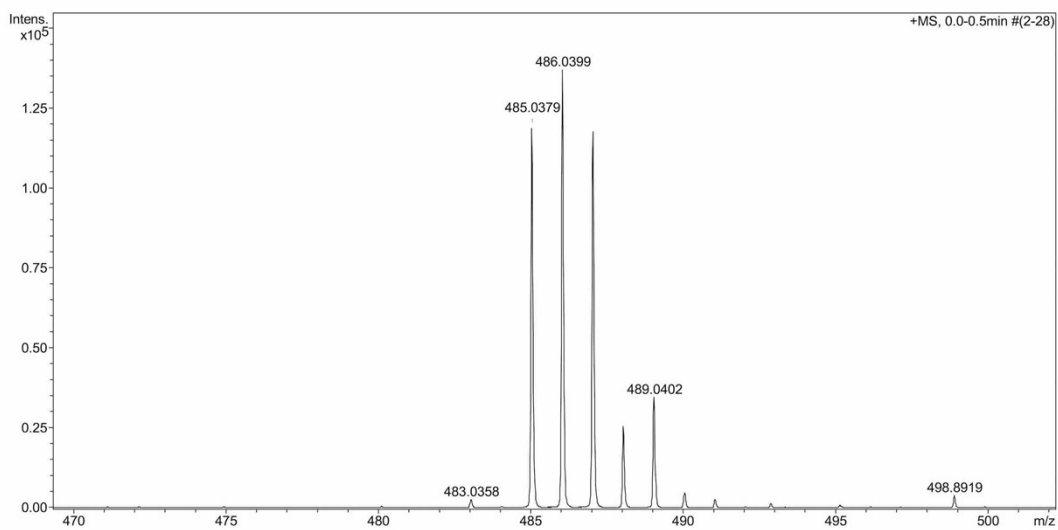
Figure S33. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4c**.

**4d**

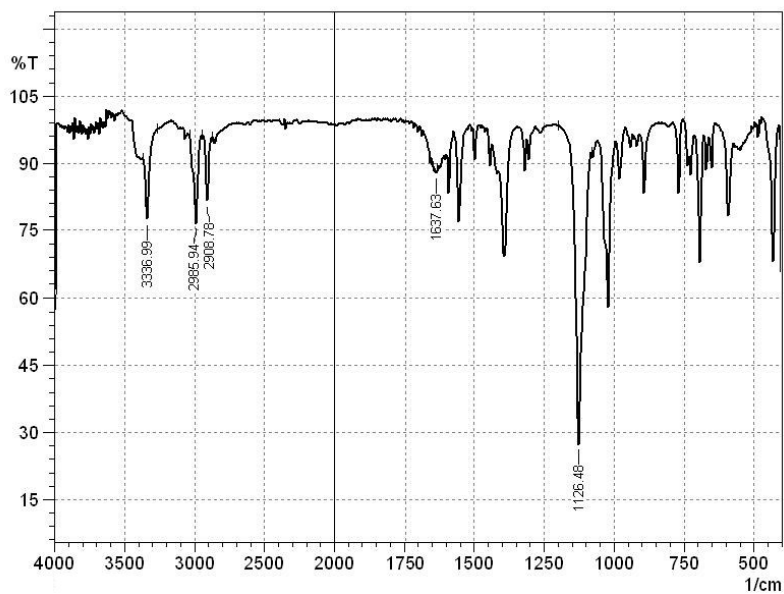


**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source



**Figure S34.** HR ESI<sup>+</sup>-MS spectrum of **4d**.



**Figure S35.** IR spectrum of **4d**.

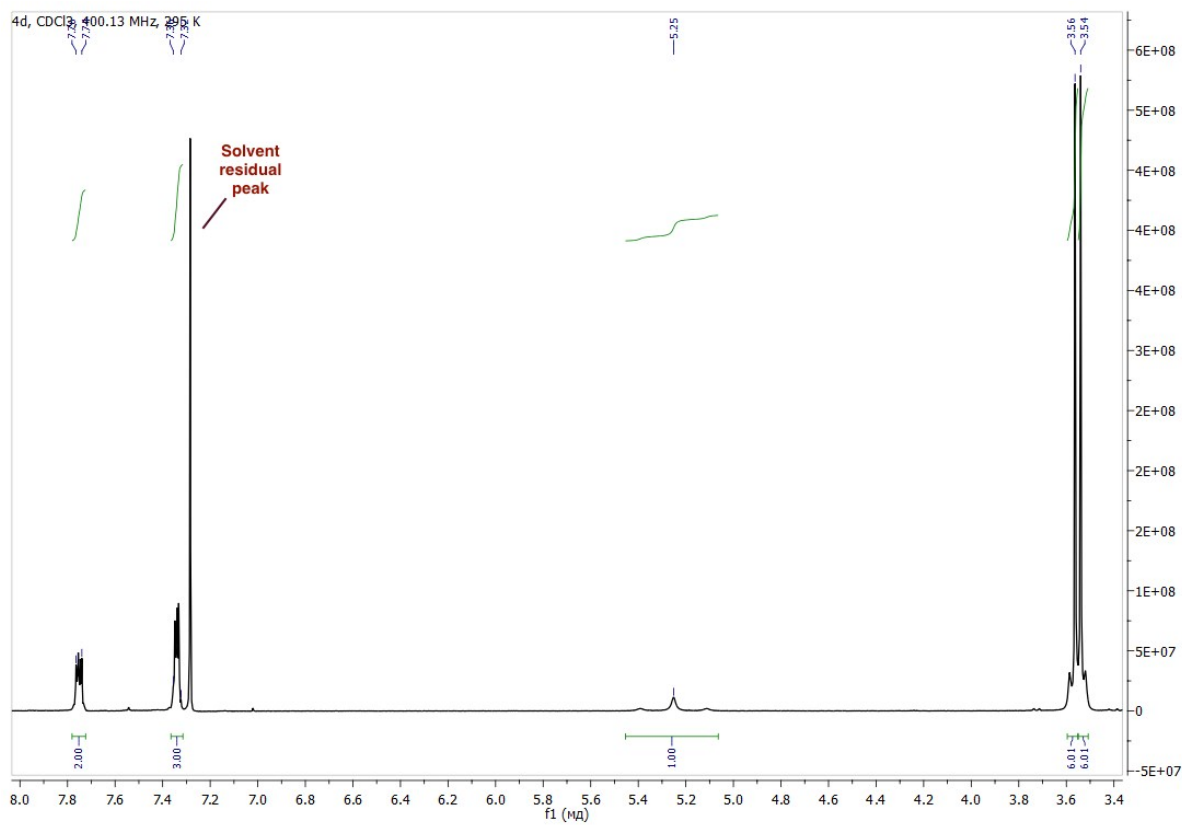


Figure S36.  $^1\text{H}$  NMR spectrum of **4d**.

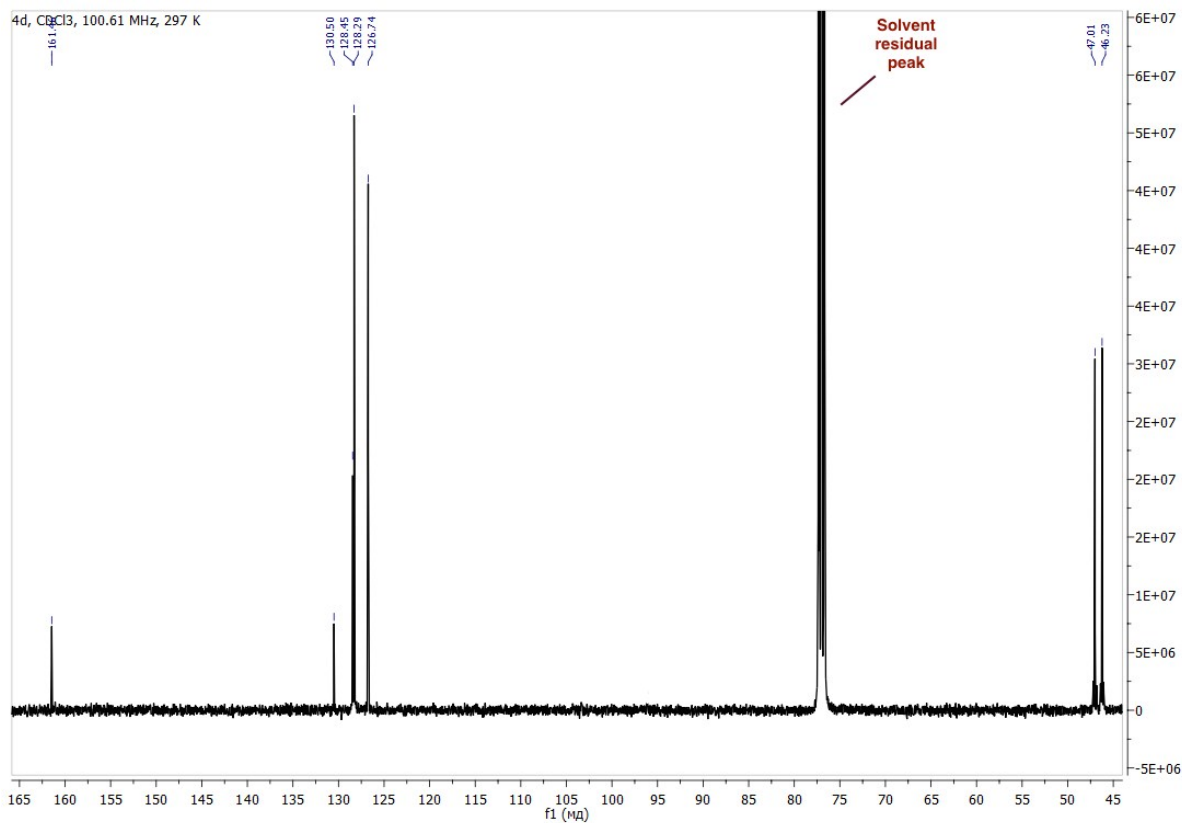
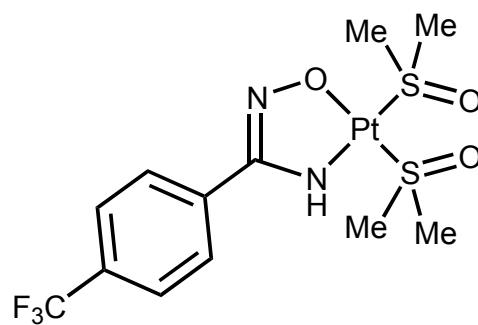


Figure S37.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4d**.

4e



Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source

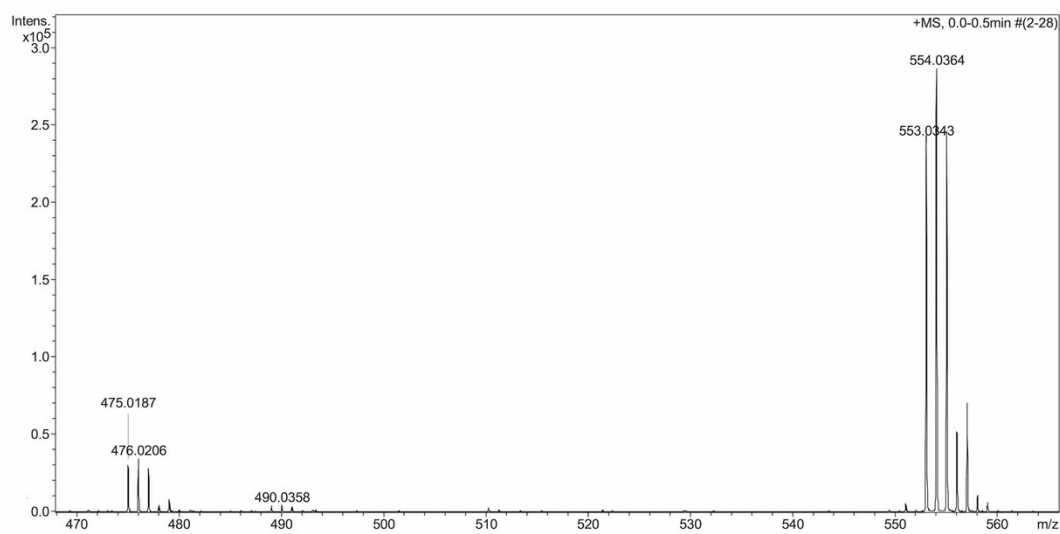


Figure S38. HR ESI<sup>+</sup>-MS spectrum of 4e.

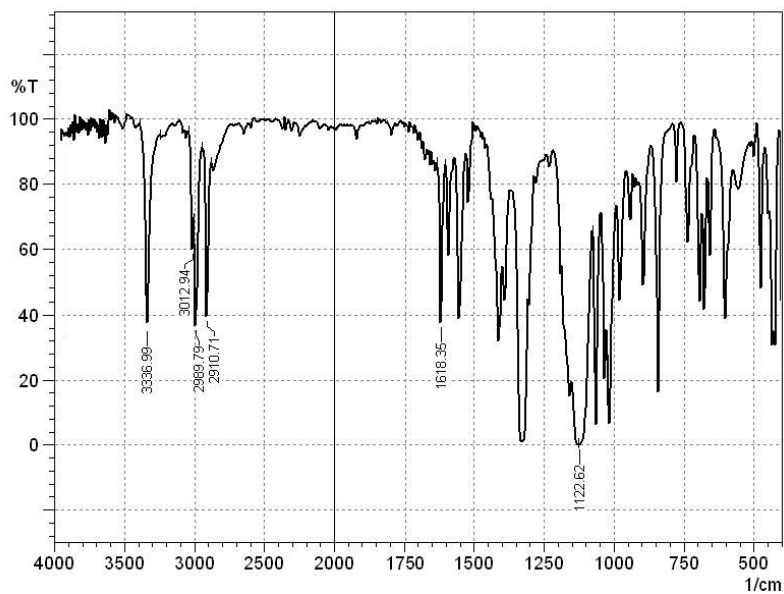


Figure S39. IR spectrum of 4e.

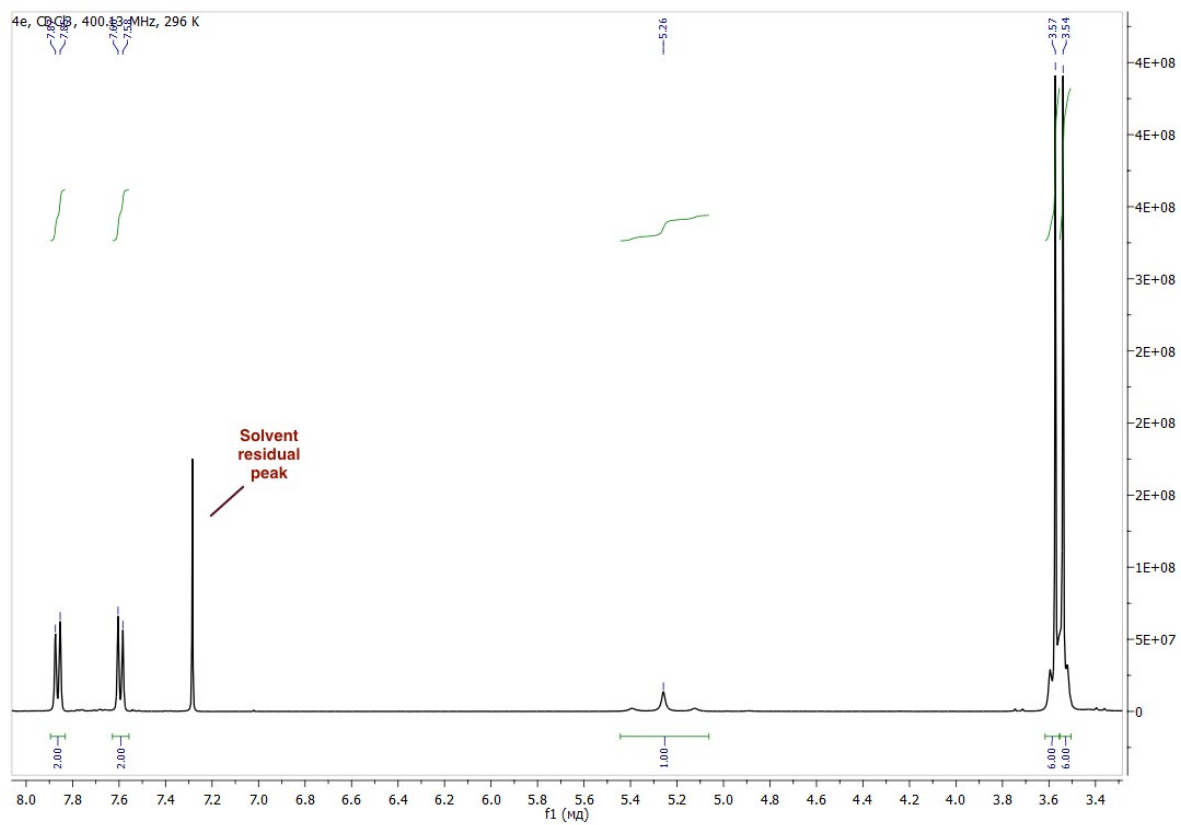


Figure S40. <sup>1</sup>H NMR spectrum of 4e.

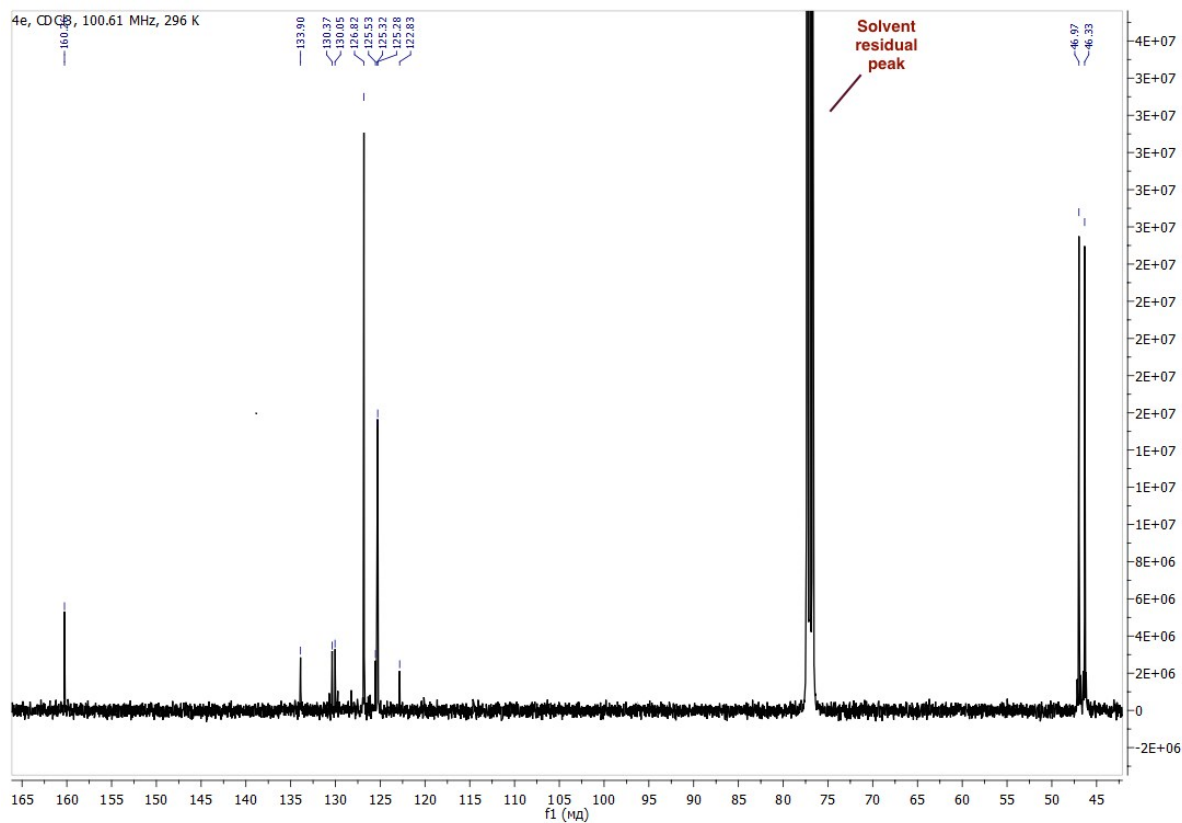
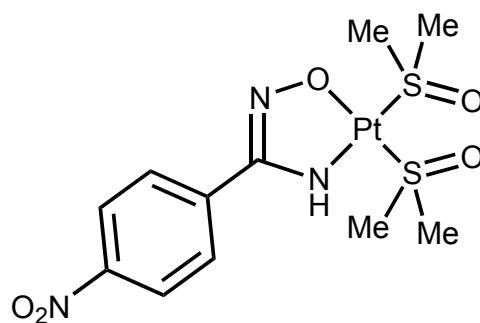


Figure S41. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4e.

4f



Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source

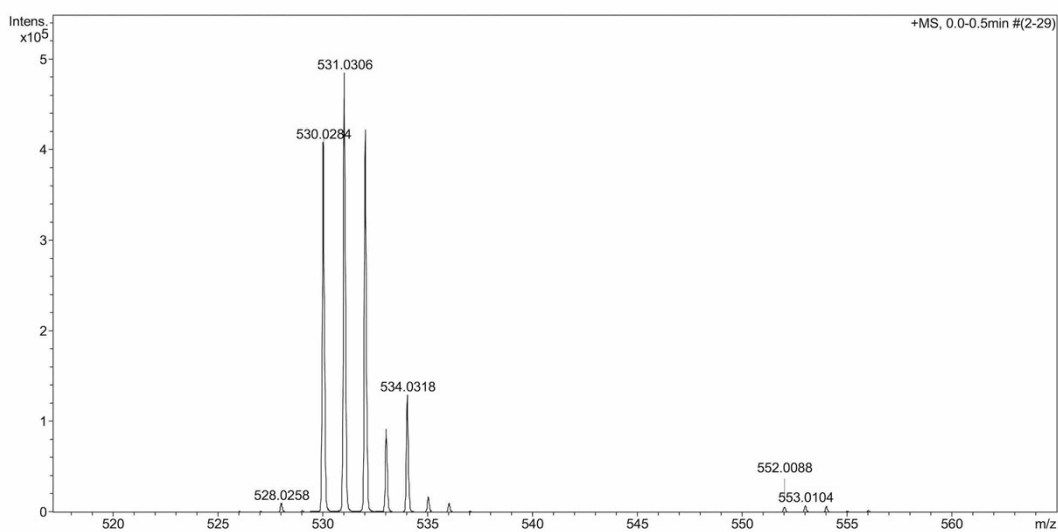


Figure S42. HR ESI<sup>+</sup>-MS spectrum of 4f.

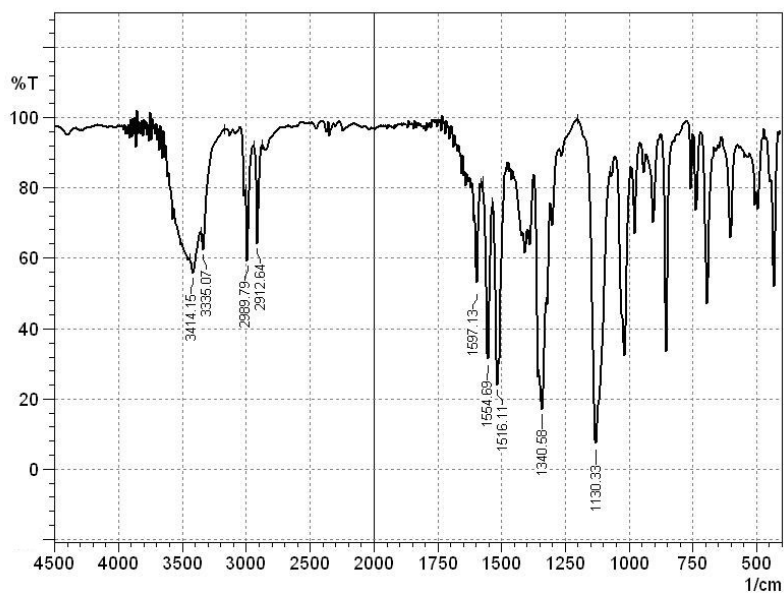


Figure S43. IR spectrum of 4f.



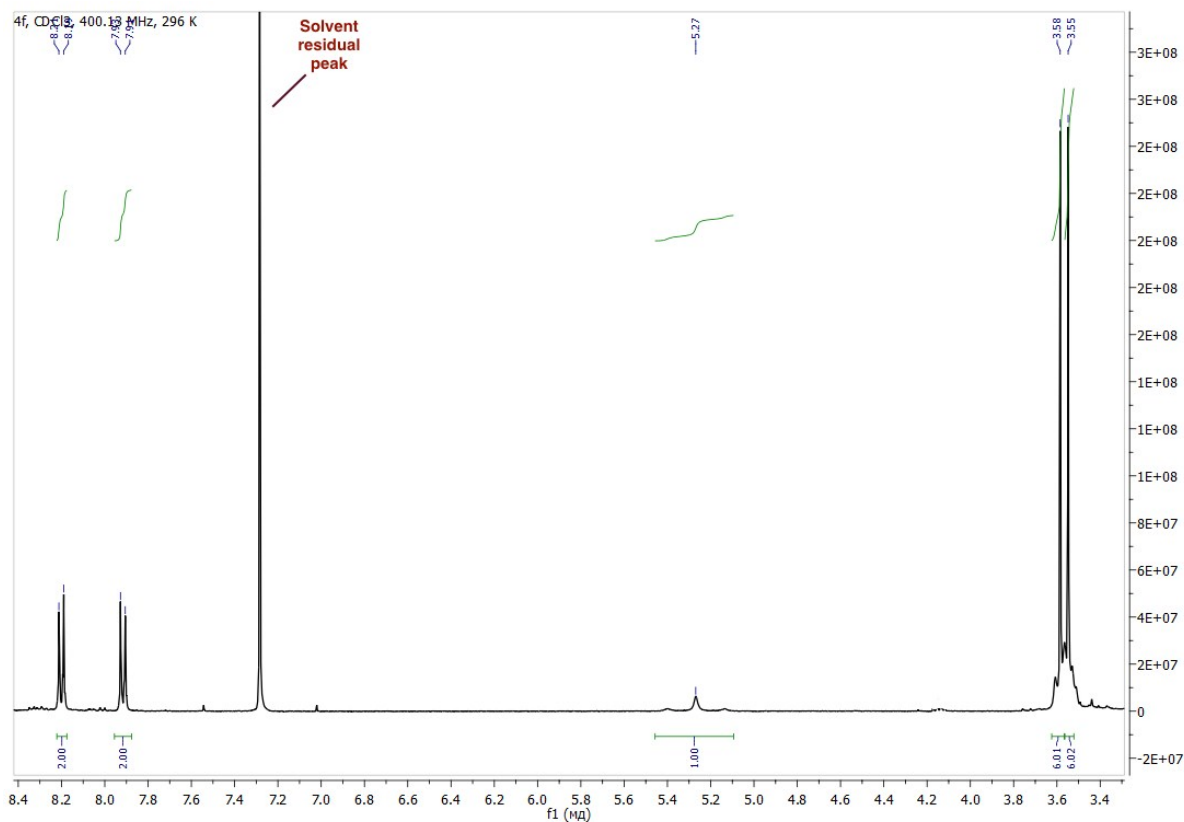


Figure S44. <sup>1</sup>H NMR spectrum of **4f**.

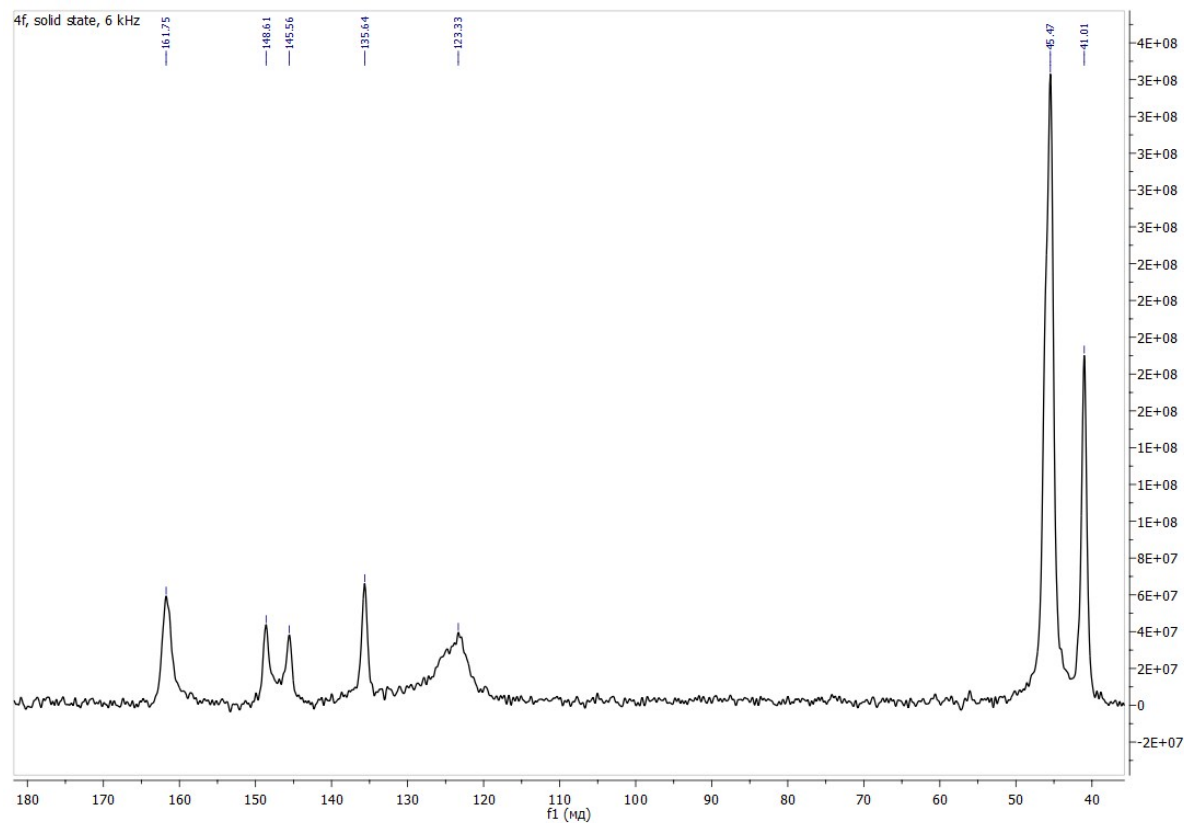
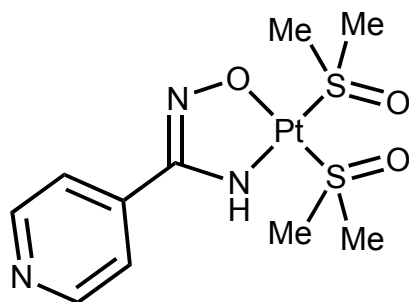


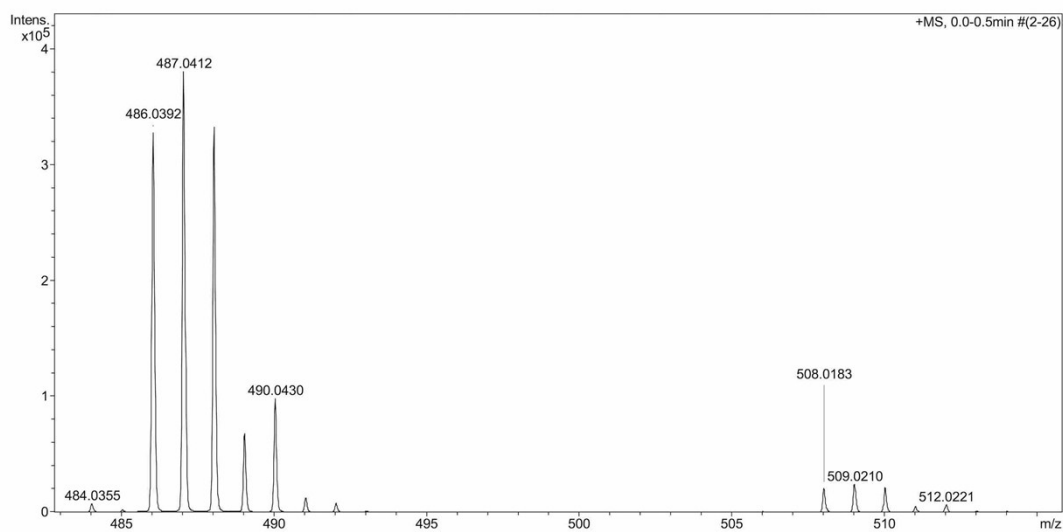
Figure S45. CP-MAS TOSS <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4f**.

4g

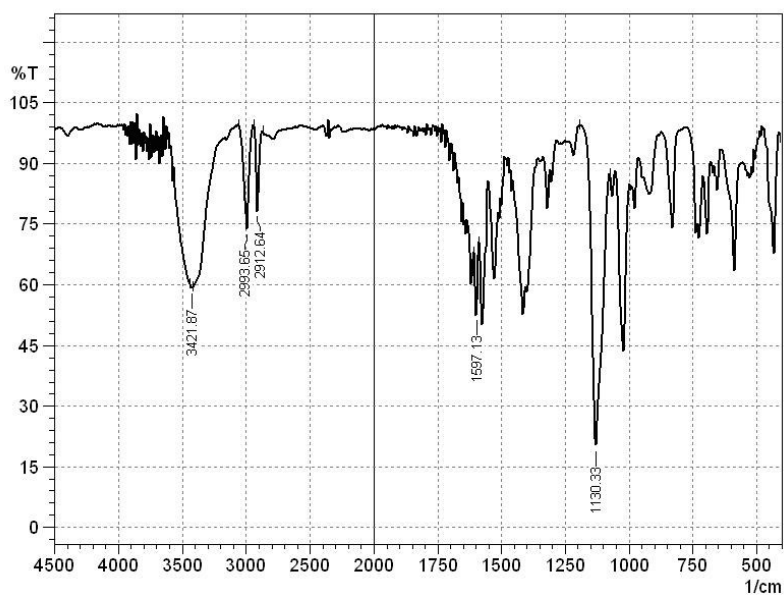


**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z			Set Divert Valve	Source



**Figure S46.** HR ESI<sup>+</sup>-MS spectrum of 4g.



**Figure S47.** IR spectrum of 4g.

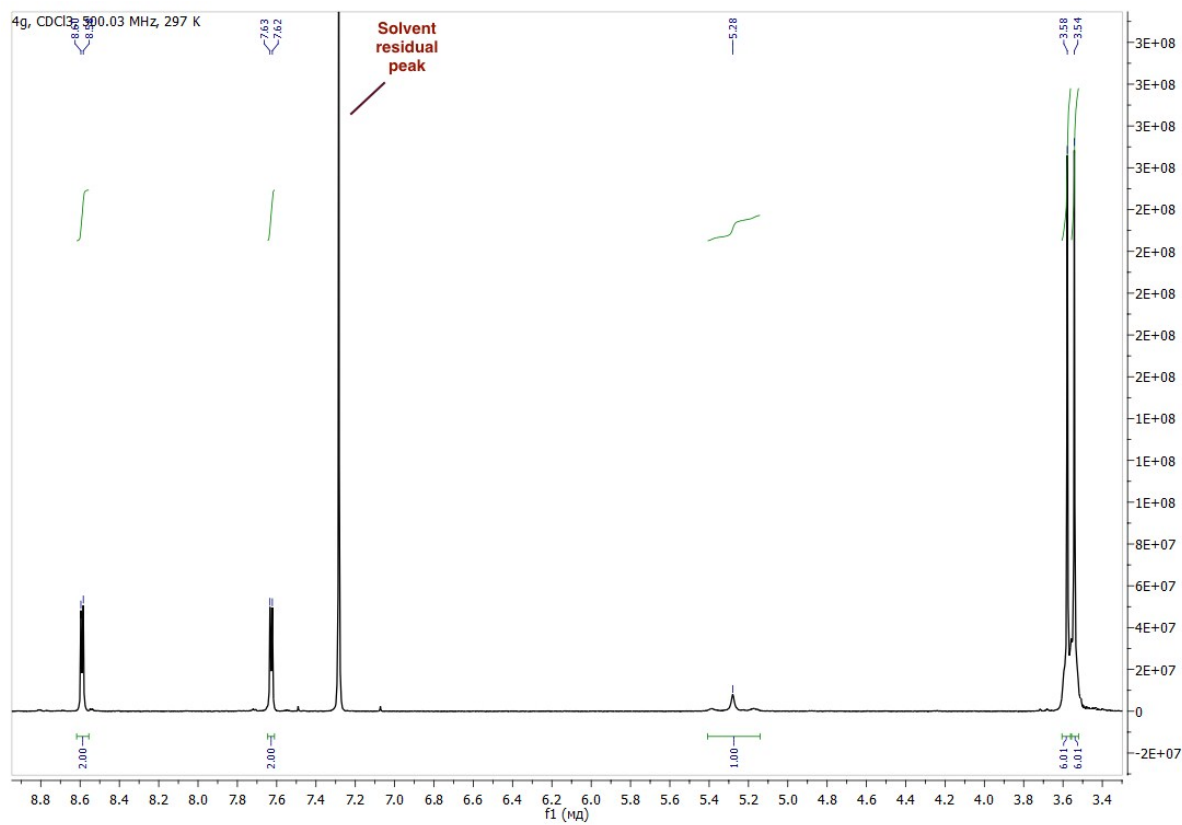


Figure S48. <sup>1</sup>H NMR spectrum of **4g**.

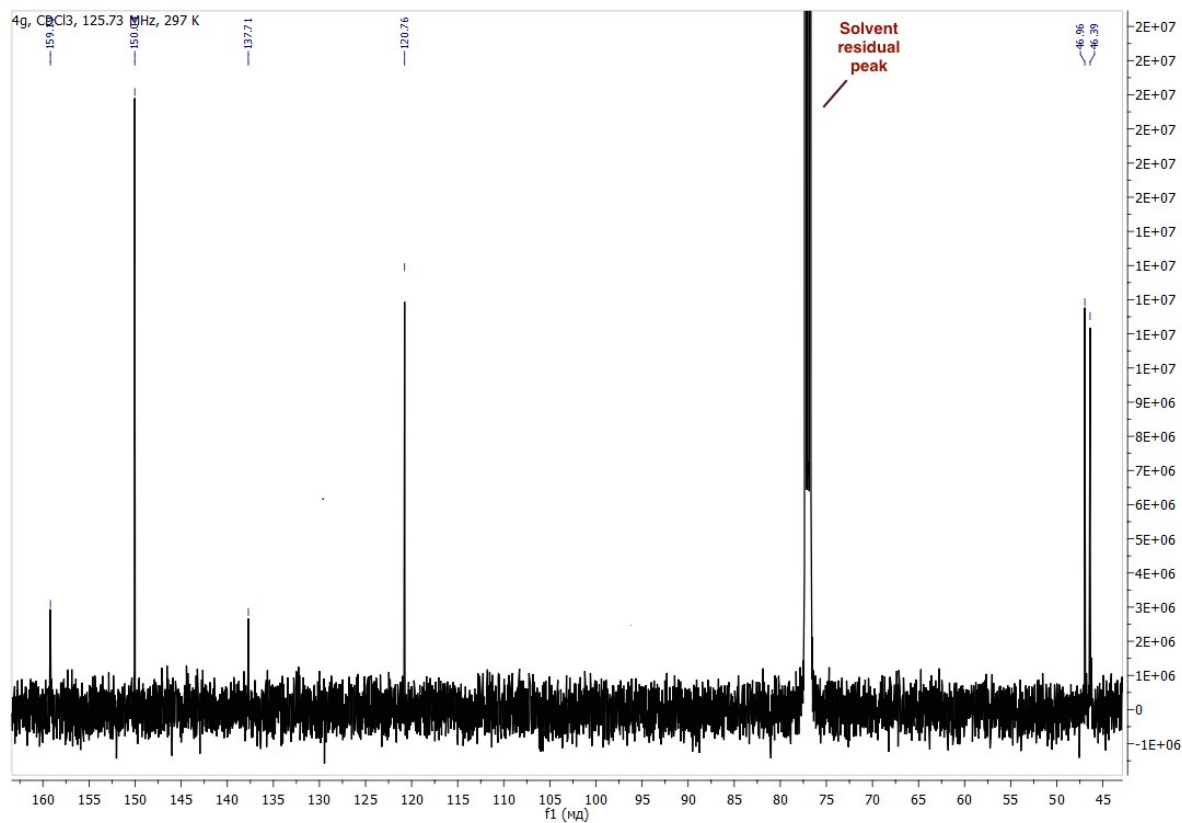


Figure S49. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4g**.

**Table S1.** Crystal data for **3a–b** and **3d–e**.

Identification code	<b>3a</b>	<b>3b</b>	<b>3d</b>	<b>3e</b>
Empirical formula	C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> PtS	C <sub>5</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> PtS	C <sub>10</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub> PtS	C <sub>10</sub> H <sub>13</sub> Cl <sub>2</sub> F <sub>3</sub> N <sub>2</sub> O <sub>2</sub> PtS
Formula weight	418.21	432.23	512.31	548.27
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	P2 <sub>1</sub> /c	P-1	P2 <sub>1</sub> /c	P-1
a/Å	8.0458(6)	7.7950(7)	7.7751(2)	7.1487(4)
b/Å	11.8336(7)	8.6094(9)	15.9278(5)	8.9180(5)
c/Å	12.2420(15)	9.4837(9)	13.8379(4)	13.5059(9)
α/°	90	99.166(8)	90	82.385(5)
β/°	112.759(8)	91.628(8)	103.110(3)	87.679(5)
γ/°	90	114.355(9)	90	66.909(6)
Volume/Å <sup>3</sup>	1074.82(18)	569.26(10)	1669.01(8)	785.01(9)
Z	4	2	4	2
ρ <sub>calc</sub> /cm <sup>3</sup>	2.584	2.522	2.039	2.320
μ/mm <sup>-1</sup>	13.712	12.950	8.856	9.444
F(000)	776.0	404.0	976.0	516.0
Crystal size/mm <sup>3</sup>	0.2 × 0.15 × 0.15	0.25 × 0.25 × 0.2	0.2 × 0.2 × 0.15	0.15 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.49 to 54.976	5.288 to 55	5.38 to 54.994	5.006 to 54.99
Index ranges	-10 ≤ h ≤ 9, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	-8 ≤ h ≤ 10, -11 ≤ k ≤ 10, -11 ≤ l ≤ 12	-10 ≤ h ≤ 7, -10 ≤ k ≤ 20, -17 ≤ l ≤ 17	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected	8752	4656	7727	12183
Independent reflections	2472 [R <sub>int</sub> = 0.0556, R <sub>sigma</sub> = 0.0530]	2607 [R <sub>int</sub> = 0.0265, R <sub>sigma</sub> = 0.0456]	3821 [R <sub>int</sub> = 0.0276, R <sub>sigma</sub> = 0.0444]	3602 [R <sub>int</sub> = 0.0345, R <sub>sigma</sub> = 0.0392]
Data/restraints/parameters	2472/0/112	2607/6/139	3821/0/177	3602/0/193
Goodness-of-fit on F <sup>2</sup>	1.020	1.038	1.066	1.023
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0273, wR <sub>2</sub> = 0.0503	R <sub>1</sub> = 0.0311, wR <sub>2</sub> = 0.0657	R <sub>1</sub> = 0.0252, wR <sub>2</sub> = 0.0475	R <sub>1</sub> = 0.0222, wR <sub>2</sub> = 0.0450
Final R indexes [all data]	R <sub>1</sub> = 0.0376, wR <sub>2</sub> = 0.0545	R <sub>1</sub> = 0.0342, wR <sub>2</sub> = 0.0679	R <sub>1</sub> = 0.0312, wR <sub>2</sub> = 0.0497	R <sub>1</sub> = 0.0270, wR <sub>2</sub> = 0.0461
Largest diff. peak/hole / e Å <sup>-3</sup>	1.32/-1.64	1.93/-2.50	1.21/-0.82	1.07/-0.87
CCDC number	<b>1475389</b>	<b>1475381</b>	<b>1475378</b>	<b>1475377</b>

**Table S2.** Crystal data for **3f**, **4c**, **4f** and **[2cH][PtCl<sub>3</sub>(Me<sub>2</sub>SO)]**.

Identification code	<b>3f</b>	<b>4c</b>	<b>4f</b>	<b>by-product_3c</b>
Empirical formula	C <sub>9</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> PtS	C <sub>9</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> PtS <sub>2</sub>	C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub> PtS <sub>2</sub>	C <sub>7</sub> H <sub>19</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>2</sub> PtS
Formula weight	525.27	465.49	530.48	496.74
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	orthorhombic	triclinic	monoclinic
Space group	P-1	Cmce	P-1	P2 <sub>1</sub> /c
a/Å	7.0238(3)	9.3250(8)	8.7261(2)	6.5859(2)
b/Å	9.0811(4)	18.8767(15)	10.2167(3)	19.2634(7)
c/Å	12.9083(3)	17.497(2)	18.8842(4)	12.7960(5)
α/°	91.147(3)	90	74.480(2)	90
β/°	94.584(3)	90	80.247(2)	116.115(3)
γ/°	111.834(4)	90	87.869(2)	90
Volume/Å <sup>3</sup>	760.73(5)	3079.9(5)	1598.67(8)	1457.66(10)
Z	2	8	4	4
ρ <sub>calc</sub> /cm <sup>3</sup>	2.293	2.008	2.204	2.264
μ/mm <sup>-1</sup>	9.724	9.382	19.111	10.308
F(000)	496.0	1792.0	1016.0	944.0
Crystal size/mm <sup>3</sup>	0.3 × 0.3 × 0.2	0.3 × 0.15 × 0.15	0.35 × 0.12 × 0.06	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.642 to 54.996	5.4 to 54.948	8.984 to 149.968	5.52 to 54.992
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16	-12 ≤ h ≤ 6, -24 ≤ k ≤ 24, -12 ≤ l ≤ 21	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -20 ≤ l ≤ 23	-6 ≤ h ≤ 8, -25 ≤ k ≤ 17, -16 ≤ l ≤ 15
Reflections collected	34901	5640	24766	7442
Independent reflections	3488 [R <sub>int</sub> = 0.0655, R <sub>sigma</sub> = 0.0289]	1809 [R <sub>int</sub> = 0.0234, R <sub>sigma</sub> = 0.0239]	6576 [R <sub>int</sub> = 0.0576, R <sub>sigma</sub> = 0.0434]	3352 [R <sub>int</sub> = 0.0284, R <sub>sigma</sub> = 0.0391]
Data/restraints/parameters	3488/0/184	1809/0/97	6576/0/399	3352/0/150
Goodness-of-fit on F <sup>2</sup>	1.055	1.121	1.084	1.050
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0208, wR <sub>2</sub> = 0.0438	R <sub>1</sub> = 0.0245, wR <sub>2</sub> = 0.0597	R <sub>1</sub> = 0.0313, wR <sub>2</sub> = 0.0760	R <sub>1</sub> = 0.0234, wR <sub>2</sub> = 0.0444
Final R indexes [all data]	R <sub>1</sub> = 0.0224, wR <sub>2</sub> = 0.0444	R <sub>1</sub> = 0.0282, wR <sub>2</sub> = 0.0615	R <sub>1</sub> = 0.0377, wR <sub>2</sub> = 0.0812	R <sub>1</sub> = 0.0292, wR <sub>2</sub> = 0.0462
Largest diff. peak/hole / e Å <sup>-3</sup>	1.27/-1.20	2.75/-1.15	1.75/-1.47	1.77/-0.96
CCDC number	<b>1475399</b>	<b>1475400</b>	<b>1475683</b>	<b>1475446</b>

Concentration-effect curves of 3b, 3d-e and 4c-e

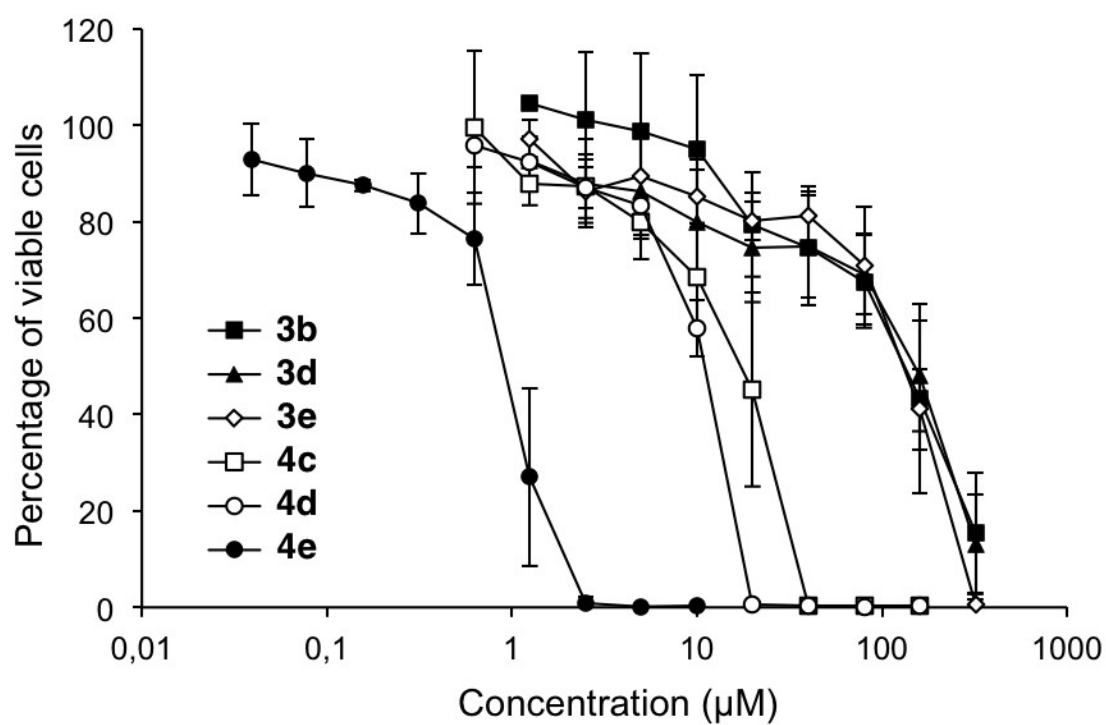


Figure S50. Concentration-effect curves of 3b, 3d-e and 4c-e in CH1/PA-1 cells.

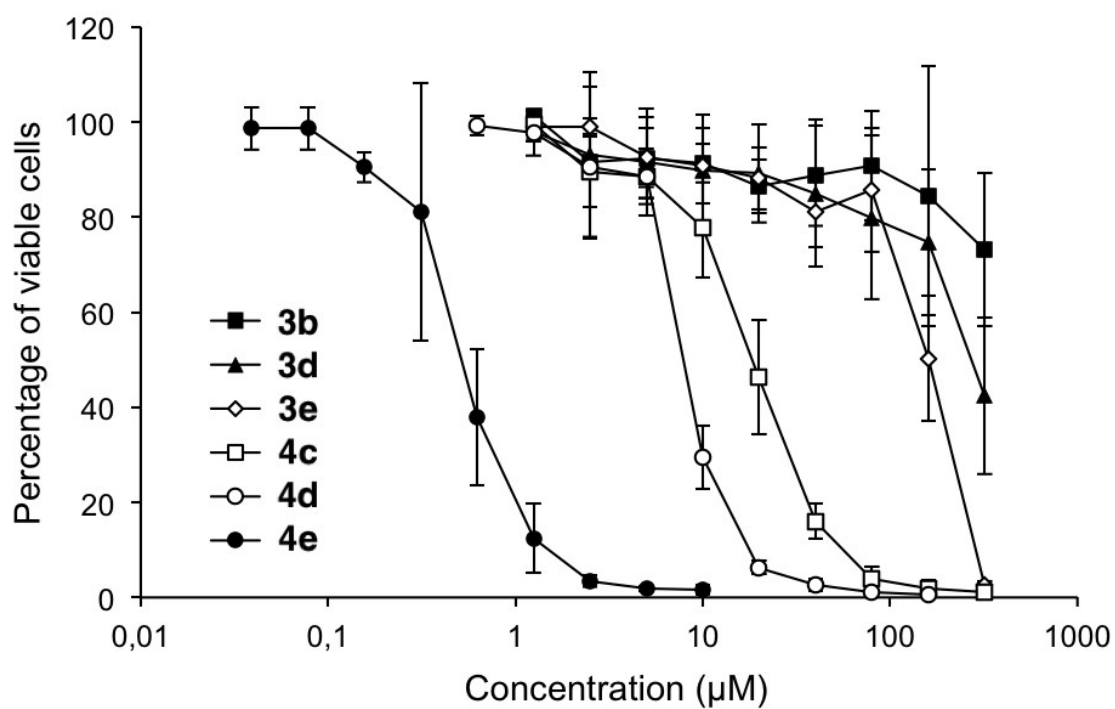


Figure S51. Concentration-effect curves of 3b, 3d-e and 4c-e in SW480 cells.

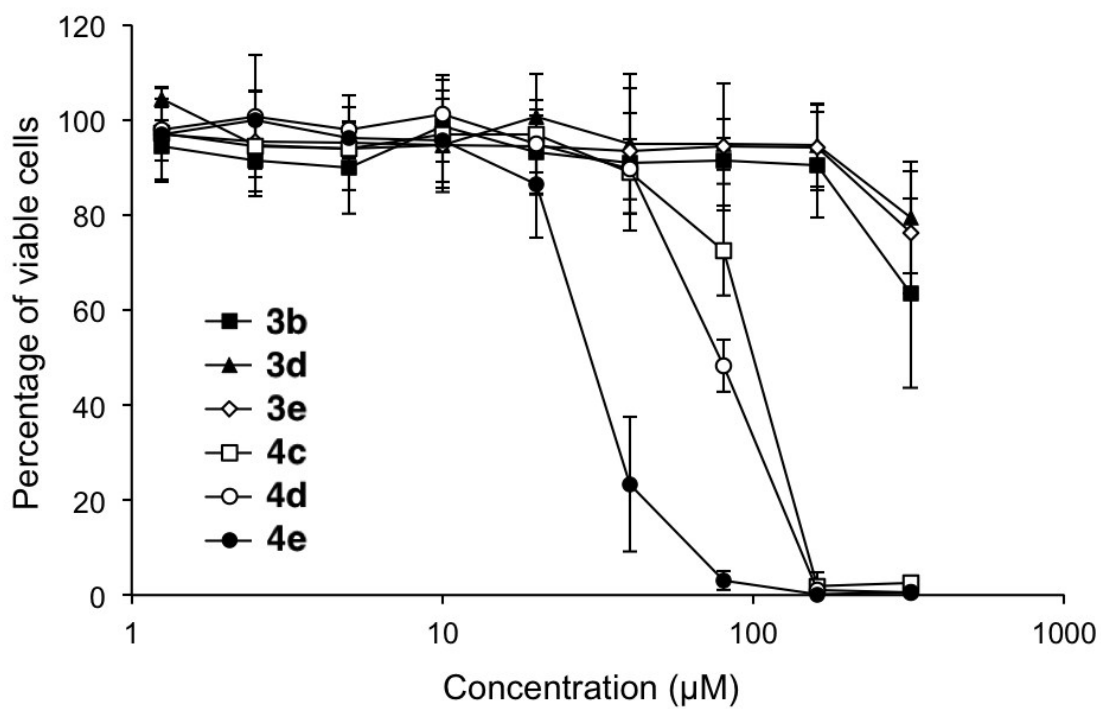


Figure S52. Concentration-effect curves of **3b**, **3d–e** and **4c–e** in A549 cells.

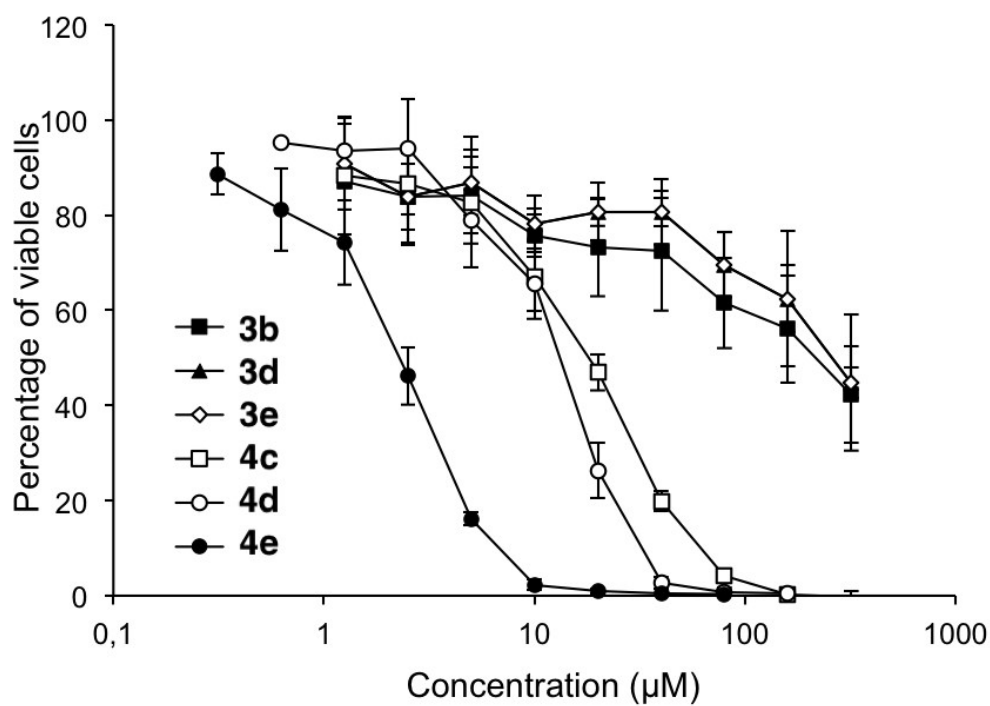


Figure S53. Concentration-effect curves of **3b**, **3d–e** and **4c–e** in SKBR3 cells.