Electronic Supplementary Information

Metal Acetylacetonate Complexes for High Energy Density Non-Aqueous Redox Flow Batteries

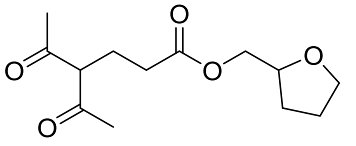
James A. Suttil, Jonathan F. Kucharyson, Ismailia L. Escalante-Garcia, Pablo J. Cabrera, Bryant R. James, Robert F. Savinell, Melanie S. Sanford, and Levi T. Thompson**

Ligand Synthesis

General Procedure:

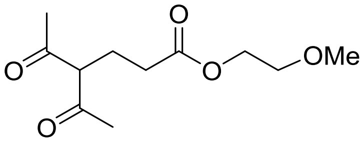
On the benchtop, potassium carbonate (0.1 eq.), the desired acrylate (1 eq.) and acetylacetone (5 eq.) were combined in a 20 mL vial, sealed and heated to 70 °C overnight with stirring. The resulting bright orange suspension was filtered through a celite pad and the solid residue was washed with 2 × 5 mL portions of acetylacetone. The washings and filtrate were combined and dried *in vacuo* to give a bright orange liquid, which was purified by vacuum distillation. Any variations from this procedure are disclosed for each individual compound. The authors note that the ^{13}C NMR data for the ligands detailed herein show less carbon signals than would be expected from the ascribed structures. The authors have attributed this to signal overlap given the structural similarity of the tautomers.

Preparation and characterization of tetrahydrofurfuryl 4-acetyl-5-oxohexanoate:



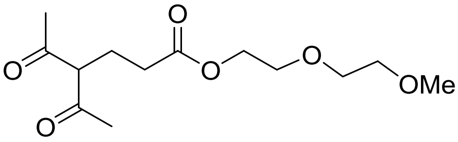
Tetrahydrofurfuryl 4-acetyl-5-oxohexanoate was prepared according to the general procedure employing tetrahydrofurfuryl acrylate (6.60 mL, 40.0 mmol), acetylacetone (20.5 mL, 200 mmol) and potassium carbonate (0.55 g, 3.98 mmol). The title compound was isolated as a yellow liquid via vacuum distillation (0.079 mm Hg, 152 °C) (9.26 g, 90 % yield, 36.1 mmol). IR (υ, cm^{-1}): 2953 (w), 1728 (s), 1698 (s), 1421 (w), 1359 (m), 1246 (w), 1154 (s), 1080 (m), 1022 (m), 992 (m). ^{1}H NMR (400 MHz, $CDCl_3$), mixture of tautomers: δ 16.72 (s, 0.16H), 4.05-4.15 (multiple peaks, 2H), 3.98 (m, 1H), 3.84 (m, 1H), 3.72-3.78 (multiple peaks, 1.7H), 2.57 (m, 0.4H), 2.41 (m, 0.4H), 2.32 (t, *J* = 4 Hz, 1.5H), 2.09-2.18 (multiple peaks, 6.46H), 1.97 (m, 1H), 1.88 (m, 2H), 1.56 (m, 1H). ^{13}C NMR (100.46 MHz, $CDCl_3$): δ 203.8, 191.4, 172.6, 108.7, 76.5, 76.5, 68.5, 68.5, 67.0, 66.8, 66.7, 34.87, 31.6, 29.4, 29.3, 28.1, 28.0, 25.7, 23.0, 23.0, 22.9. HR-MS (ESI, positive ion mode) *m/z* calcd. for $C_{13}H_{21}O_5$ $[M+H]^+$: 257.1384, found: 257.1377.

Preparation and characterization of 2-methoxyethyl 4-acetyl-5-oxohexanoate:



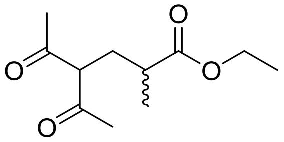
2-Methoxyethyl 4-acetyl-5-oxohexanoate was prepared according to the general procedure employing ethylene glycol methyl ether acrylate (2.57 mL, 20 mmol). The title compound was isolated as a yellow liquid via vacuum distillation (0.092 mm Hg, 119 °C) (2.66 g, 58 %, 11.5 mmol). IR (υ, cm^{-1}): 2934 (w), 1728 (s), 1698 (s), 1420 (w), 1359 (m), 1248 (w), 1152 (m), 1127 (s), 1032 (m). ^1H NMR (400 MHz, $CDCl_3$), mixture of tautomers: δ 16.77 (s, 0.3H), 4.22-4.25 (multiple peaks, 2H), 3.75 (t, *J* = 6.8 Hz, 0.8H), 3.57-3.60 (multiple peaks, 2H), 3.38-3.39 (multiple peaks, 3H), 2.60 (m, 0.6H), 2.44 (m, 0.6H), 2.35 (t, *J* = 6.8 Hz, 1.6H), 2.12 – 2.20 (multiple peaks, 7.2H). ^{13}C NMR (175.95 MHz, $CDCl_3$), mixture of tautomers: δ 203.8, 191.4, 172.6, 108.7, 70.4, 70.4, 67.0, 63.7, 63.7, 59.0, 59.0, 34.7, 31.6, 29.4, 23.0, 22.9. HR-MS (ESI, positive ion mode) *m/z* calcd. for $C_{11}H_{18}O_5Na$ $[M+Na]^+$: 253.1046, found: 253.1044.

Preparation and characterization of 2-(2-methoxyethyl)ethyl 4-acetyl-5-oxohexanoate:



(2-(2-Methoxyethoxy)ethyl 4-acetyl-5-oxohexanoate was prepared according to the general procedure employing 2-(2-methoxyethoxy)ethyl acrylate (4.05 g, 23.2 mmol), 2,4-pentanedione (11.9 mL, 116 mmol) and potassium carbonate (0.32 g, 2.32 mmol). The title compound was isolated as a yellow liquid via vacuum distillation (0.092 mm Hg, 119 °C) (4.81 g, 76 % yield, 17.5 mmol). IR (υ, cm^{-1}): 2880 (m), 1729 (s), 1698 (s), 1612 (w), 1421 (w), 1359 (m), 1248 (m), 1139 (m), 1107 (s), 958 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 16.67 (s, 0.3H), 4.12-4.13 (multiple peaks, 2H), 3.66 (t, *J* = 7.2 Hz, 0.7H), 3.57-3.60 (multiple peaks, 2H), 3.51-3.54 (multiple peaks, 2H), 3.43-3.45 (multiple peaks, 2H), 3.26-3.27 (multiple peaks, 3H), 2.49 (m, 0.7H), 2.32 (m, 0.7H), 2.23 (t, *J* = 7.2 Hz, 1.4H), 2.00 – 2.10 (multiple peaks, 7H). ^{13}C NMR (100.46 MHz, $CDCl_3$): δ 203.9, 191.4, 172.6, 108.7, 72.0, 70.6, 70.6, 69.2, 69.1, 67.1, 63.8, 63.8, 59.1, 59.1, 34.8, 31.6, 29.4, 23.0, 22.9.HR-MS (ESI, positive ion mode) *m/z* calcd. for $C_{14}H_{25}O_6$ $[M+H]^+$: 289.1646, found: 289.1645.

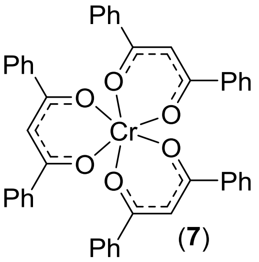
Preparation and characterization of ethyl 2-methyl-4-acetyl-5-oxohexanoate:

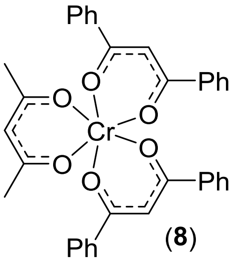


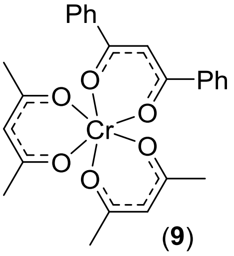
On the benchtop, potassium fluoride dihydrate (4.71 g, 50 mmol), 2,4-pentanedione (20.5 mL, 200 mmol) and ethyl methacrylate (12.4 mL, 100 mmol) were combined in 30 mL of ethanol and refluxed for three days. The bright orange suspension was filtered, concentrated *in vacuo* and refiltered to remove any insoluble species. The bright orange residue was first purified by vacuum distillation (0.050 mm Hg, 60 °C) to give a colourless liquid. This was further purified by silica gel column chromatography employing dichloromethane eluent. The title compound was isolated in 22% yield (4.71 g, 22 mmol) as a mixture contaminated with ethyl 2-methyl-5-oxohexanoate. The mixture was used without further purification. IR (υ, cm^{-1}): 2978 (w), 1716 (s), 1462 (w), 1369 (m), 1251 (w), 1159 (s), 1026 (m). HR-MS (ESI, positive ion mode) *m/z* calcd. for $C_{13}H_{21}O_5$ $[M+Na]^+$: 237.1097, found: 237.1098.

Complex Synthesis

One-pot preparation of tris(1,3-diphenyl-1,3-propanedionato)chromium(III) (7), (2,4-pentanedionato)bis(1,3-diphenyl-1,3-propanedionato)chromium(III) (8) and bis(2,4-pentanedionato)(1,3-diphenyl-1,3-propanedionato)chromium(III) (9):


(**7**)

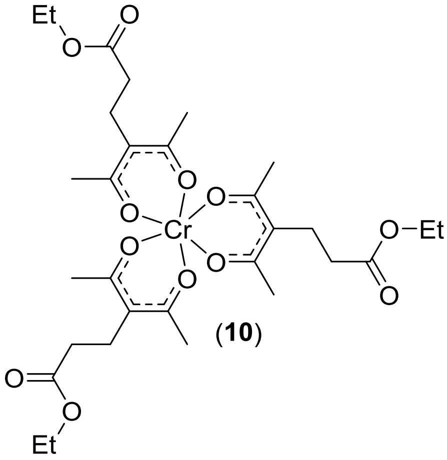

(**8**)


(**9**)

Chromium acetylacetonate (6.00 g, 17.2 mmol) and 1,3-diphenyl-1,3-propanedione (3.85 g, 17.2 mmol) were ground together in a mortar and pestle until a homogeneous, pink powder was obtained. The powder was transferred to a 250 mL Erlenmeyer flask and heated to 175 °C for four hours under a flow of nitrogen. Upon cooling, the title products were separated by silica gel column chromatography employing dichloromethane as the eluent. Tris(1,3-diphenyl-1,3-propanedionato)chromium(III) (**7**) was isolated as a dark brown solid (0.32 g, 3% yield, 0.45 mmol, $R_f = 0.84$ in CH_2Cl_2). Mp = 280-281 °C (from CH_2Cl_2); elemental analysis calcd. for $C_{45}H_{33}O_6Cr$: C 74.89, H 4.61; found: C 75.08, H 4.63; IR (υ, cm^{-1}) 3062 (w), 1588 (m), 1515 (s), 1475 (s), 1452 (s), 1440 (m), 1365 (s), 1316 (s), 1226 (m), 1180 (w), 1067 (m), 1024 (m), 941 (w); HRMS (EI) *m/z* calcd. for $C_{45}H_{33}O_6Cr$: 721.1682; found = 721.1680. (2,4-Pentanedionato)bis(1,3-diphenyl-1,3-propanedionato)chromium(III) (**8**) was isolated as a dark brown solid (1.55 g, 15% yield, 2.60 mmol; $R_f = 0.59$ CH_2Cl_2). Crystals suitable for X-ray diffraction were grown by vapour diffusion of hexanes into a chloroform solution of 8. Mp = 257-258 °C (from hexanes/chloroform); elemental analysis calcd. for $C_{35}H_{29}O_6Cr$: C 70.34, H 4.89; found: C 70.23, H 4.90; IR (υ, cm^{-1}) 1584 (w), 1517 (m), 1472 (w), 1450 (w), 1366 (m), 1316 (w), 1224 (w), 1066 (w), 1024 (w), 927 (w); HRMS (EI) *m/z* calcd. for $C_{35}H_{29}O_6Cr$: 597.1369; found: 597.1354. Bis(2,4-Pentanedionato)(1,3-diphenyl-1,3-propanedionato)chromium(III)

(**9**) was isolated as a dark brown solid (2.72 g, 33% yield, 5.73 mmol, R_f = 0.19 in CH_2Cl_2). Crystals suitable for X-ray diffraction were grown by vapour diffusion of hexanes into a chloroform solution of the complex. Mp = 237-239 °C (from hexanes/chloroform); elemental analysis calcd. for $C_{25}H_{25}O_6Cr$: C 63.42, H 5.32; found: C 63.17, H 5.31; IR (υ, cm^{-1}): 1572 (m), 1517 (s), 1476 (m), 1372 (s), 1314 (w), 1278 (m), 1230 (w), 1069 (m), 1023 (m), 931 (m); HRMS (EI) *m/z* calcd. for $C_{25}H_{25}O_6Cr$: 473.1056; found: 473.1048.

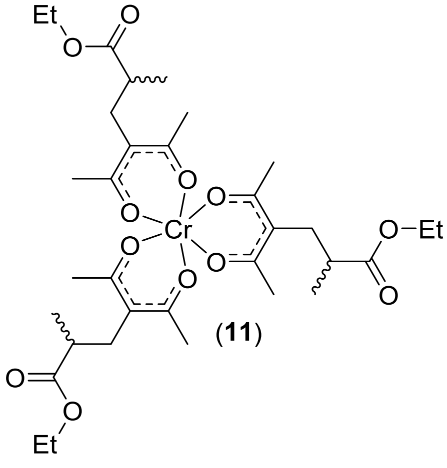
Preparation of 10:



(**10**)

A solution of ethyl 4-acetyl-5-oxohexanoate (1.86 g, 9.30 mmol) in 25 mL of anhydrous tetrahydrofuran was slowly added to a suspension of sodium hydride (0.22 g, 9.30 mmol) in 25 mL of anhydrous tetrahydrofuran at 0 °C. The resulting yellow solution was allowed to warm to room temperature and stirred for three hours. Subsequently, $CrCl_3(thf)_3$ (1.12 g, 3.00 mmol) was added in a single portion, and the mixture was heated to 90 °C overnight. On the benchtop, the green/purple suspension was quenched with 1 mL of degassed water and dried under vacuum. The residue was purified via silica gel chromatography and then dried under vacuum overnight to afford **10** as a dark purple tar (1.45 g, 74% yield, 2.23 mmol, R_f = 0.31 in 95% CH_2Cl_2/5% THF). Elemental analysis calcd. for $C_{30}H_{45}O_{12}Cr$: C 55.46, H 6.98; found: C 55.54, H 6.80; IR (υ, cm^{-1}) 2980 (w), 1727 (s), 1563 (s) 1454 (s), 1358 (s), 1339 (s), 1291 (s), 1238 (w), 1154 (m), 1054 (w), 1020 (m), 985 (m); HRMS (ESI, positive ion mode) *m/z* calcd. for $C_{30}H_{46}O_{12}Cr$ $[M+H]^+$ 650.2389; found 650.2383.

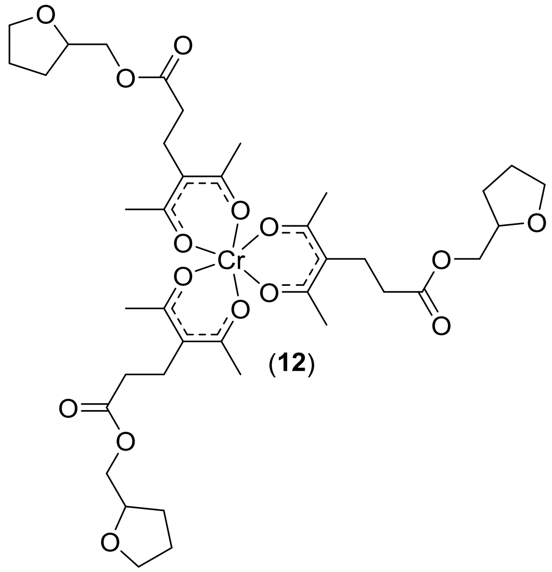
Preparation of 11:



(**11**)

Complex **11** was prepared by an analogous procedure to complex **10** employing 2-methyl-4-acetyl-5-oxohexanoate (2.12 g, 9.90 mmol), sodium hydride (0.22 g, 9.30 mmol) and $CrCl_3(thf)_3$ (1.12 g, 3.00 mmol). Purification via silica gel column chromatography yielded **11** as a dark purple tar (0.84 g, 41% yield, 1.22 mmol, $R_f = 0.30$ in 98% CH_2Cl_2/2% THF). Elemental analysis calcd. for $C_{33}H_{51}O_{12}Cr$: C 57.30, H 7.43; found: C 57.57, H 7.32; IR (υ, cm^{-1}) 2979 (w), 1726 (s), 1562 (s), 1450 (s), 1340 (s) 1289 (m), 1229 (w), 1172 (s), 1100 (m), 1051 (w), 1010 (s), 923 (m); HRMS (ESI, positive ion mode) *m/z* calcd. for $C_{33}H_{52}O_{12}Cr$ $[M+H]^+$ 692.2858, found 692.2851.

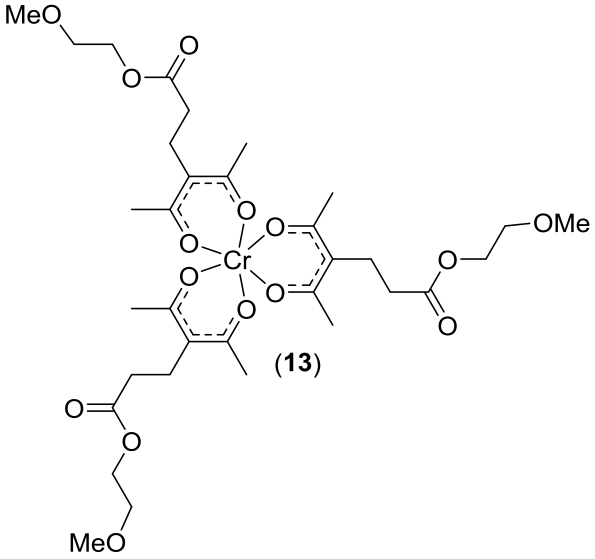
Preparation of 12:



(**12**)

Complex **12** was prepared by an analogous procedure to **10** employing tetrahydrofurfuryl 4-acetyl-5-oxohexanoate (4.10 g, 16.0 mmol), sodium hydride (0.38 g, 16.0 mmol) and $CrCl_3(thf)_3$ (1.93 g, 5.16 mmol). Purification via silica gel column chromatography yielded **12** as a dark purple tar (3.00 g, 71% yield, 3.67 mmol, $R_f = 0.56$ in 80% CH_2Cl_2/20% THF). Elemental analysis calcd. for $C_{39}H_{57}O_{15}Cr$: C 57.27, H 7.02; found: C 57.33, H 6.69; IR (υ, cm^{-1}) 2954 (w), 1729 (s), 1563 (s), 1455 (m), 1340 (s), 1292 (m), 1159 (m), 1082 (m), 985 (m); HRMS (ESI, positive ion mode) *m/z* calcd. for $C_{39}H_{58}O_{15}Cr$ $[M+H]^+$ 818.3175; found 818.3165.

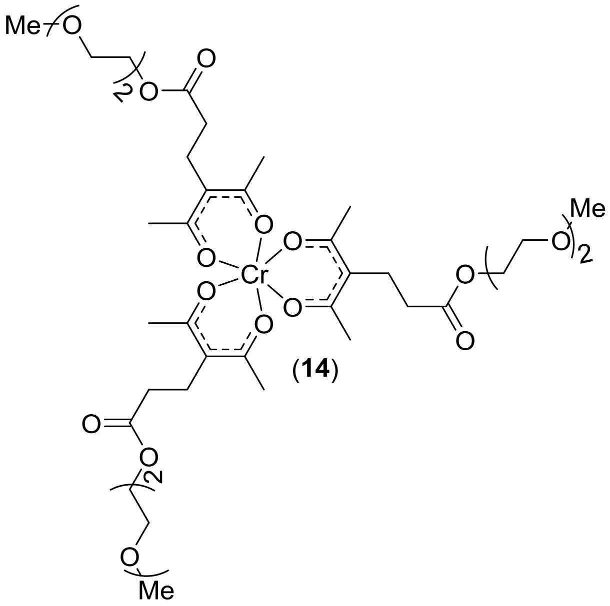
Preparation of 13:



(**13**)

Complex **13** was prepared by an analogous procedure to **10** employing 2-methoxyethyl 4-acetyl-5-oxohexanoate (2.28 g, 9.90 mmol), sodium hydride (0.22 g, 9.30 mmol) and $CrCl_3(thf)_3$ (1.12 g, 3.00 mmol). Purification via silica gel column chromatography yielded **13** as a dark purple tar (1.99 g, 90% yield, 2.69 mmol, R_f = 0.60 in 80% CH_2Cl_2/20% THF. Elemental analysis calcd. for $C_{33}H_{51}O_{15}Cr$: C 53.58, H 6.95; found: C 53.69, H 6.84; IR (υ, cm^{-1}) 2925 (w), 1729 (s), 1564 (s), 1454 (s), 1340 (s), 1291 (m), 1160 (m), 1125 (m), 1056 (w), 1025 (w), 984 (m);). HRMS (ESI, positive ion mode) *m/z* calcd. for $C_{33}H_{52}O_{15}Cr$ $[M+H]^+$ 740.2706; found 740.2703.

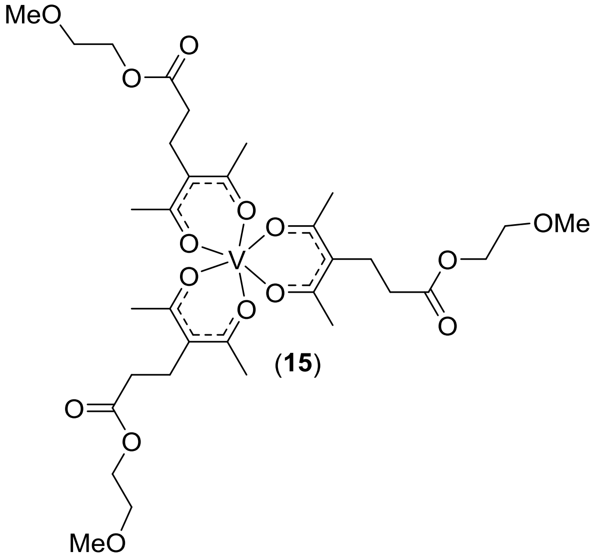
Preparation of 14:



(**14**)

Complex **14** was prepared by an analogous procedure to **10** employing 2-(2-methoxyethoxy)ethyl 4-acetyl-5-oxohexanoate (2.26 g, 8.25 mmol), sodium hydride (0.19 g, 7.75 mmol) and $CrCl_3(thf)_3$ (0.94 g, 2.50 mmol). Purification via silica gel column chromatography yielded **14** as a dark purple tar (1.30 g, 60% yield, 1.49 mmol, R_f = 0.10 in ethyl acetate). Elemental analysis calcd. for $C_{39}H_{63}O_{18}Cr$: C 53.72, H 7.29; found: C 53.77, H 7.16; IR (υ, cm^{-1}) 2878 (m), 1729 (s), 1564 (s), 1341 (s), 1292 (m), 1106 (m), 1057 (w), 1020 (w), 985 (m); HRMS (ESI, positive ion mode) *m/z* calcd. for $C_{39}H_{64}O_{18}Cr$ $[M+H]^+$ 872.3492; found 872.3488.

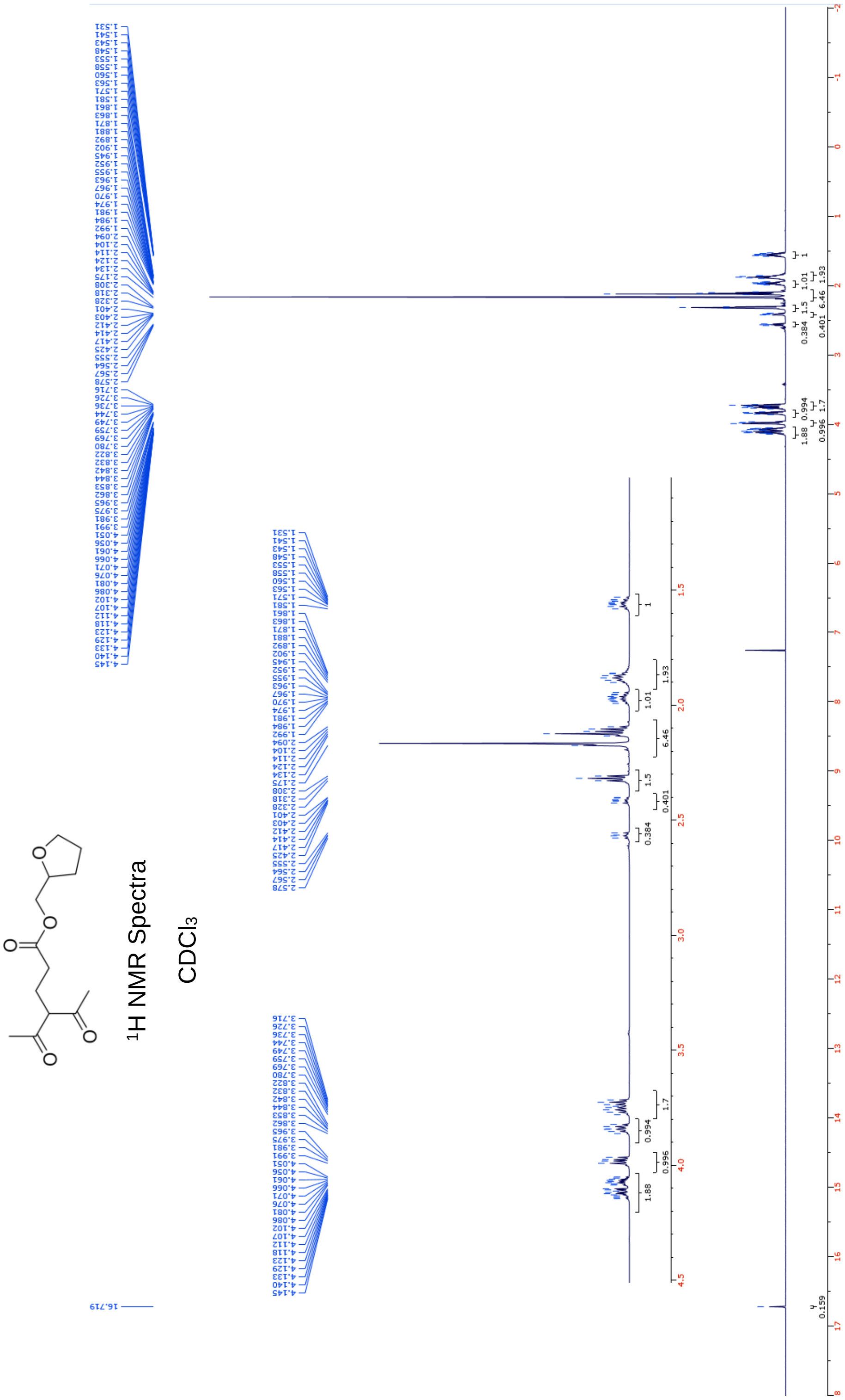
Preparation of 15:

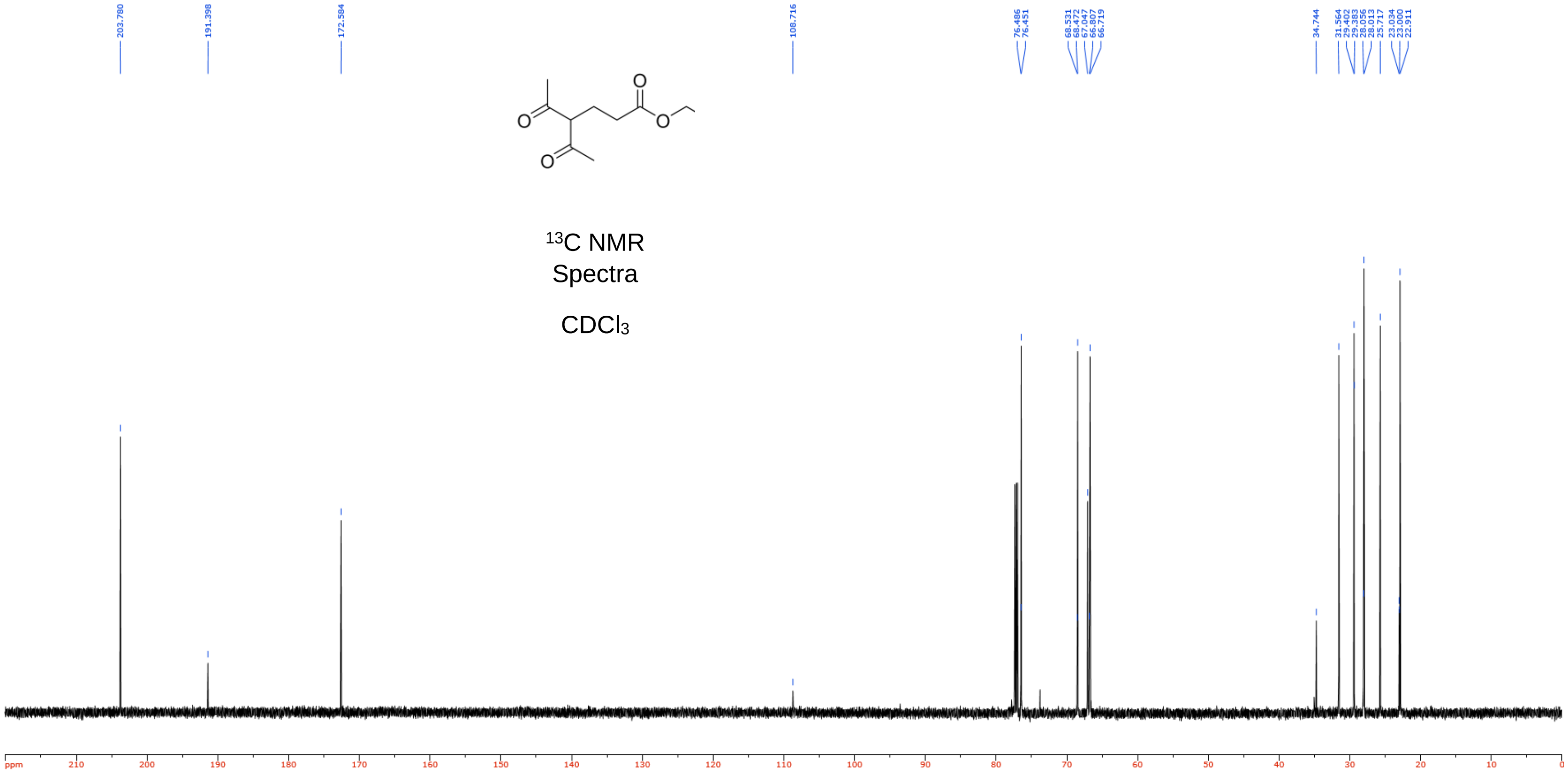


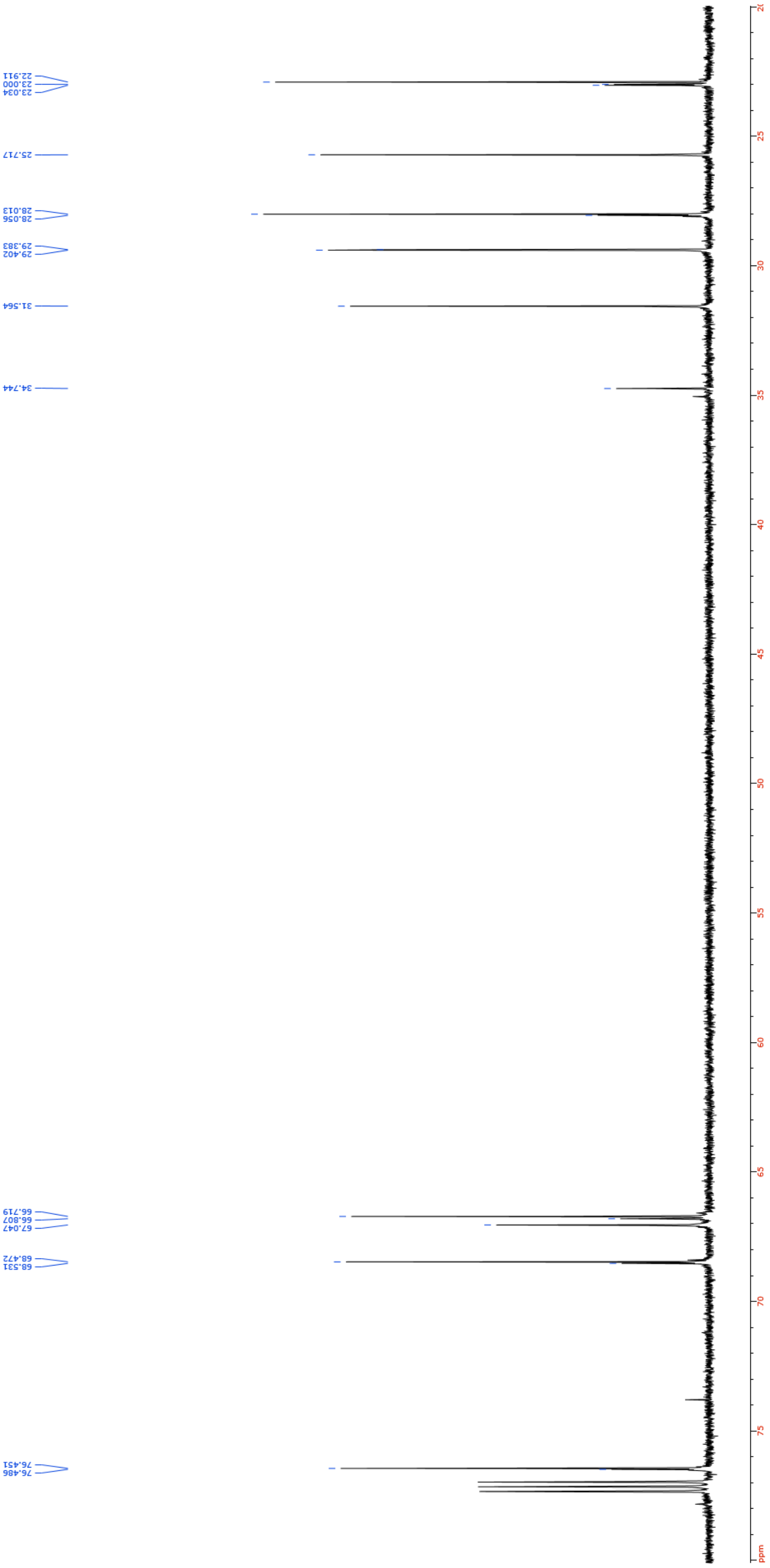
(**15**)

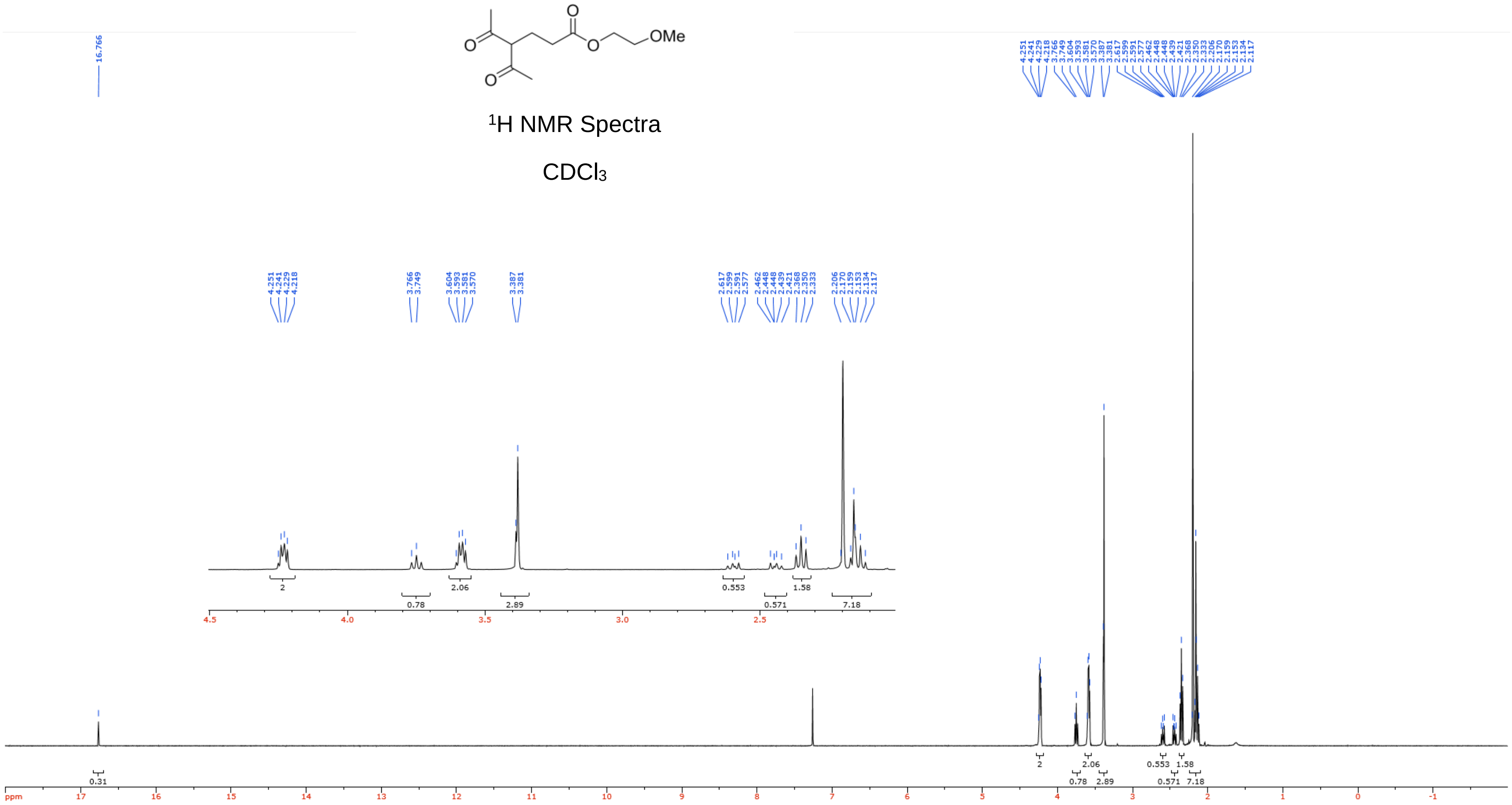
A solution of 2-methoxyethyl 4-acetyl-5-oxohexanoate (3.66 g, 15.9 mmol) in 50 mL of anhydrous tetrahydrofuran was slowly added via cannula to a suspension of sodium hydride (0.38 g, 16.0 mmol) in 100 mL of anhydrous tetrahydrofuran at 0 °C. The resulting solution was stirred for 15 min at 0 °C and then allowed to warm to room temperature where it was stirred for 3 h. $VCl_3(thf)_3$ (2.00 g, 5.36 mmol) was added to the reaction mixture in a single portion. The resulting dark brown suspension was heated to 90 °C overnight. On the benchtop, the solvent was removed *in vacuo*. The dark brown residue was purified by passage through a 4-inch silica gel plug using 85% CH_2Cl_2/15% ethyl acetate as the eluent. The solvent was removed under vacuum, and the product was dried overnight at 80 ºC to afford **15** as a dark brown tar (1.36 g, 35% yield, 1.88 mmol). The product was stored under an inert atmosphere to prevent oxidation. Elemental analysis calcd. for $C_{33}H_{51}O_{15}V$: C 53.67, H 6.96; found: C 53.61, H 6.91; IR (υ, cm^{-1}) = 2890 (w), 2361 (w), 2337 (w), 1278 (s), 1699 (m), 1559 (s), 1456 (s), 1356 (m), 1286 (m), 1242 (w), 1157 (m), 1126 (m), 1030 (m), 983 (m); HRMS (ESI, positive ion mode) *m/z* calcd. for $C_{33}H_{51}O_{15}V$ $[M]^+$ 738.2662; found 738.2659.

NMR Spectra



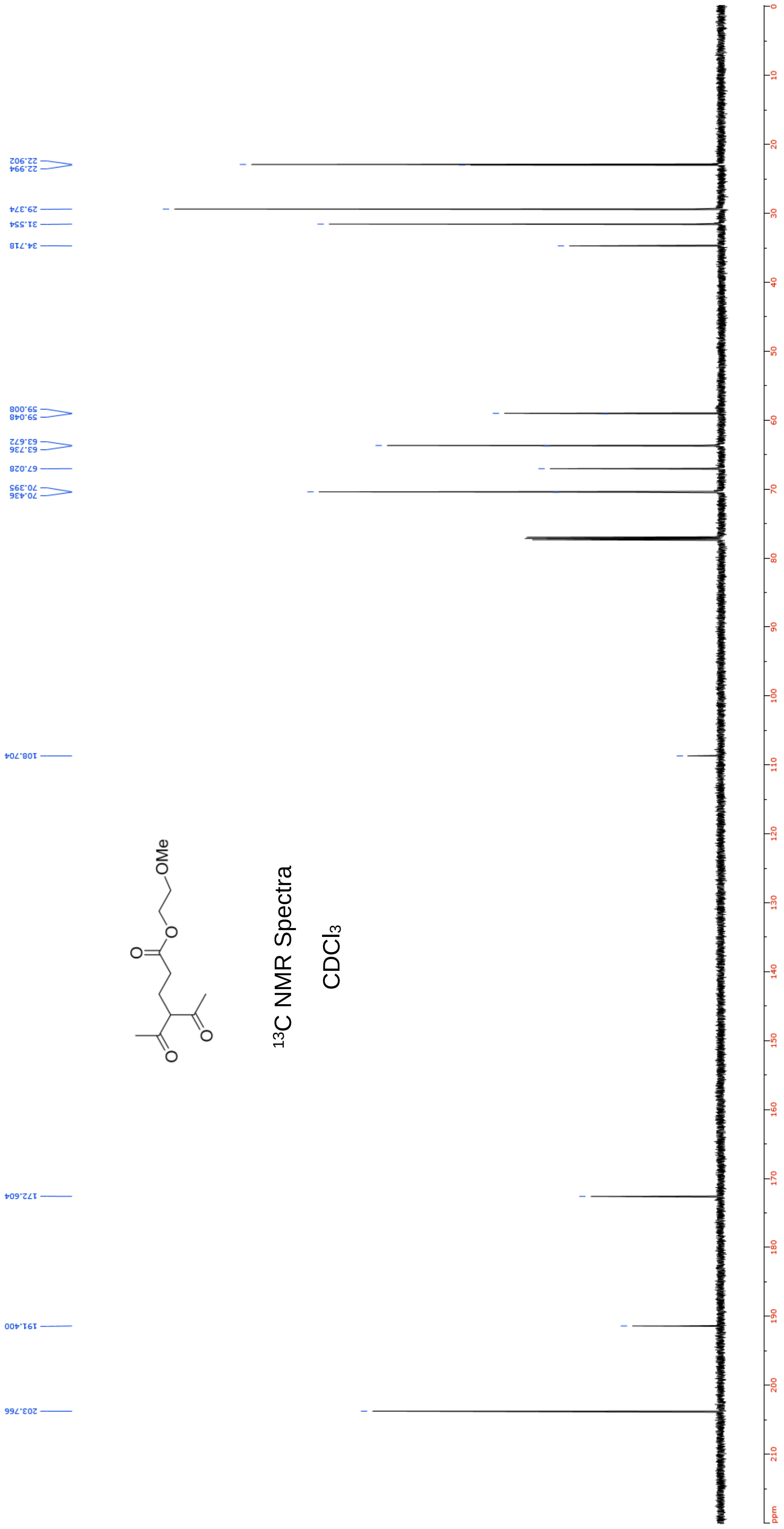
203.780
191.398
172.584
108.716
76.486
76.451
68.531
68.472
67.047
66.807
66.719
34.744
31.564
29.402
29.383
28.056
28.013
25.717
23.034
23.000
22.911
^{13}C NMR
Spectra
CDCl$_3$
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

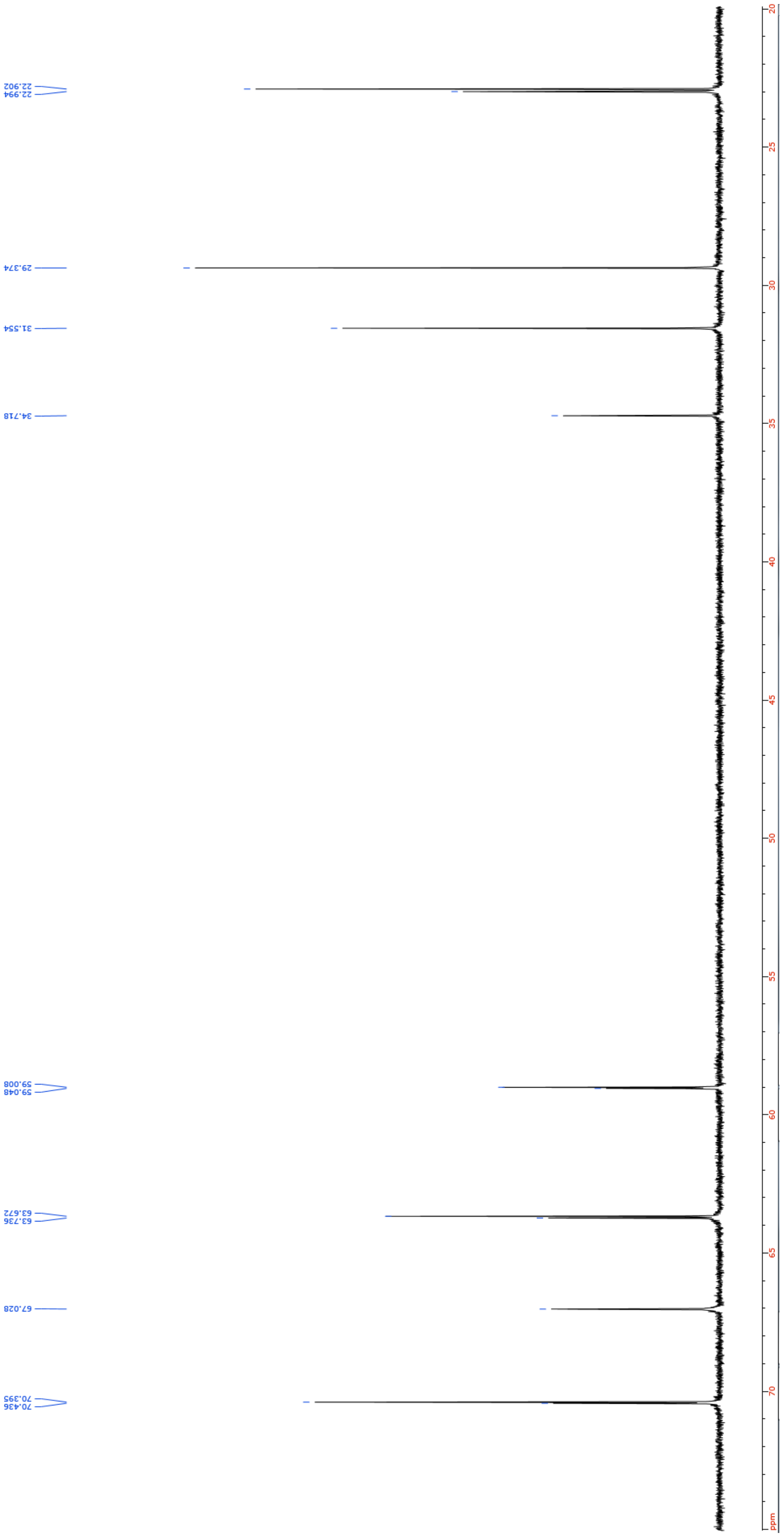

22.911
23.000
23.034
25.717
28.013
28.056
29.383
29.402
31.564
34.744
66.719
66.807
67.047
68.472
68.531
76.451
76.486
20
25
30
35
40
45
50
55
60
65
70
75
ppm

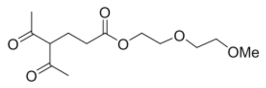


^{1}H NMR Spectra

$CDCl_3$

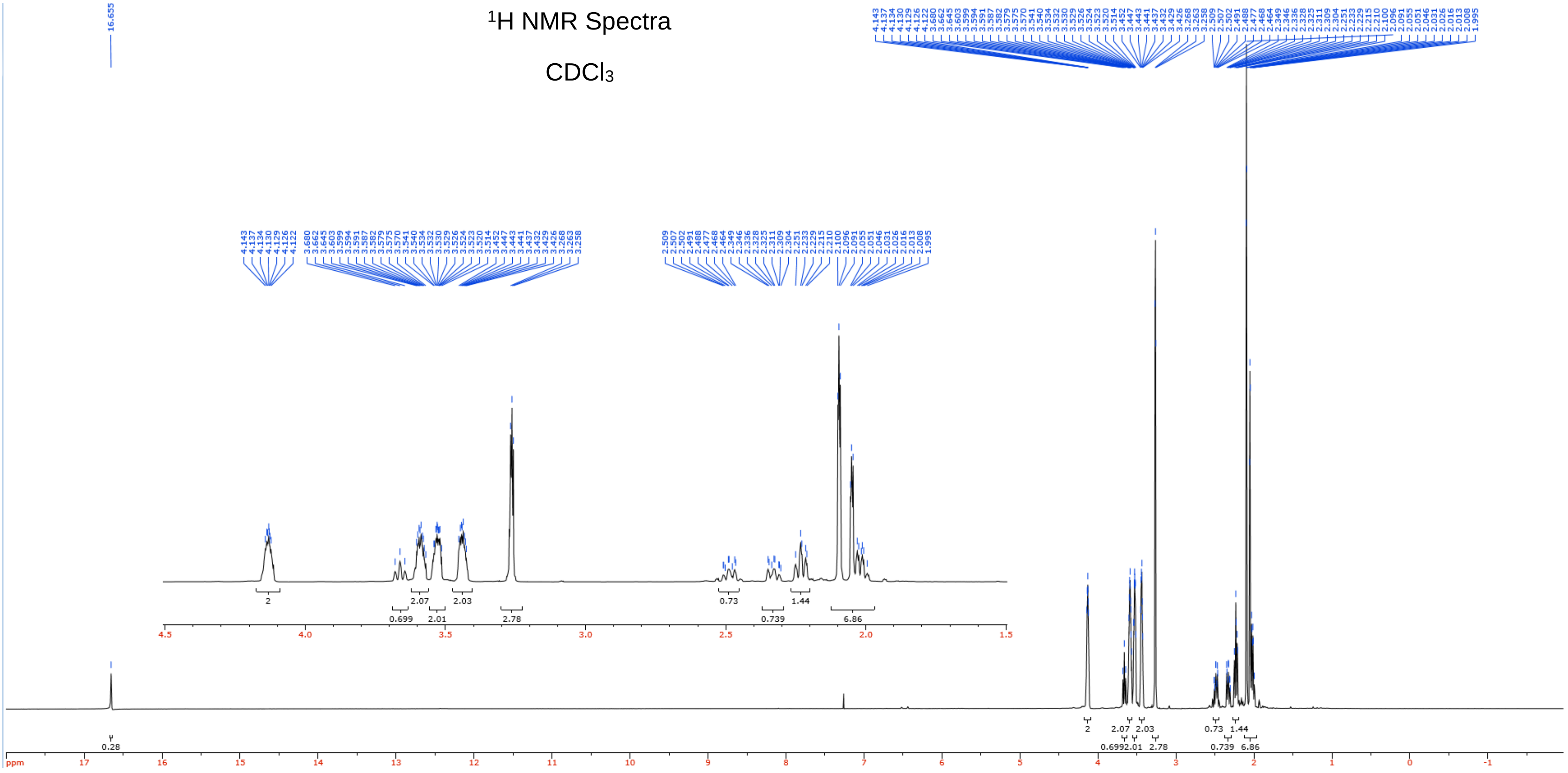

13C NMR Spectra
CDCl3
OMe
O
O
O
O
203.766
191.400
172.604
108.704
70.436
70.395
67.028
63.736
63.672
59.048
59.008
34.718
31.554
29.374
22.994
22.902
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

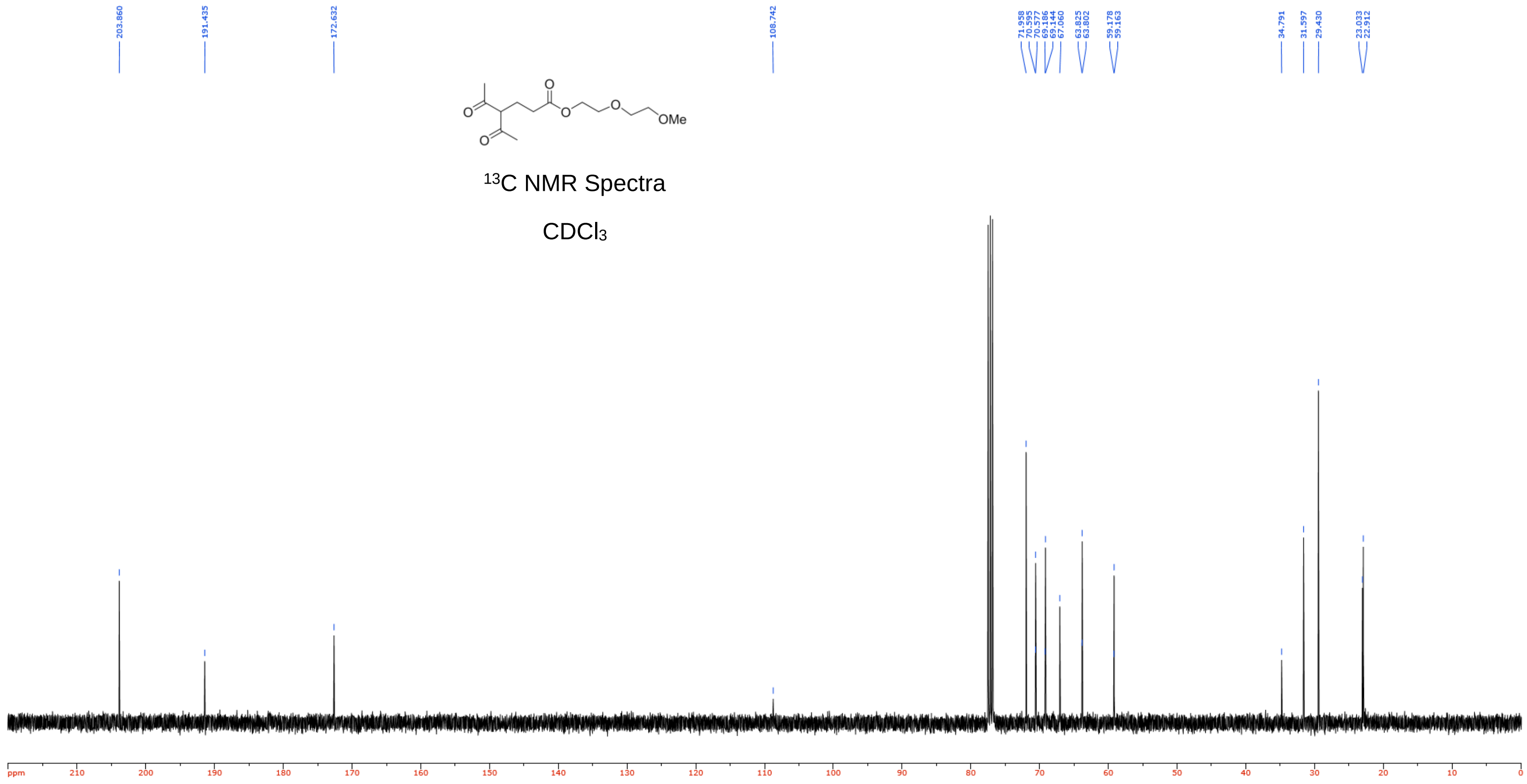

22.902
22.994
29.374
31.554
34.718
59.008
59.048
63.672
63.736
67.028
70.395
70.436
20
25
30
35
40
45
50
55
60
65
70
ppm



^{1}H NMR Spectra

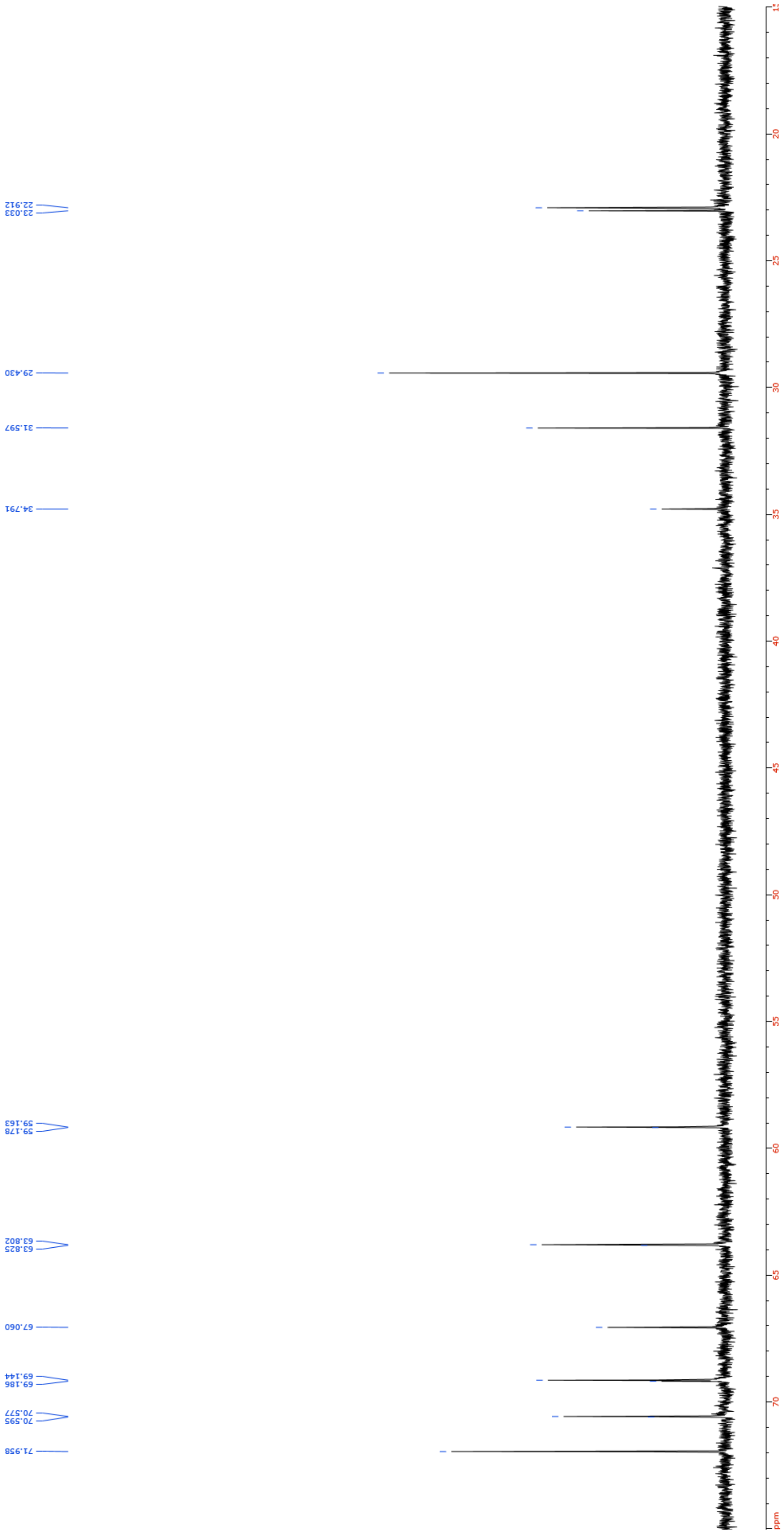
CDCl$_3$





^{13}C NMR Spectra

$CDCl_3$


22.912
23.033
29.430
31.597
34.791
59.163
59.178
63.802
63.825
67.060
69.144
69.186
70.577
70.595
71.958
20
25
30
35
40
45
50
55
60
65
70
ppm

Solubility Measurements

The solubility of complexes **1** – **15** in acetonitrile were determined as per the general procedure outlined in the full paper. The concentration of standard solutions, dilution factors for saturated solutions and wavelengths of absorption for each complex are listed in Table S1.

Complex	λ abs. (nm)	Standard Solutions (mM)	Saturated Solution Dilutions	Max. Solubility in MeCN
1	550	1.0, 5.0, 10.0, 20.0	70 µL into 5 mL	0.653 ± 0.003 M
2	570	1.0, 5.0, 10.0, 15.0	250 µL into 10 mL	0.404 ± 0.002 M
3	564	0.05, 0.10, 0.50, 1.00	1.25 mL into 5 mL	0.00212 ± 0.00002 M
4	558	1.0, 5.0, 10.0, 20.0	500 µL into 5 mL	0.0547 ± 0.0003 M
5	564	1.0, 5.0, 10.0, 20.0	25 µL into 5 mL	1.92 ± 0.04 M
6	567	1.0, 5.0, 10.0, 20.0	200 µL into 10 mL	0.43 ± 0.02 M
7	366	0.02, 0.03, 0.06, 0.13	250 µL into 5 mL	$5.7 \times 10^{-5} \pm 7 \times 10^{-6}$ M
8	418	0.03, 0.06, 0.13, 0.25	1.25 mL into 5 mL	$7.99 \times 10^{-4} \pm 4 \times 10^{-7}$ M
9	564	1.0, 5.0, 10.0, 20.0	1 mL into 5 mL	0.0434 ± 0.0003 M
10	571	1.0, 5.0, 10.0, 15.0	50 µL into 5 mL	0.86 ± 0.05 M
11	566	1.0, 5.0, 10.0, 20.0	50 µL into 5 mL	1.25 ± 0.01 M
12	572	1.0, 5.0, 10.0, 15.0	50 µL into 5 mL	1.13 ± 0.01 M
13	572	1.0, 5.0, 10.0, 15.0	25 µL into 5 mL	1.80 ± 0.04 M
15	600	1.0, 5.0, 10.0, 20.0	20 µL into 5 mL	1.32 ± 0.04 M

Table S1: Solubility parameters and determinations for complexes **1** – **13** and **15** in acetonitrile.

Complex	λ abs. (nm)	Experimental ε ($cm^{-1} \cdot M^{-1}$)	Literature ε ($cm^{-1} \cdot M^{-1}$)
1	550	51.48	72.44 (λ = 560 nm, $CHCl_3$)[1]
2	570	45.35	39.81 (λ = 550 nm, EtOH)[2]
3	564	74.41	83.18 (λ = 570 nm, $CHCl_3$)[1]
4	558	71.56	70.79 (λ = 558 nm, $CHCl_3$)[1]
5	564	65.9	~80 (λ = 56 nm, not reported)[3]
6	567	78.56	-
7	366	19012	28183 (λ = 360 nm, $CHCl_3$)[1]
8	418	6442	-
9	564	76.92	-
10	571	69.30	N/A
11	566	74.64	N/A
12	572	68.66	N/A
13	572	65.91	N/A
15	600	74.51	N/A

Table S2: Experimental extinction coefficients for complexes **1** – **13** and **15** in acetonitrile and a comparison to literature values where appropriate.

X-Ray Structure Determination

Complex 6: Purple blocks of **6** were grown from a hexanes/benzene solution of the complex at 25 °C. A crystal of dimensions 0.18 x 0.08 x 0.07 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 3805 images were collected with an oscillation width of 1.0° in ω The exposure time was 1 sec. for the low angle images, 4 sec. for high angle. The integration of the data yielded a total of 69181 reflections to a maximum 2θ value of 136.48° of which 4837 were independent and 4520 were greater than 2σ(I). The final cell constants Table S3) were based on the xyz centroids 34219 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{21}H_{24}N_3O_6Cr$, C_6H_6. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0354 and wR2 = 0.1012 [based on I > 2sigma(I)], R1 = 0.0400 and wR2 = 0.1195 for all data. Additional details are presented in Table S3 and are given as Supporting Information in a CIF file.

Identification code	Complex **5**
Empirical formula	C_{27} H_{30} Cr N_3 O_6
Formula weight	544.54
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.7622(16) A, α = 90 °
	b = 15.3268(3) A, β = 114.351(9) °
	c = 14.8815(11) A, γ = 90 °
Volume	2651.9(4) A^3
Z, Calculated density	4, 1.364 Mg/m^3
Absorption coefficient	3.935 mm^{-1}
F(000)	1140
Crystal size	0.18 x 0.08 x 0.07 mm
Theta range for data collection	4.35 to 68.24 °
Limiting indices	$-15\le h\le 15$, $-18\le k\le 18$, $-17\le l\le 16$
Reflections collected / unique	69181 / 4837 [R(int) = 0.0681]
Completeness to theta = 68.24	99.90%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7702 and 0.5377
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4837 / 0 / 340
Goodness-of-fit on F^2	1.181
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.1012
R indices (all data)	R1 = 0.0400, wR2 = 0.1195
Largest diff. peak and hole	0.304 and -0.577 e.A^{-3}

Table S3: Crystal data and structure refinement for complex **5**.

Complex 8: Green blocks of complex **8** were grown from a chloroform/hexanes solution at 25 °C. A crystal of dimensions 0.13 x 0.12 x 0.07 mm was mounted on a Bruker SMART APEX-I CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.070 cm from the crystal. A total of 4460 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 30 s/frame. The integration of the data yielded a total of 87026 reflections to a maximum 2θ value of 74.16° of which 14372 were independent and 10727 were greater than 2σ(I). The final cell constants (Table S4) were based on the xyz centroids of 9870 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P1bar with Z = 2 for the formula $C_{35}H_{29}O_6Cr$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0468 and wR2 = 0.1090 [based on I > 2sigma(I)], R1 = 0.0722 and wR2 = 0.1231 for all data. Additional details are presented in Table S4 and are given as Supporting Information in a CIF file.

Identification code	Complex **8**
Empirical formula	$C_{35}H_{29}CrO_6$
Formula weight	597.58
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.1881(2) A, α = 94.4750(10) °
	b = 10.8140(2) A, β = 92.6810(10) °
	c = 13.9887(3) A, γ = 112.3820(10) °
Volume	1415.84(5) A^3
Z, Calculated density	2, 1.402 Mg/m^3
Absorption coefficient	0.451 mm^{-1}
F(000)	622
Crystal size	0.13 x 0.12 x 0.7 mm
Theta range for data collection	2.05 to 37.08 °
Limiting indices	-17≤h≤17, -18≤k≤18, -23≤l≤23
Reflections collected / unique	87026 / 14372 [R(int) = 0.0702]
Completeness to theta = 37.08	99.20%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9691 and 0.9436
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14372 / 0 / 381
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.109
R indices (all data)	R1 = 0.0722, wR2 = 0.1231
Largest diff. peak and hole	0.867 and -0.419 $e.A^{-3}$

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

Complex 9: Orange blocks of complex **9** were grown from a chloroform/hexanes solution of the complex at 25 °C. A crystal of dimensions 0.18 x 0.14 x 0.13 mm was mounted on a Bruker SMART APEX-I CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube ($\lambda = 0.71073$ A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.070 cm from the crystal. A total of 2425 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 30 s/frame. The integration of the data yielded a total of 223213 reflections to a maximum 2θ value of 56.64° of which 28072 were independent and 17169 were greater than $2\sigma(I)$. The final cell constants (Table S5) were based on the xyz centroids of 9951 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/n with Z = 20 for the formula $C_{25}H_{25}O_6Cr$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0587 and wR2 = 0.1446 [based on I > 2sigma(I)], R1 = 0.1040 and wR2 = 0.1774 for all data. Additional details are presented in Table S5 and are given as Supporting Information in a CIF file.

Identification code	Complex **8**
Empirical formula	$C_{25}\ H_{25}\ Cr\ O_6$
Formula weight	473.45
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 23.612(2) A, α = 90 °
	b = 14.2939(13) A, β = 95.048(2) °
	c = 33.570(3) A, γ = 90 °
Volume	11286.3(18) A^3
Z, Calculated density	20, 1.393 Mg/m^3
Absorption coefficient	0.545 mm^{-1}
F(000)	4940
Crystal size	0.18 x 0.14 x 0.13 mm
Theta range for data collection	1.01 to 28.32 °
Limiting indices	$-31\leq h\leq 31$, $-19\leq k\leq 19$, $-44\leq l\leq 44$
Reflections collected / unique	223213 / 28072 [R(int) = 0.0790]
Completeness to theta = 28.32	99.90%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9325 and 0.9082
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	28072 / 0 / 1461
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1446
R indices (all data)	R1 = 0.1040, wR2 = 0.1774
Largest diff. peak and hole	1.375 and -0.414 $e.A^{-3}$

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

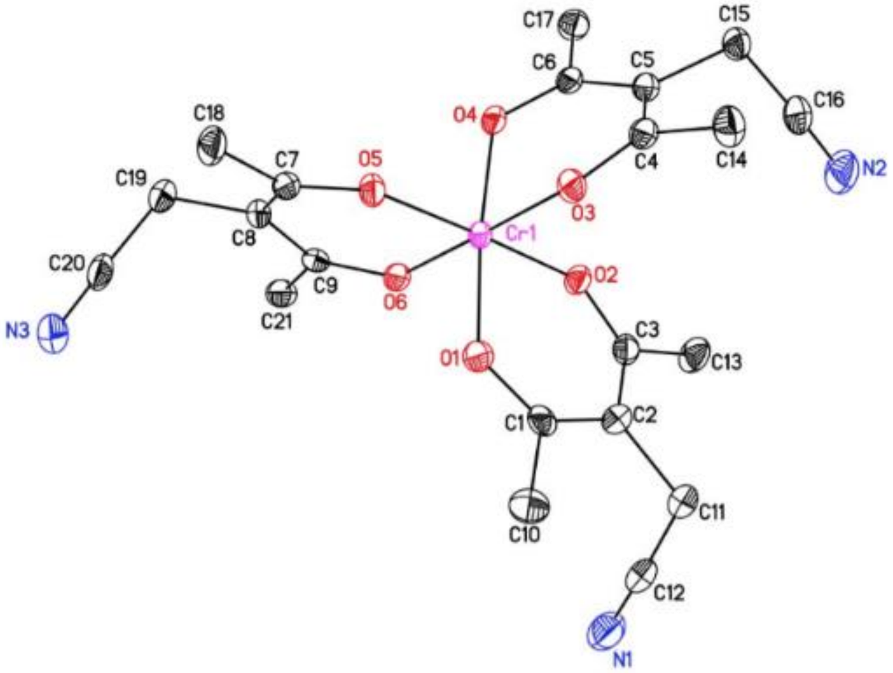


Figure S1: X-ray crystal structure of complex **6**.

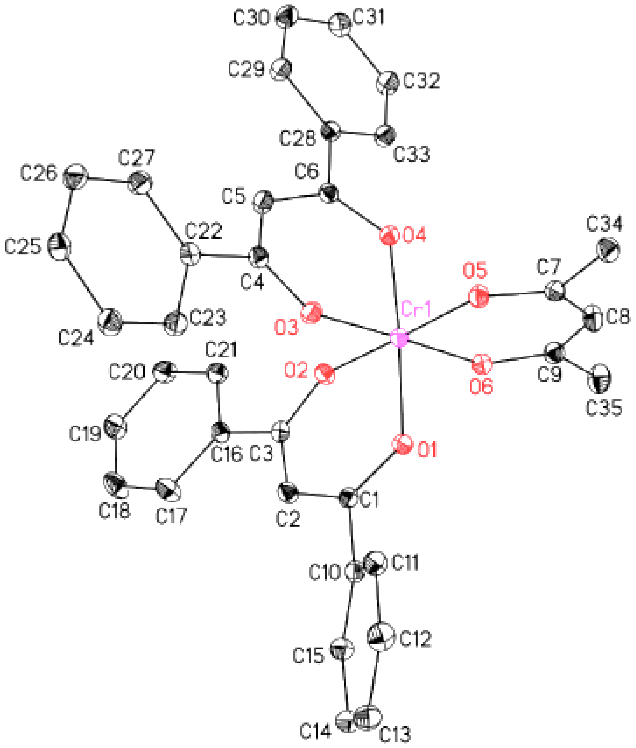


Figure S2: X-ray crystal structure of complex **8**.

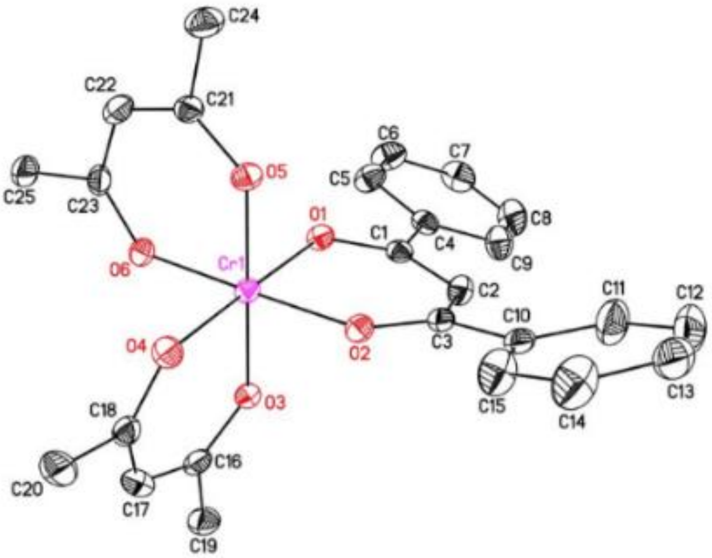
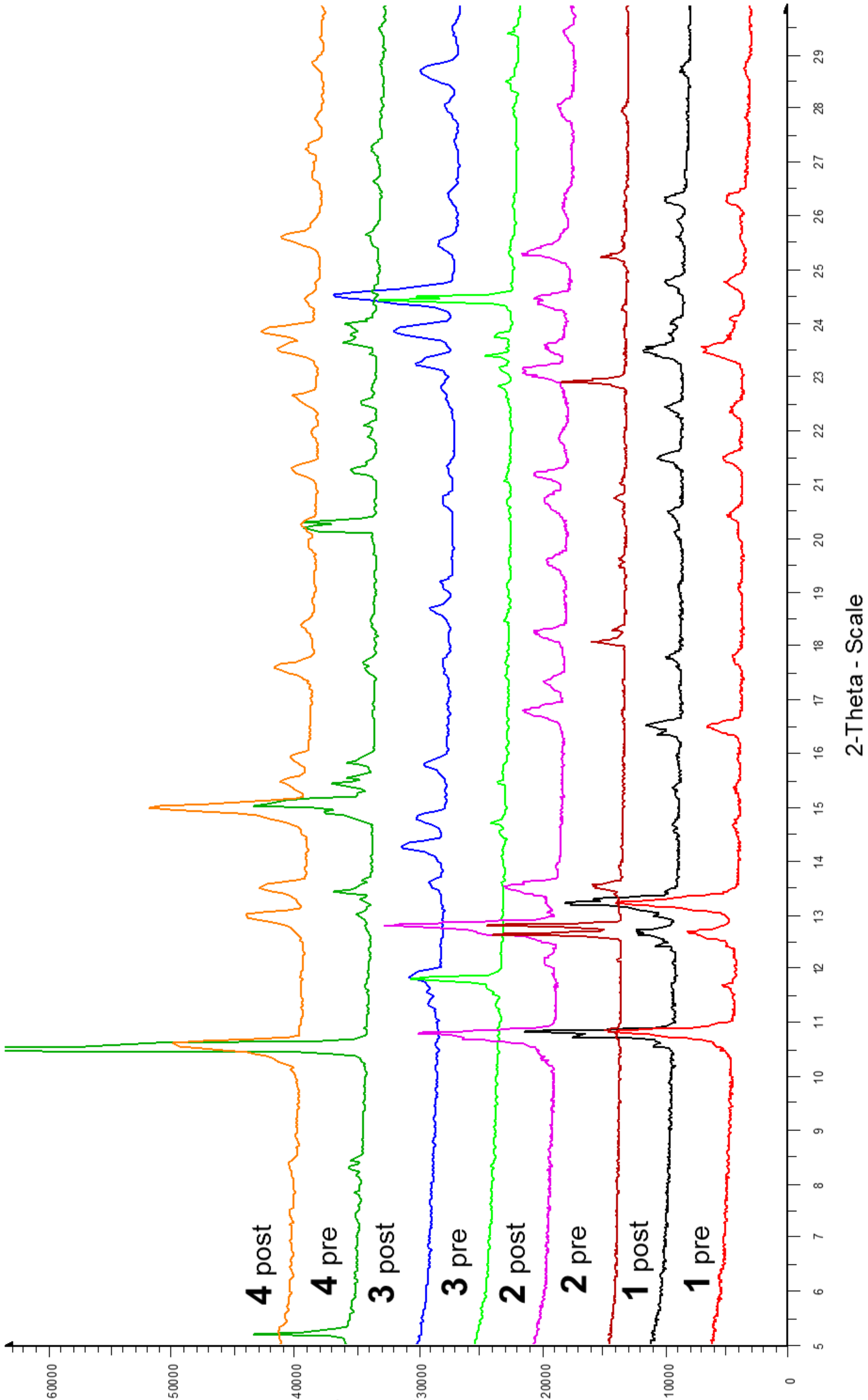


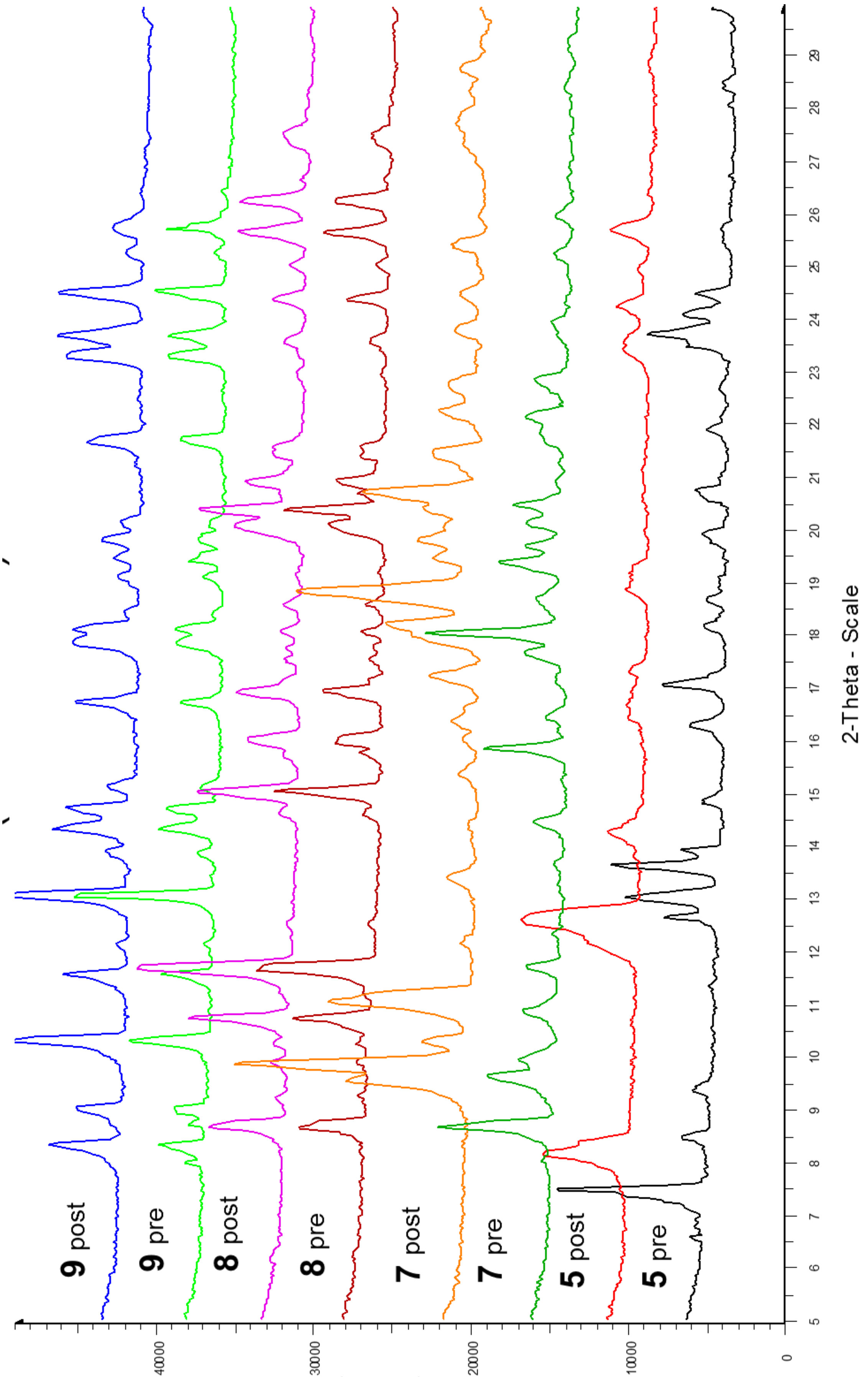
Figure S3: X-ray crystal structure of complex **9**.

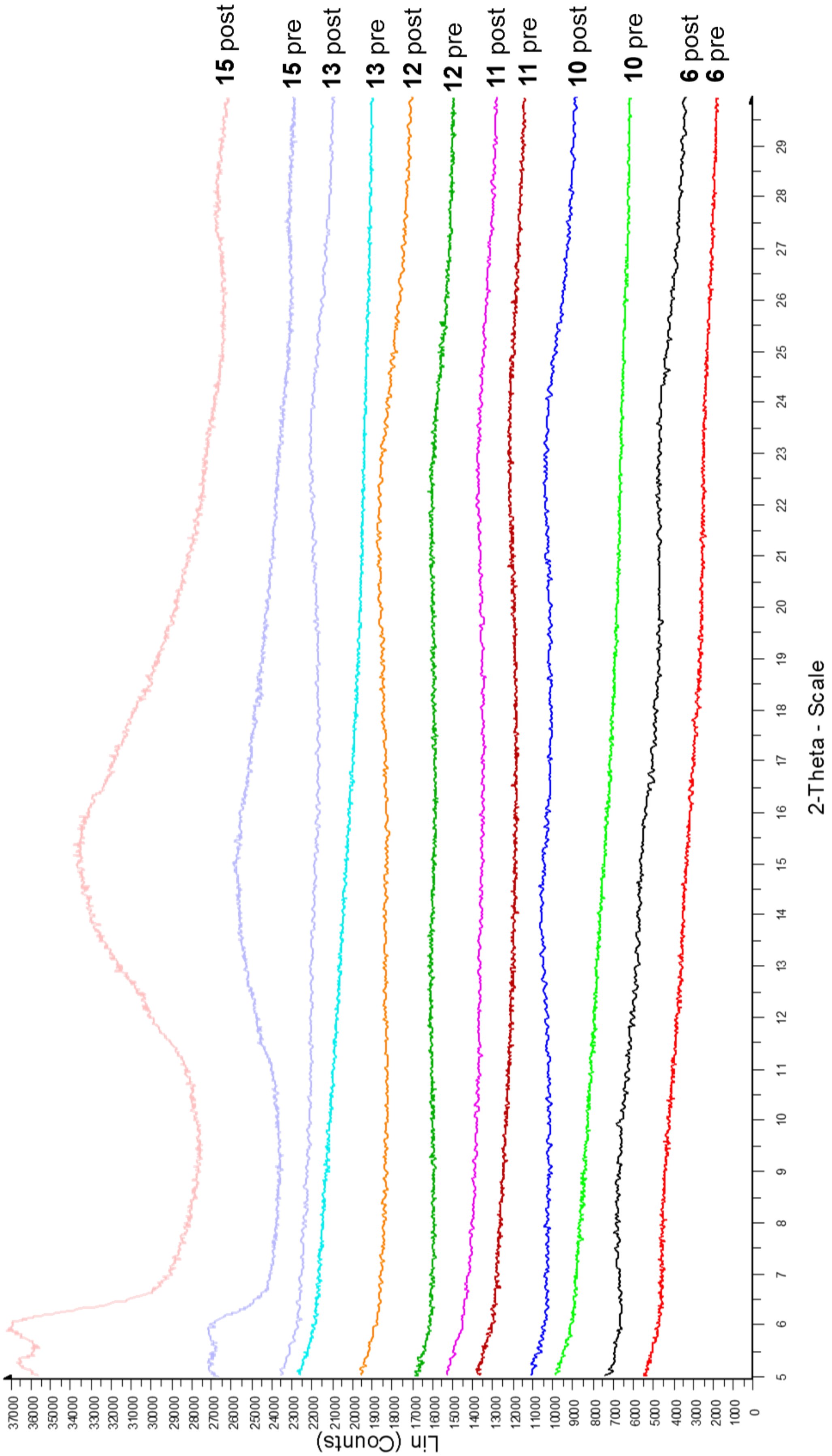
Powder X-ray Diffraction Patterns

PXRD data were recorded at room temperature on a Bruker AXS D8 Advance powder diffractometer at 40 kV, 40 mA with a CuKα source (λ=1.5406 Å) between 5 and 30° 2θ with a scan speed of 0.1 s/ step and a step size of 0.04. Samples were measured on a glass microscope slide in an aluminum holder.

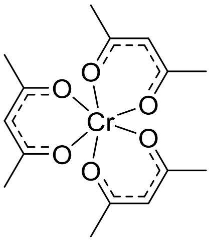


Lin (Counts)
60000
50000
40000
30000
20000
10000
0
2-Theta - Scale
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
4 post
4 pre
3 post
3 pre
2 post
2 pre
1 post
1 pre

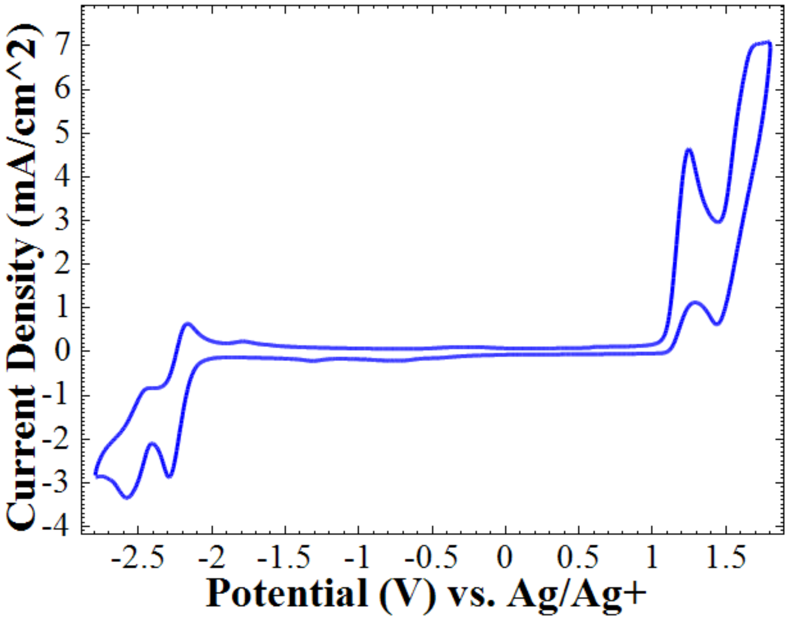

9 post
9 pre
8 post
8 pre
7 post
7 pre
5 post
5 pre
Lin (Counts)
0
10000
20000
30000
40000
2-Theta - Scale
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29

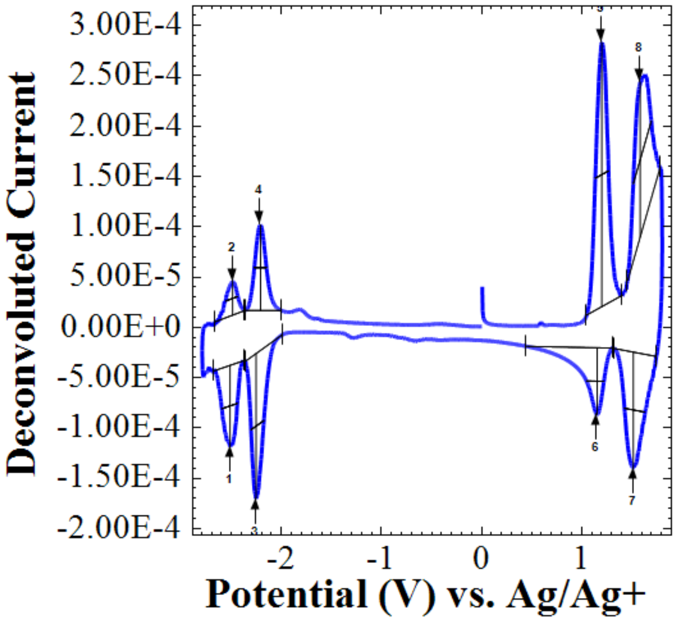

15 post
15 pre
13 post
13 pre
12 post
12 pre
11 post
11 pre
10 post
10 pre
6 post
6 pre
Lin (Counts)
37000
36000
35000
34000
33000
32000
31000
30000
29000
28000
27000
26000
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
2-Theta - Scale
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29

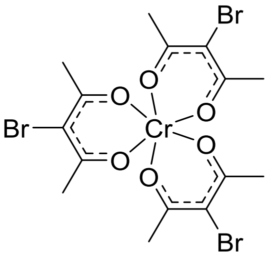
Cyclic Voltammograms



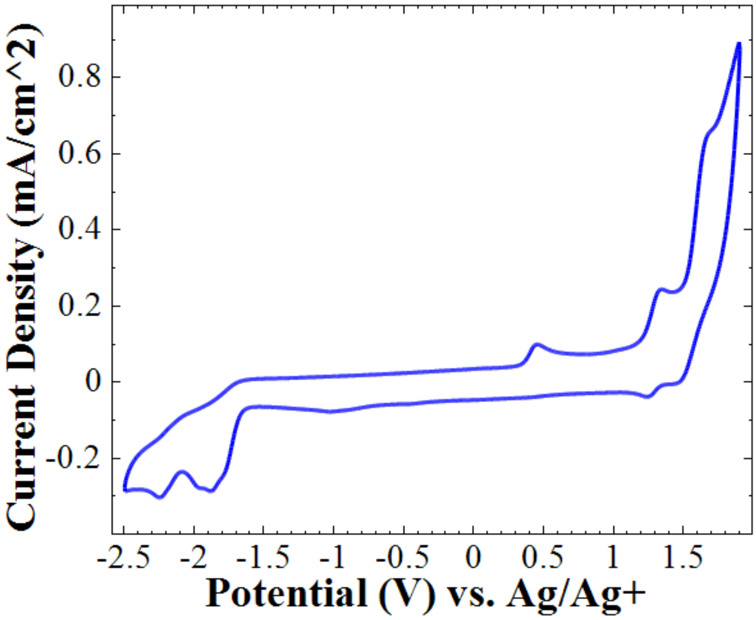
CV taken in acetonitrile using 0.01 M complex and 0.1 M $TBABF_4$.

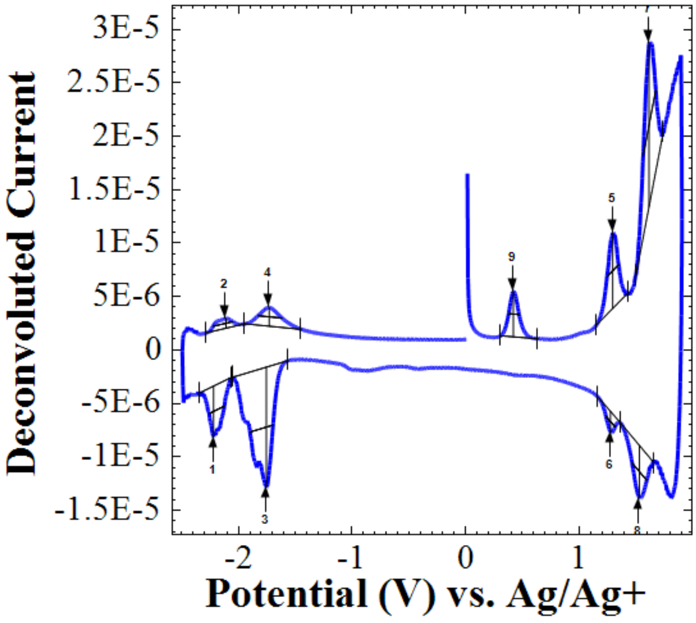


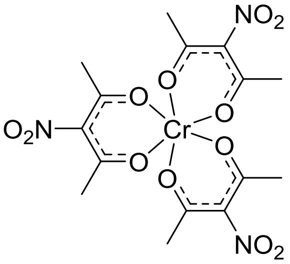




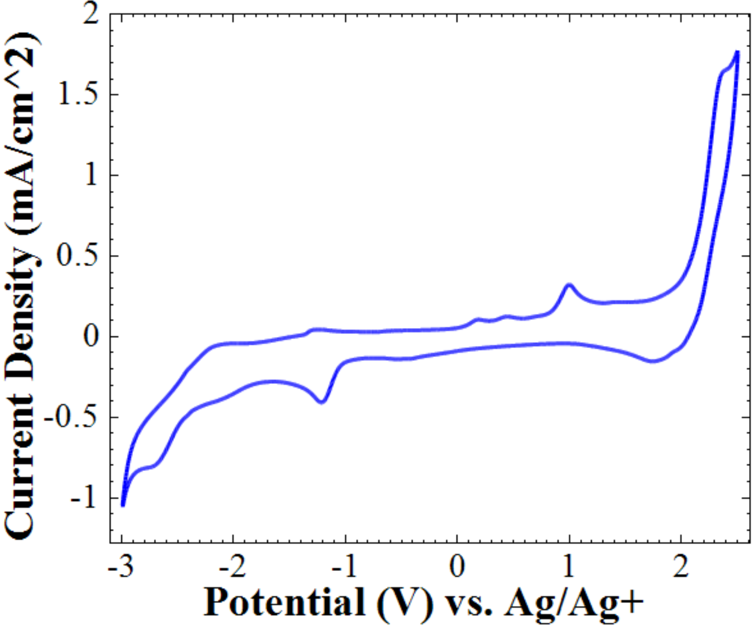
CV taken in acetonitrile using 0.001 M complex and 0.01 M TBABF$_4$.

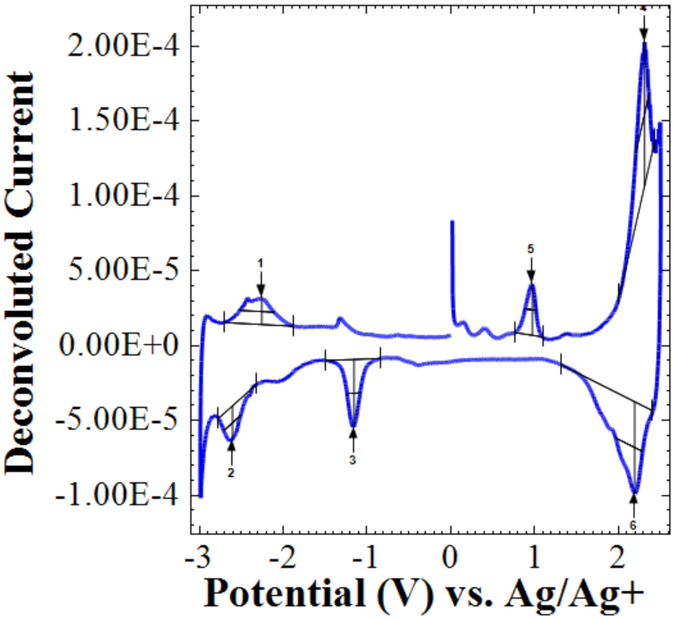


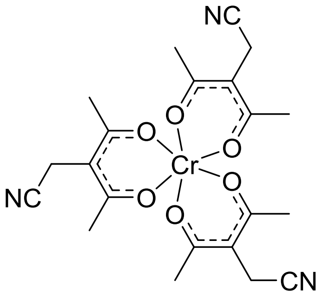




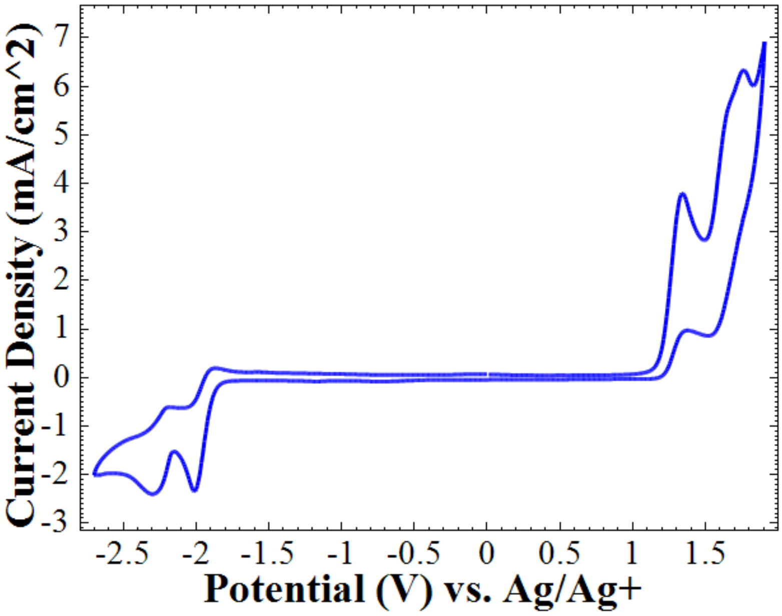
CV taken in acetonitrile using 0.001 M complex and 0.01 M TBABF$_4$.

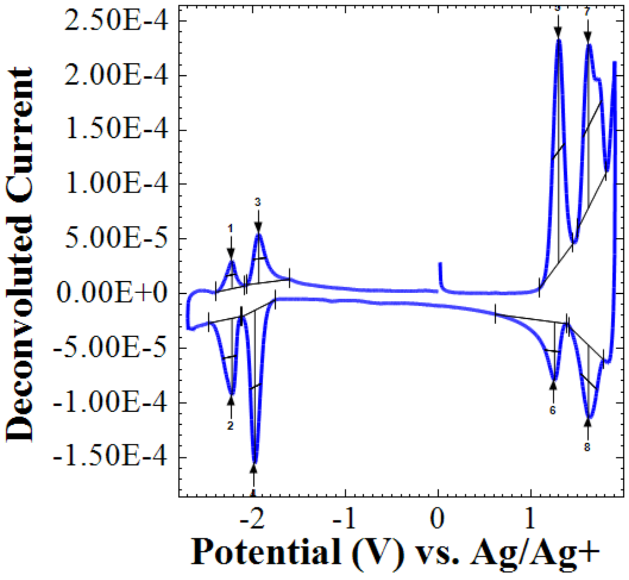


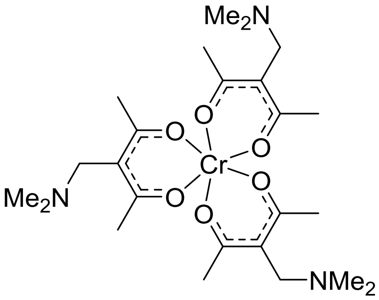




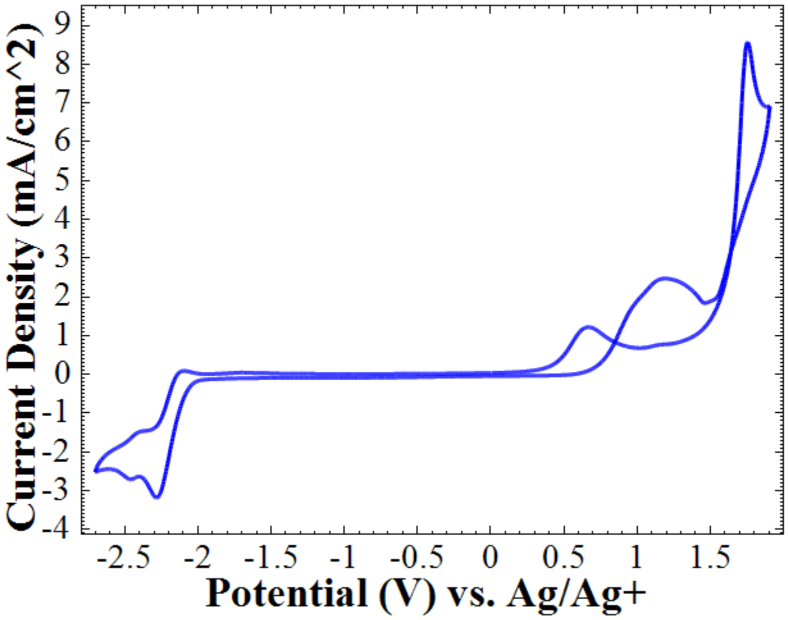
CV taken in acetonitrile using 0.01 M complex and 0.1 M TBABF$_4$.

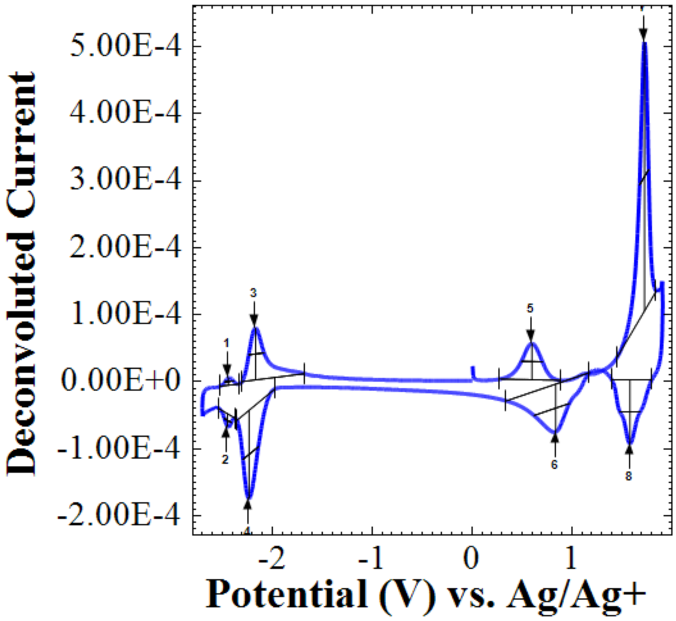


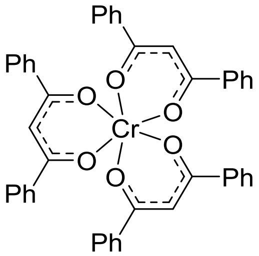




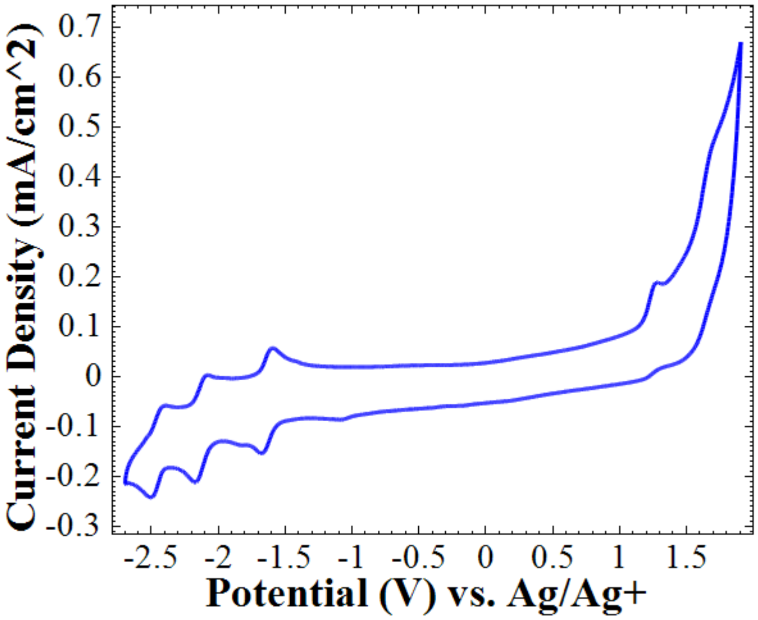
CV taken in acetonitrile using 0.01 M complex and 0.1 M TBABF$_4$.

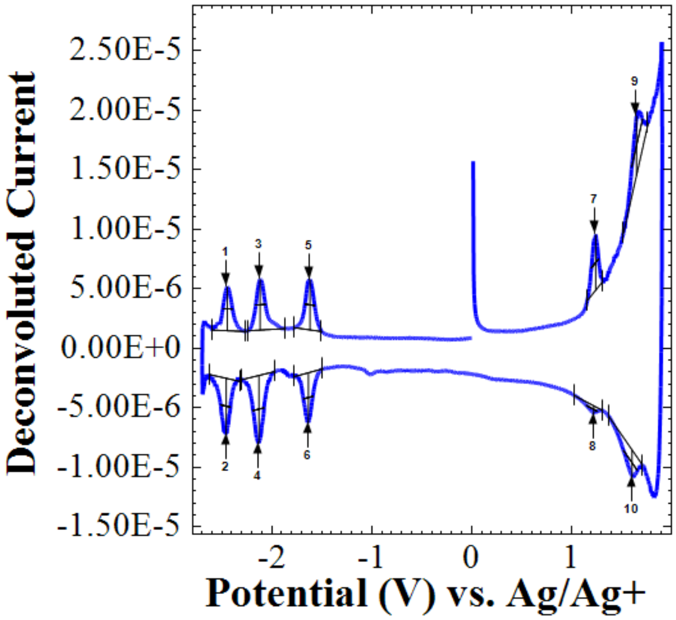


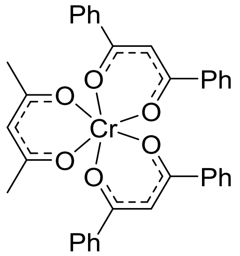




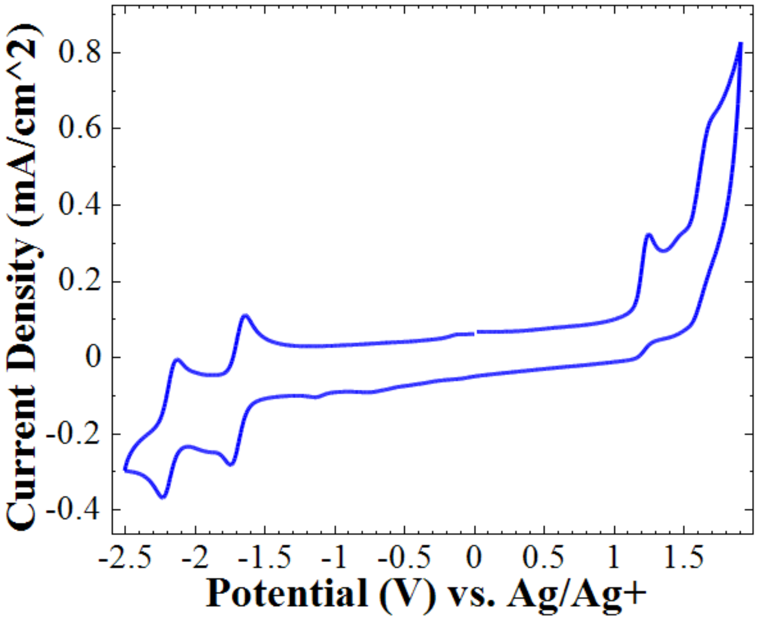
CV taken in acetonitrile using 0.00014 M complex and 0.1 M $TBABF_4$.

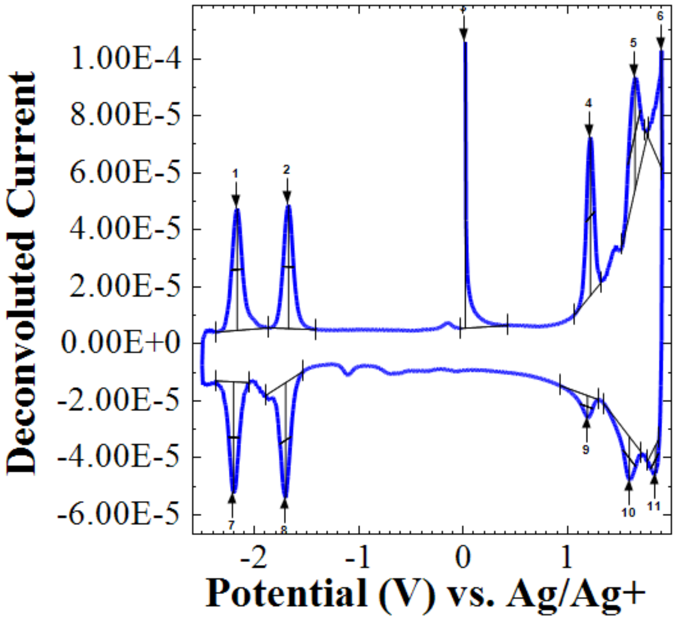


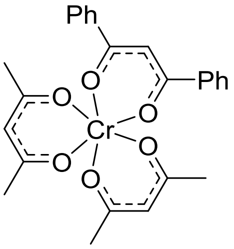




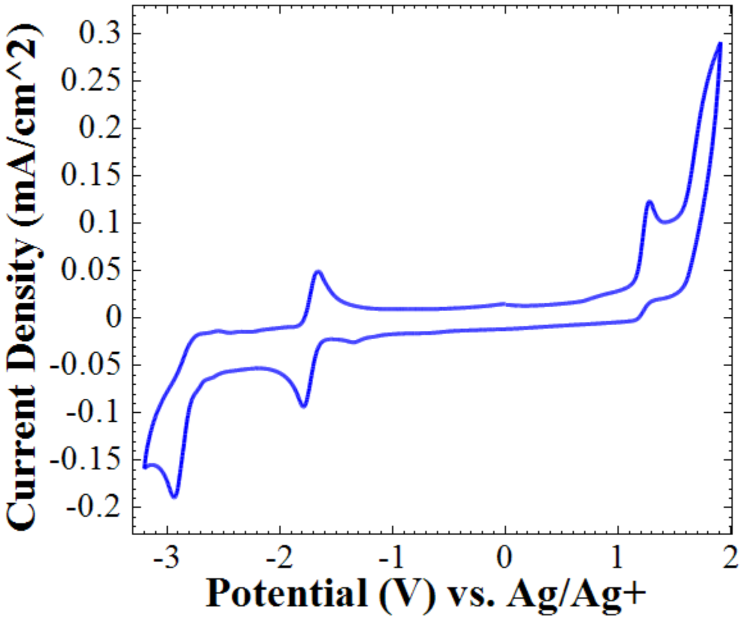
CV taken in acetonitrile using 0.001 M complex and 0.1 M TBABF_4.

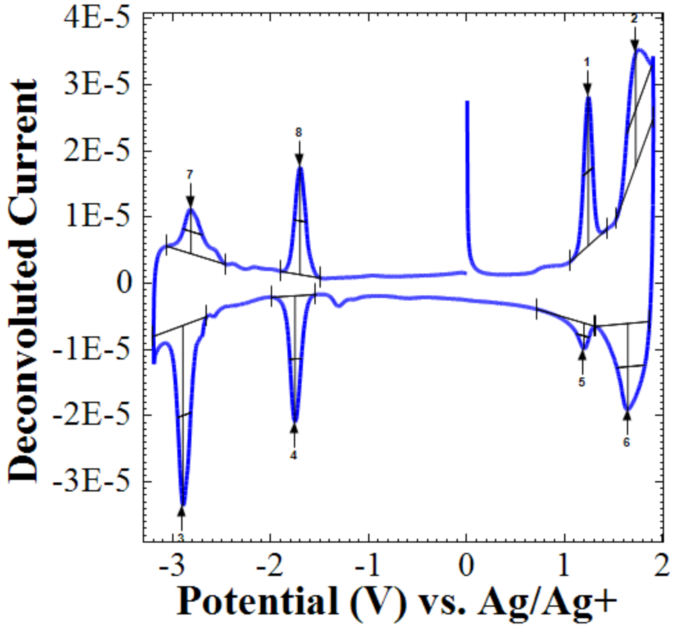


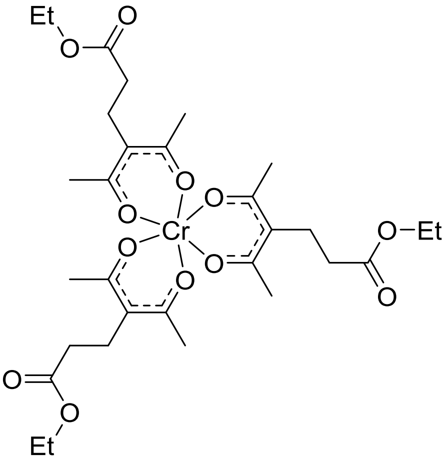




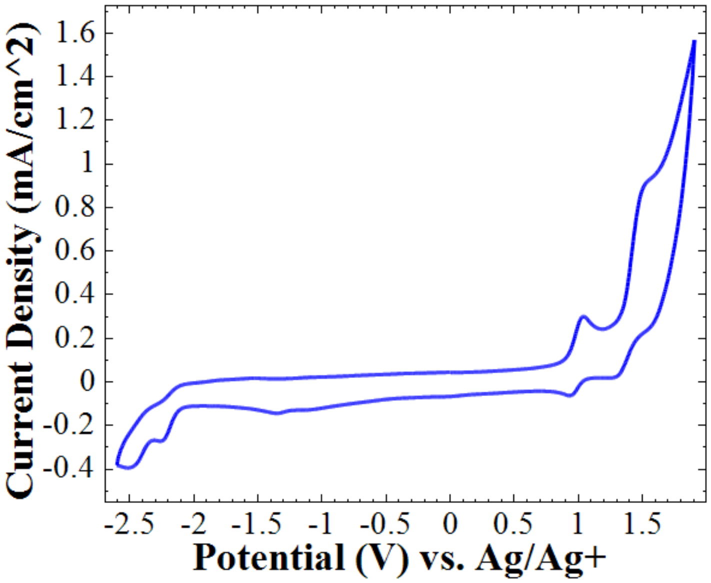
CV taken in acetonitrile using 0.001 M complex and 0.1 M $TBABF_4$.

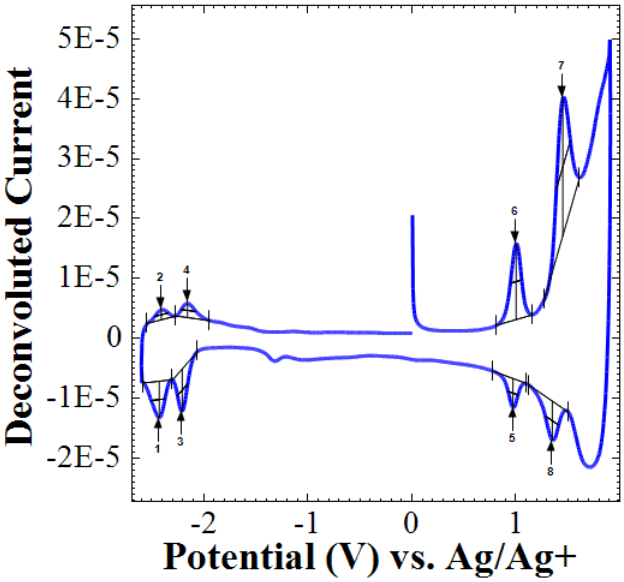


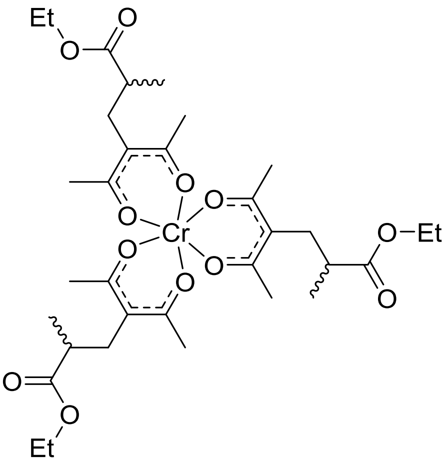




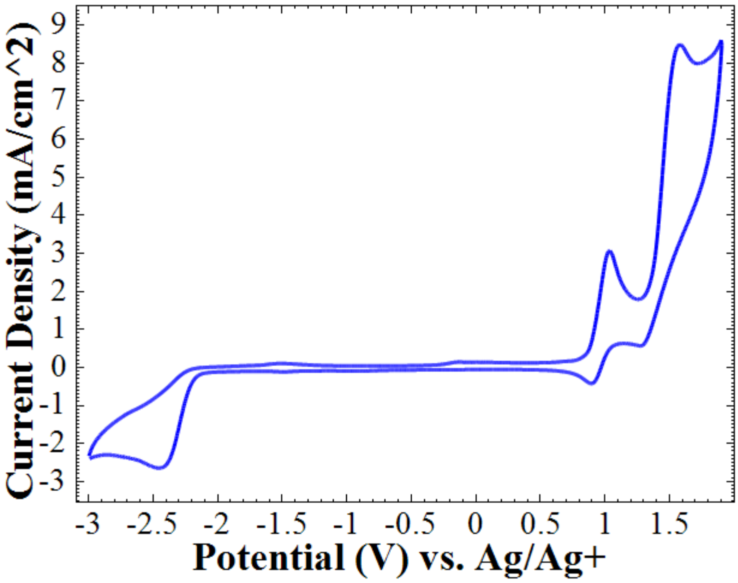
CV taken in acetonitrile using 0.001 M complex and 0.1 M $TBABF_4$.

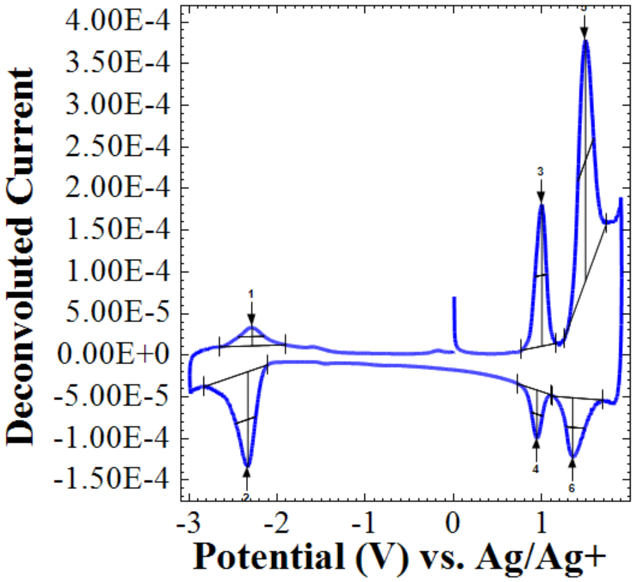


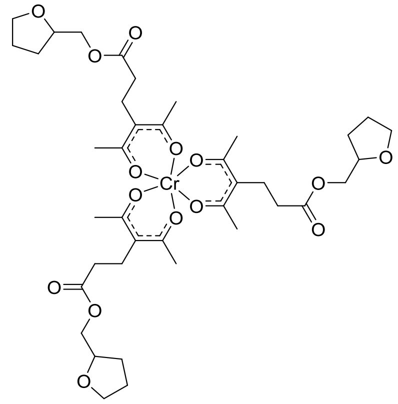




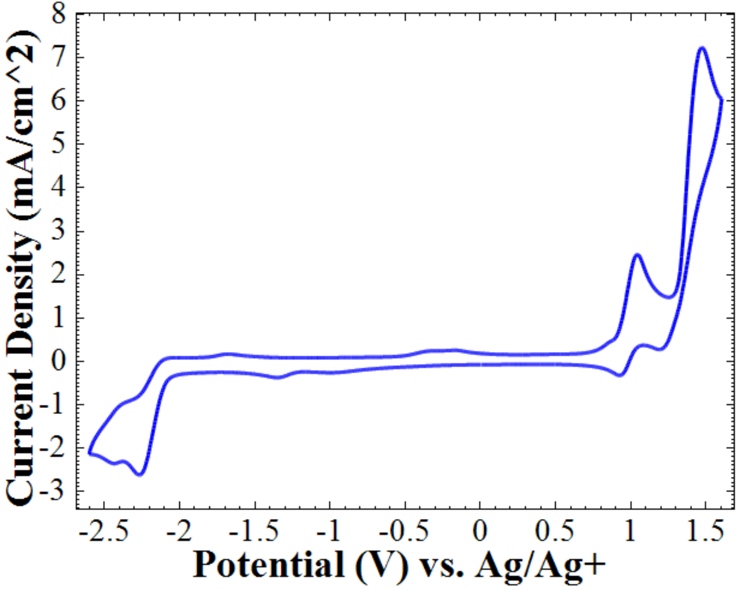
CV taken in acetonitrile using 0.01 M complex and 0.1 M $TBABF_4$.

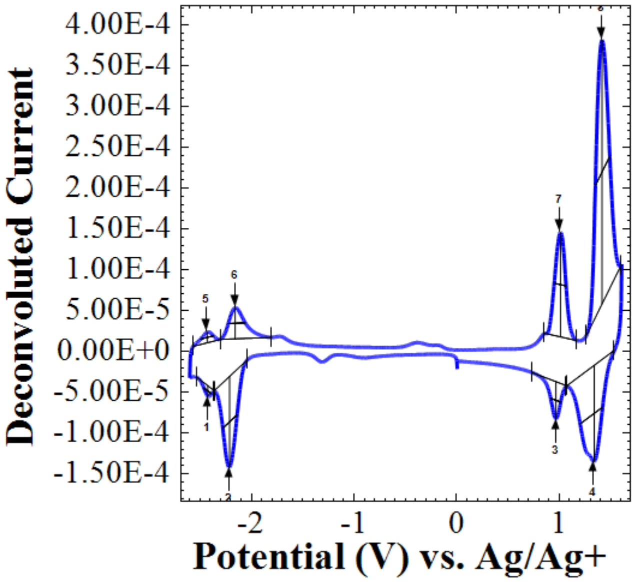


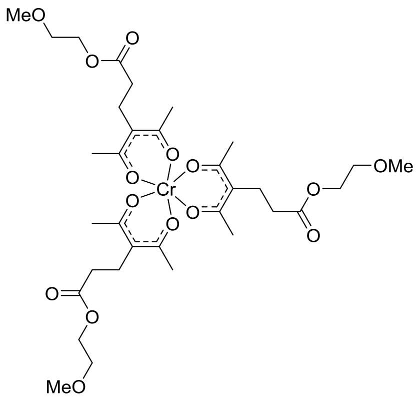




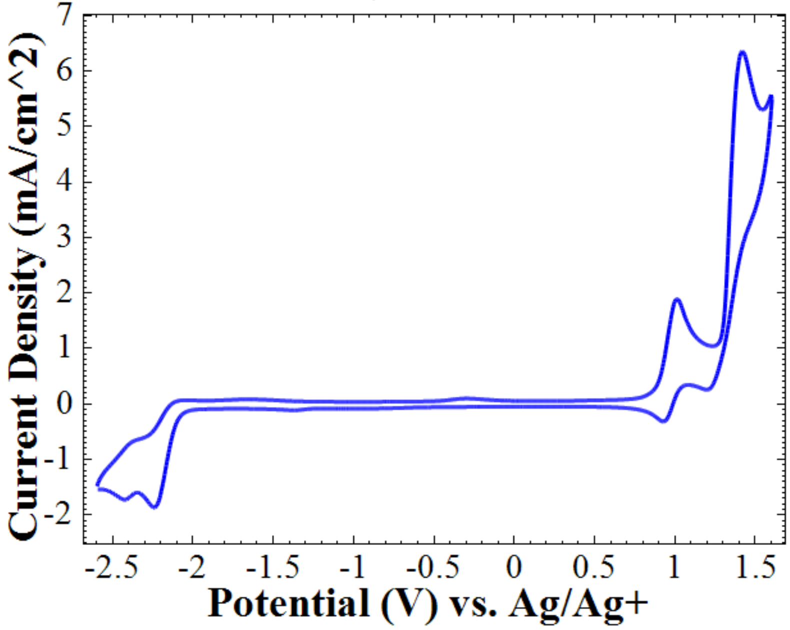
CV taken in acetonitrile using 0.01 M complex and 0.1 M $TBABF_4$.

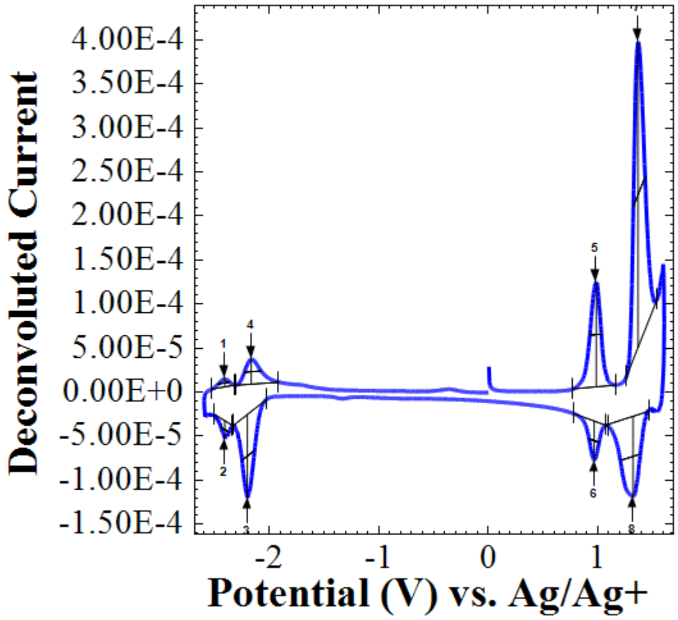


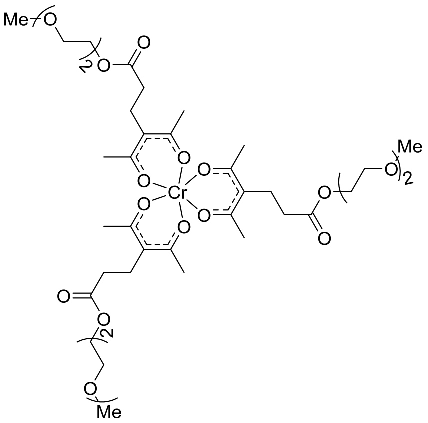




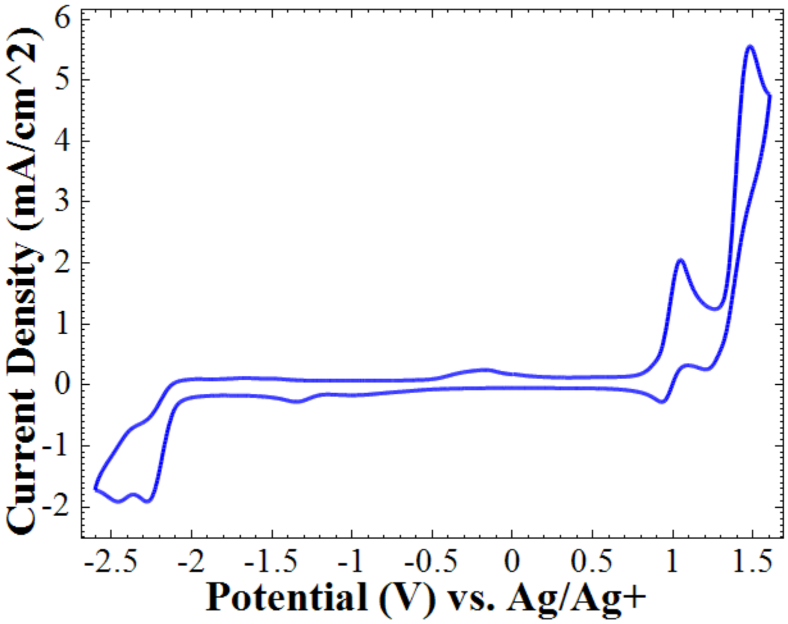
CV taken in acetonitrile using 0.01 M complex and 0.1 M TBABF$_4$.

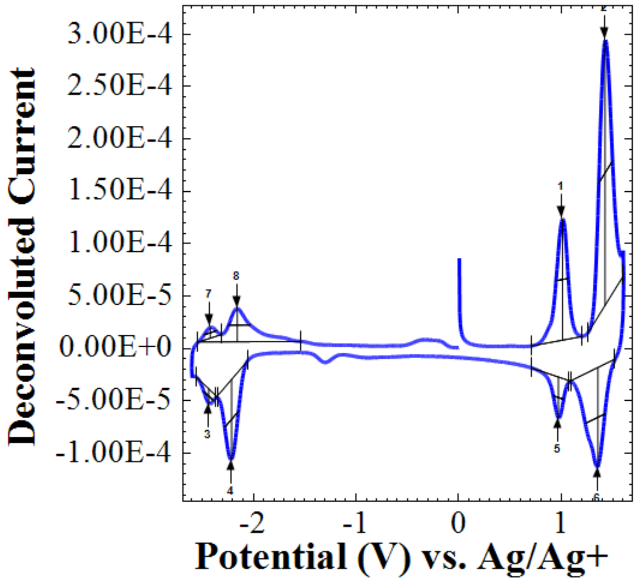


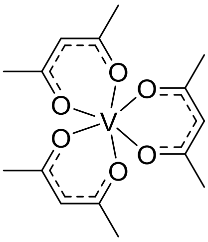




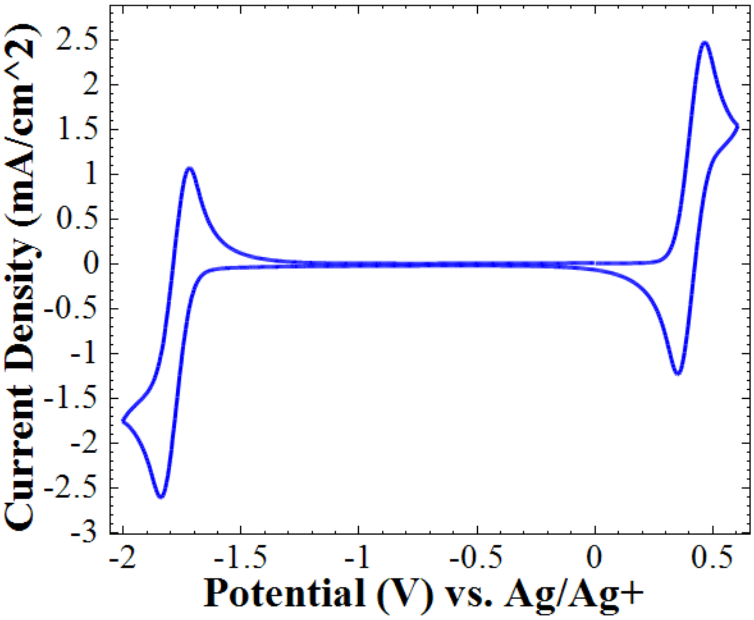
CV taken in acetonitrile using 0.01 M complex and 0.1 M TBABF$_4$.

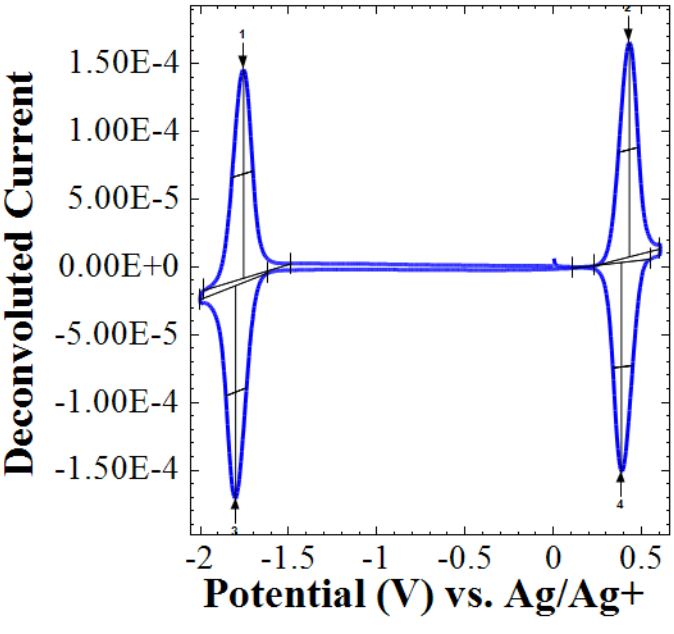


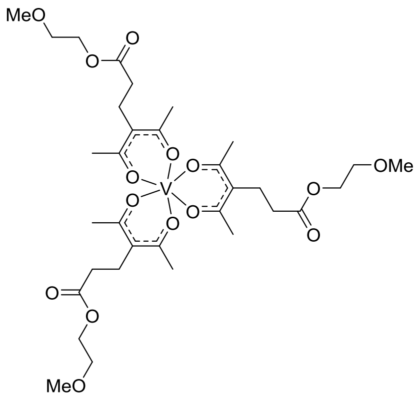




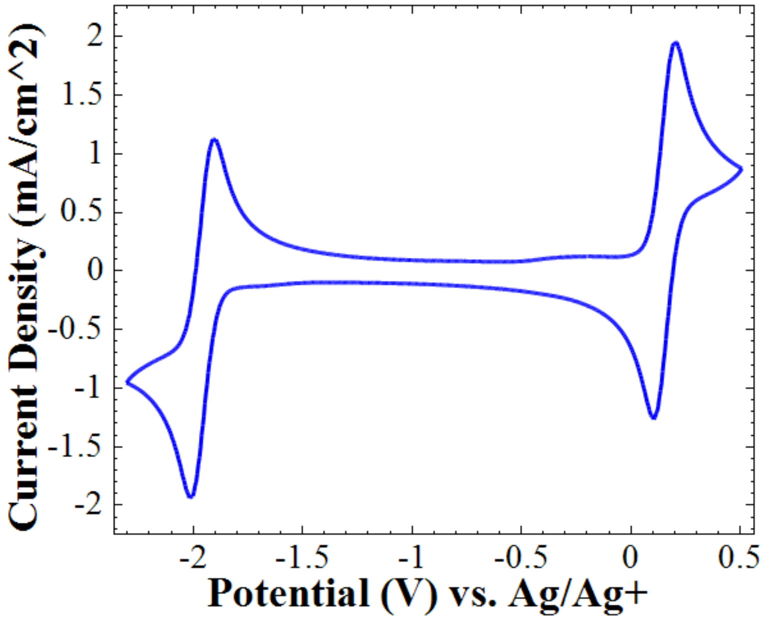
CV taken in acetonitrile using 0.01 M complex and 0.1 M TBABF$_4$.

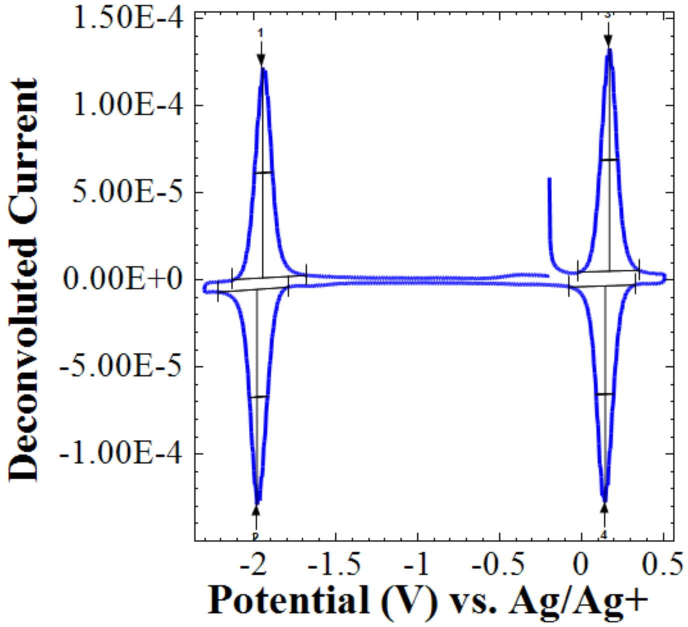






CV taken in acetonitrile using 0.01 M complex and 0.1 M $TBABF_4$.





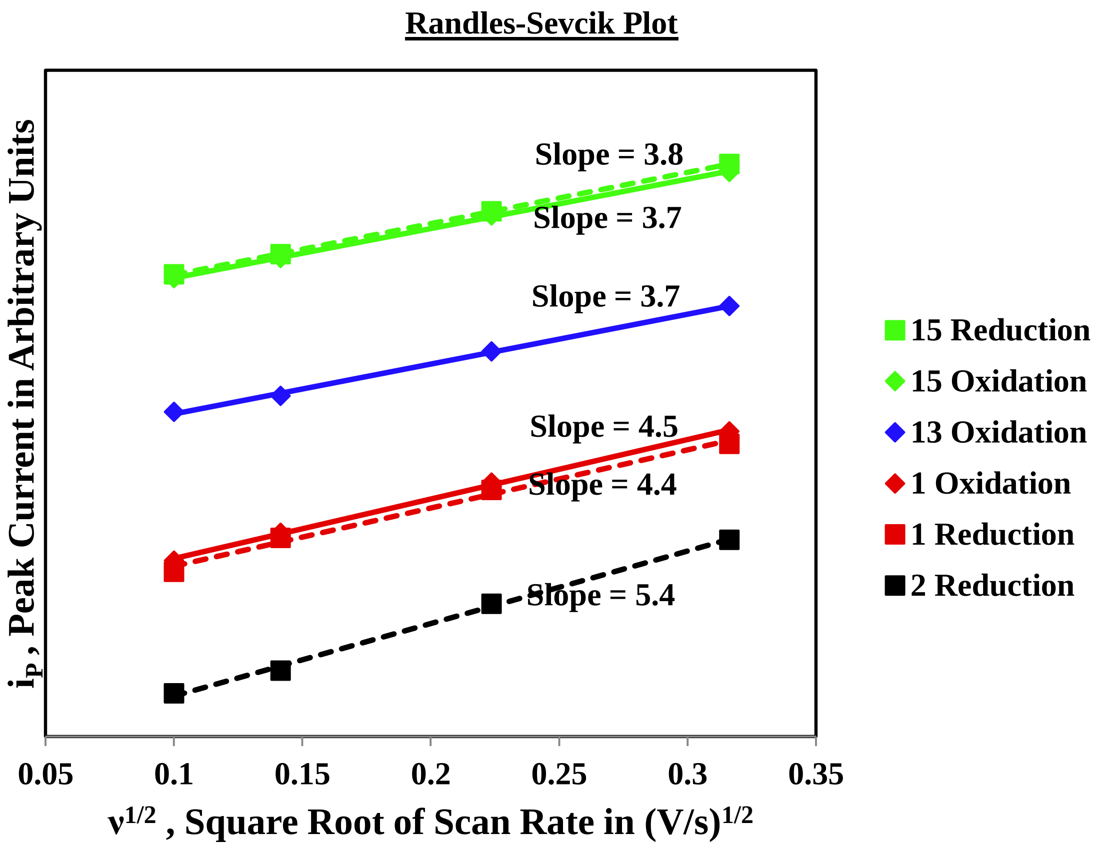


Figure S4: Plot of peak current (adjusted to increase separation) versus square root of the scan rate. Diamonds are for oxidation reactions, and squares are for reduction reactions. Linear fitting lines are solid for oxidation reactions and dashed for reduction reactions. Reduction peak currents are not available for **13** and oxidation peak currents are not available for **2**, due to irreversible reactions.

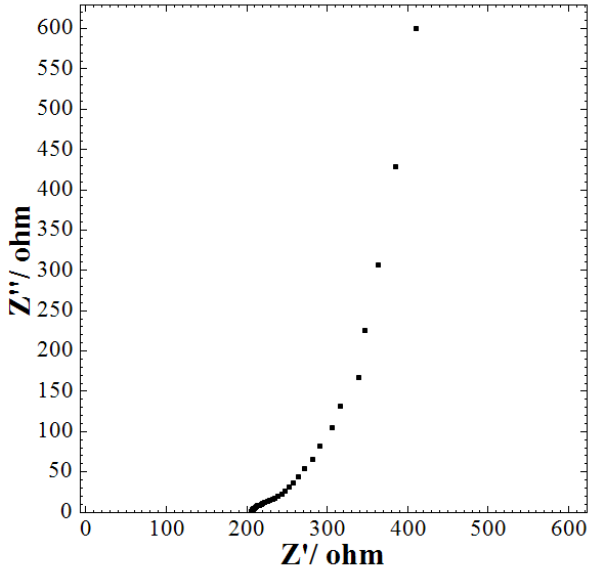


Figure S5: EIS Nyquist plot of H-cell with 0.5M $TBABF_4$ from 0.01-1x10^6 Hz at open circuit potential. R_S = 206Ω.

References

1. P. R. Singh and R. Sahai, *Aust. J. Chem.* 1969, **22**, 1169-1175.
2. D. W. Barnum, *J. Inorg. Nucl. Chem.* 1961, **21**, 221-237.
3. K. B. Takvorian and R. H. Barker, *Inorganic Syntheses* 1970, **12**, 85-88.