Electronic Supplementary Information

Synthesis and characterization of a dipyriamethyrin-uranyl complex

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Contents

Materials & General Methods

All reagents and solvents were purchased from commercial supplies and used without further purification. Analytical thin-layer chromatography (TLC) was performed using commercial precoated silica gel plates containing a fluorescent indicator. Column chromatography was carried out using silica gel (0.040-0.063 mm) or basic alumina (aluminum oxide, basic, Brockmann 1, 50-200 μm, 60A; Acros Organics). High-resolution mass spectra (HRMS) were measured using an Ion Spec Fourier Transform mass spectrometer (9.4 T). Proton and carbon NMR spectra were recorded using a Varian 400 spectrometer at room temperature and chemical shifts are reported in ppm using TMS or solvent residual signals as internal reference standards. All NMR spectroscopic solvents were purchased from Cambridge Isotope Laboratories. UV-Vis spectra were recorded from 250 to 800 nm using a Varian Cary 5000 spectrophotometer at room temperature. Unless otherwise indicated, a cell length of 10 mm was used for all UV-Vis spectra studies.

Synthesis and Characterization Data

*meso-Dipyriamethyrin (**6a**)*

To a 500 mL round bottom flask was added 2,6-bis(3,4-diethyl-2-pyrryl)pyridine (**5**) (500 mg, 1.55 mmol) and CH_2Cl_2 (350 mL). The reaction mixture was degassed with N_2 followed by addition of boron trifluoride diethyl etherate (2.6 mL, 21 mmol, 13.5 equiv.) and 37% aqueous formaldehyde (0.151 mL, 1.87 mmol, 1.2 equiv.). The mixture was stirred at room temperature for 24 h and 2,3-dichloro-5,6-dicyanoquinone (DDQ) (427 mg, 1.87 mmol, 1.2 equiv.) was added. The resulting mixture was stirred for another 30 min at room temperature, then transferred to a separatory funnel and washed with saturated $NaHCO_3$ (aq.) (2 x 50 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The resulting solid was subjected to flash chromatography using silica (CH_2Cl_2 to 20% acetone/ CH_2Cl_2, eluent) or basic alumina (Al_2O_3) (CH_2Cl_2 to 15% acetone/ CH_2Cl_2) to yield **6a** as a red-orange powder.[1] Yield: 97% (500 mg), 99% (510 mg) (two runs).

^{1}H NMR (400 MHz, δ-value in $CDCl_3$) δ 7.74 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 4H), 6.93 (s, 2H), 2.67 (q, *J* = 9.3, 8.4 Hz, 8H), 2.55 (q, *J* = 7.5 Hz, 8H), 1.22 (t, *J* = 7.6 Hz, 12H), 1.07 (t, *J* = 7.5 Hz, 12H). UV-Vis (λ_{max} (nm) in CH_2Cl_2; (ε, $M^{-1}cm^{-1}$)) 290 (11,600), 334 (8,400), 453 (18,500). HRMS (ESI^+) calcd. for $C_{44}H_{50}N_6$ ($M+H^+$) 663.42, found 663.42.[2]

*meso-Bis(pentafluorophenyl)dipyriamethyrin (**6b**)*

To a 500 mL round bottom flask was charged with 2,6-bis(3,4-diethyl-2-pyrryl)pyridine (**5**) (50 mg, 0.16 mmol), pentafluorobenzaldehyde (0.04 mL, 0.33 mmol, 2.1 equiv.), and propionic acid: butyric acid (1:1) (200 mL) previously degassed with N_2. The reaction mixture was heated at reflux for 16 h, then concentrated under vacuum and subsequently suspended in dry CH_2Cl_2 (100 mL). 2,3-Dichloro-5,6-dicyanoquinone (DDQ) (42 mg, 0.19 mmol, 1.2 equiv.) was added. The mixture was stirred for 1 h at room temperature then transferred to a separatory funnel and washed with saturated $NaHCO_3$ (aq.) (2 x 25 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The resulting solid was subjected to flash

chromatography over silica gel (CH_2Cl_2 to 15% acetone/ CH_2Cl_2, eluent) or basic alumina (Al_2O_3) (CH_2Cl_2 to 15% acetone/ CH_2Cl_2) to yield **6a** as a red powder. Yield: 10% (15 mg).

^{1}H NMR (400 MHz, δ-value in $CDCl_3$) δ 12.53 (s, 2H), 7.76 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 4H), 2.41 (q, *J* = 7.5 Hz, 8H), 1.85 (q, *J* = 7.4 Hz, 8H), 0.99 (t, *J* = 7.5 Hz, 12H), 0.83 (t, J =7.5 12H). ^{13}C NMR (101 MHz, δ-value in $CDCl_3$) δ 153.82, 153.36, 140.48, 137.85, 135.95, 133.68, 121.76, 108.16, 77.20, 18.94, 17.78, 15.79, 15.24. UV-Vis (λ_{max} (nm) in CH_2Cl_2; (ε, $M^{-1}cm^{-1}$)) 290 (19,100), 464 (25,500). HRMS (ESI^+) calcd. for $C_{56}H_{48}F_{10}N_6$ ($M+H^+$) 995.38, found 995.3839

*meso-Dipyriamethyrin uranyl complex (**7a**)*

(a) In an inert atmosphere glove box, $UO_2[N(SiMe_3)_2]_2$-2THF (55 mg, 0.075 mmol) was added to a stirred solution of macrocycle **6a** (50 mg, 0.075 mmol) in 5 mL of dry THF. The mixture was heated to reflux for 8 h, at which time the solution was observed to turn a dark purple. The reaction mixture was removed from the inert atmosphere glove box and concentrated *in vacuo*. The residue was purified by basic alumina (Al_2O_3) chromatography (eluent: CH_2Cl_2) on the bench top to yield **7a** as a dark purple solid. Yield: 80% (56 mg).

(b) To a 50 mL round bottom was added **6a** (15.6 mg, 0.024 mmol), uranyl acetate dihydrate (25 mg, 0.059 mmol, 2.5 equiv.), and 10 mL of CH_2Cl_2: MeOH (1:1, v/v). The reaction was stirred at room temperature overnight. Upon completion, the mixture was concentrated *in vacuo* and purified by flash chromatography over basic alumina (Al_2O_3) (CH_2Cl_2, eluent) to yield **7a** as a dark purple solid. Yield: 14% (3 mg).

^{1}H NMR (400 MHz, δ-value in $CDCl_3$) δ 7.80 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 4H), 7.37 (s, 2H), 2.72 (q, *J* = 7.6 Hz, 8H), 2.63 (q, *J* = 7.4 Hz, 8H), 1.25 – 1.19 (m, 24H). ^{13}C NMR (101 MHz, δ-value in $CDCl_3$) δ 160.23, 156.53, 146.29, 143.76, 139.09, 130.02, 128.61, 119.57, 18.19, 18.07, 17.62, 16.03. UV-Vis (λ_{max} (nm) in CH_2Cl_2; (ε, $M^{-1}cm^{-1}$)) 315 (28,100), 543 (39,300), 618 (19,600). HRMS (ESI^+) calcd. for $C_{44}H_{48}N_6O_2U$ ($M+H^+$) 931.442, found 931.4406.

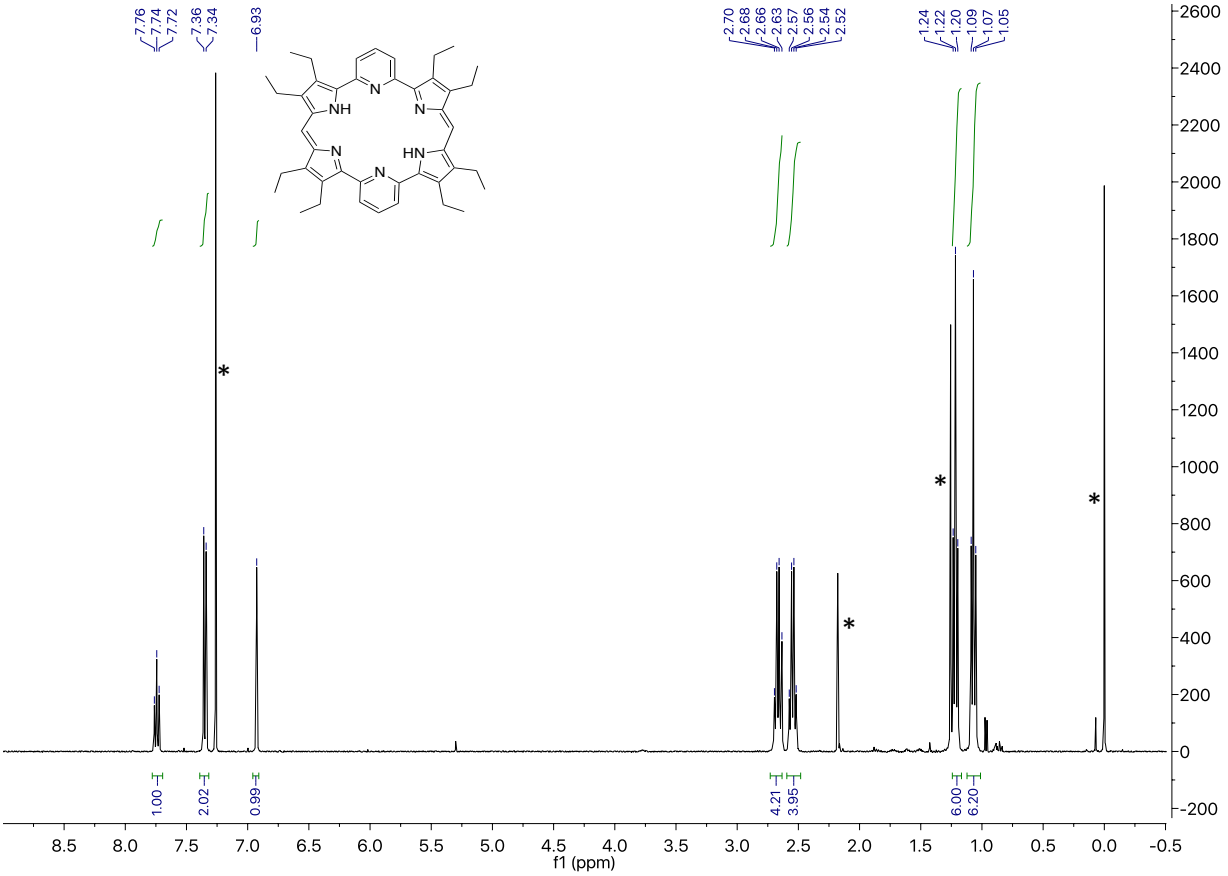
*meso-Bis(pentafluorophenyl)dipyriamethyrin uranyl complex (**7b**)*

In an inert atmosphere glove box, $UO_2[N(SiMe_3)_2]_2$-2THF (19 mg, 0.026 mmol) was added to a stirring solution of macrocycle **6b** (25 mg, 0.025 mmol) in 5 mL of dry THF. The reaction was heated to reflux for 8 h, at which time the solution was observed to turn a dark purple. The mixture was removed from the inert atmosphere glove box and concentrated under vacuum. The resulting residue was purified by basic alumina (Al_2O_3) column chromatography (eluent: CH_2Cl_2) on the bench top to yield **7b** as a dark purple solid. Yield: 72% (23 mg).

^{1}H NMR (400 MHz, δ-value in $CDCl_3$) δ 7.82 (t, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 4H), 2.57 (q, *J* = 7.5 Hz, 8H), 1.92 (q, *J* = 7.5 Hz, 8H), 1.16 (t, *J* = 7.5 Hz, 12H), 0.72 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, δ-value in $CDCl_3$) δ 160.21, 156.20, 153.79, 146.61, 144.35, 138.72, 134.05, 121.76, 119.75, 19.75, 18.10, 15.83, 15.73. UV-Vis (λ_{max} (nm) in CH_2Cl_2; (ε, $M^{-1}cm^{-1}$))) 315 (17,580), 373 (10,700), 572 (30,200). HRMS (ESI^+) calcd. for $C_{56}H_{46}F_{10}N_6O_2U$ ($M+H^+$) 1263.410, found 1263.4105.

NMR Spectral & HRMS-ESI Data

*meso-Dipyriamethyrin (**6a**)*



Target Compound Screening Report

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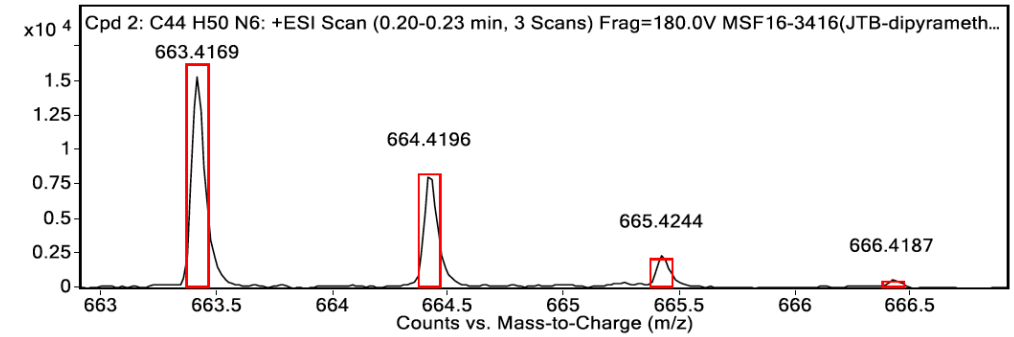
MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
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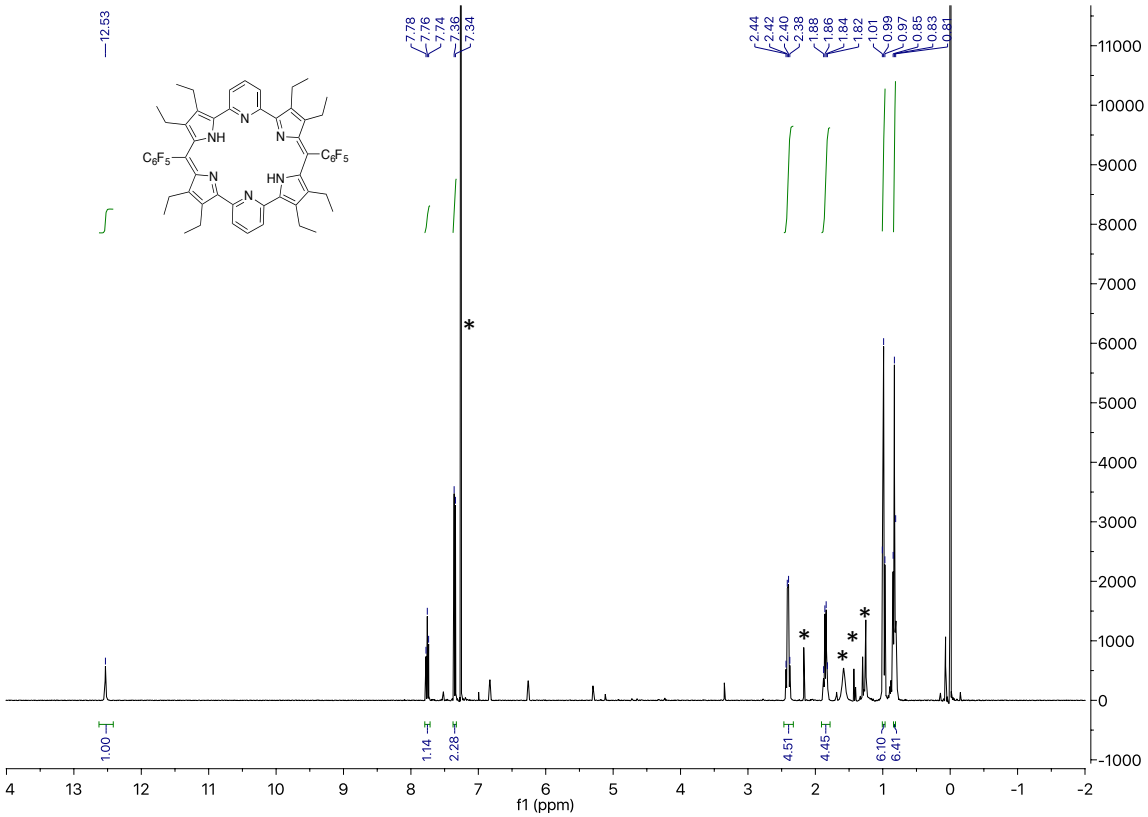
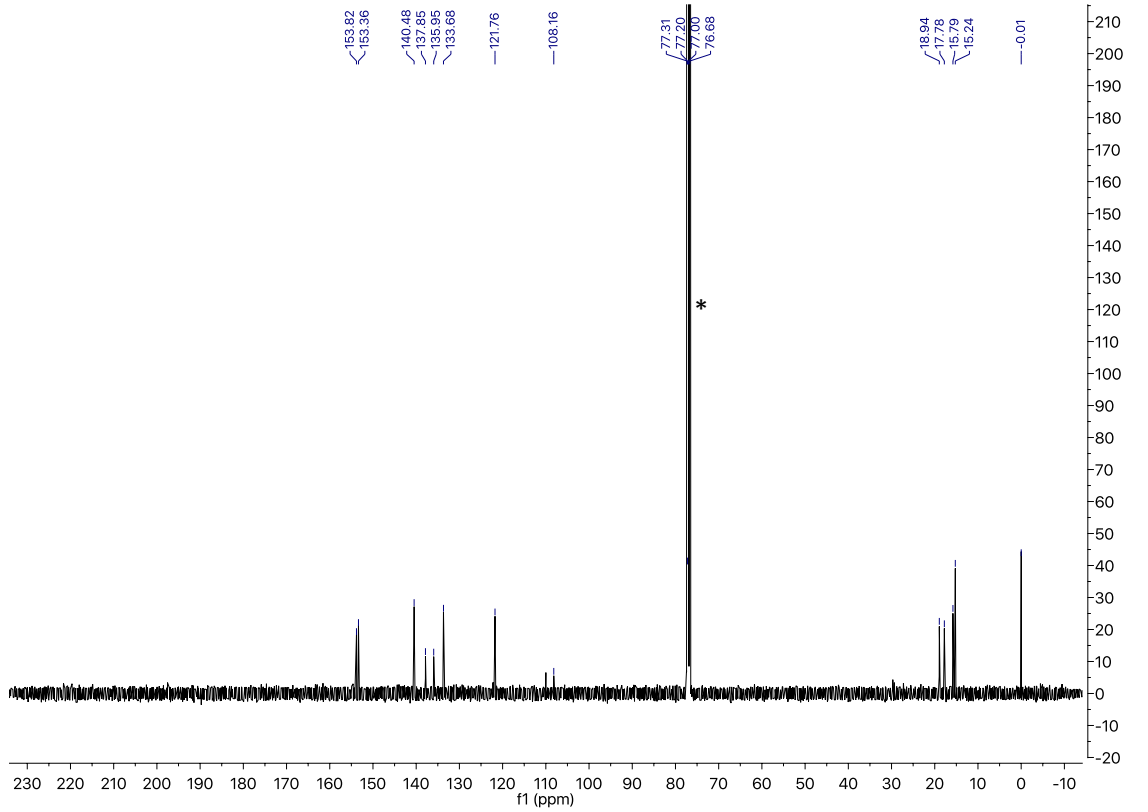
664.41960	664.42010	1	8333.7	C44H50N6	(M+H)+	0.8
665.42440	665.42320	1	2389.47	C44H50N6	(M+H)+	-1.76
666.41870	666.42630	1	624.3	C44H50N6	(M+H)+	11.38
695.44230			31252.63			

--- End Of Report ---

*meso-Bis(pentafluorophenyl)dipyriamethyrin (**6b**)*





Target Compound Screening Report

Data File	MSF16-3416(JTB-dipyramethyrin-UO2)_hrESIpos2.d	**Sample Name**	3416(JTB-dipyramethyrin-UO2)	**Comment**	3416(JTB-dipyramethyrin-UO2)
Position	P1-A8	**Instrument Name**	Instrument 1	**User Name**	
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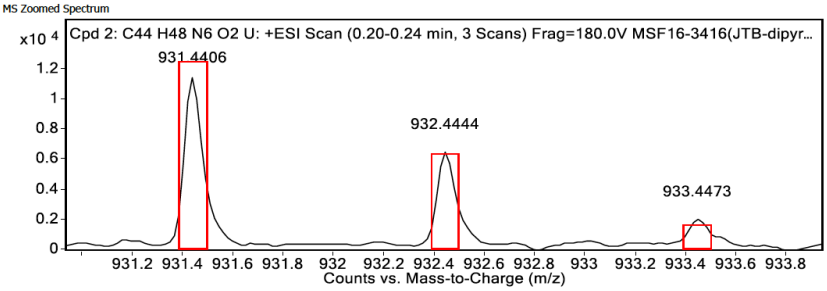

MS Spectrum Peak List

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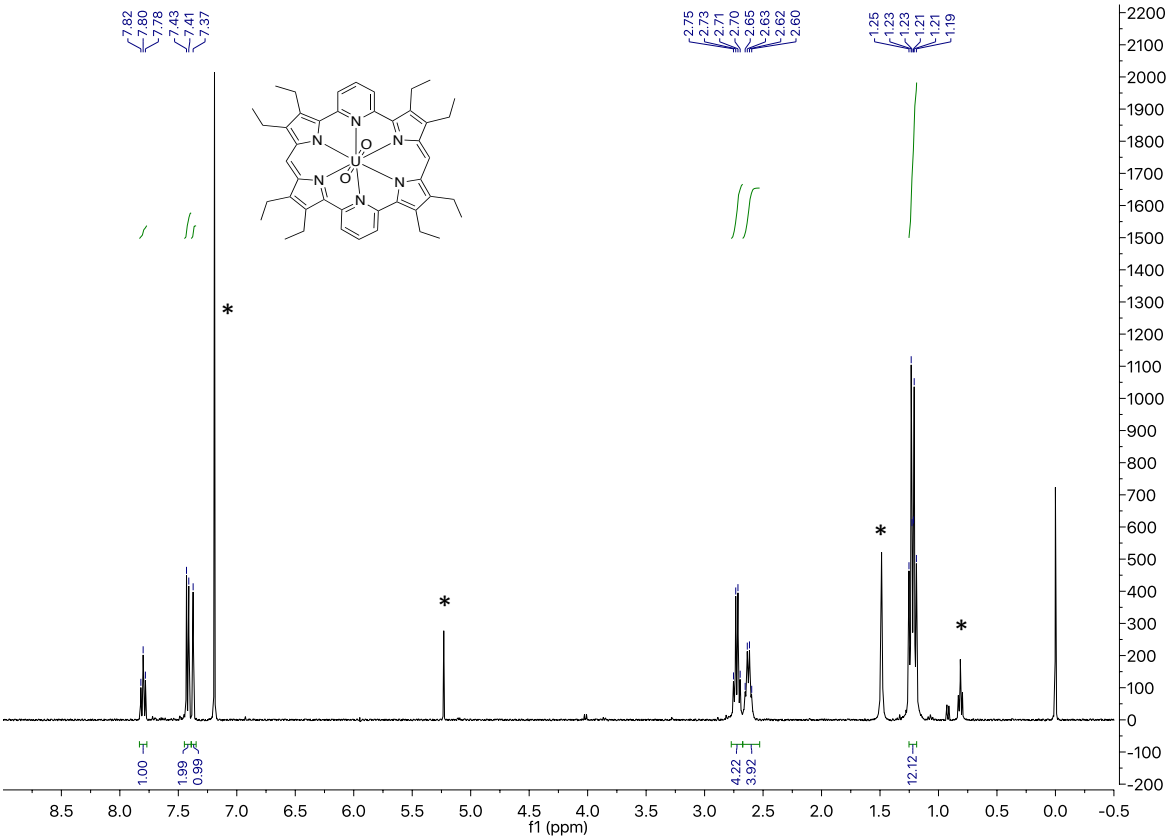
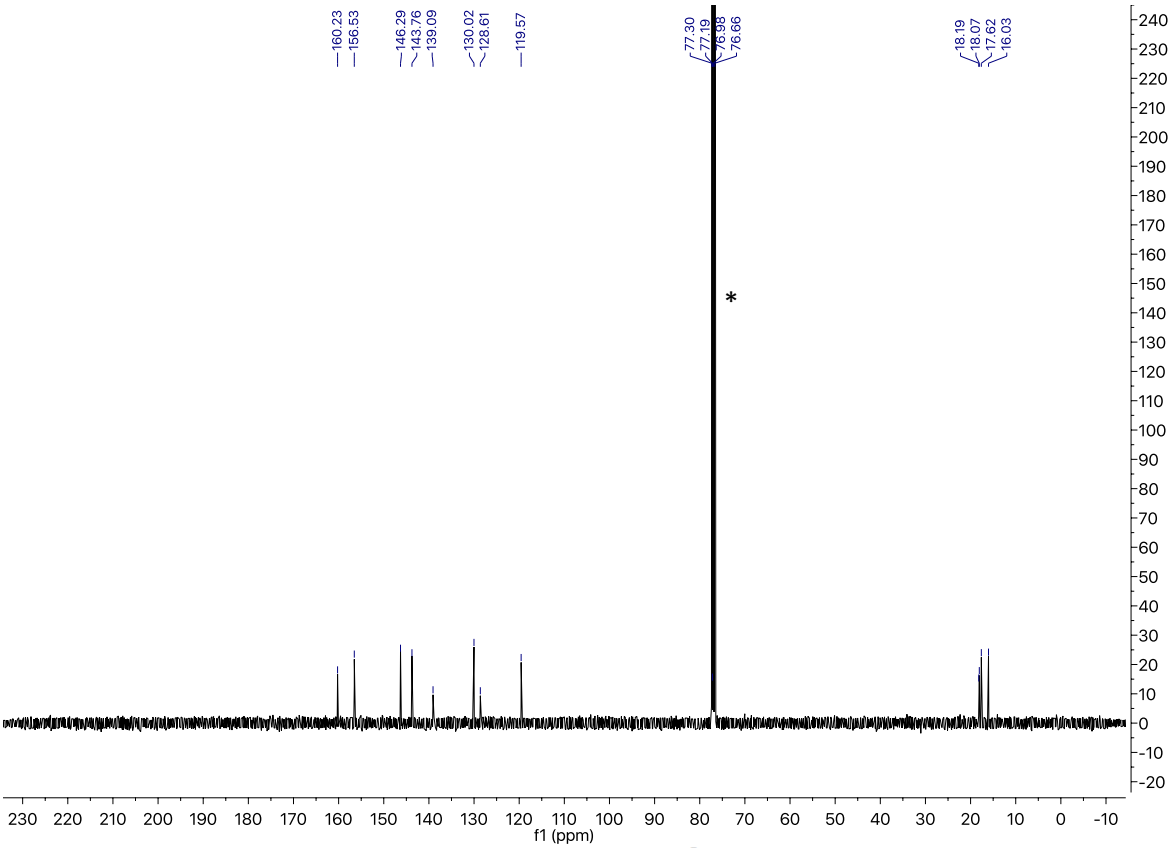
931.44060	931.44190	1	11440.82	C44H48N6O2U	(M+H)+	1.38
932.44440	932.44500	1	6527.8	C44H48N6O2U	(M+H)+	0.75
933.44730	933.44810	1	2048.92	C44H48N6O2U	(M+H)+	0.89
934.43420	934.45110	1	640.92	C44H48N6O2U	(M+H)+	18.05

--- End Of Report ---

*meso-Dipyriamethyrin uranyl complex (**7a**)*

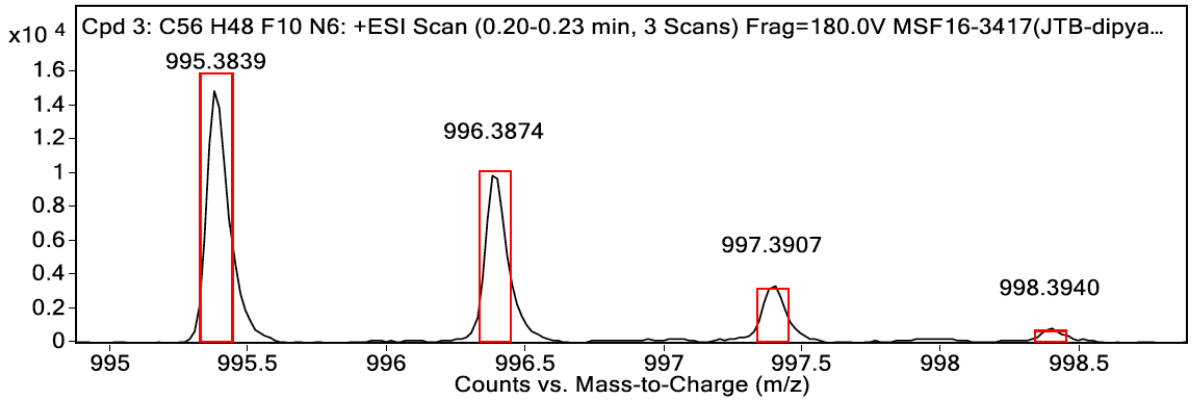




Target Compound Screening Report

Data File	MSF16-3417(JTB-dipyamc6f5)_hrESIpos1.d	**Sample Name**	3417(JTB-dipyamc6f5)	**Comment**	3417(JTB-dipyamc6f5)
Position	P1-B8	**Instrument Name**	Instrument 1	**User Name**	
Acq Method	pos.m	**Acquired Time**	11/23/2016 9:06:48 AM	**DA Method**	KS.m

MS Zoomed Spectrum

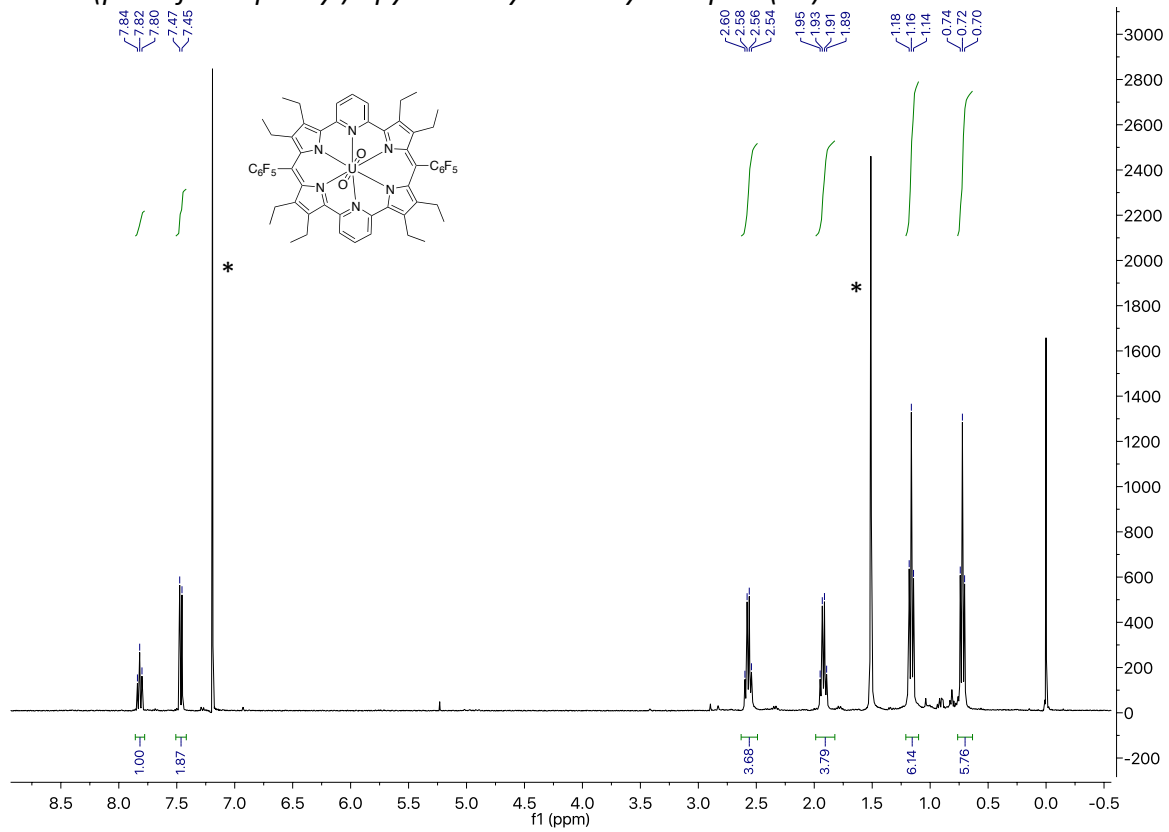


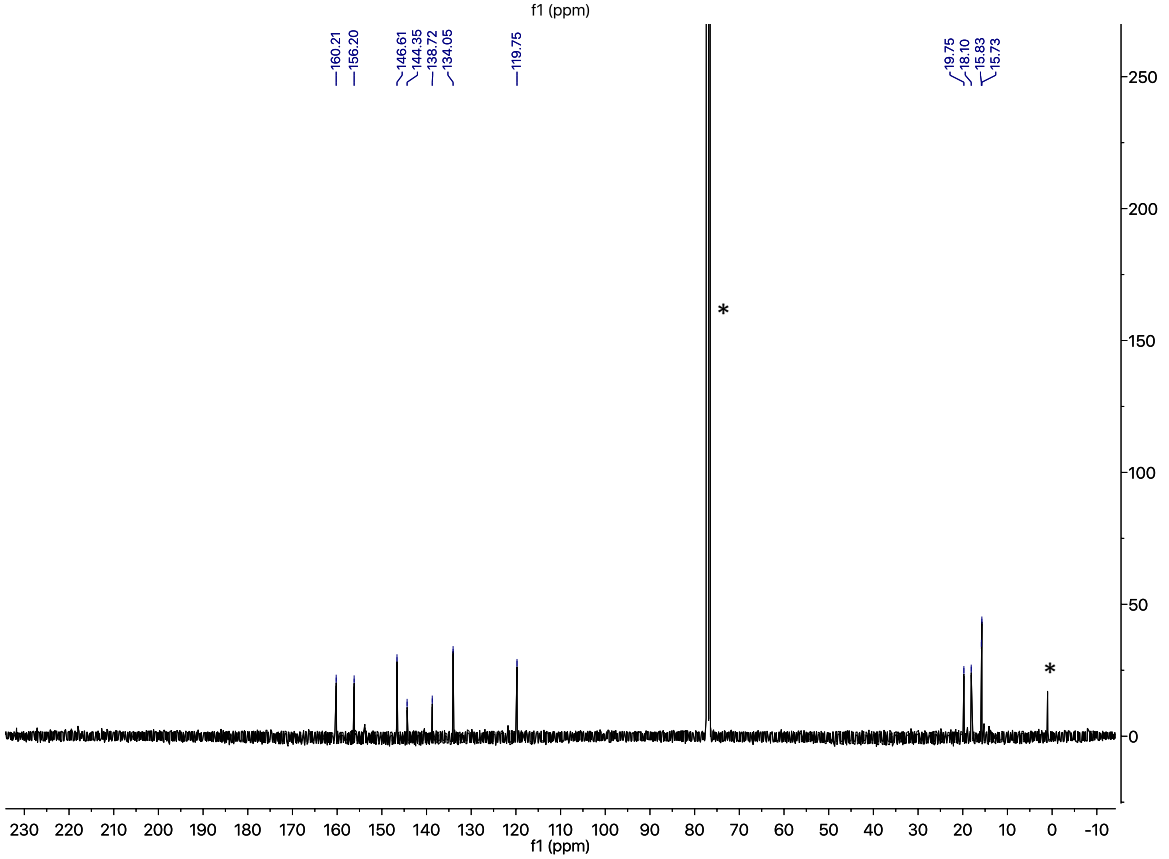
MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
498.19750			28231.89			
995.38390	995.38540	1	15040.2	C56H48F10N6	(M+H)+	1.49
996.38740	996.38850	1	10126.4	C56H48F10N6	(M+H)+	1.14
997.39070	997.39170	1	3396.86	C56H48F10N6	(M+H)+	0.98
998.39400	998.39480	1	863.7	C56H48F10N6	(M+H)+	0.84
999.38560	999.39800	1	306.53	C56H48F10N6	(M+H)+	12.36

End Of Report

*meso-Bis(pentafluorophenyl)dipyriamethyrin uranyl complex (**7b**)*

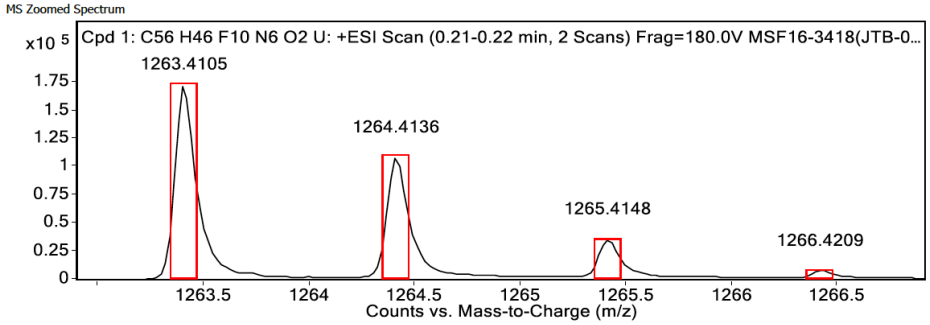




Target Compound Screening Report

Data File	MSF16-3418(JTB-02-45_C6F5-UO2)_hrESIpos1.d	**Sample Name**	3418(JTB-02-45_C6F5-UO2)	**Comment**	3418(JTB-02-45_C6F5-UO2)
Position	P1-E6	**Instrument Name**	Instrument 1	**User Name**	
Acq Method	pos.m	**Acquired Time**	11/29/2016 1:41:01 PM	**DA Method**	KS.m

MS Zoomed Spectrum



MS Spectrum Peak List

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301.14170			2131797.18			
1263.41050	1263.41030	1	172703.52	C56H46F10N6O2U	(M+H)+	-0.12
1264.41360	1264.41350	1	108050.31	C56H46F10N6O2U	(M+H)+	-0.1
1265.41480	1265.41660	1	35363.68	C56H46F10N6O2U	(M+H)+	1.44
1266.42090	1266.41970	1	7194.24	C56H46F10N6O2U	(M+H)+	-0.94
1267.36710	1267.42270	1	1997.88	C56H46F10N6O2U	(M+H)+	43.85
1268.39030	1268.42570	1	579.66	C56H46F10N6O2U	(M+H)+	27.91

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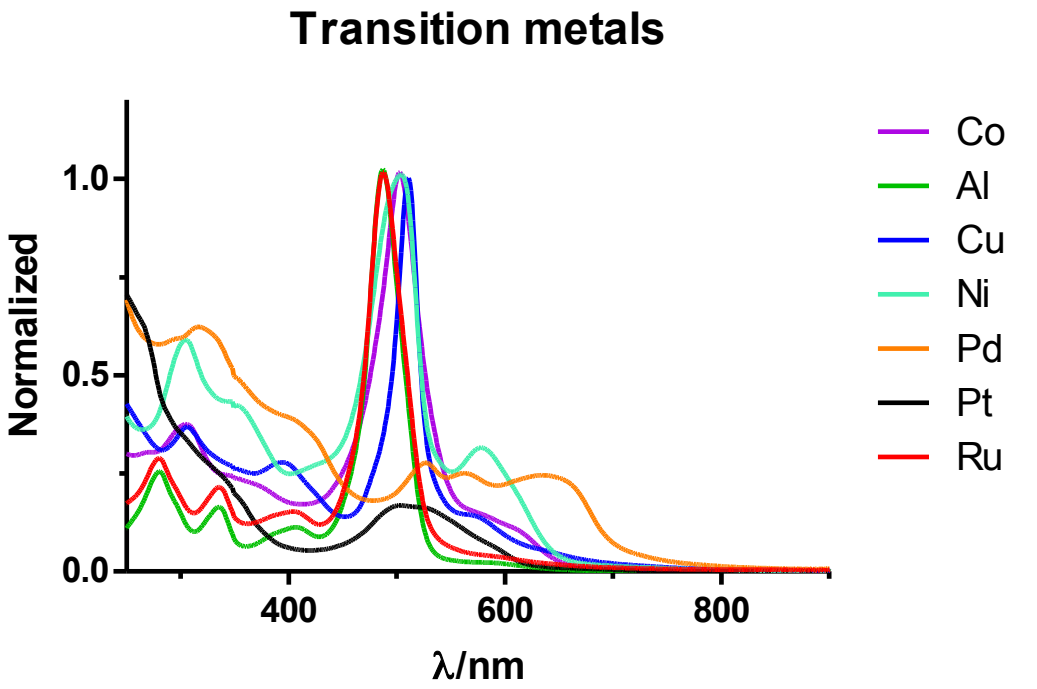
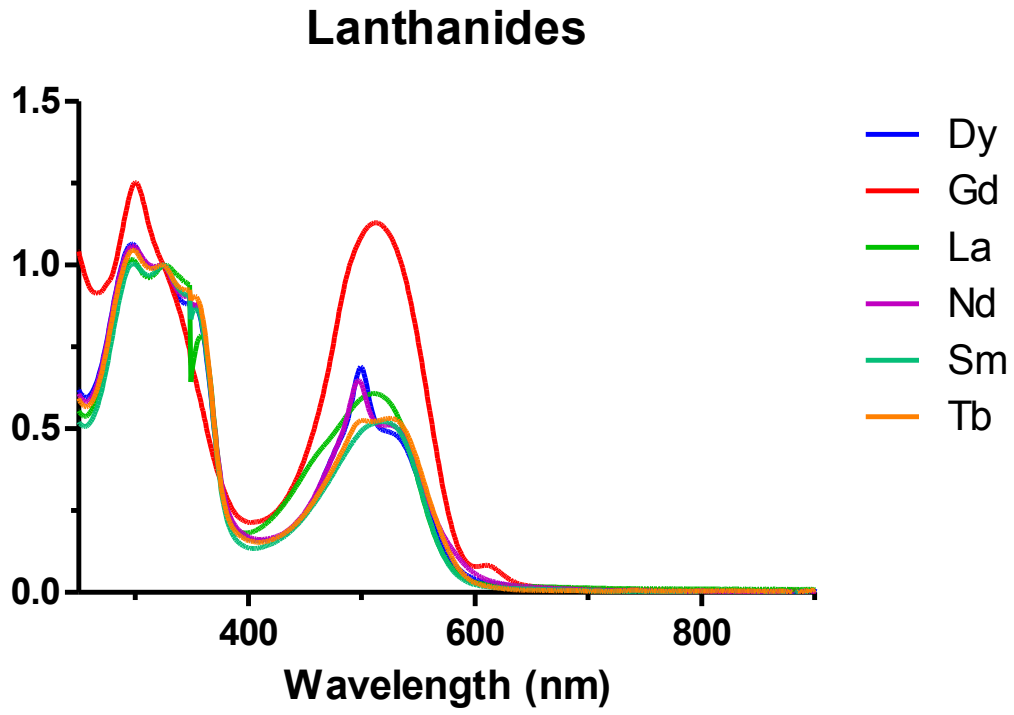
Competition Experiment Procedures

To a 50 mL round bottom was added **6a** (25 mg, 0.038 mmol), uranyl acetate dihydrate (16 mg, 0.038 mmol, 1 equiv.), lanthanum acetate (13 mg, 0.038 mmol, 1 equiv.), gadolinium acetate (15 mg, 0.038 mmol, 1 equiv.), neodymium acetate (12 mg, 0.038 mmol, 1 equiv.), terbium acetate (15 mg, 0.038 mmol, 1 equiv.), and dysprosium acetate (15 mg, 0.038 mmol, 1 equiv.). The flask was charged with 10 mL of CH_2Cl_2: MeOH (1:1, v/v) and stirred at room temperature for 16 h. The mixture was concentrated *in vacuo* and purified by flash chromatography over basic alumina (Al_2O_3) (CH_2Cl_2, eluent) to yield **7a** as a dark purple solid. Yield: 5% (1.6 mg).

UV-vis, LR- and HR ESI MS, and ^{1}H NMR Spectroscopic Data for the Products Obtained using Other Metal Precursors

UV-vis:

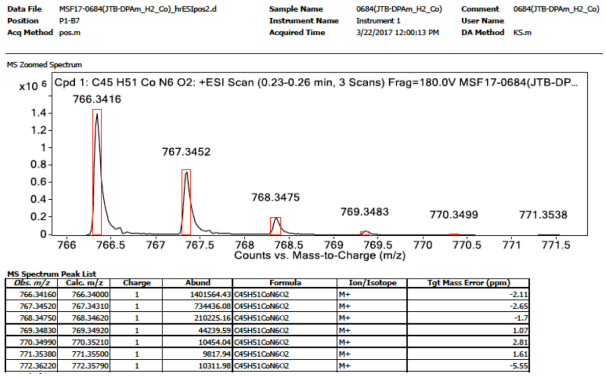




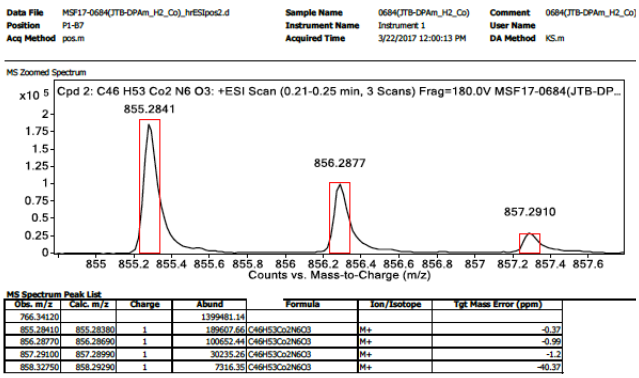
Low Resolution or High Resolution Mass Spectrometric-ESI Data for Obtained after Test Metallation Studies:

Cobalt: $[LCoH+HCOOH]^+$ ($C_{45}H_{51}N_6O_2Co$) at 766 amu

$[LCo_2+CH_3OH+HCOO^-]^+$ ($C_{46}H_{53}N_6O_3Co_2$) at 855 amu



Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
766.34160	766.34000	1	1401564.43	C45H51CoN6O2	M+	-2.11
767.34520	767.34310	1	734436.08	C45H51CoN6O2	M+	-2.65
768.34750	768.34620	1	210225.16	C45H51CoN6O2	M+	-1.7
769.34830	769.34920	1	44239.59	C45H51CoN6O2	M+	1.07
770.34990	770.35210	1	10454.04	C45H51CoN6O2	M+	2.81
771.35380	771.35500	1	9817.94	C45H51CoN6O2	M+	1.61
772.36220	772.35790	1	10311.98	C45H51CoN6O2	M+	-5.55



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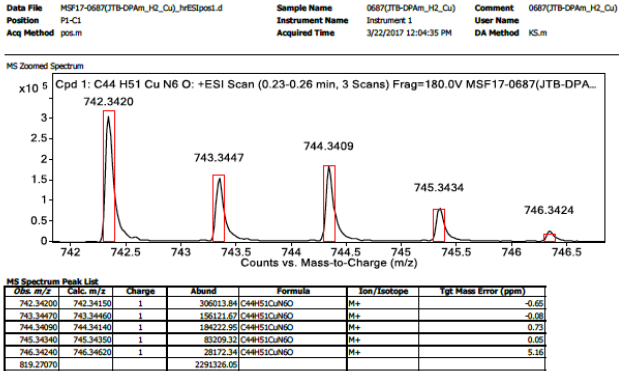
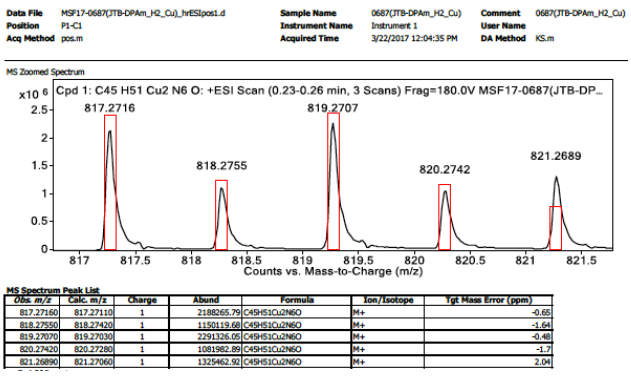
855.28410	855.28380	1	189607.66	C46H53Co2N6O3	M+	-0.37
856.28770	856.28690	1	100652.44	C46H53Co2N6O3	M+	-0.99
857.29100	857.28990	1	30235.26	C46H53Co2N6O3	M+	-1.2
858.32750	858.29290	1	7316.35	C46H53Co2N6O3	M+	-40.37

Copper: $[LCuH+H_2O]^+$ ($C_{44}H_{51}N_6OCu$) at 742 amu

$[LCu_2+CH_3O^-]^+$ ($C_{45}H_{51}N_6OCu_2$) at 817 amu



Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
742.34200	742.34150	1	306013.84	C44H51CuN6O	M+	-0.65
743.34470	743.34460	1	156121.67	C44H51CuN6O	M+	-0.08
744.34690	744.34140	1	184222.95	C44H51CuN6O	M+	0.73
745.34340	745.34350	1	83209.32	C44H51CuN6O	M+	0.05
746.34240	746.34620	1	28172.34	C44H51CuN6O	M+	5.16
819.27070			2291326.05			

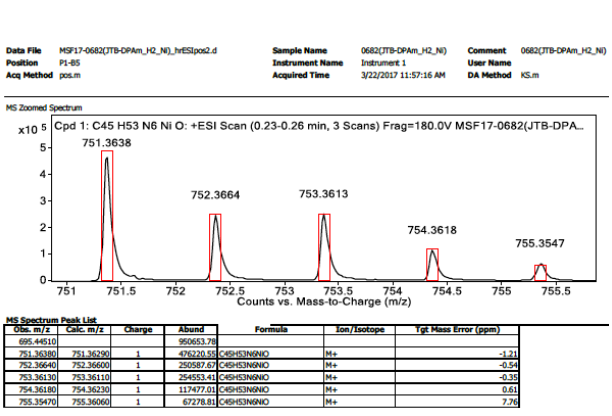


Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
817.27160	817.27110	1	2188265.79	C45H51Cu2N6O	M+	-0.65
818.27550	818.27420	1	1150119.68	C45H51Cu2N6O	M+	-1.64
819.27070	819.27030	1	2291326.05	C45H51Cu2N6O	M+	-0.48
820.27420	820.27280	1	1081982.89	C45H51Cu2N6O	M+	-1.7
821.26890	821.27060	1	1325462.92	C45H51Cu2N6O	M+	2.04

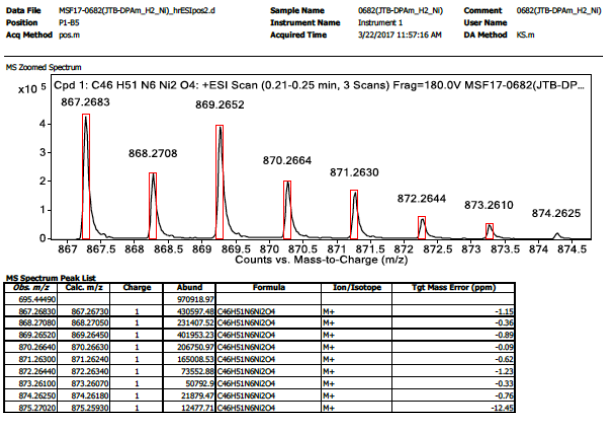
Nickel:

$[LNiH+CH_3OH]^+$ ($C_{45}H_{53}N_6ONi$) at 751 amu

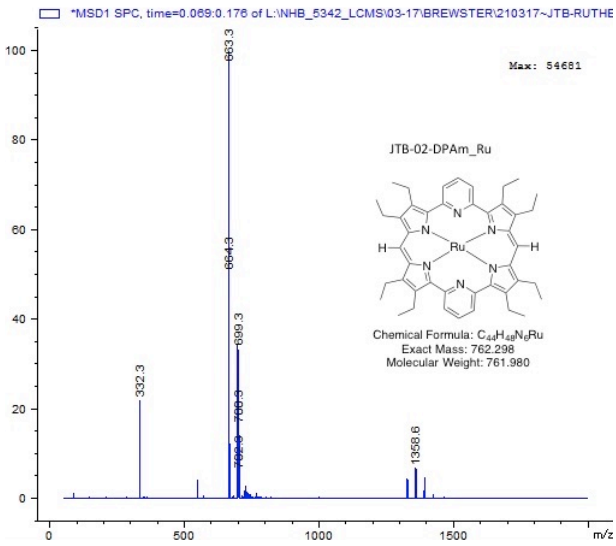
$[LNi_2+HCOOH+HCOO^-]^+$ ($C_{46}H_{51}N_6O_4Ni_2$) at 867 amu

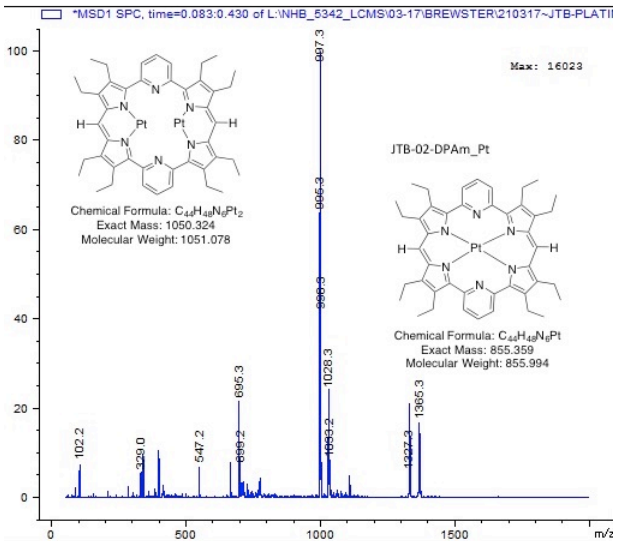


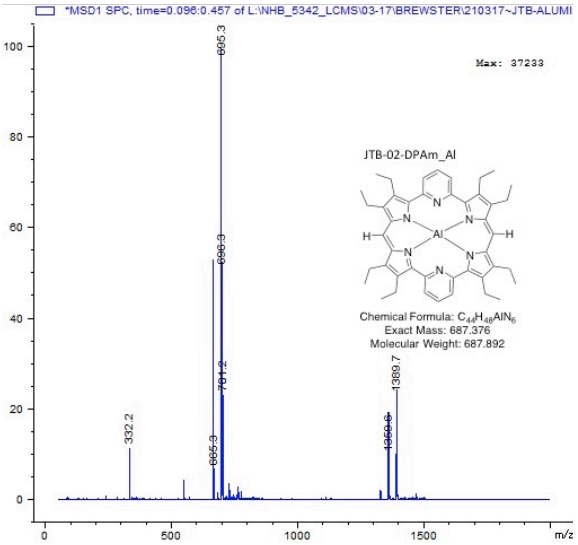
Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
695.44510			950653.78			
751.36380	751.36290	1	476220.59	C45H53N6NiO	M+	-1.21
752.36640	752.36600	1	250587.67	C45H53N6NiO	M+	-0.54
753.36130	753.36110	1	254553.41	C45H53N6NiO	M+	-0.35
754.36180	754.36230	1	117477.01	C45H53N6NiO	M+	0.61
755.35470	755.36060	1	67278.81	C45H53N6NiO	M+	7.76

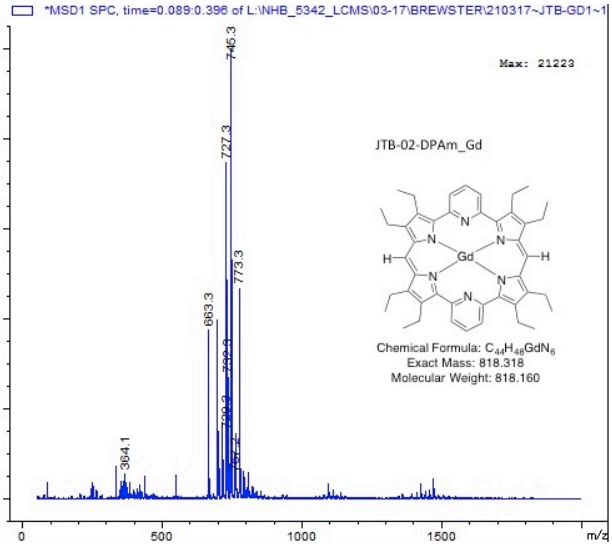


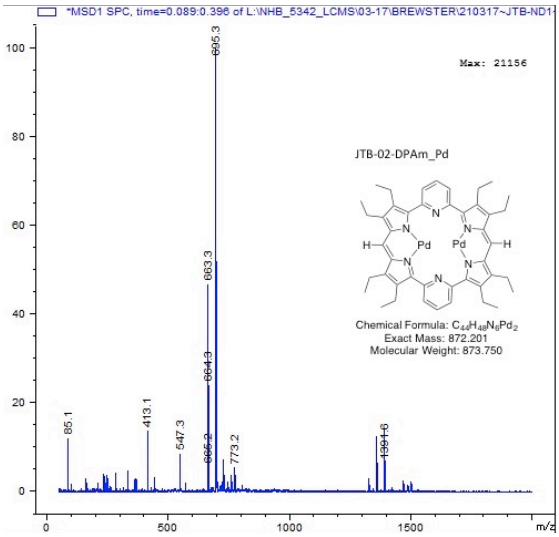
Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
695.44490			970918.97			
867.26830	867.26730	1	430597.48	C46H51N6Ni2O4	M+	-1.15
868.27080	868.27050	1	231407.52	C46H51N6Ni2O4	M+	-0.36
869.26520	869.26450	1	401953.23	C46H51N6Ni2O4	M+	-0.89
870.26640	870.26630	1	206750.97	C46H51N6Ni2O4	M+	-0.09
871.26300	871.26240	1	165008.53	C46H51N6Ni2O4	M+	-0.62
872.26440	872.26340	1	73552.88	C46H51N6Ni2O4	M+	-1.23
873.26100	873.26070	1	50792.9	C46H51N6Ni2O4	M+	-0.33
874.26250	874.26180	1	21879.47	C46H51N6Ni2O4	M+	-0.76
875.27020	875.25930	1	12477.71	C46H51N6Ni2O4	M+	-12.45


*MSD1 SPC, time=0.069:0.176 of L:\NHB_5342_LCMS\03-17\BREWSTER\210317~JTB-RUTHE
Max: 54681
JTB-02-DPAm_Ru
Chemical Formula: C44H48N8Ru
Exact Mass: 762.298
Molecular Weight: 761.980
663.3
664.3
699.3
332.3
1358.6
m/z

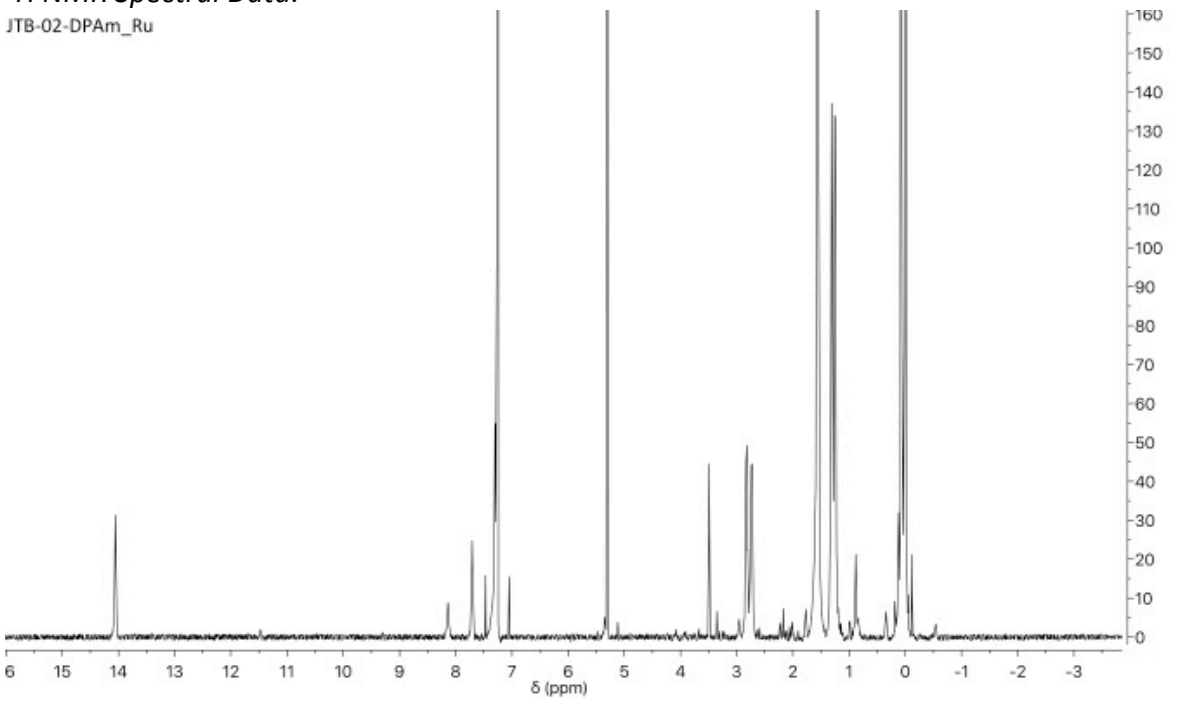

*MSD1 SPC, time=0.083:0.430 of L:\NHB_5342_LCMS\03-17\BREWSTER\210317~JTB-PLATII
Max: 16023
JTB-02-DPAm_Pt
Chemical Formula: C44H48N8Pt2
Exact Mass: 1050.324
Molecular Weight: 1051.078
Chemical Formula: C44H48N8Pt
Exact Mass: 855.359
Molecular Weight: 855.994
997.3
996.3
695.3
1028.3
1365.3
102.2
329.0
547.2
695.2
1327.3
m/z

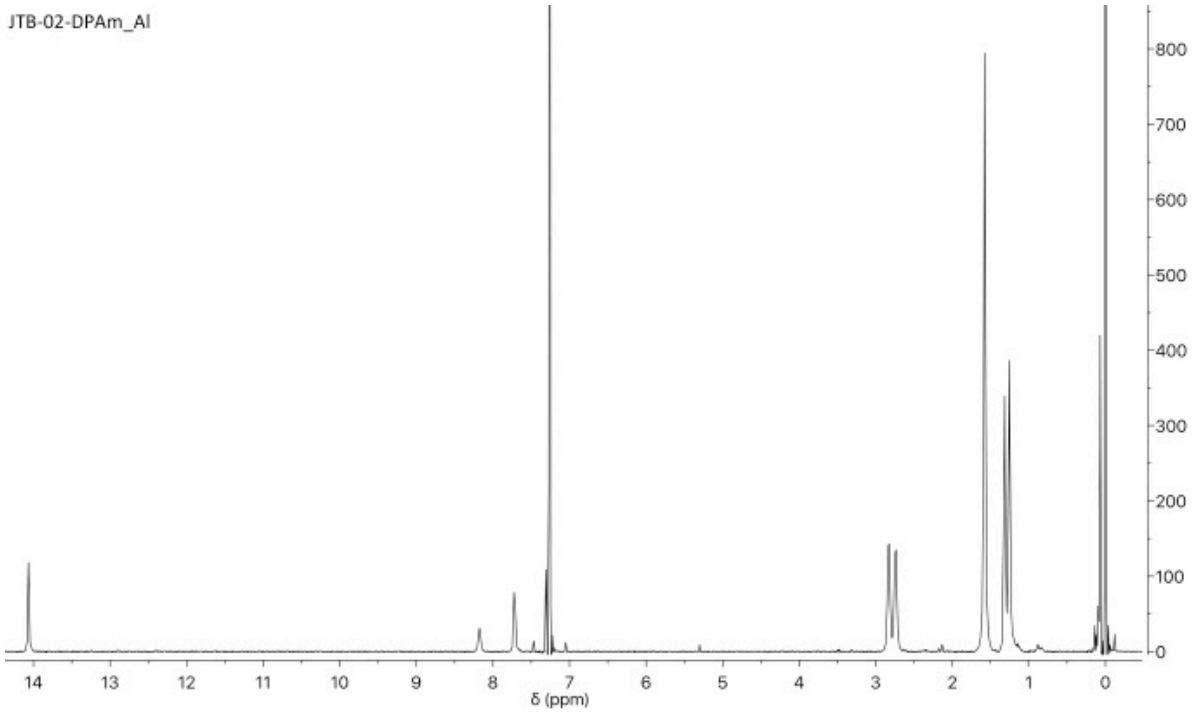

*MSD1 SPC, time=0.096:0.457 of L:\NHB_5342_LCMS\03-17\BREWSTER\210317~JTB-ALUMI
Max: 37233
JTB-02-DPAm_Al
Chemical Formula: C44H48AlN8
Exact Mass: 687.376
Molecular Weight: 687.892
695.3
696.3
781.2
332.2
665.3
1369.7
m/z

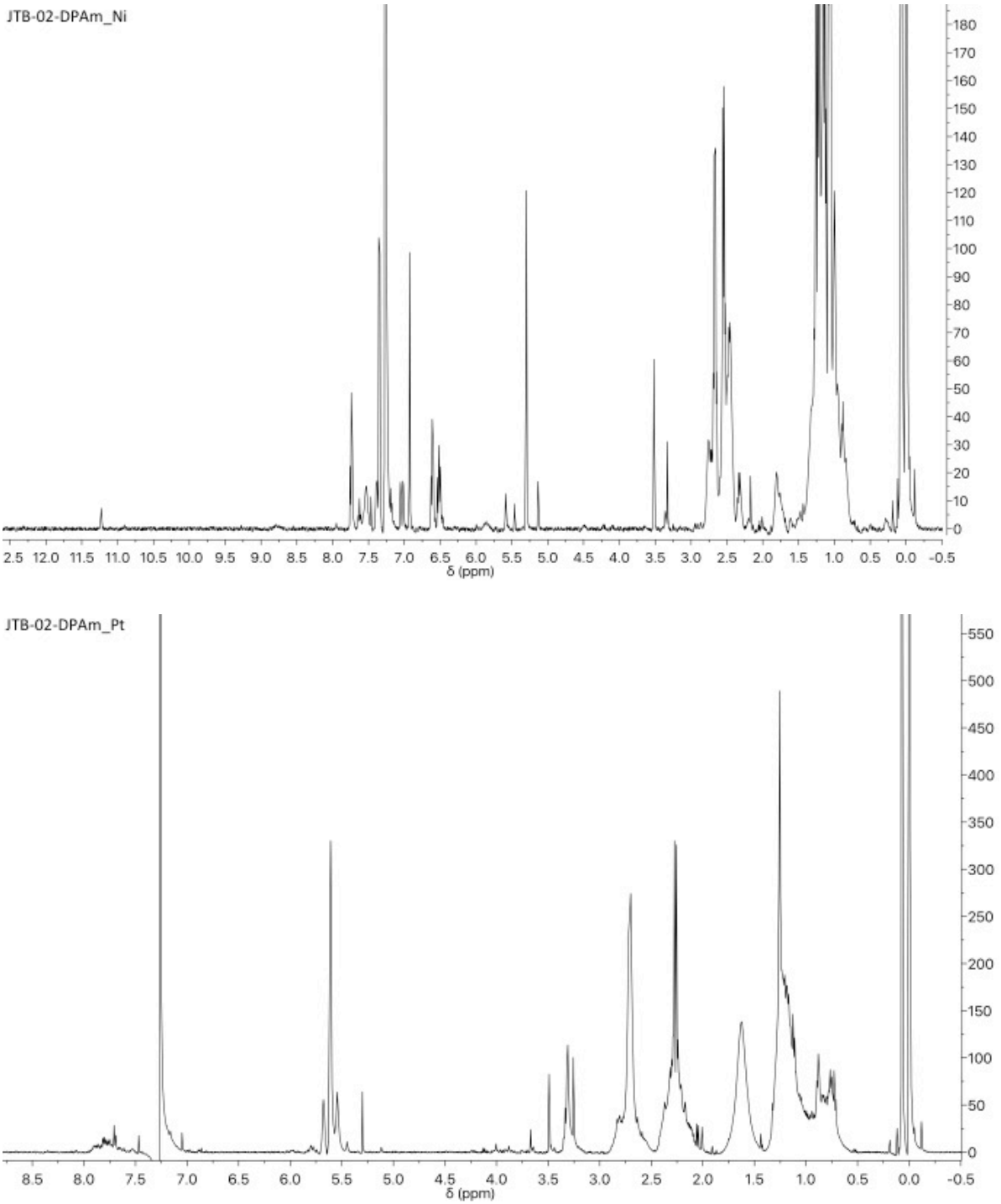

*MSD1 SPC, time=0.089:0.396 of L:\NHB_5342_LCMS\03-17\BREWSTER\210317~JTB-GD1~1
Max: 21223
JTB-02-DPAm_Gd
Chemical Formula: C44H48GdN8
Exact Mass: 818.318
Molecular Weight: 818.160
745.3
727.3
773.3
663.3
364.1
m/z


*MSD1 SPC, time=0.089:0.396 of L:\NHB_5342_LCMS\03-17\BREWSTER\210317~JTB-ND1
Max: 21156
JTB-02-DPAm_Pd
Chemical Formula: C44H48N8Pd2
Exact Mass: 872.201
Molecular Weight: 873.750
695.3
663.3
664.3
85.1
413.1
547.3
773.2
1391.6
m/z

^{1}H NMR Spectral Data:







Calculations

Density Functional Theory (DFT) Calculations

Theoretical calculations were performed with the *Gaussian09* program suite using supercomputers (Stampeded, UT Austin, TACC).[3] Calculations were carried out using the density functional theory method with Becke's three-parameter hybrid exchange functionals and the

Lee-Yang-Parr correlation (B3LYP) employing the 6-311++G** basis set for the C, H, N, O atoms.[4] The uranium atom was treated with a Stuttgart-Dresden pseudopotential in combination with the appropriate basis set, which is labeled as SDD(U).[5] Geometry coordinates were inputted based on crystal structures.

X-Ray Crystallographic Data[6-8]

Crystallographic data for **6b** (from CH_2Cl_2/*n*-hexane): $C_{56}H_{48}N_6F_{10}\cdot 2(CH_2Cl_2)$, M = 1164.85, triclinic, red needle, P-1, a = 8.5433(5), b = 18.7105(10), c = 19.0289(13) Å, α = 68.396(6)°, β = 82.032(5)°, γ = 77.230(5)°, V = 2752.6(3) Å^3, Z = 2, D_{calc} = 1.405 g/cm^3, CuKα = 1.54184 Å, T = 100(2) K, R_1 = 0.0969, wR_2 = 0.2604, GOF (on F^2) = 1.027 ($I > 2.00\sigma(I)$), CCDC 1534773. **7b** (from CH_2Cl_2/*n*-hexane): $C_{56}H_{48}N_6F_{10}UO_2$, M = 1263.02, orthorhombic, red prism, Pbcn, a = 14.8944(4), b = 9.8978(3), c = 32.5727(7) Å, α = 90°, β = 90°, γ = 90°, V = 4801.9(2) Å^3, Z = 4, D_{calc} = 1.747 g/cm^3, CuKα = 1.54184 Å, T = 100(2) K, R_1 = 0.0375, wR_2 = 0.0947, GOF (on F^2) = 1.100 ($I > 2.00\sigma(I)$), CCDC 1534774.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

```
Bond precision:  C-C = 0.0080 A          Wavelength=1.54184

Cell:          a=8.5433(5)       b=18.7105(10)    c=19.0289(13)
               alpha=68.396(6)   beta=82.032(5)   gamma=77.230(5)
Temperature:   100 K
```

	Calculated	Reported
Volume	2752.6(3)	2752.6(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C56 H48 F10 N6, 2(C H2 Cl2)	C56 H48 N6 F10, 2 C H2 Cl2
Sum formula	C58 H52 Cl4 F10 N6	C58 H52 Cl4 F10 N6
Mr	1164.86	1164.85
Dx,g cm-3	1.405	1.405
Z	2	2
Mu (mm-1)	2.632	2.632
F000	1200.0	1200.0
F000'	1206.69	
h,k,lmax	10,23,23	10,23,23
Nref	11115	10869
Tmin,Tmax	0.910,0.924	0.678,1.000
Tmin'	0.275	

```
Correction method= # Reported T Limits: Tmin=0.678 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.978          Theta(max)= 73.570

R(reflections)= 0.0969( 6954)     wR2(reflections)= 0.2604( 10869)

S = 1.027                  Npar= 719
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.

PLAT084_ALERT_3_C	High wR2 Value (i.e. > 0.25)	0.26 Report
PLAT097_ALERT_2_C	Large Reported Max. (Positive) Residual Density	1.30 eA-3
PLAT222_ALERT_3_C	Non-Solvent Resd 1 H Uiso(max)/Uiso(min) Range	5.1 Ratio
PLAT244_ALERT_4_C	Low 'Solvent' Ueq as Compared to Neighbors of	C2 Check
PLAT244_ALERT_4_C	Low 'Solvent' Ueq as Compared to Neighbors of	C77 Check
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00797 Ang.
PLAT352_ALERT_3_C	Short N-H (X0.87,N1.01A) N3 - H3N ..	0.71 Ang.
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	15.354 Check
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	3.107 Check
PLAT911_ALERT_3_C	Missing # FCF Refl Between THmin & STh/L= 0.600	27 Report
PLAT978_ALERT_2_C	Number C-C Bonds with Positive Residual Density.	0 Note

---

Alert level G

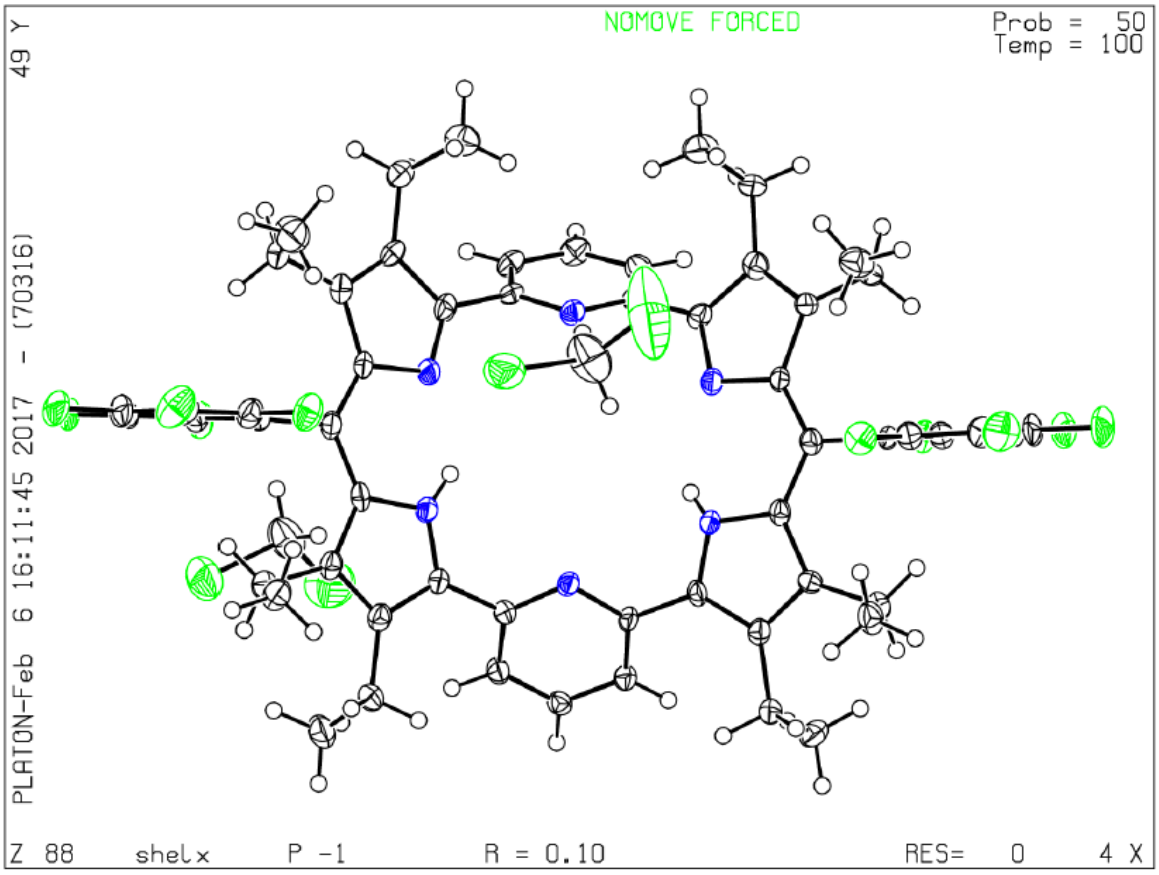
PLAT042_ALERT_1_G	Calc. and Reported MoietyFormula Strings Differ	Please Check
PLAT072_ALERT_2_G	SHELXL First Parameter in WGHT Unusually Large	0.10 Report
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	7.99 Why ?
PLAT802_ALERT_4_G	CIF Input Record(s) with more than 80 Characters	1 Info
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	220 Note

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
12 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
7 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Datablock shelx - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

```
Bond precision:  C-C = 0.0084 A          Wavelength=1.54184

Cell:             a=14.8944(4)     b=9.8978(3)     c=32.5727(7)
                  alpha=90         beta=90         gamma=90
Temperature:      100 K

                  Calculated                  Reported
Volume            4801.9(2)                   4801.9(2)
Space group       P b c n                     P b c n
Hall group        -P 2n 2ab                   -P 2n 2ab
Moiety formula    C56 H46 F10 N6 O2 U         C56 H46 N6 F10, U O2
Sum formula       C56 H46 F10 N6 O2 U         C56 H46 F10 N6 O2 U
Mr                1263.02                     1263.02
Dx,g cm-3         1.747                       1.747
Z                 4                           4
Mu (mm-1)         10.303                      10.303
F000              2488.0                      2488.0
F000'             2478.86
h,k,lmax          18,12,40                    18,11,40
Nref              4839                        4750
Tmin,Tmax         0.261,0.597                 0.518,1.000
Tmin'             0.136

Correction method= # Reported T Limits: Tmin=0.518 Tmax=1.000
AbsCorr = 'G

Data completeness= 0.982          Theta(max)= 73.463

R(reflections)= 0.0375( 3785)     wR2(reflections)= 0.0947( 4750)

S = 1.100                 Npar= 344
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT976_ALERT_2_A Check Calcd Residual Density 0.70A From O1 -2.72 eA-3

Author Response: This peak is close to the U ion and is probably due to series terminat effects.

Alert level B

PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers .... 2 Check
PLAT971_ALERT_2_B Check Calcd Residual Density 1.02A From U1 3.02 eA-3

Author Response: see above

PLAT972_ALERT_2_B Check Calcd Residual Density 0.70A From O1 -2.72 eA-3

Author Response: see above

Alert level C

PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00845 Ang.
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 2.451 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 6 Report
PLAT975_ALERT_2_C Check Calcd Residual Density 0.69A From O2 1.05 eA-3
PLAT975_ALERT_2_C Check Calcd Residual Density 0.66A From O1 0.89 eA-3
PLAT975_ALERT_2_C Check Calcd Residual Density 0.99A From N2 0.64 eA-3
PLAT976_ALERT_2_C Check Calcd Residual Density 1.06A From N2 -1.19 eA-3

Author Response: This peak is close to the U ion and is probably due to series terminat effects.

PLAT976_ALERT_2_C Check Calcd Residual Density 0.73A From N1 -0.57 eA-3

Author Response: This peak is close to the U ion and is probably due to series terminat effects.

PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Note

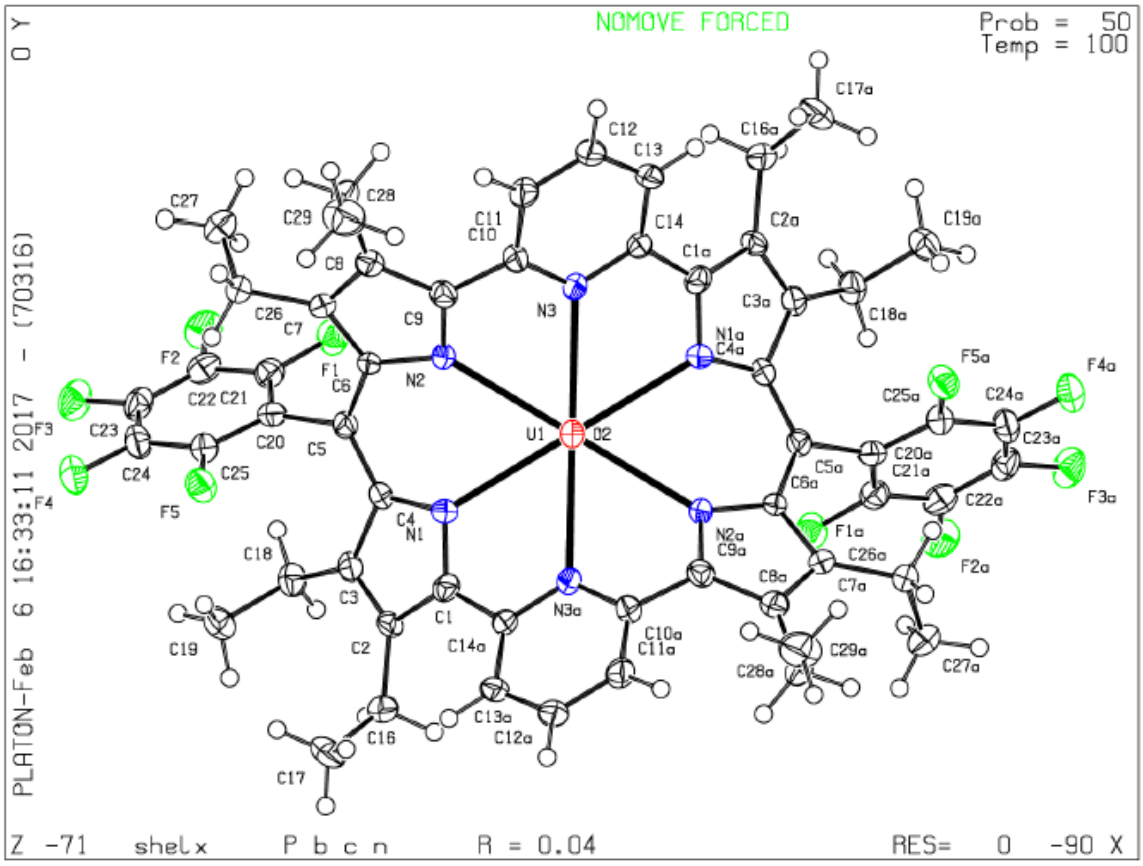
---

Alert level G

ABSTY01_ALERT_1_G Extra text has been found in the _exptl_absorpt_correction_type field, which should be only a single keyword. A literature citation should be included in the _exptl_absorpt_process_details field.
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 39.05 Why ?
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) U1 -- O2 .. 6.0 s.u.

PLATON version of 24/11/2016; check.def file version of 23/11/2016

Datablock shelx - ellipsoid plot



References & Notes

1. The presence of residual DDQ caused unsuccessful recrystallization in our hands. Thus, prepared materials were subjected to column chromatography. After flash passage through a silica gel column, the product required further purification to remove trace amounts of DDQ. This was accomplished via recrystallization from CH_2Cl_2/hexanes (1 mL/ 5 mL). It was subsequently found that purification by basic aluminum proved was more effective. In this case, after concentrating the necessary fractions the resulting solid could be simply washed with pentane (2 x 5 mL) to remove any residual organic-soluble impurities.
2. J.-i., Setsune, K. Yamato, *Chem. Commun.*, 2012, **48**, 4447.
3. Gaussian 09, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.;

Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J., Gaussian, Inc., Wallingford CT, **2009**.

4. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
5. (a) W. Kuchle, M. Dol, H. Stoll, H. Preuss, *Mol. Phys.*, 1991, **74**, 1245. (b) W. Kuchle, M. Dolg, H. Stol, H. Preuss, *J. Phys. Chem.*, 1994, **100**, 7535.
6. CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31
7. Sheldrick, G. M. *Acta Cryst.*, 2015, **A71**, 3-8. SHELXT. An Integrated Space Group and Crystal Structure Determination Program.
8. Farrugia, L. J. *J. Appl. Cryst.*, 1999, **32**, 837-838. An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data.
9. Sheldrick, G. M. (2015). SHELXL-2016/6. Acta Cryst., C71, 9-18. Spek, A. L. (1998) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.