Supporting Information for:

Radical Reductive Elimination from Tetrabenzyluranium Mediated by an Iminoquinone Ligand

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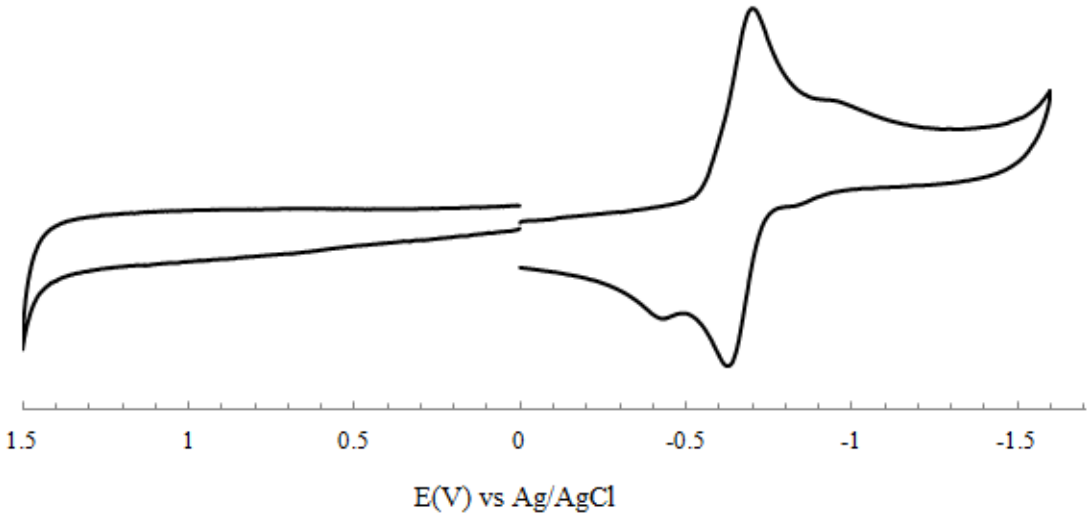

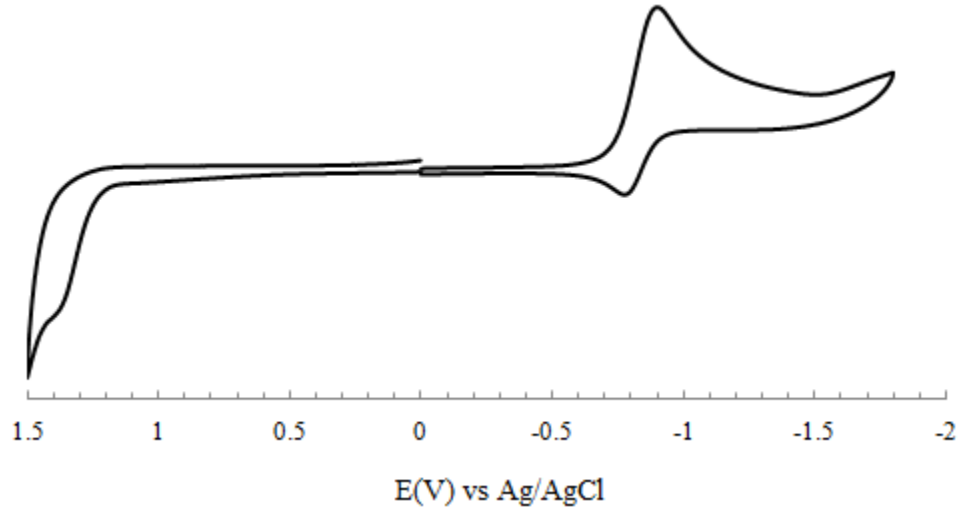

Figure S1. Top: Cyclic voltammogram of ^{dipp}iq recorded in 0.20 M THF solution of (n-Bu)$_4$NPF$_6$ at a scan rate of 0.1 V/s. $E_{1/2}$: -0.664 V. i_b/i_f: 0.815. **Bottom:** Cyclic voltammogram of ^{Mes}DAB^{Mes} recorded in 0.20 M THF solution of (n-Bu)$_4$NPF$_6$ at a scan rate of 0.1 V/s. $E_{1/2}$: -0.839. i_b/i_f: 0.462.

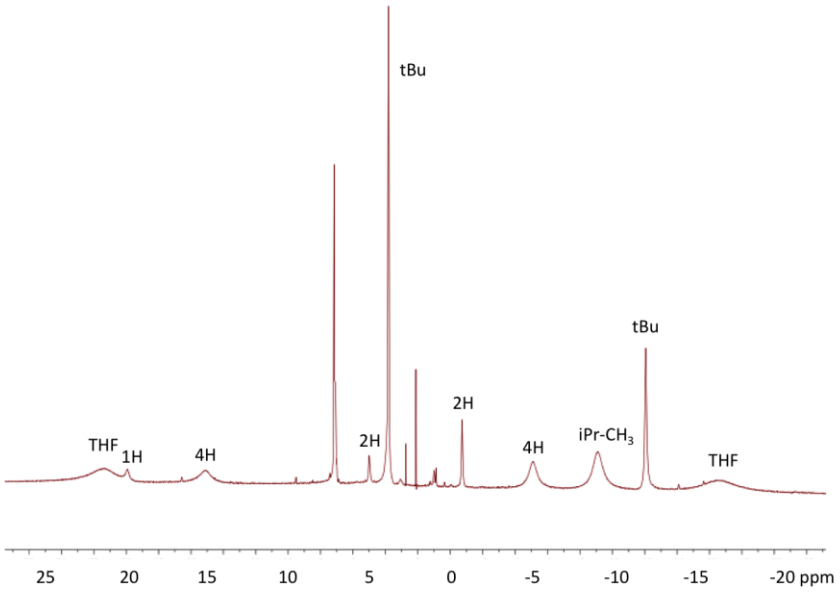

Figure S2. ^{1}H NMR spectrum (C_6D_6, 25 °C) of **2**

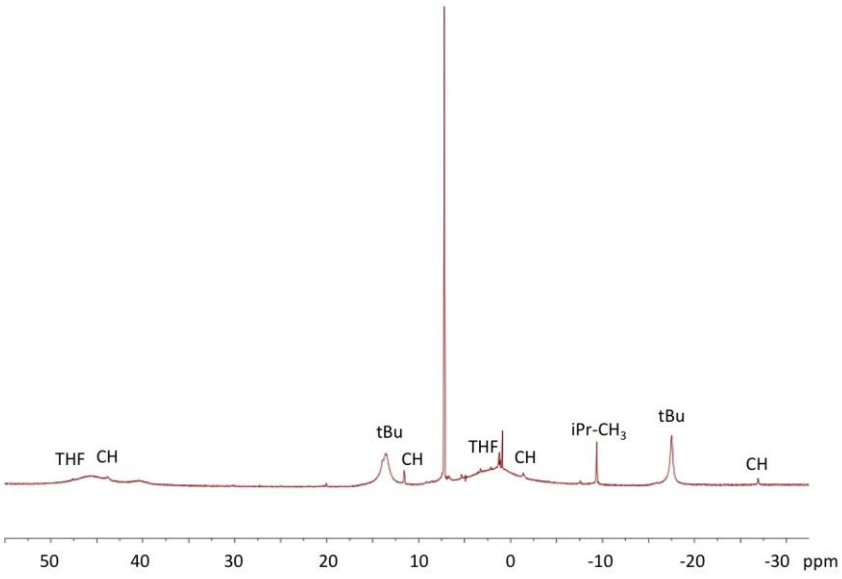

Figure S3. ^{1}H NMR spectrum (C_6D_6, 25 °C) of **3**

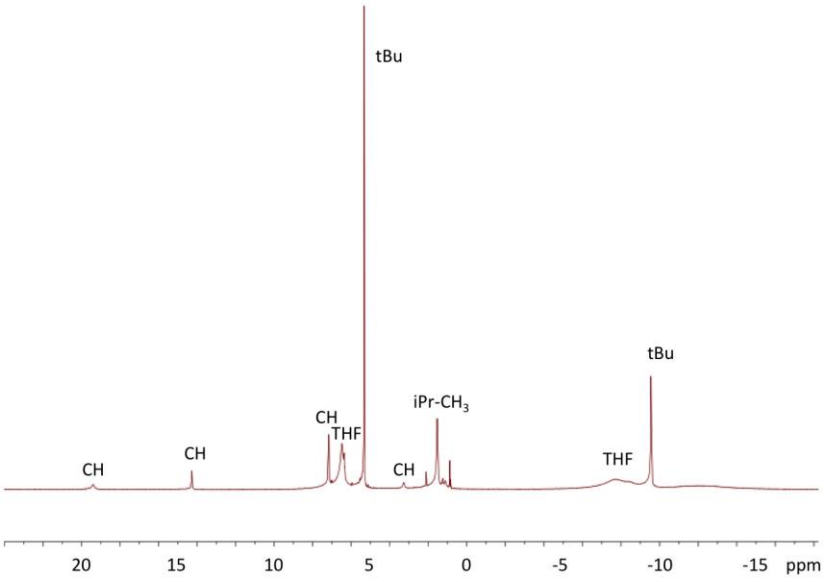

Figure S4. ^{1}H NMR spectrum (C_6D_6, 25 °C) of **4**

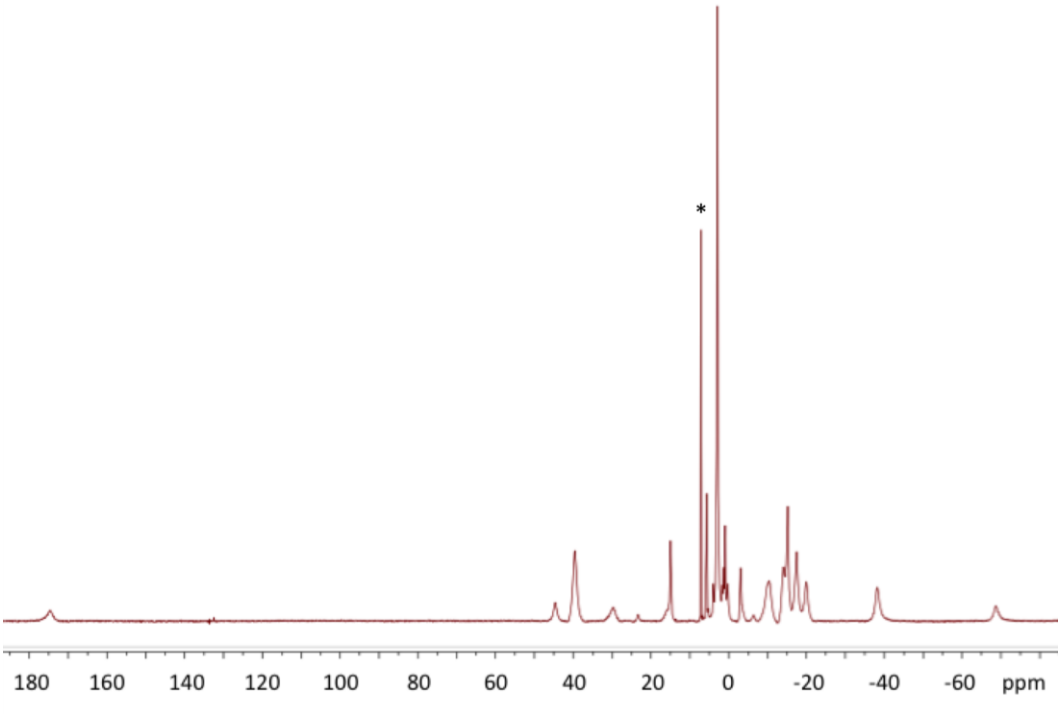

Figure S5. ^{1}H NMR spectrum (C_6D_6, 25 °C) of **5**. Residual solvent denoted as (*).

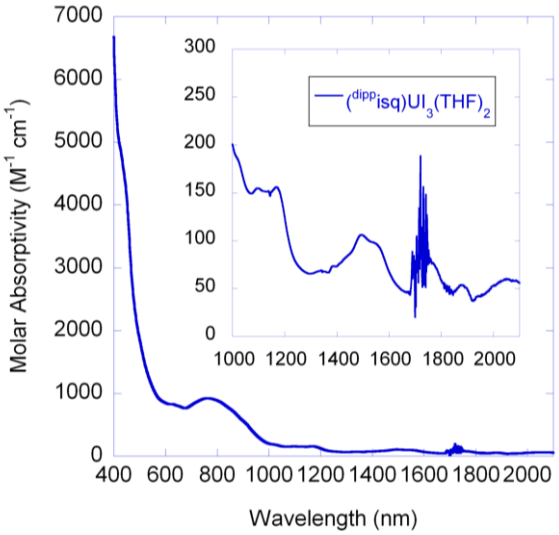

Figure S6. Electronic absorption spectrum of (^{dipp}isq)U(I)$_3$(THF)$_2$ (**3**) (blue) in THF at ambient temperature. Inset shows the near-infrared region of the spectrum. Solvent overtones are present in between 1600 and 1800 nm.

Figure S7. GC/MS data for crossover experiment. M/Z: 182 ($C_6H_5CH_2CH_2C_6H_5$), 189 ($C_6D_5CD_2CH_2C_6H_5$), 196 ($C_6D_5CD_2CD_2C_6D_5$).

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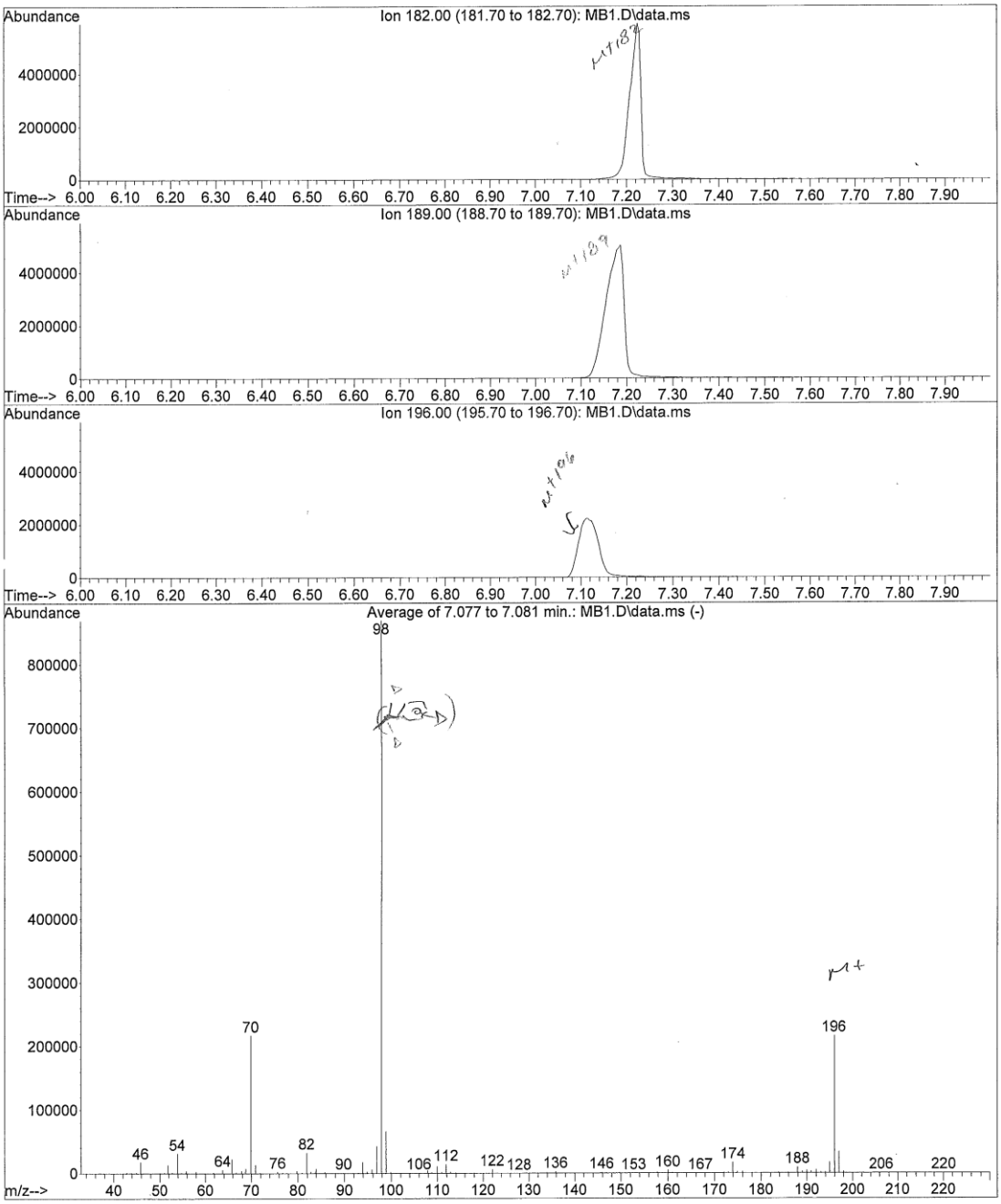

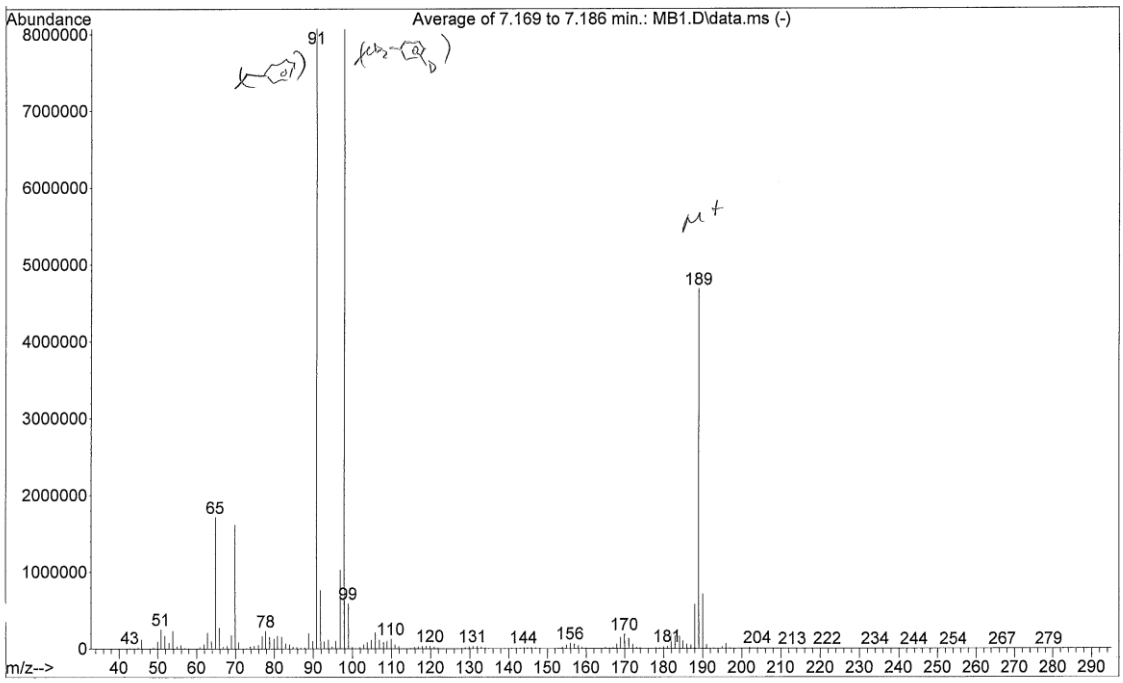
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78
110
120
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144
156
170
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234
244
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267
279
m/z-->
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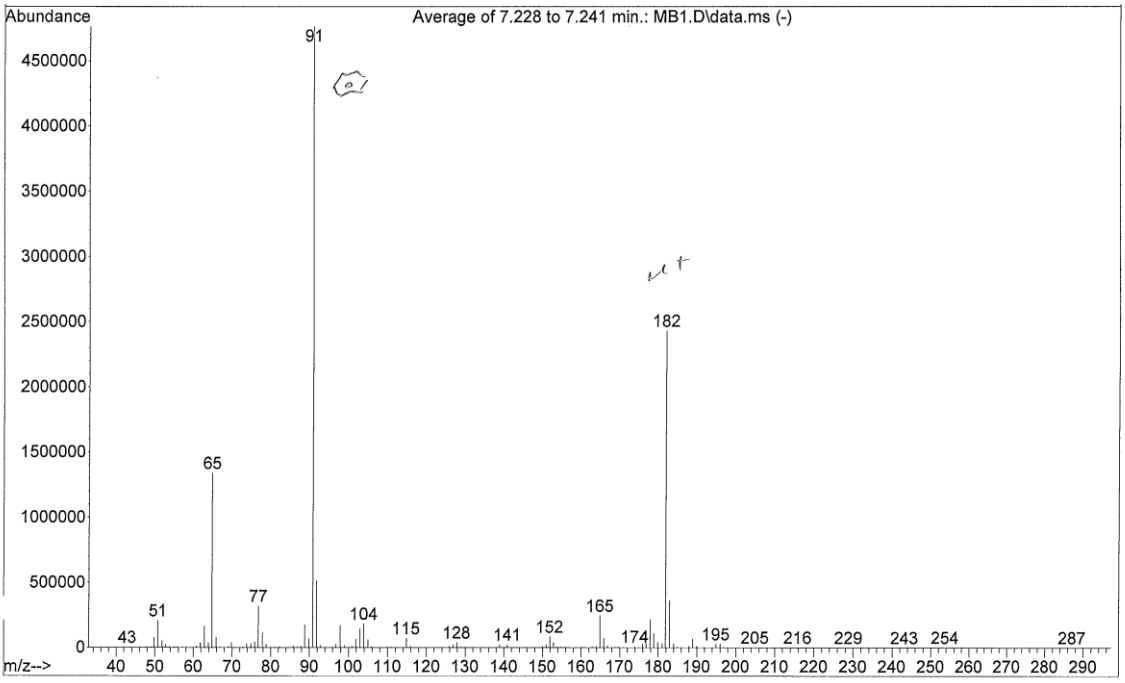
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65
77
51
104
115
128
141
152
165
174
195
205
216
229
243
254
287
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290

EXPERIMENTAL: (^{dipp}ap)U($CH_2Ph)_2(THF)_2$ (**2**)

DATA COLLECTION

A red plate of $C_{48}H_{66}NO_3U$ having approximate dimensions of 0.14 x 0.12 x 0.04 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu K_a radiation (λ = 1.54184Å) on a Rigaku Rapid II equipped with confocal optics.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 34099 reflections in the range 3 < q < 66°. The triclinic cell parameters and calculated volume are: a = 11.1218(7), b = 11.7622(7), c = 17.4818(13)Å, a = 77.253(6), b =77.037(5), g = 87.418(4)°, V = 2173.7(2)Å^3. For Z = 2 and F.W. = 944.10 the calculated density is 1.44 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[1] was 0.95° indicating moderate crystal quality. The space group was determined by the program XPREP.[2] There were no systematic absences; the space group was determined to be P -1(# 2).

The data were collected at a temperature of 150(1)K. Data were collected to a maximum 2q of 133.3°.

DATA REDUCTION

A total of 34099 reflections were collected, of which 5441 were unique. Frames were integrated with DENZO-SMN.[1]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 108.1 /mm for Cu K_a radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.478 to 0.649. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 8.0% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99.[3] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $Sw(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[s^2(Fo^2)+(0.0948P)^2+5.0051P]$ where $P=(Fo^2 +2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[4] 5441 reflections were used in the refinements. However, only the 5115 reflections with $F_o^2>2s(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 498 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S |Fo - Fc| / S Fo = 0.051$$

$$R2 = SQRT (S w (Fo^2 - Fc^2)^2 / S w (Fo^2)^2) = 0.133$$

The goodness-of-fit parameter was 1.08. The highest peak in the final difference Fourier had a height of 2.32 e/A^3. The minimum negative peak had a height of -0.69 e/A^3.

Refinement was performed on a LINUX PC using SHELX-97.[2] Crystallographic drawings were done using programs ORTEP[5] and PLUTON[6].

EXPERIMENTAL: (^{dipp}isq)$UI_3(THF)_2$ (**3**)

DATA COLLECTION

A brown plate of $C_{34}H_{53}I_3NO_3U,C_4H_8O$ having approximate dimensions of 0.20 x 0.15 x 0.08 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu K_a radiation (λ = 1.54184Å) on a Rigaku Rapid II equipped with confocal optics.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 33999 reflections in the range 2 < q < 68°. The monoclinic cell parameters and calculated volume are: a = 11.1652(3), b = 11.1044(3) c = 35.4297(10) Å, b = 92.594(2)°, V = 4388.2(2)$Å^3$. For Z = 4 and F.W. = 1214.66 the calculated density is 1.84 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[1] was 0.42° indicating good crystal quality. The space group was determined by the program XPREP.[2] From the systematic presences of:

h0l l=2n
0k0 k=2n

and from subsequent least-squares refinement, the space group was determined to be P 1 21/c 1(# 14).

The data were collected at a temperature of 150(1)K. Data were collected to a maximum 2q of 136.8°.

DATA REDUCTION

A total of 33999 reflections were collected, of which 7882 were unique. Frames were integrated with DENZO-SMN.[1]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 272.5 /mm for Cu K_a radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.073 to 0.113. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 6.6% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program PATTY in DIRDIF99.[3] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $Sw(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[s^2(Fo^2)+(0.0908P)^2+18.0363P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[4] 7882 reflections were used in the refinements. However, only the 7628reflections with $F_o^2>2s(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 434 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S\ |Fo - Fc| / S\ Fo = 0.046$$

$$R2 = SQRT\ (\ S\ w\ (\ Fo^2 - Fc^2\ )^2 / S\ w\ (Fo^2)^2\ ) = 0.130$$

The goodness-of-fit parameter was 1.10. The highest peak in the final difference Fourier had a height of 2.85 e/A^3. The minimum negative peak had a height of -3.56 e/A^3.

Refinement was performed on a LINUX PC using SHELX-97.[2] Crystallographic drawings were done using programs ORTEP[5] and PLUTON[6].

EXPERIMENTAL: (^{dipp}ap)UI(CH_2Ph)$(THF)_2$ (**5**)

DATA COLLECTION

A red plate of $C_{41}H_{60}INO_3U,0.5(C_7H_8)$ having approximate dimensions of 0.20 x 0.14 x 0.03 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Cu K_a radiation (λ = 1.54184Å) on a Rigaku Rapid II equipped with confocal optics.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of121346 reflections in the range $2 < q < 68°$. The monoclinic cell parameters and calculated volume are: a = 28.2048(9), b = 15.3209(5) c = 22.6313(7) Å, b = 108.301(2)°, V = 9284.8(5)Å^3. For Z = 8 and F.W. = 1025.95 the calculated density is 1.47 g/cm^3. The refined mosaicity from DENZO/SCALEPACK[1] was 0.41° indicating good crystal quality. The space group was determined by the program XPREP.[2] From the systematic presences of:

h0l l=2n
0k0 k=2n

and from subsequent least-squares refinement, the space group was determined to be P 1 21/c 1(# 14).

The data were collected at a temperature of 150(1)K. Data were collected to a maximum 2q of 136.7°.

DATA REDUCTION

A total of121346 reflections were collected, of which 13745 were unique. Frames were integrated with DENZO-SMN.[1]

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 153.2 /mm for Cu K_a radiation. An empirical absorption correction using SCALEPACK[1] was applied. Transmission coefficients ranged from 0.161 to 0.631. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 10.9% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $Sw(|Fo|^2-|Fc|^2)^2$ and the weight w is defined as $1/[s^2(Fo^2)+(0.1441P)^2+25.1546P]$ where $P=(Fo^2+2Fc^2)/3$. Scattering factors were taken from the "International Tables for Crystallography".[4] 13745 reflections were used in the refinements. However, only the 11340reflections with $F_o^2>2s(F_o^2)$ were used in, calculating R1. The final cycle of refinement included 932 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = S\ |Fo - Fc| / S\ Fo = 0.070$$

$$R2 = SQRT\ (\ S\ w\ (\ Fo^2 - Fc^2\ )^2 / S\ w\ (Fo^2)^2\ ) = 0.201$$

The goodness-of-fit parameter was 1.08. The highest peak in the final difference Fourier had a height of 1.86 e/A^3. The minimum negative peak had a height of -2.08 e/A^3. Residual electron density was adjusted using the SQUEEZE option in PLATON (ref 5).

Refinement was performed on a LINUX PC using SHELX-97.[2] Crystallographic drawings were done using programs ORTEP[5] and PLUTON[6].

Experimental for Magnetic Measurements:

Magnetism data of crystalline powdered samples (20 – 30 mg) were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe (2 – 300 K for **2** and **3**). Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment (χ_{dia} = – 550.04 × 10^{-6} cm^3mol^{-1} (**2**), – 542.15 × 10^{-6} cm^3mol^{-1} (**3**)) by using tabulated Pascal constants and the effect of the blanksample holders (gelatin capsule/ straw).[7] Samples used for magnetization measurements were recrystallized multiple times and checked for chemical composition and purity by elemental analysis (C, H, N) and ^{1}H NMR spectroscopy. Data reproducibility was also carefully checked on independently synthesized samples. "

References:

[1] Z. M. Otwinowski, W., *Methods Enzymol.* **1997**, *276*, 307.
[2] G. M. Sheldrick, *Acta Crystallographica Section A* **2008**, *112*, 64.
[3] P. T. B. Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M., *DIRDIF2008 Program System*, University of Nijmegen: The Netherlands, **2008**.
[4] *International Tables for Crystallography, Vol. C*, Kluwer Academic Publishers, Utrecht, The Netherlands, **1992**.
[5] C. K. Johnson, *ORTEPII, Report ORNL-5138*, Oak Ridge National Laboratory, Tennessee, USA, **1976**.
[6] A. L. Spek, *J. Apply. Cryst.* **2003**, *36*, 7.
[7] G. A. Bain and J. F. Berry, *J. Chem. Educ.* **2008**, *85*, 532-536.