

# Reductive Heterocoupling Mediated by $\text{Cp}^*_2\text{U}(2,2'\text{-bpy})$

*Adil Mohammad, Dennis P. Cladis, William P. Forrest, Phillip E. Fanwick, and Suzanne C. Bart\**

Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907

[sbart@purdue.edu](mailto:sbart@purdue.edu)

## Table of Contents

General Considerations.....	Page 2
Preparation of $\text{Cp}^*_2\text{UI}(\text{THF})$ .....	Page 4
Preparation of $\text{Cp}^*_2\text{U}(2,2'\text{-bpy})$ .....	Page 5
Preparation of 3a-3d.....	Page 5-7
UV-Visible spectrum of 2.....	Page 7
Near IR spectrum of 2.....	Page 8
$^1\text{H}$ - $^1\text{H}$ correlation (COSY) Spectroscopy of 3a.....	Page 9
$^1\text{H}$ - $^1\text{H}$ correlation (COSY) Spectrum of 3a.....	Page 10
Crystallographic Experimental Information for 3a.....	Page 13
References.....	Page 14

## Experimental Section

**General Considerations.** All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as two  $-35^{\circ}\text{C}$  freezers for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.<sup>1</sup> Benzene- $d_6$  was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze-pump-thaw cycles. 2,2'-Bipyridine and benzophenone were purchased from Sigma Aldrich, dried overnight on the Schlenk line, and recrystallized from dry diethyl ether. Furfuraldehyde and *p*-tolualdehyde were purchased from Aldrich, dried over magnesium sulfate, filtered and degassed by three freeze-pump-thaw cycles. Acetone and acetone- $d_6$  were purchased from Aldrich, dried over  $\text{CaH}_2$ , and vacuum transferred before use. Depleted uranium was purchased from Manufacturing Sciences in Oak Ridge, TN. 1,2,3,4,5-Pentamethylcyclopentadiene ( $\text{Cp}^*\text{H}$ ) was purchased from Norquay Technology Inc. Potassium pentamethylcyclopentadienide ( $\text{KCp}^*$ )<sup>2</sup>,  $\text{KC}_8$ <sup>3</sup> and  $\text{U}_3(1,4\text{-dioxane})_{1.5}$ <sup>4</sup> were prepared according to literature procedures.

$^1\text{H}$  NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.992 MHz. All chemical shifts are reported relative to the peak for  $\text{SiMe}_4$  using  $^1\text{H}$  (residual) chemical shifts of the solvent as a secondary standard. The spectra for paramagnetic molecules were obtained using an acquisition time of 0.5, thus the peak widths reported have an error of  $\pm 2$  Hz. For paramagnetic molecules, the  $^1\text{H}$  NMR data are reported with the chemical shift, followed by the peak width at half height in Hertz, the integration value, and where possible, the peak

assignment. Pulsed-field gradient COSY spectra were obtained using a Bruker DRX 500 spectrometer equipped with a 5mm Z-gradient TX1 cryoprobe. Spectra were acquired using sweep widths of 47619 Hz in both dimensions. In F2, 4 scans per increment were acquired using 4096 data points and a relaxation delay of 1 second. In F1, 512 increments were acquired. The raw data were Fourier transformed into a final data matrix consisting of 4K points in F2 and 2K points in F1. Infra-red spectra were recorded using a Perkin-Elmer FT-IR RX I spectrometer. Samples were made by crushing the solids, mixing with dry KBr, and pressing into a pellet. Electronic absorption spectroscopic measurements were recorded at 294 K in toluene in 1 cm quartz cuvettes on a Jasco V-670 spectrophotometer. Elemental analyses were obtained at Midwest Microlab, LLC, in Indianapolis, IN.

Single crystals for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of a Rigaku Rapid II image plate diffractometer equipped with a MicroMax002+ high intensity copper X-ray source with confocal optics. Preliminary examination and data collection were performed with CuK $\alpha$  radiation ( $\lambda = 1.54184$  Å). Cell constants for data collection were obtained from least-squares refinement. The space group was identified using the program XPREP.<sup>5</sup> The structures were solved using the structure solution program PATTY in DIRDIFF99.<sup>6</sup> Refinement was performed on a LINUX PC using SHELX-97.<sup>5</sup> The data were collected at a temperature of 150(1) K.

**Preparation of Cp\*<sub>2</sub>UI(THF) (1).** Prepared according to the modified literature procedure.<sup>7</sup> A 20-mL scintillation vial was charged with 0.300 g (0.399 mmol) of UI<sub>3</sub>(1,4-dioxane)<sub>1.5</sub> and approximately 10 mL of THF were stirred for one hour. Next, 0.139 g (0.799 mmol) of solid KCp\* was added to the purple solution, which caused a color change to green. This solution was stirred for 30 minutes after which a white precipitate was formed, and the reaction mixture was

filtered through Celite using THF, followed by removal of the volatiles *in vacuo*. The solid was washed with 1 mL pentane and then dried to obtain a bright green solid (0.250 g, 0.350 mmol, 83%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = -55.59$  (168, 4H,  $-\text{CH}_2$ , THF),  $-17.79$  (73, 4H,  $-\text{CH}_2$ , THF),  $-1.07$  (123, 30H,  $-\text{CH}_3$ ,  $\text{Cp}^*$ ).

**Preparation of  $\text{Cp}^*_2\text{U}(2,2'\text{-bpy})$  (**2**).** Prepared according to modified literature procedure.<sup>8</sup> A 20 mL scintillation vial was charged with 0.210 g (0.297 mmol) of  $\text{Cp}^*_2\text{UI}(\text{THF})$  (**1**) in 10 mL toluene and solid 0.046 g (0.297 mmol) 2,2'-bipyridine and 0.080 g (0.594 mmol) of  $\text{KC}_8$  were added while stirring. The resulting mixture was stirred at room temperature for 3 h. The KI and graphite were removed by filtration over Celite and a dark green powder was obtained after removal of toluene *in vacuo* (0.170 g, 0.256 mmol, 86%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = -93.89$  (17, 2H,  $-\text{CH}$ , bpy),  $-81.31$  (16, 2H,  $-\text{CH}$ , bpy),  $-41.35$  (21, 2H,  $-\text{CH}$ , bpy),  $-19.95$  (17, 2H,  $-\text{CH}$ , bpy),  $0.138$  (6, 30H,  $-\text{CH}_3$ ,  $\text{Cp}^*$ ). IR (KBr pellet): bipy radical,  $1499, 916\text{ cm}^{-1}$ ;  $\mu_{\text{eff}} = 2.37\ \mu\text{B}$ .

**One pot preparation of  $\text{Cp}^*_2\text{U}(2,2'\text{-bpy})$  (**2**).** A 20 mL scintillation vial was charged with 0.200 g (0.266 mmol) of  $\text{UI}_3(\text{dioxane})_{1.5}$ , and stirred in 5 mL THF for one hour. To the mixture was added solid 0.092 g (0.527 mmol) of  $\text{KCp}^*$ , resulting in an immediate color change from bright blue to bright green. After 2 hours of additional stirring, 0.041 g (0.266 mmol) of 2,2'-bipyridine followed by 0.072 g (0.527 mmol) of  $\text{KC}_8$  were added and stirred for an additional 3 hours at room temperature. The resulting, KI and graphite were filtered through Celite and the volatiles were removed *in vacuo* to yield dark green solid. The solid was washed with 3 mL pentane and dried to obtain a dark green solid (0.150 g, 0.225 mmol, 85%). The  $^1\text{H NMR}$  of the solid matches with the spectra of **2** made by the above mentioned route.

**Preparation of 3a.** A 20 mL scintillation vial was charged with 0.340 g (0.511 mmol) of **Cp\*<sub>2</sub>U(2,2'-bpy) (2)** and 0.061 g (0.511 mmol) of *p*-tolualdehyde was added, using a microsyringe, in 10 mL toluene. Color of the solution immediately changed to dark pink-red and was stirred for 3 hours. A dark red-pink solid (0.360 g, 0.459 mmol, 89%) was isolated by removing the solvent *in vacuo*. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25° C): δ = -6.95 (9, 1H, -O-CH-), -6.56 (5, 1H, -CH, bpy), -3.93 (18, 1H, -CH, bpy), 0.340 (4, 15H, -CH<sub>3</sub>, Cp\*), 1.40 (4, 15H, -CH<sub>3</sub>, Cp\*), -6.08 (4, 3H, Ar-CH<sub>3</sub>), 8.31 (4, 1H, -CH, bpy), 13.74 (4, 1H, -CH, bpy), 14.04 (12, 2H, Ar-H), 16.30 (14, 1H, -CH, bpy), 16.37 (14, 1H, -CH, bpy), 26.63 (7, 2H, Ar-H), 60.34 (23, 1H, -CH, bpy), 82.24 (21, 1H, -CH, bpy). IR (KBr pellet): No C=O stretch; μ<sub>eff</sub> = 2.04 μ<sub>B</sub>. Analysis for C<sub>38</sub>H<sub>46</sub>N<sub>2</sub>O<sub>2</sub>U: Calcd. C, 58.15; H, 5.91; N, 3.57. Found C, 57.74; H, 5.69; N, 3.50.

**Preparation of 3b.** A 20 mL scintillation vial was charged with 0.150 g (0.225 mmol) of **Cp\*<sub>2</sub>U(2,2'-bpy) (2)** in 10 mL toluene and added 0.021 g (0.225 mmol) of furfuraldehyde, using a microsyringe; resulting in immediate color change from dark green to dark red-pink. The solvent was removed *in vacuo* to yield dark red-pink solid (0.15g, 0.197mmol, 87%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25° C): δ = -7.34 (10, 1H, -O-CH-), -6.96 (14, 1H, -CH, bpy), -3.42 (21, 1H, -CH, bpy), 1.13 (6, 15H, -CH<sub>3</sub>, Cp\*), 1.96 (6, 15H, -CH<sub>3</sub>, Cp\*), 12.12 (7, 1H, ), 12.70 (5, 1H, ), 13.75 (16, 1H, ), 13.83 (5, 1H, ), 17.06 (21, 1H, ), 18.36 (7, 1H, ), 52.2 (23, 1H, -CH, bpy), 60.96 (22, 1H, -CH, bpy). IR (KBr pellet): No C=O stretch; μ<sub>eff</sub> = 2.07 μ<sub>B</sub>. Analysis for C<sub>35</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>U: Calcd. C, 55.25; H, 5.56; N, 3.68. Found C, 55.16; H, 5.04; N, 3.77.

**Preparation of 3c.** A 20 mL scintillation vial was charged with 0.210 g (0.316 mmol) of **Cp\*<sub>2</sub>U(2,2'-bpy) (2)** in 10 mL toluene. While stirring, a few drops of acetone (excess) were added using microsyringe. The color of the resulting mixture immediately changed from dark green to dark purple-pink and the mixture was stirred for 4 hours. The solvent was removed *in*

*vacuo* to yield bright purple solid (0.21 g, 0.290 mmol, 92%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = -6.44$  (13, 1H, -CH, bpy),  $-4.77$  (10, 1H, -CH, bpy),  $-0.883$  (10, 1H, -CH, bpy)  $-0.63$  (6, 15H, -CH<sub>3</sub>, Cp\*),  $0.009$  (7, 15H, -CH<sub>3</sub>, Cp\*),  $14.37$  (17, 1H, -CH, bpy),  $15.42$  (16, 1H, -CH, bpy),  $19.63$  (16, 1H, -CH, bpy),  $25.72$  (13, 1H, -CH, bpy),  $28.92$  (9, 3H, acetone-CH<sub>3</sub>),  $36.38$  (8, 3H, acetone-CH<sub>3</sub>),  $105.97$  (26, 1H, bipy-H). IR (KBr pellet): No C=O stretch;  $\mu_{\text{eff}} = 2.49 \mu_{\text{B}}$ . Analysis for  $\text{C}_{33}\text{H}_{44}\text{N}_2\text{OU}$ : Calcd. C, 54.84; H, 6.14 ; N, 3.88. Found C, 54.51; H, 5.78 ; N, 3.74.

**Preparation of 3c-d<sub>6</sub>.** Same procedure as above.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = -6.42$  (4, 1H, -CH, bpy),  $-4.87$  (4, 1H, -CH, bpy),  $-1.02$  (4, 1H, -CH, bpy),  $-0.68$  (4, 15H, -CH<sub>3</sub>, Cp\*),  $0.06$  (4, 15H, -CH<sub>3</sub>, Cp\*),  $14.49$  (3, 1H, -CH, bpy),  $15.32$  (4, 1H, -CH, bpy),  $19.88$  (13, 1H, -CH, bpy),  $25.28$  (10, 1H, -CH, bpy),  $107.15$  (22, 1H, -CH, bpy);  $^2\text{H}$  NMR (PhMe,  $25^\circ\text{C}$ ):  $\delta = 28.78$  (acetone-CD<sub>3</sub>),  $36.30$  (acetone-CD<sub>3</sub>).

**Preparation of 3d.** To a 20 mL scintillation vial, was added 0.250 g (0.376 mmol) of  $\text{Cp}^*_2\text{U}(2,2'\text{-bpy})$  (**2**) and 0.068 g (0.376 mmol) of solid benzophenone, in 10 mL toluene. The color of solution changed immediately from dark green to purple and was stirred for 2 hours. Removing of solvent *in vacuo* yielded purple solid (0.300 g, 0.354 mmol, 94%) as product.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = -5.60$  (5, 1H, -CH, bpy),  $1.39$  (3, 15H, -CH<sub>3</sub>, Cp\*),  $1.94$  (3, 15H, -CH<sub>3</sub>, Cp\*),  $5.91$  (19, 1H, -CH, bpy),  $7.71$  (16, 1H, -CH, bpy),  $9.16$  (4, 1H, Ar-H),  $9.74$  (5, 1H, -CH, bpy),  $10.08$  (4, 1H, Ar-H),  $10.62$  (19, 1H, Ar-H),  $18.84$  (22, 1H, -CH, bpy),  $19.01$  (22, 2H, Ar-H),  $19.95$  (21, 2H, Ar-H),  $46.54$  (12, 1H, -CH, bpy),  $51.19$  (25, 1H, -CH, bpy). IR (KBr pellet): No C=O stretch;  $\mu_{\text{eff}} = 1.93 \mu_{\text{B}}$ . Analysis for  $\text{C}_{43}\text{H}_{48}\text{N}_2\text{OU}$ : Calcd. C, 60.98; H, 5.71; N, 3.31. Found C, 60.69; H, 5.62; N, 3.46.

Figure S1. UV-Visible spectrum of **2** in toluene at 294 K.

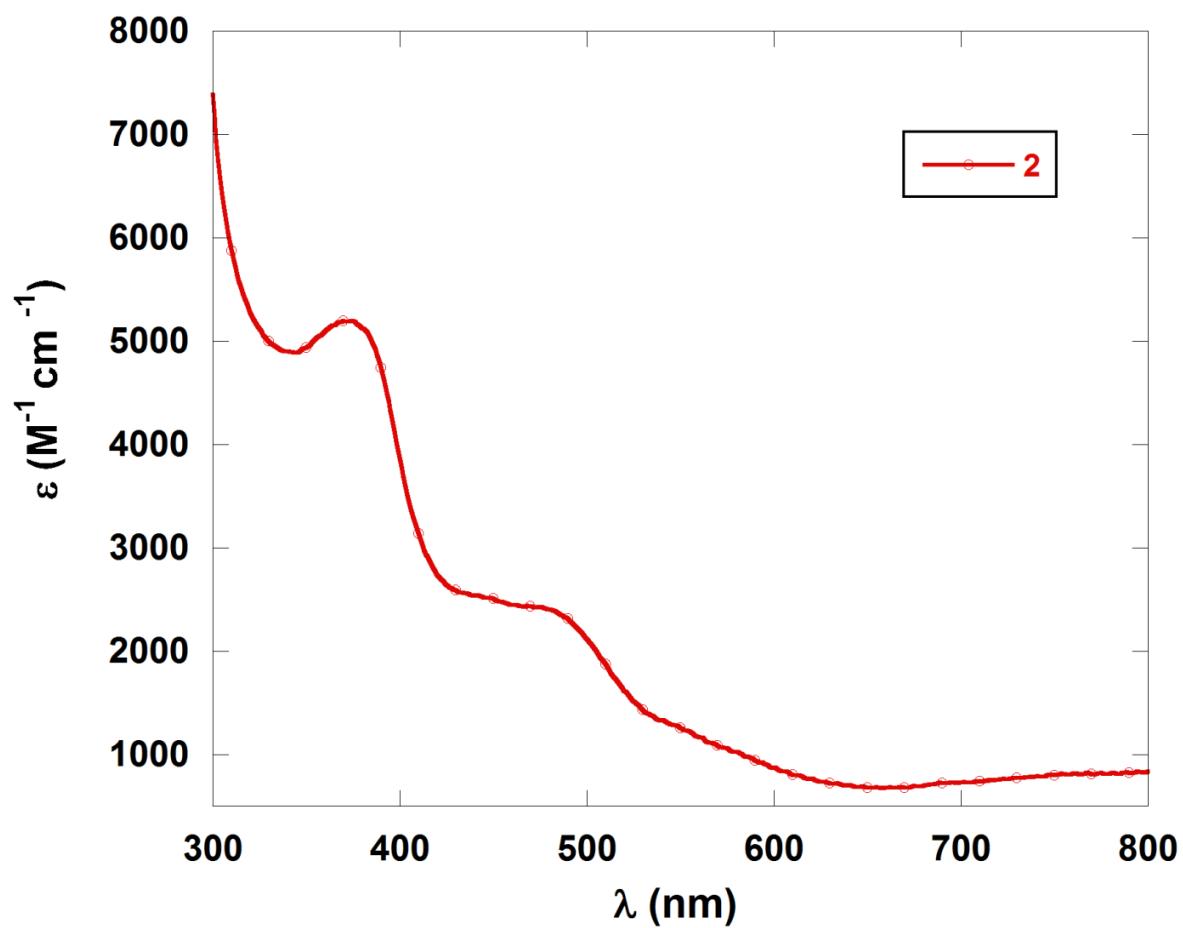
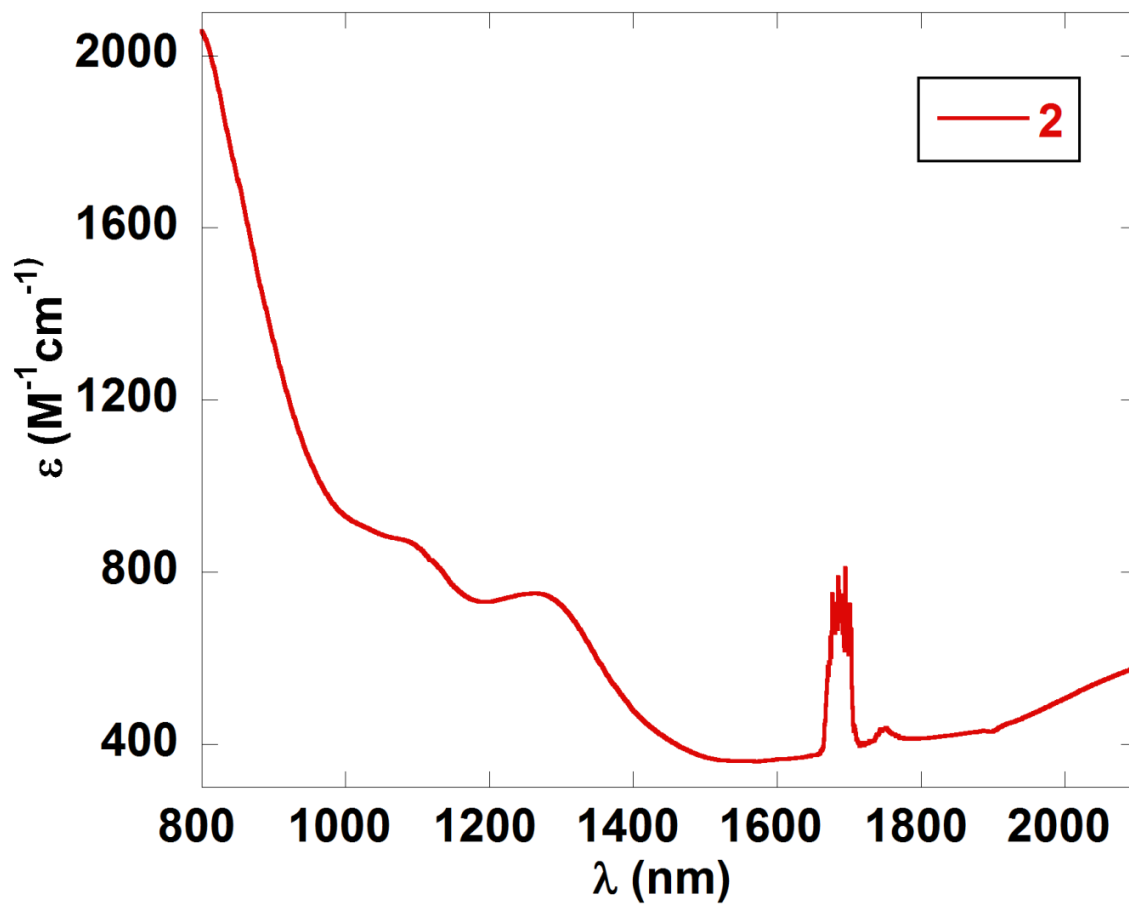


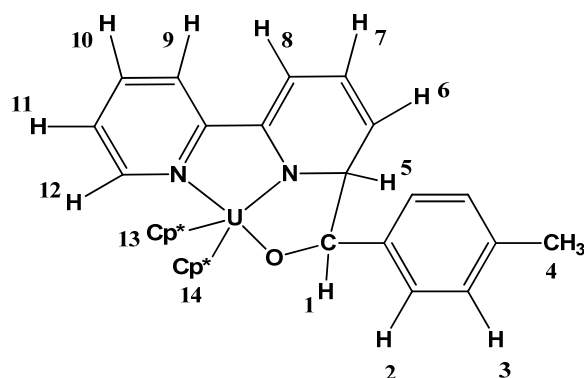
Figure S2. Near-IR spectrum for **2** in toluene at 294 K.



Note: Sharp peaks at ~1650-1750 nm are due to the second harmonic of toluene solvent.

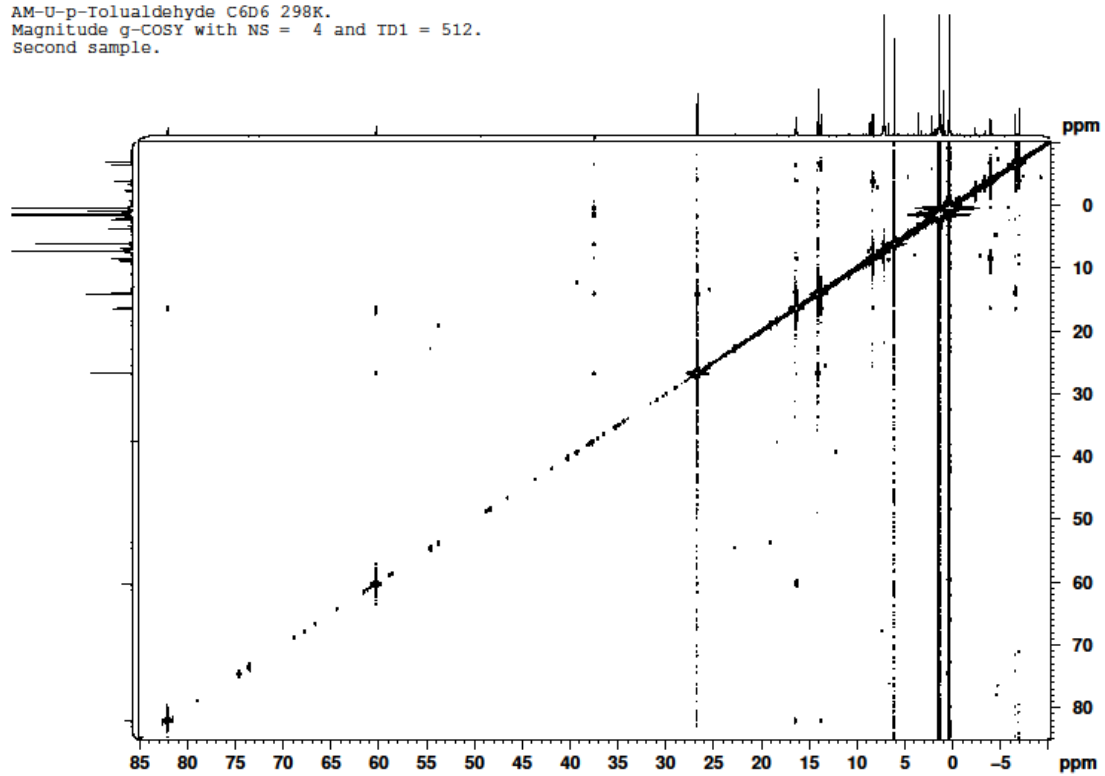


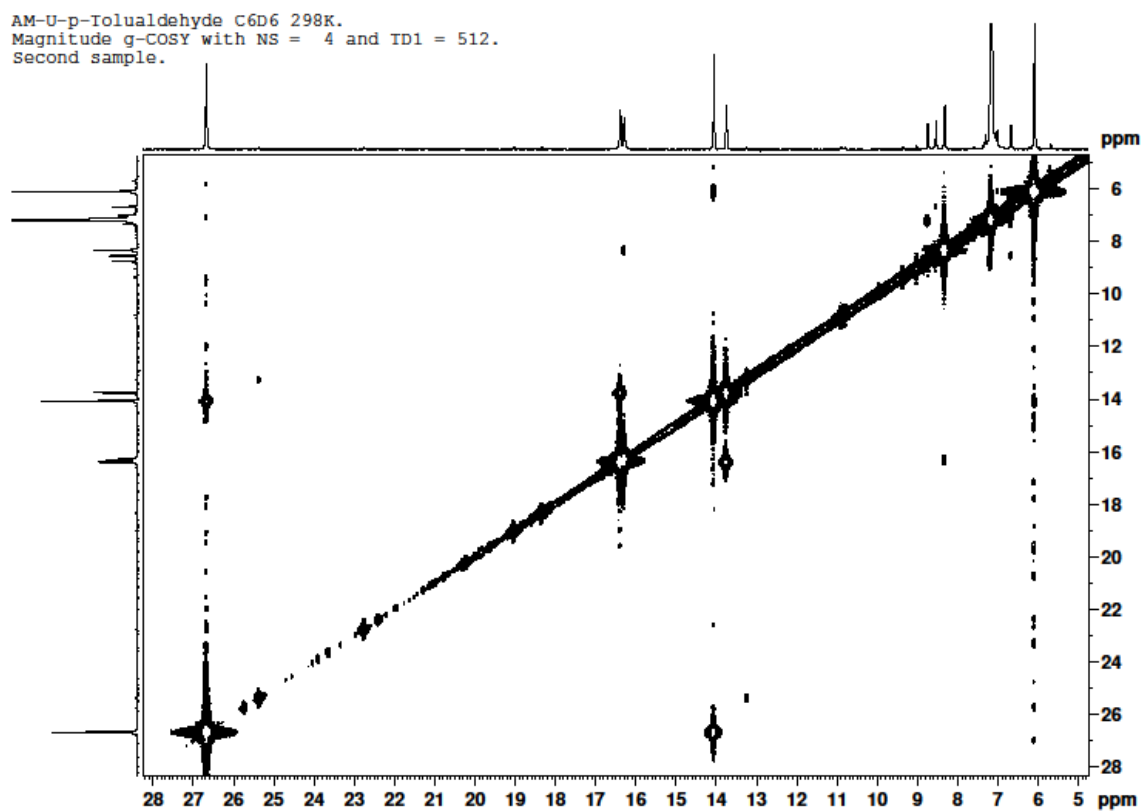
**Figure S3.** Structure of **3a** for COSY spectroscopy.



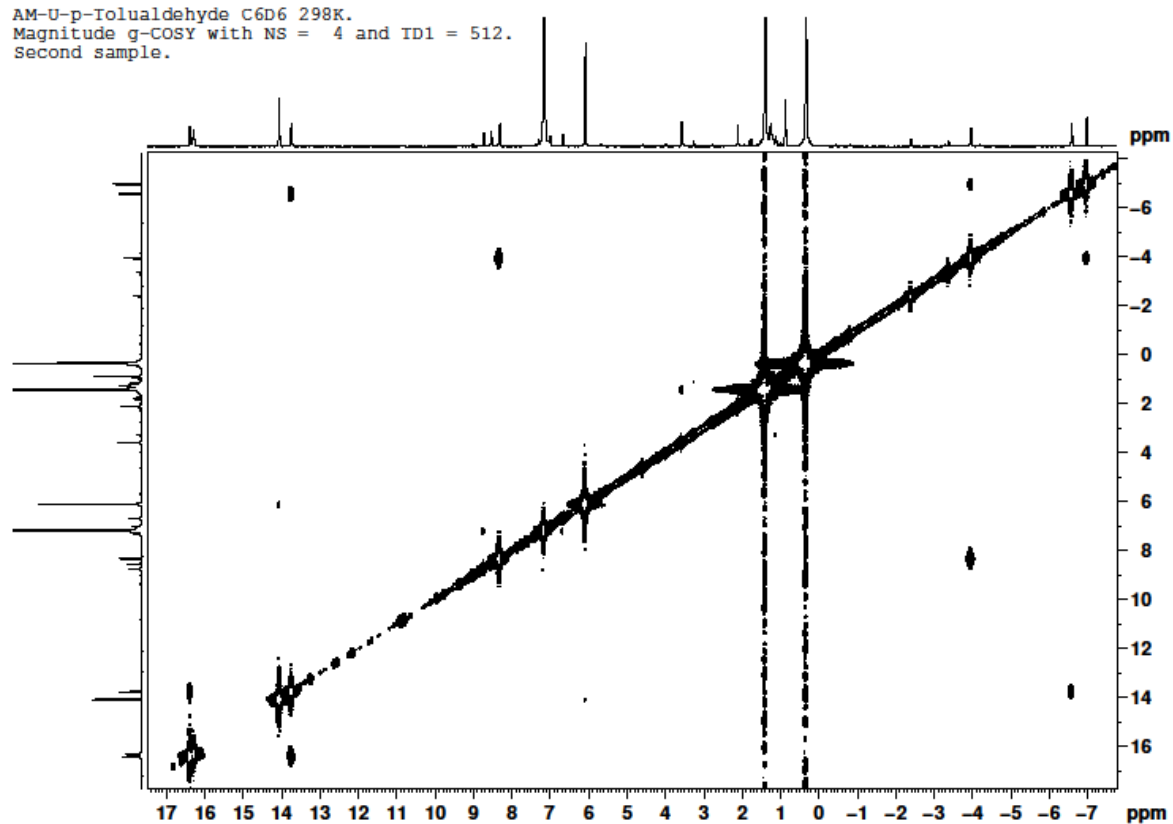
**$^1\text{H}$ - $^1\text{H}$  correlation (COSY) Spectroscopy of **3a**.**  $^1\text{H}$ - $^1\text{H}$  correlation (COSY) experiments were done to thoroughly assign the NMR spectrum of **3a**. Proton H-1 is closest to the uranium centre and appears as a singlet at -6.98 ppm. This proton has only one cross peak in the COSY spectrum and should correspond to the proton H-5 at -3.93 ppm. The proton H-5 is connected to protons H-1 (-6.98 ppm) and H-6 (8.33 ppm) and COSY spectrum shows these two peaks correlated. Proton H-6 shows two cross peaks for H-5 and H-7 (16.30 ppm) and H-7 is further correlated to H-8. Proton H-8 (60.10 confirm) is connected to only one proton H-7 and should have only one peak correlated. Proton H-12 is also in proximity to the uranium centre in complex **3a** and appears at -6.59 ppm. This proton H-12 shows only one cross peak at 13.75 ppm and therefore this peak corresponds to proton H-11. Proton H-11 has two neighboring protons H-12 and H-10 and shows these two cross peaks in the COSY spectrum. The peak at 16.36 ppm corresponds to proton H-10. Proton H-10 is further connected to proton H-9 (80.10 ppm confirm) and this proton H-9 has only one cross peak i.e. for H-10 proton. The protons for the *p*-tolyl group H-2 and H-3 are correlated to one another and therefore appear at 14.06 and 26.67 ppm. The methyl group of the *p*-tolyl group (H-4) appears at 6.09 ppm.

AM-U-p-Tolualdehyde C6D6 298K.  
Magnitude g-COSY with NS = 4 and TD1 = 512.  
Second sample.





AM-U-p-Tolualdehyde C6D6 298K.  
Magnitude g-COSY with NS = 4 and ID1 = 512.  
Second sample.



## X-RAY DATA COLLECTION

A violet needle of **3a** ( $C_{38}H_{47}N_2OU$ ) \*  $C_{10}H_8N_2$  having approximate dimensions of 0.50 x 0.20 x 0.14 mm was mounted on a fiber in a random orientation. Preliminary examination and data collection were performed Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073\text{\AA}$ ) on a Nonius KappaCCD equipped with a graphite crystal, incident beam monochromator.

Cell constants for data collection were obtained from least-squares refinement, using the setting angles of 25742 reflections in the range  $2 < \theta < 25^{\circ}$ . The triclinic cell parameters and calculated volume are:  $a = 9.9120(4)$ ,  $b = 10.4913(5)$ ,  $c = 17.3261(9)\text{\AA}$ ,  $\alpha = 86.613(3)$ ,  $\beta = 88.157(2)$ ,  $\gamma = 82.654(2)^{\circ}$ ,  $V = 1783.27(14)\text{\AA}^3$ . For  $Z = 1$  and F.W. = 1727.87 the calculated density is  $1.61\text{ g/cm}^3$ . The refined mosaicity from DENZO/SCALEPACK<sup>9</sup> was  $2.43^{\circ}$ . The space group was determined by the program ABSEN<sup>10</sup>. There were no systematic absences; the space group was determined to be  $P-1(\#2)$ . The data were collected at a temperature of  $150(1)\text{K}$ . Data were collected to a maximum  $2\theta$  of  $50.8^{\circ}$ .

## DATA REDUCTION

A total of 25742 reflections were collected, of which 4633 were unique. Frames were integrated with DENZO-SMN<sup>9</sup>.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is  $45.9\text{ /mm}$  for Mo  $K_{\alpha}$  radiation. An empirical absorption correction using SCALEPACK<sup>9</sup> was applied. Transmission coefficients ranged from 0.432 to 0.526. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 9.4% 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  $\sum w(|F_o|^2 -$

$|F_c|^2$ )<sup>2</sup> and the weight  $w$  is defined as  $1/[s^2(F_o^2)+(0.0886P)^2+30.6475P]$  where  $P=(F_o^2 +2F_c^2)/3$ . Scattering factors were taken from the "International Tables for Crystallography"<sup>12</sup>. 4633 reflections were used in the refinements. However, only the 4291 reflections with  $F_o^2 > 2s(F_o^2)$  were used in, calculating R1. The final cycle of refinement included 444 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of:

$$R1 = \sum |F_o - F_c| / \sum F_o = 0.075$$

$$R2 = \text{SQRT} ( \sum w ( F_o^2 - F_c^2 )^2 / \sum w ( F_o^2 )^2 ) = 0.185$$

The goodness-of-fit parameter was 1.24. The highest peak in the final difference Fourier had a height of 3.83 e/A<sup>3</sup>. The minimum negative peak had a height of -2.00 e/A<sup>3</sup>.

Refinement was performed on a LINUX PC using SHELX-97<sup>11</sup>. Crystallographic drawings were done using programs ORTEP<sup>13</sup>, and PLUTON<sup>14</sup>.

### References

- 1 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
- 2 Z. J. Tonzetich and R. Eisenberg, *Inorganica Chimica Acta*, 2003, **345**, 340.
- 3 S. Chakraborty, J. Chattopadhyay, W. Guo, and W. E. Billups, *Angew. Chem. Int. Ed.*, 2007, **46**, 4486.
- 4 M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott, and J. L. Kiplinger, *Organometallics*, 2011, **30**, 2031.
- 5 G. Sheldrick, *Acta Crystallogr. Section A*, 2008, **64**, 112.
- 6 P. T. B. Beurskens, G.; de Gelder, R.; Garcia-Grands, S.; Gould R. O.; Smits, J. M. M., *The DIRDIF2008 Program System*, 2008, Crystallography Laboratory.
- 7 L. R. Avens, C. J. Burns, R. J. Butcher, D. L. Clark, J. C. Gordon, A. R. Schake, B. L. Scott, J. G. Watkin, and B. D. Zwick, *Organometallics*, 2000, **19**, 451.
- 8 T. Mehdoui, J.-C. Berthet, P. Thuéry, L. Salmon, E. Rivière, and M. Ephritikhine, *Chem. – Eur. J.*, 2005, **11**, 6994.
- 9 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1977, **276**, 307.
- 10 P.C. McArdle, *J. Appl. Cryst.*, 1996, **29**, 306.
- 11 G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.
- 12 The structure was solved using the solution program SHELXS97. "International Tables for Crystallography", Vol. C, Kluwer Academic Publishers, Utrecht, The Netherlands, (1992), Tables 4.2.6.8 and 6.1.1.4.
- 13 C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).
- 14 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.