Supporting Information for:

Synthesis and reactivity of a uranyl-imidazolyl complex

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of nitrogen or argon. Hexanes, diethyl ether, THF and toluene were dried by passage over activated molecular sieves using a Vacuum Atmospheres solvent purification system. C_6D_6 and 1-methylimidazole (MeIm) were dried over activated 4Å molecular sieves, while CH_2Cl_2 and CD_2Cl_2 were dried over activated 3Å molecular sieves for 24 h. $UO_2Cl_2(THF)_3$,[1] Li(Ar$_2$nacnac),[2] Li($C_5H_4N_2$),[3] [UO$_2$(Ar$_2$nacnac)Cl]$_2$ (**1**),[4] were prepared by the published procedures. All other reagents were purchased from commercial sources and used as received.

NMR spectra and Evans method determinations[5] were recorded on a Varian UNITY INOVA 400, a Varian UNITY INOVA 500 spectrometer, a Varian UNITY INOVA 600, or a Bruker Avance III Ultrashield Plus 800 MHz spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). ^{13}C assignments were confirmed via HSQC and HMBC experiments. ^{7}Li{^{1}H} NMR spectra were referenced to external LiCl. Elemental analyses were performed by the Microanalytical Laboratory at UC Berkeley. UV/vis spectra were recorded on an Ocean Optics USB4000 UV/Vis spectrometer equipped with a USB-DT light source. IR spectra were recorded on a Mattson Genesis FTIR spectrometer. Raman samples were prepared by forming a 1:1 (w/w) KBr mull, and measured in a 5mm diameter NMR tube. Raman spectra were recorded on a Thermo

Scientific Nicolet 6700 FT-IR Spectrometer with NXR FT-Raman Accessory using an excitation wavelength of 1064 nm.

Synthesis of [Li(MeIm)][UO(μ-O)(Ar$_2$nacnac)(μ-*C*,*N*-$C_5H_4N_2$)$_2$] (2). To a toluene solution (2 mL) of [UO_2(Ar$_2$nacnac)Cl]$_2$ (106 mg, 0.073 mmol) was added MeIm (14 μL, 0.18 mmol). The resulting deep green solution was cooled to -25 °C, whereupon a cold (-25 °C) THF solution (2 mL) of Li($C_4H_5N_2$) (26 mg, 0.30 mmol) was added. This resulted in an immediate color change to red, concomitant with the deposition of white solid. After 20 minutes of stirring, the volatiles were removed in vacuo, and the resulting solid was extracted into toluene (5 mL). This solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The volume of filtrate was then reduced in vacuo (0.5 mL), and the solution was layered with hexane (2 mL) and stored at -25 °C for 12 hrs. This resulted in the deposition of red plates (71 mg). Yield 52%. Anal Calcd for $C_{41}H_{57}N_8O_2ULi$: C, 52.45; H, 6.12; N, 11.93. Found C, 52.17; H, 6.12; N, 11.93. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.92 (d, 6H, J_{HH} = 6.4 Hz, CH*Me$_2$*), 1.24 (d, 6H, J_{HH} = 6.8 Hz, CH*Me$_2$*), 1.29 (d, 6H, J_{HH} = 6.4 Hz, CH*Me$_2$*), 1.37 (d, 6H, J_{HH} = 6.8 Hz, CH*Me$_2$*), 1.84 (s, 6H, Me), 2.28 (s, 3H, NMe), 3.05 (s, 6H, NMe), 3.90 (m, 2H, J_{HH} = 6.4 Hz, C*H*Me$_2$), 4.30 (m, 2H, J_{HH} = 6.8 Hz, C*H*Me$_2$), 4.73 (s, 1H, γ-CH), 5.98 (s, 1H, 5-H, MeIm), 6.36 (s, 2H, 5-H, imidazolyl), 6.89 (s, 1H, 4-H, MeIm), 7.09 – 7.19 (m, 7H, overlapping CH), 7.31 (d, 2H, J_{HH} = 7.6 Hz, meta CH). ^{7}Li{^{1}H} NMR (194 MHz, 25 °C, C_6D_6): δ 1.20. ^{13}C{^{1}H} NMR (125 MHz, 25 °C, C_6D_6): δ 24.20 (CH*Me$_2$*), 24.32 (CH*Me$_2$*), 25.93 (CH*Me$_2$*), 26.34 (CH*Me$_2$*), 28.29 (*CH*Me$_2$), 28.55 (Me), 28.82 (*CH*Me$_2$), 32.02 (N*Me*, MeIm), 34.99 (N*Me*, imidazolyl), 97.62 (γ-C), 116.54 (C-4, imidazolyl), 119.75 (C-4, MeIm), 124.35 (meta CH), 124.61 (meta CH), 127.08 (para CH), 129.17 (C-

5, MeIm), 129.28 (C-5, imidazolyl), 138.32 (C-2, MeIm), 142.58 (ortho CH), 146.53 (ortho CH), 147.52 (C-ipso), 167.39 (β-CN), 329.4 (C-2, imidazolyl). UV/Vis (Toluene, 8.0×10^{-4} M): 425 nm ($\varepsilon = 410$ $L\cdot mol^{-1}\cdot cm^{-1}$), 514 nm ($\varepsilon = 160$ $L\cdot mol^{-1}\cdot cm^{-1}$). IR (KBr pellet, cm^{-1}): 1552 (m), 1523 (s), 1465 (s), 1435 (s), 1402 (s), 1368 (m), 1339 (w), 1318 (s), 1285 (w), 1267 (w), 1253 (w), 1233 (w), 1191 (sh), 1168 (m), 1109 (m), 1097 (m), 1089 (sh), 1059 (w), 1043 (sh), 1026 (w), 969 (w), 930 (m), 886 (s, ν_{asym}(U=O)), 839 (w), 818 (m), 790 (m), 761 (w), 732 (m), 696 (w), 674 (sh), 663 (w), 618 (w), 533 (m), 507 (m), 491 (m), 469 (m), 447 (sh), 430 (sh), 413 (w). Raman (KBr mull, cm^{-1}): 806 (ν_{sym}(U=O)).

Synthesis of [FeCl(MeIm)][UO$_2$(Ar$_2$nacnac)(μ-*N,C*-C$_5$H$_4$N$_2$)$_2$] (3): A THF solution (1 mL) of **2** (43 mg, 0.046 mmol) was added to a THF suspension (1 mL) of $FeCl_2$ (6 mg, 0.05 mmol). This solution was stirred for 1 hour, whereupon the solution changed color from red to light green. The volatiles were removed in vacuo and the resulting green solid was dissolved in toluene (2 mL) and filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The filtrate was collected and the volatiles were removed in vacuo. The solid was then dissolved in THF (0.5 mL). This solution was layered with Et_2O (2 mL) and stored at -25 °C for 12 hrs. This resulted in the deposition of **3** as yellow green plates (21 mg). Yield 42 %. Anal Calcd for $C_{41}H_{57}N_8O_2ClUFe\cdot C_4H_{10}O$: C, 49.25; H, 6.15; N, 10.21. Found C, 49.15; H, 6.00; N, 10.52. ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ -10.87 (br s, 2H, Ar or Me$_2$C*H* or imidazolyl CH), -10.37 (br s, 1H, MeIm), -2.40 (s, 6H, Ar$_2$nacnac Me or imidazolyl Me), 0.52 (s, 6H, *Me*$_2$CH), 1.62 (s, 6H, *Me*$_2$CH), 1.78 (s, 6H, *Me*$_2$CH), 2.30 (s, 6H, *Me*$_2$CH), 4.27 (s, 1H, γ-CH), 5.49 (br s, 2H, Me$_2$C*H*), 7.46 (s, 2H, Ar or Me$_2$C*H* or imidazolyl CH), 8.12 (s, 2H, Ar or Me$_2$C*H* or imidazolyl CH), 14.01 (br s, 6H, Ar_2nacnac Me or imidazolyl Me), 14.59 (s, 2H, Ar or Me_2CH or imidazolyl CH), 16.46 (s, 3H, MeIm), 26.67 (s, 2H, Ar or Me_2CH or imidazolyl CH), 40.43 (s, 1H, MeIm), 46.32 (br s, 1H, MeIm). One resonance integrating to 2H was not observed. UV/Vis (Toluene, 4.2×10^{-4} M): 437 nm ($\varepsilon = 610$ $L \cdot mol^{-1} \cdot cm^{-1}$), 591 ($\varepsilon = 270$ $L \cdot mol^{-1} \cdot cm^{-1}$). IR (KBr pellet, cm^{-1}): 1561 (sh), 1552 (sh), 1544 (m), 1535 (sh), 1524 (s), 1512 (sh), 1500 (w), 1493 (w), 1466 (sh), 1461 (m), 1450 (sh), 1436 (s), 1423 (sh), 1398 (s), 1370 (sh), 1345 (m), 1318 (s), 1286 (w), 1267 (w), 1254 (w), 1235 (w), 1208 (w), 1169 (w), 1138 (w), 1108 (m), 1060 (w), 1027 (w), 985 (sh), 944 (sh), 934 (w), 911 (m, ν_{asym}(U=O)), 892 (w), 845 (w), 827 (w), 793 (w), 760 (w), 741 (w), 687 (w), 671 (sh), 661 (w), 647 (sh), 621 (w), 604 (w), 581 (w), 557 (w), 540 (w), 516 (w), 494 (w), 474 (w), 451 (w), 429 (w). Evans' method (C_6D_6, 20.1 °C, 0.0158 M): $\mu_{eff} = 4.95$ B.M.

Synthesis of [CoCl(MeIm)][$UO_2(Ar_2nacnac)(\mu$-*N*,*C*-$C_5H_4N_2)_2$] (4): A THF solution (1 mL) of **2** (61 mg, 0.065 mmol) was added to a THF (1 mL) suspension of $CoCl_2$ (9 mg, 0.07 mmol). This solution was stirred for 35 minutes, whereupon the solution turned deep green. The volatiles were removed in vacuo and the resulting green solid was dissolved in toluene (2 mL) and filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The filtrate was collected and the volatiles were removed in vacuo. The solid was then dissolved in THF (1 mL). The volume of the solution was reduced in vacuo (0.5 mL), and the solution was layered with Et_2O (2 mL) and stored at -25 °C for 12 hrs. This resulted in the deposition of **4** as dark green plates (28 mg). Yield: 39%. Anal Calcd for $C_{41}H_{57}N_8O_2ClUCo \cdot C_4H_{10}O$: C, 49.11; H, 6.14; N, 10.18. Found C, 49.12; H, 6.06; N, 9.67. ^1H NMR (400 MHz, 25 °C, C_6D_6): δ -5.13 (br s, 6H,

Ar_2nacnac Me or imidazolyl Me), -4.15 (br s, 1H, MeIm), -4.01 (br s, 1H, MeIm), -3.28 (br s, 2H, Ar or Me_2CH or imidazolyl CH), -0.79 (s, 6H, *Me_2*CH), 0.63 (s, 6H, *Me_2*CH), 1.83 (s, 6H, *Me_2*CH), 2.86 (s, 1H, γ-C), 3.32 (s, 6H, *Me_2*CH), 5.78 (s, 2H, Ar or Me_2CH or imidazolyl CH), 7.35 (s, 2H, Ar or Me_2CH or imidazolyl CH), 8.01 (s, 2H, Ar or Me_2CH or imidazolyl CH), 8.70 (s, 2H, Ar or Me_2CH or imidazolyl CH), 14.37 (s, 3H, MeIm), 23.50 (s, 2H, Ar or Me_2CH or imidazolyl CH), 43.37 (br s, 2H, Ar or Me_2CH or imidazolyl CH), 44.38 (br s, 1H, MeIm). One resonance integrating to 6H was not observed. UV/Vis (Toluene, 5.4×10^{-4} M): 446 ($\varepsilon = 690$ $L \cdot mol^{-1} \cdot cm^{-1}$) 567 ($\varepsilon = 480$ $L \cdot mol^{-1} \cdot cm^{-1}$) 617 ($\varepsilon = 520$ $L \cdot mol^{-1} \cdot cm^{-1}$) 652 ($\varepsilon = 450$ $L \cdot mol^{-1} \cdot cm^{-1}$). IR (KBr pellet cm^{-1}): 1552 (sh), 1530 (m), 1465 (m), 1435 (m), 1397 (s), 1362 (sh), 1317 (m), 1287 (w), 1278 (sh), 1265 (w), 1253 (w), 1242 (w), 1229 (sh), 1168 (w), 1109 (s), 1060 (w), 1027 (m), 946 (w), 932 (w), 911 (s, ν_{asym}(U=O)), 841 (w), 793 (m), 761 (w), 726 (w), 687 (w), 659 (w), 621 (w), 508 (w), 488 (w), 483 (w), 446 (w), 429 (w), 407 (w). Evans' method (C_6D_6, 21.7 °C, 0.0182 M): $\mu_{eff} = 4.42$ B.M.

Reaction of 3 with excess 1-methylimidazole. Complex **3** (10 mg, 9.8 µmol) was dissolved in C_6D_6 (0.4 mL). A ^1H NMR spectrum of the sample was recorded. Subsequently, MeIm (1.1 µL, 13 µmol) was added to the solution and the ^1H NMR spectrum was immediately re-recorded. This spectrum revealed the disappearance of peaks at -10.37 ppm, 16.46 ppm, 40.43 ppm and 46.32 ppm, presumably due to rapid exchange with free MeIm. Accordingly, these peaks were assigned as belonging to coordinated 1-methylimidazole.

Reaction of 4 with excess 1-methylimidazole. Complex **4** (10 mg, 9.7 μmol) was dissolved in C_6D_6 (0.4 mL). A ^1H NMR spectrum of the sample was recorded. Subsequently, MeIm (6.1 μL, 72 μmol) was added to the solution and the ^1H NMR spectrum was immediately re-recorded. This spectrum revealed a broadening of peaks at -4.15 ppm, -4.01 ppm, and 44.3 ppm, presumably due to exchange with free MeIm. Accordingly, these peaks were assigned as belonging to coordinated 1-methylimidazole.

Raman spectrum for $[UO_2(Ar_2nacnac)Cl]_2$: Raman (KBr mull, cm^{-1}): 850 (ν_{sym}(U=O)).

X-ray Crystallography. The crystal structures of complexes **2**$\cdot 0.5C_7H_8$, **3**$\cdot Et_2O$, and **4**$\cdot Et_2O$ were determined similarly with exceptions noted in subsequent paragraphs. Crystals were mounted on a glass fiber under Paratone-N oil. Data collection was carried out using a Bruker 3-axis platform diffractometer with SMART-1000 CCD detector. The instrument was equipped with graphite monochromatized MoKα X-ray source (λ = 0.71073 Å). All data were collected at 150(2) K using Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans, with 20 s (for **2**$\cdot 0.5C_7H_8$), 30 s (for **3**$\cdot Et_2O$), or 25 s (for **4**$\cdot Et_2O$) frame exposures, and 0.3° frame widths. Data collection and cell parameter determination were conducted using the SMART program.[6] The raw frame data were processed using SAINT.[7] The empirical absorption correction was applied based on Psi-scan. Subsequent calculations were carried out using SHELXTL.[8] The structures were solved using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. The final refinement included anisotropic temperature factors on all nonhydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.

The methyl group of the toluene solvate molecule in complex **2** was found to be disordered over two orientations in a 50:50 ratio. In addition, the C-C bond lengths were fixed at 1.4 Å for the aromatic carbons, while the C-C bond length for the methyl carbon was fixed at 2.3 Å, both using the DFIX command. The diethyl ether solvate molecule found in both complexes **3** and **4** was found to be disordered over two orientations, also in a 50:50 ratio. The C-O bond lengths for the diethyl ether solvate molecule were fixed at 1.4 Å, while the C-C bond lengths were fixed at 1.54 Å, both using the DFIX command. For each structure, idealized hydrogen atoms were not assigned to the disordered carbon atoms. A summary of relevant crystallographic data for **2**$\cdot 0.5C_7H_8$, **3**$\cdot Et_2O$, and **4**$\cdot Et_2O$ is presented in Table S1.

Table S1. X-ray Crystallographic Data for Complexes **2**·0.5C_7H_8, **3**·Et_2O, **4**·Et_2O

	2·0.5C_7H_8	**3**·Et_2O	**4**·Et_2O
Empirical formula	$C_{44.5}H_{61}N_8LiO_2U$	$C_{45}H_{67}ClFeN_8O_3U$	$C_{45}H_{67}ClCoN_8O_3U$
Crystal Habit, color	plate, red	plate, yellow-green	plate, green
Crystal size (mm)	0.4 × 0.4 × 0.2	0.3 × 0.25 × 0.05	0.8 × 0.4 × 0.05
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/m$	$P2_1/m$
Volume (Å^3)	2288.3(3)	2392.9(4)	2384.65(19)
a (Å)	9.1577(7)	8.9781(9)	8.9376(4)
b (Å)	12.3878(9)	21.304(2)	21.3006(10)
c (Å)	21.4749(16)	12.9440(13)	12.9545(6)
α (°)	75.3080(10)	90	90
β (°)	84.9700(10)	104.866(2)	104.7780(10)
γ (°)	76.2780(10)	90	90
Z	2	2	2
Formula weight (g/mol)	984.98	1097.40	1100.48
Density (calculated) (Mg/m^3)	1.430	1.523	1.533
Absorption coefficient (mm^{-1})	3.590	3.785	3.841
F_{000}	990	1104	1106
Total no. reflections	19442	21204	21198
Unique reflections	9113	5273	5365
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0390 wR2 = 0.0828	R1 = 0.0342 wR2 = 0.0829	R1 = 0.0408 wR2 = 0.0963
Largest diff. peak and hole (e$^-$Å^{-3})	1.476 and -1.918	1.684 and -1.351	2.404 and -1.983
GOF	1.150	0.781	1.004

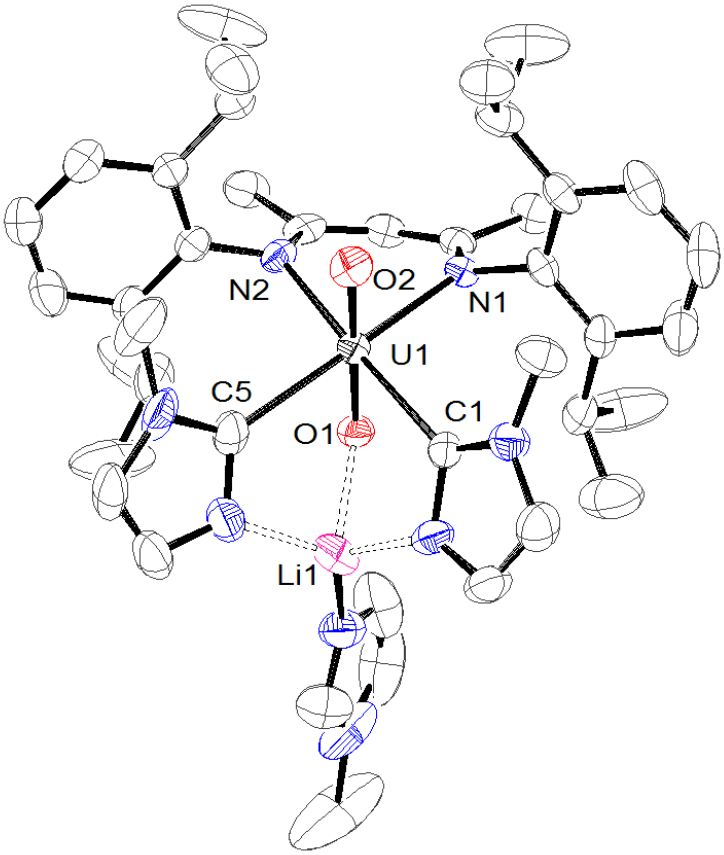

Figure S1. Solid-state molecular structure of [Li(MeIm)][UO(μ-O)(Ar$_2$nacnac)(μ-*C*,*N*-C$_5$H$_4$N$_2$)$_2$] (**2**·0.5C$_7$H$_8$) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U1-O1 = 1.788(4), U1-O2 = 1.778(4), U1-N1 = 2.446(5), U1-N2 = 2.459(5), U1-C1 = 2.498(6), U1-C5 = 2.499(7), O1-U1-O2 = 176.1(2).

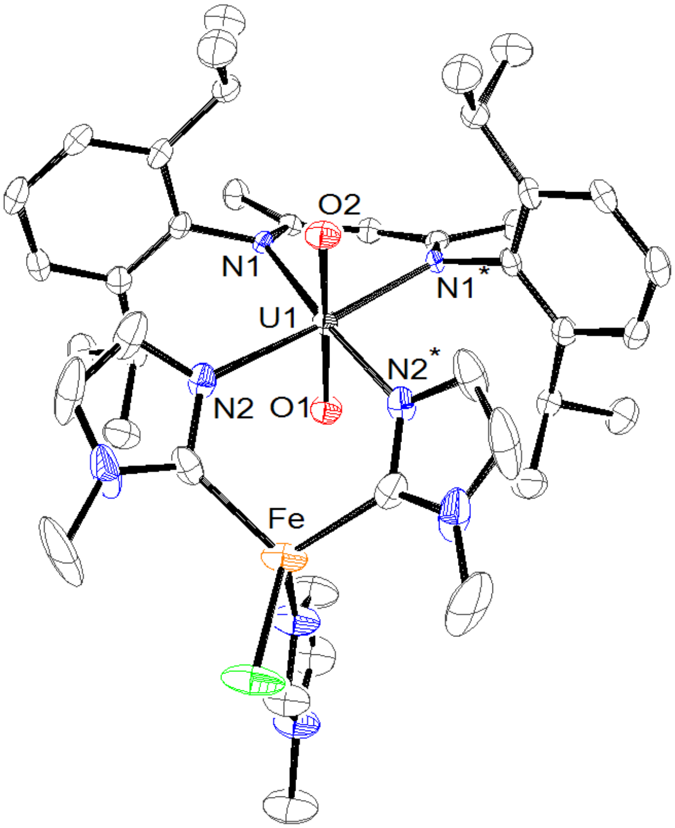

Figure S2. Solid-state molecular structure of [FeCl(MeIm)][UO$_2$(Ar$_2$nacnac)(μ-*N*,*C*-C$_5$H$_4$N$_2$)$_2$] (**3**·Et$_2$O) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U1-O1 = 1.780(4), U1-O2 = 1.777(4), U1-N1 = 2.438(3), U1-N2 = 2.432(4), Fe1-C16 = 2.095(5), Fe1-N4 = 2.083(6), O1-U1-O2 = 177.2(2).

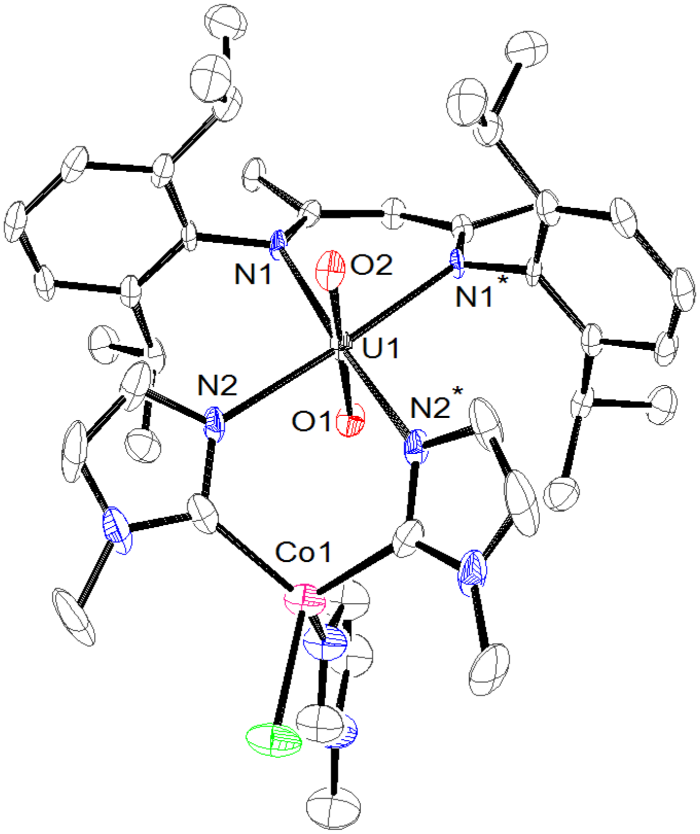

Figure S3. Solid-state molecular structure of [CoCl(MeIm)][UO_2(Ar_2nacnac)(μ-*N*,*C*-$C_5H_4N_2$)$_2$] (**4**·Et_2O) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): U1-O2 = 1.767(5), U1-O1 = 1.771(4), U1-N1 = 2.434(3), U1-N2 = 2.431(4), Co1-C16 = 2.047(6), Co1-N4 = 2.034(6), O1-U1-O2 = 178.0(2).

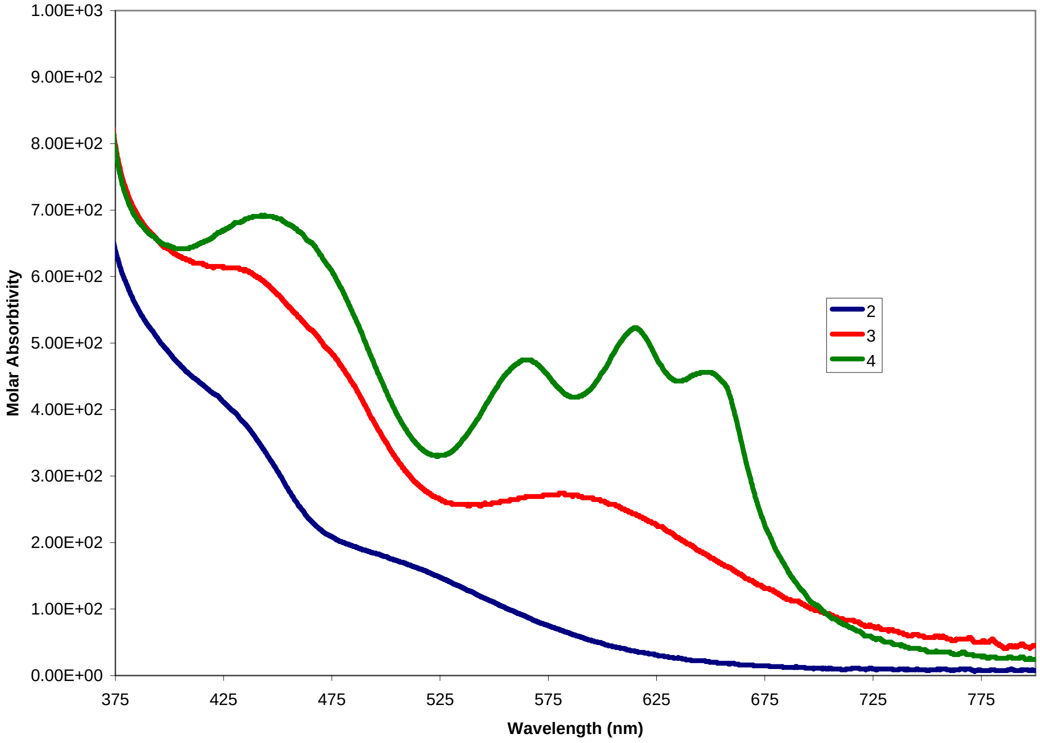

Figure S4. Optical absorption spectra of **2** (toluene, 0.80 mM), **3** (toluene, 0.42 mM) and **4** (toluene, 0.54 mM)

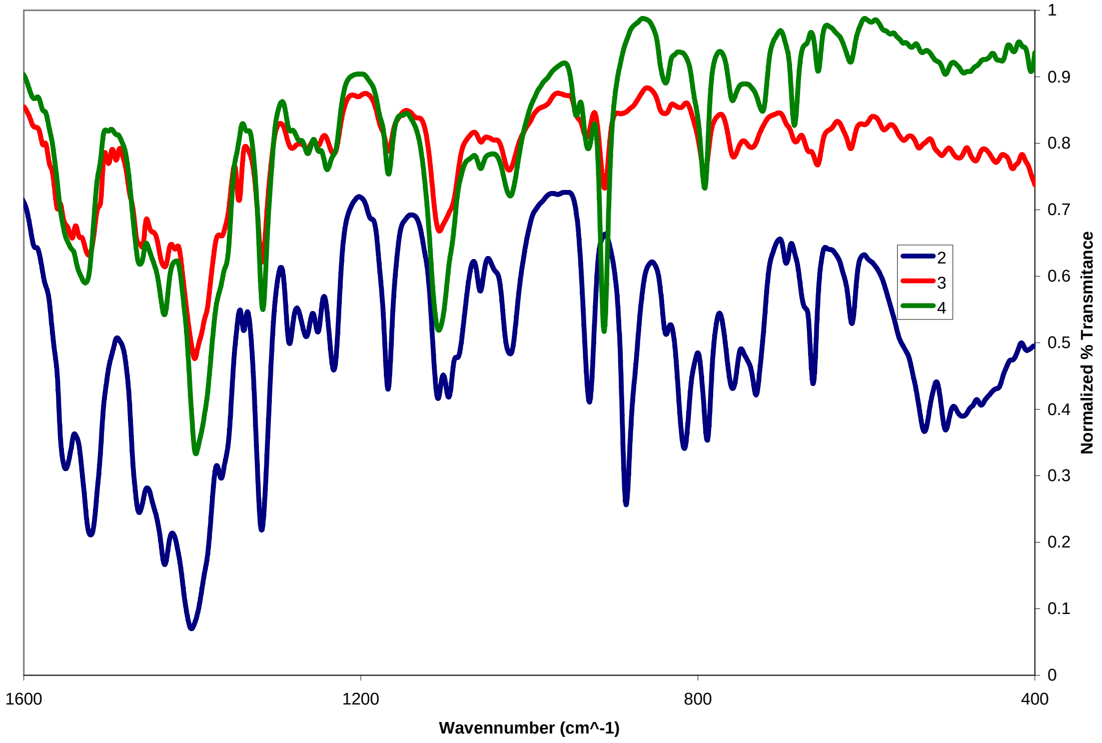

Figure S5. IR spectra (KBr pellet) of complexes **2**, **3**, and **4**.

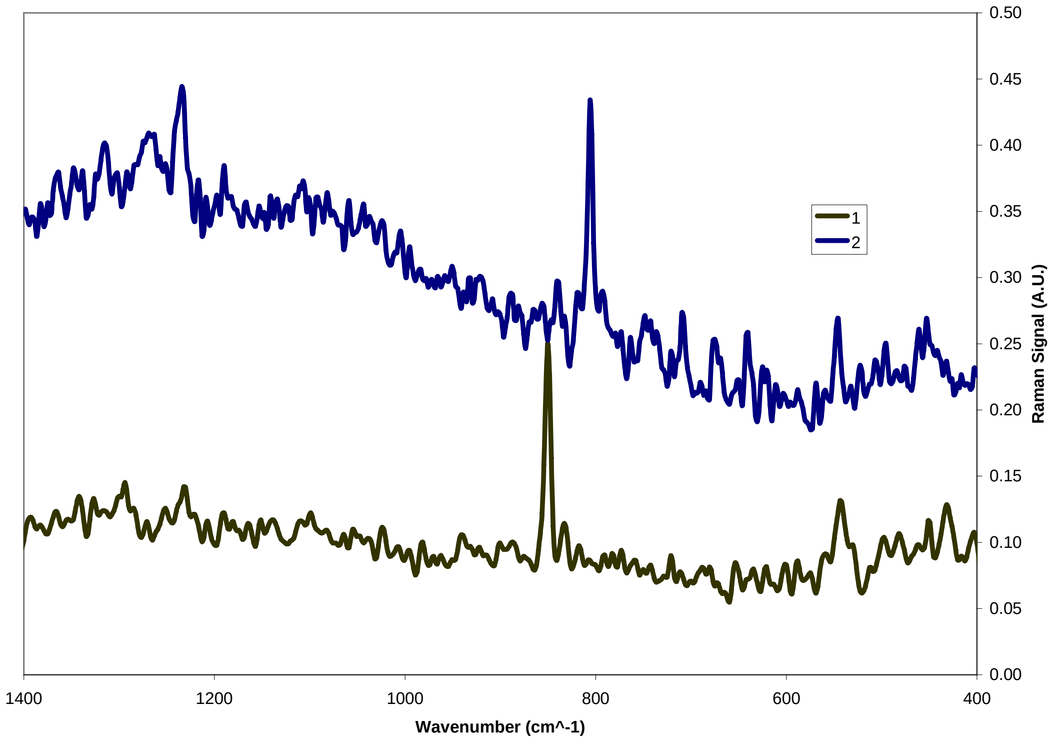

Figure S6. Raman spectra (KBr mull) of complexes **1** and **2**.

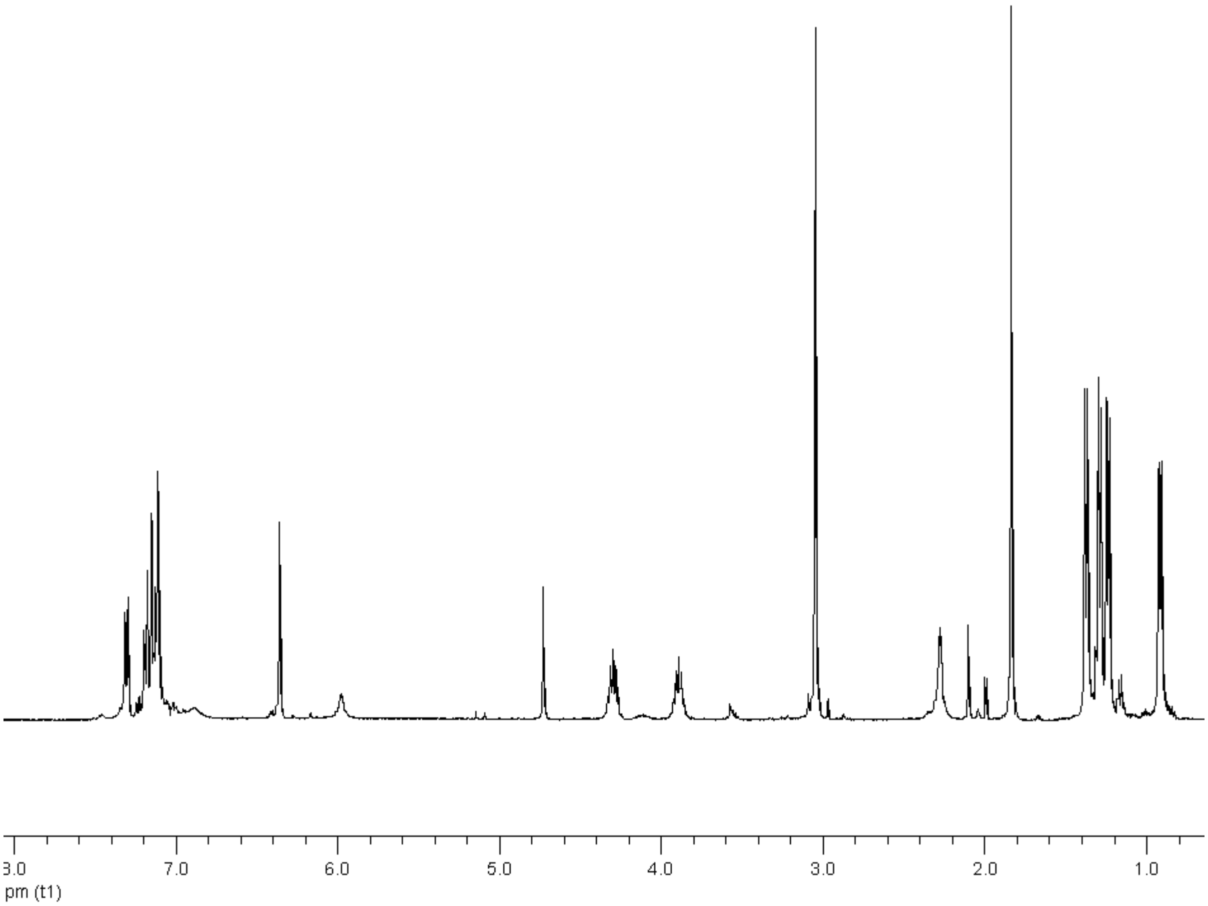

Figure S7. ^{1}H NMR spectrum of **2** (C_6D_6).

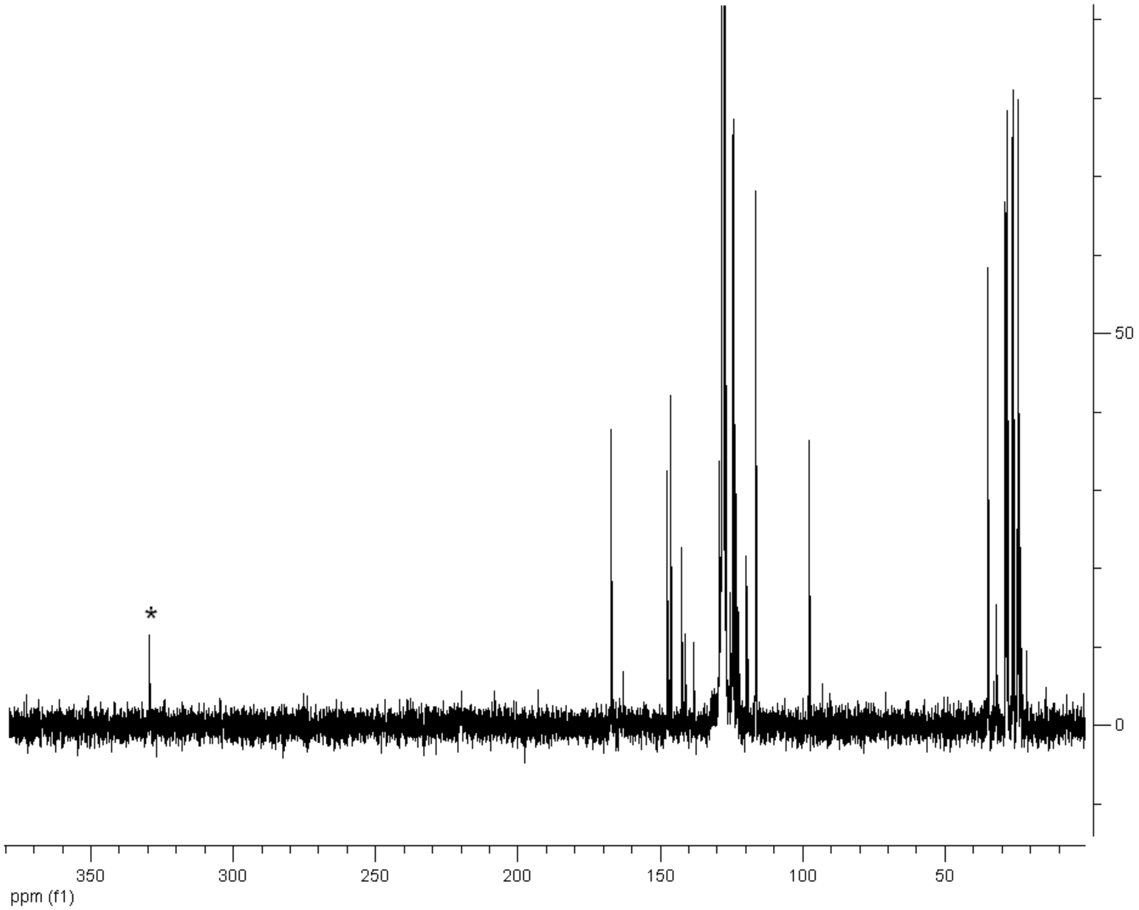

Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **2** in C_6D_6. * denotes C-2 carbon of the imidazolyl ligand.

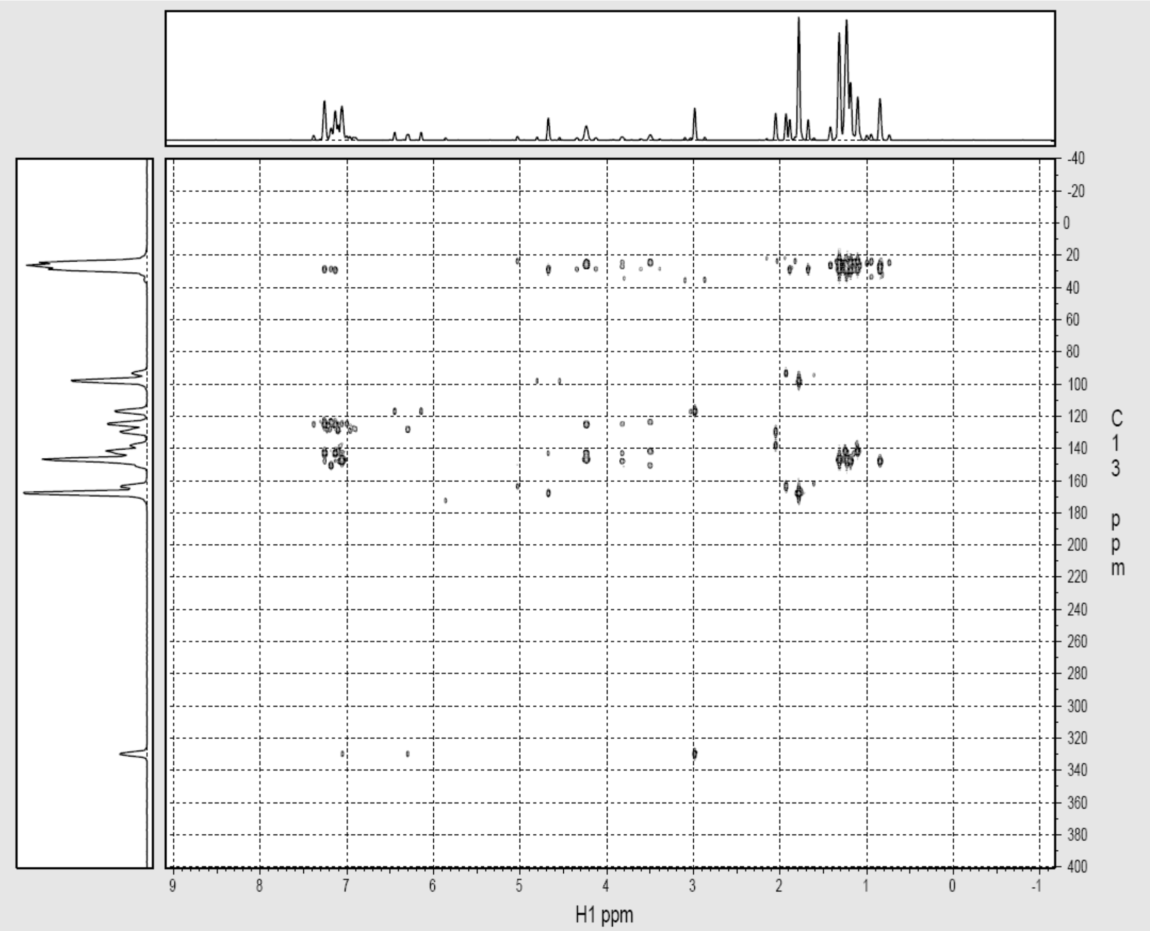

Figure S9. HMBC spectrum of **2** in C_6D_6.

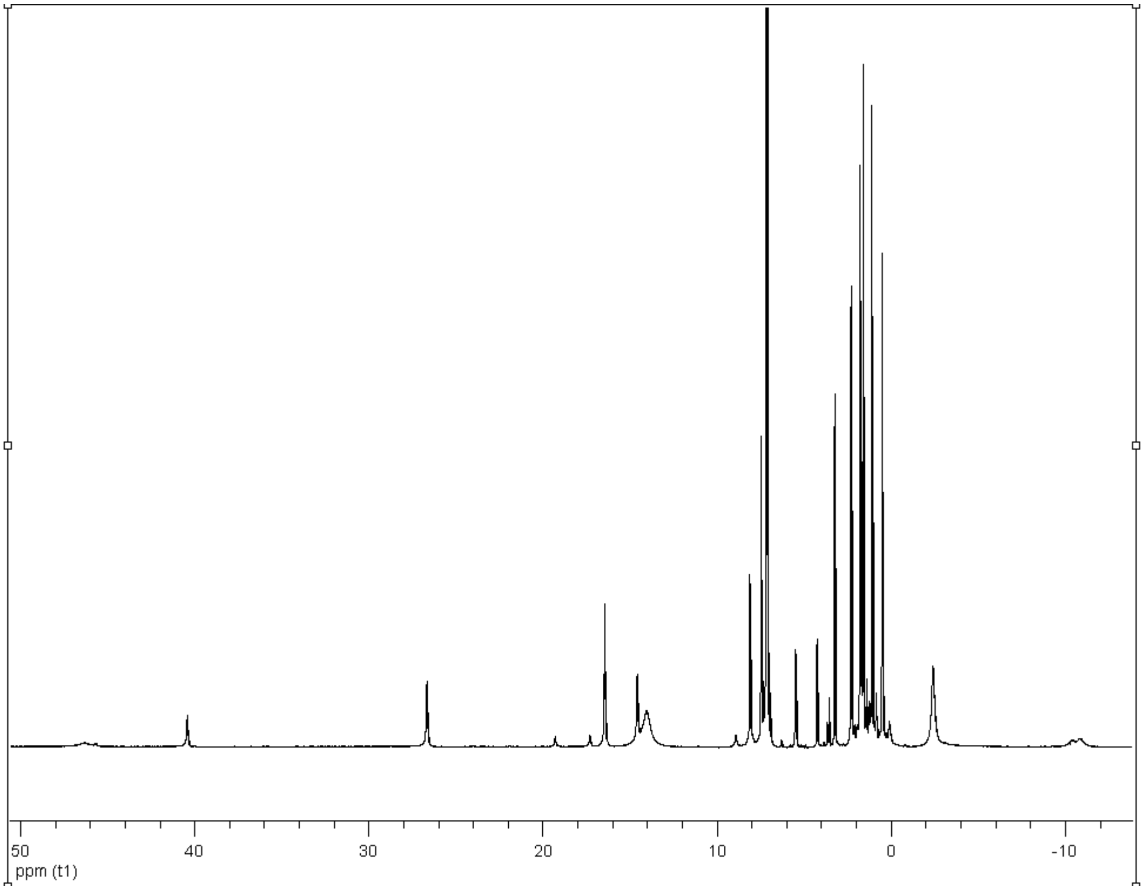

Figure S10. ^{1}H NMR spectrum for **3** (C_6D_6).

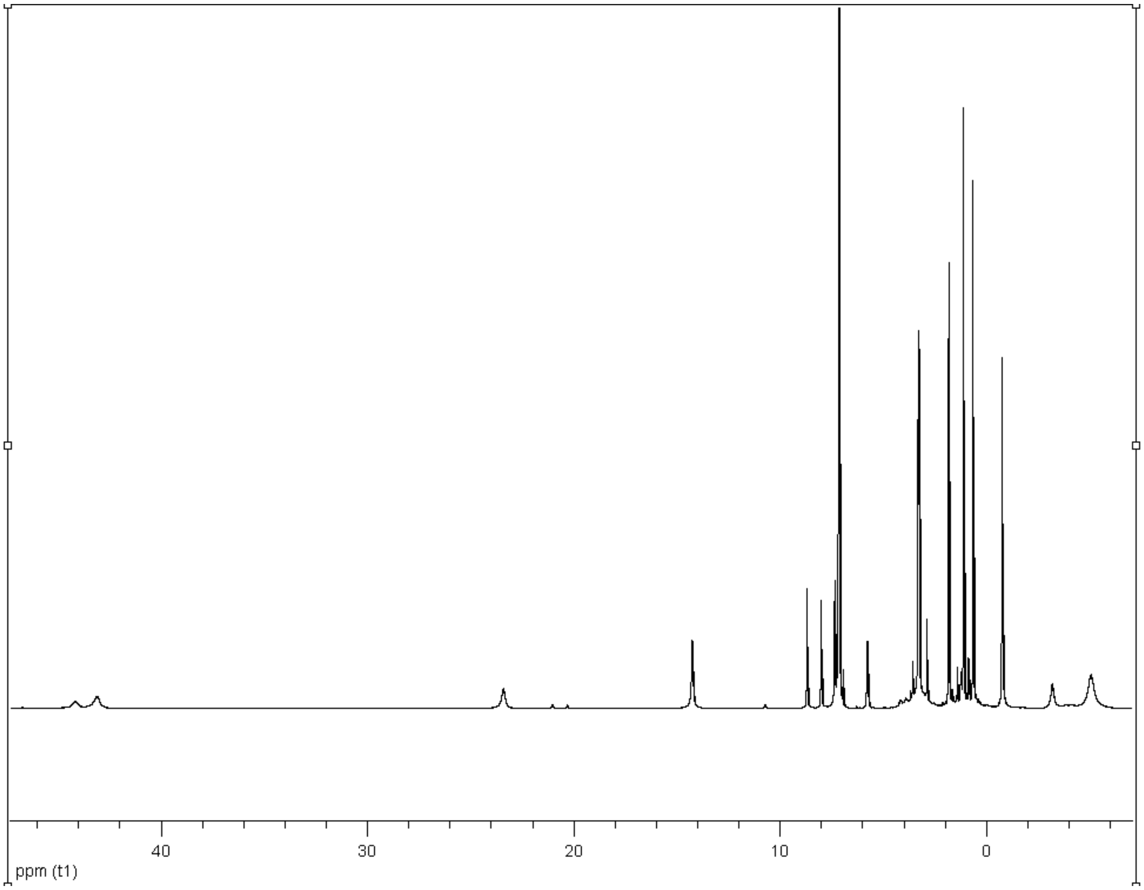

Figure S11. ^{1}H NMR spectrum for **4** (C_6D_6).

References

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