Supporting Information:

Selective Recognition and Extraction of the Uranyl Ion from Aqueous Solutions with a Recyclable Chelating Resin

Aaron C. Sather, Orion B. Berryman, and Julius Rebek, Jr.*

The Skaggs Institute for Chemical Biology and Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla California, 92037

e-mail: jrebek@scripps.edu

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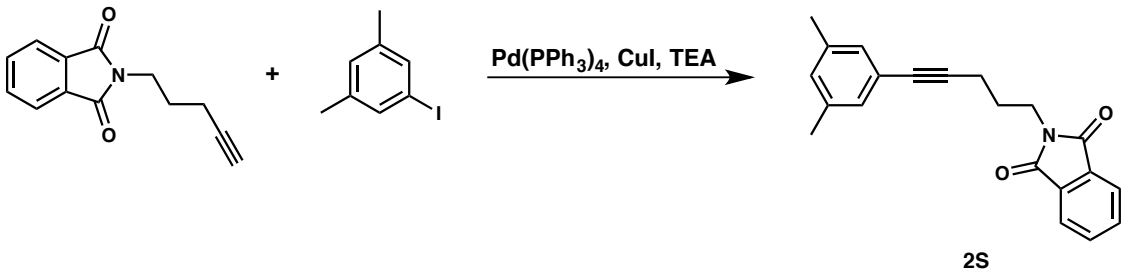
Experimental Details for the Synthesis of Reported Compounds

All NMR spectra were taken on a Bruker 600 MHz instrument using Top Spin software to acquire the data. After acquisition spectra were prepared using the MestReNova software package for Mac.

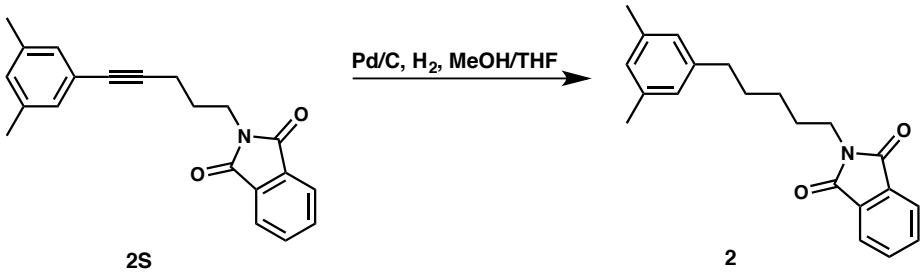
Alkyne (2S)



2S

$Pd(Ph_3)_4$ (2.7 g, 2.3 mmol), CuI (1.12 g, 5.8 mmol), and *N*-(4-pentynyl)phthalimide (25 g, 117 mmol) were added to a 2-neck round bottom flask equipped with a reflux condenser. The solids were placed under a nitrogen atmosphere. 5-iodo-m-xylene (29.9 g, 18.6 mL, 129 mmol) and triethylamine (240 mL) were added via syringe. The reaction mixture was refluxed for 24 hours. The resulting black mixture was cooled to room temperature and the volatiles were removed under reduced pressure. Once dry, the black residue was dissolved in 1:1 hexanes:dichloromethane and loaded onto a silica column. The eluent was gradually converted from 1:1 hexanes:dichloromethane to 100% dichloromethane to give **2S** (34.457 g, 92%) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.70 – 7.64 (m, 2H), 6.88 (s, 2H), 6.86 (s, 1H), 3.86 (t, *J* = 7.0 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.23 (s, 6H), 2.01 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.42, 137.55, 133.82, 132.22, 129.49, 129.21, 123.28, 123.20, 88.00, 81.53, 37.52, 27.46, 21.10, 17.41. ESI-TOF high-acc: m/z: 318.1488 ([MH]+, $C_{21}H_{19}NO_2$+, calc. 318.1488).

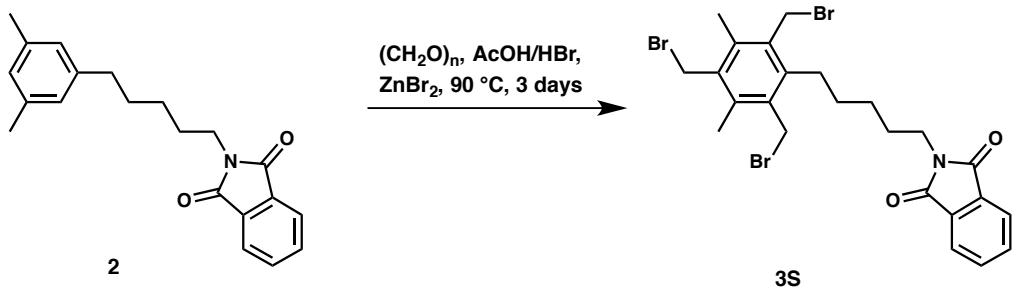
1,3,5-Dimethylalkyl benzene (2)



2S 2

Alkyne **2S** (34.45 g, 108 mmol) was placed in a 100 mL round bottom flask and dissolved in 60 mL THF. Pd/C 10% (3 g) was added and the reaction mixture was put in a pressure vessel under H_2 at 40 bar. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was then filtered through celite to give a pale yellow solution. The filtrate was concentrated under reduced pressure to give **2** (33.5 g, 96 %) as a white crystalline solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.73 – 7.68 (m, 2H), 6.80 (s, 1H), 6.78 (s, 2H), 3.68 (t, *J* = 7.3 Hz, 2H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.27 (s, 6H), 1.71 (p, *J* = 7.5 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.39 (p, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.57, 142.50, 137.84, 133.96, 132.33, 127.45, 126.37, 123.29, 38.12, 35.75, 31.22, 28.61, 26.73, 21.40. ESI-TOF high-acc: m/z: 344.1621 ([MNa]+, $C_{21}H_{23}NO_2$+, calc. 344.1621).

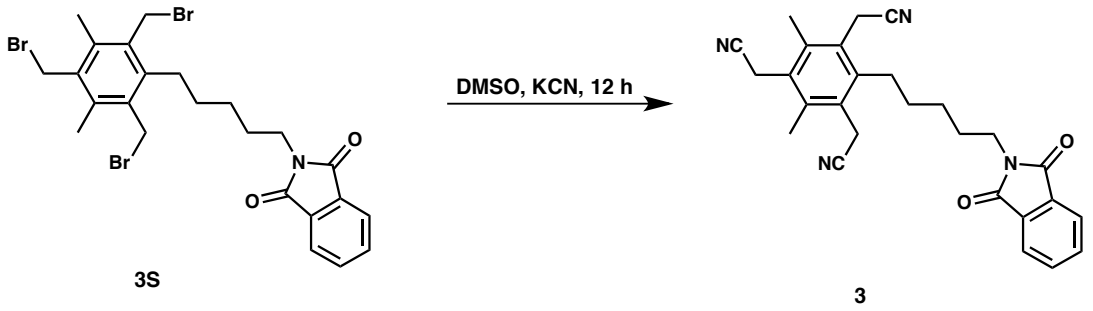
Tribromomethyl (3S)



2 3S

1,3,5-Dimethylalkyl benzene **2** (15 g, 46.7 mmol) paraformaldehyde (22.0 g, 734 mmol), and AcOH/HBr 33% (500 mL) were added to a dry 1000 mL round bottom flask with stir bar. The mixture was stirred while $ZnBr_2$ (26.0 g, 115 mmol) was slowly added. The reaction mixture was heated to 90 °C. After 24 hours an additional 22 g paraformaldehyde and 26 g $ZnBr_2$ was added. The yellow solution was heated an additional 48 hours. The reaction mixture was then cooled to room temperature and concentrated under vacuum. The residue was then dissolved in DCM and ran through a plug of silica to remove impurities. The DCM was then concentrated under reduced pressure to give **3S** (21.57 g, 77 %) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.74 – 7.71 (m, 2H), 4.57 (s, 4H), 4.56 (s, 2H), 3.74 (t, *J* = 7.1 Hz, 2H), 2.87 – 2.78 (m, 2H), 2.46 (s, 6H), 1.79 (p, *J* = 7.3 Hz, 2H), 1.71 (bs, 2H), 1.63 – 1.54 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.52, 141.91, 138.68, 134.00, 133.82, 132.93, 132.19, 123.29, 37.71, 30.88, 30.02, 30.00, 29.56, 28.35, 27.44, 15.58. ESI-TOF high-acc: m/z: 619.9420 ([MNa]+, $C_{24}H_{26}Br_3NO_2$+, calc. 619.9406).

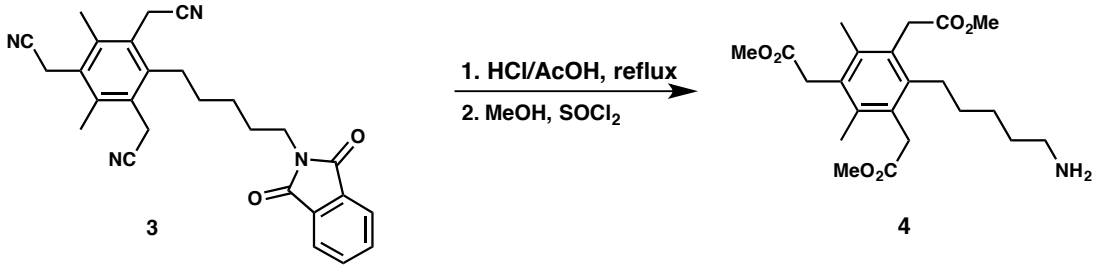
Tricyanomethyl (3)



3S 3

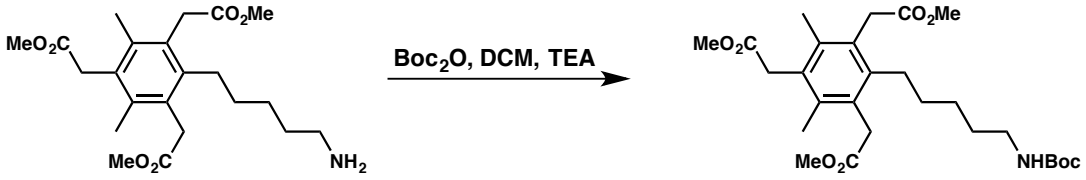
Potassium cyanide (7.06 g, 109 mmol) was dissolved in 320 mL dry DMSO under an argon atmosphere. The mixture was heated to 50 °C for 10 min then tribromomethyl **3S** (21.0 g, 35.0 mmol) was added and stirred at 50 °C for 15 min. The reaction mixture was cooled to room temperature and stirred 24 hours to yield a yellow/red solution. The reaction mixture was poured onto 600 mL ice water to give an off white precipitate. The precipitate was filtered and washed with 200 mL deionized water. The resulting off-white solid was placed in a beaker with a large stir bar and 800 mL fresh deionized water. The suspension was stirred vigorously stirred for 30 min. The suspension was then filtered and washed with 100 mL deionized water. The white solid was dissolved in DCM, washed with 300 mL brine, dried over Na_2SO_4, and concentrated under reduced pressure to give **3** (14.7 g, 96 %) as an off white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.75 – 7.70 (m, 2H), 3.76 (s, 4H), 3.74 (t, *J* = 7.0 Hz, 2H), 3.73 (s, 2H), 2.74 – 2.70 (m, 2H), 2.47 (s, 6H), 1.78 (p, *J* = 7.0 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.54 (p, *J* = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.49, 139.94, 136.50, 134.03, 132.02, 128.03, 127.37, 123.22, 117.34, 116.84, 37.15, 31.08, 29.51, 28.02, 26.76, 19.03, 18.74, 17.08. ESI-TOF high-acc: m/z: 439.2124 ([MH]+, $C_{27}H_{26}N_4O_2$+, calc. 439.2128).

Trimethylester free amine (4)



Tricyanomethyl **3** (11.0 g, 25.1 mmol) was added to a 1 L round bottom flask with stir bar. Glacial acetic acid (220 mL) and conc. HCl (220 mL) were added and the reaction mixture was heated to reflux for 48 hours. The yellow solution was then cooled to room temperature and the volatiles were removed under vacuum. The residue was dried in a desiccator, under vacuum, overnight. The dried solid was then suspended in MeOH (440 mL) and cooled to 0 °C in an ice bath. $SOCl_2$ (45 mL) was then added dropwise while maintaining the reaction temperature at 0 °C. After addition was complete the reaction mixture was allowed to warm to room temperature. The reaction mixture was then refluxed for 2 hours, cooled to room temperature, and the solvents were removed under vacuum. The resulting off white residue was dissolved in water and placed in a separatory funnel. The aqueous layer was extracted with Et_2O (3 × 200 mL). The aqueous portion was then placed in a beaker and basified with solid $NaHCO_3$. The basified aqueous solution was then returned to the separatory funnel and extracted with DCM (3 × 250 mL). The combined DCM extracts were dried over Na_2SO_4 and concentrated under reduced pressure to give **4** (8.18 g, 80% yield) as a light brown oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 (s, 2H), 3.77 (s, 4H), 3.71 (s, 9H), 2.75 (bs, 2H), 2.72 – 2.66 (m, 2H), 2.27 (s, 6H), 1.72 (s, 2H), 1.59 – 1.40 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.29, 172.05, 139.75, 136.23, 130.53, 129.66, 52.15, 52.09, 42.04, 36.47, 36.08, 31.04, 30.28, 27.53, 17.23. ESI-TOF high-acc: m/z: 408.2386 ([MH]+, $C_{22}H_{33}NO_6$+, calc. 408.2381).

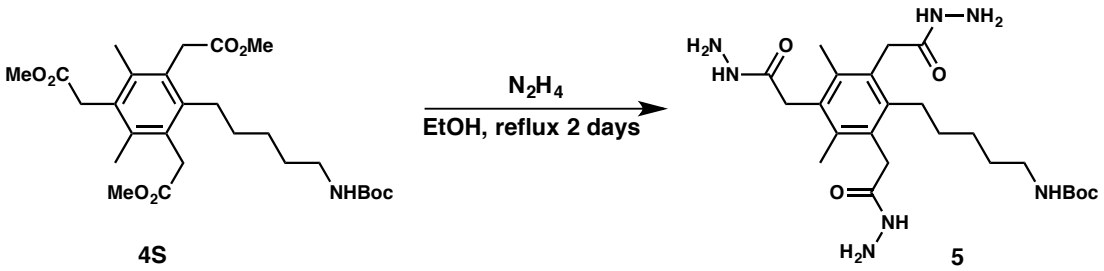
Trimethylester Boc-amine (4S)



4 **4S**

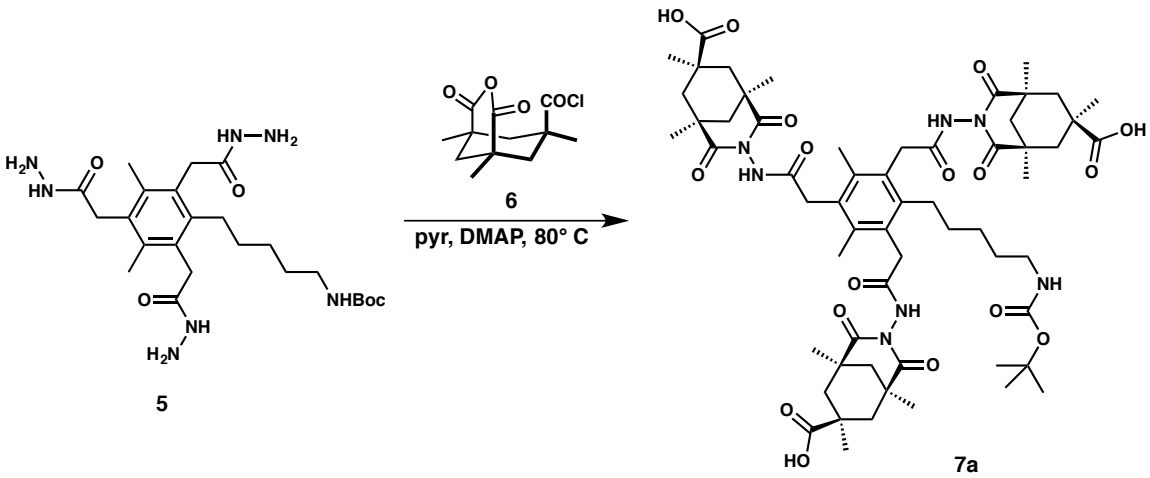
Free-amine **4** (8.0 g, 19.6 mmol) was added to a 500 mL round-bottom flask, dissolved in DCM (300 mL), and cooled in an ice bath. Once cool, TEA (5.48 mL, 39.2 mmol) was added dropwise followed by addition of Boc_2O (6.43 g, 29.4 mmol) was added. The reaction mixture was stirred and allowed to warm to room temperature overnight. The organics were evaporated to give a light brown oil. The oil was purified with column chromatography using 2:1 Hex:EtOAc as the eluent to give **4S** (8.072 g, 81% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.54 (bs, 1H), 3.75 (s, 2H), 3.74 (s, 4H), 3.68 (s, 9H), 3.19 – 3.07 (m, 2H), 2.70 – 2.62 (m, 2H), 2.25 (s, 6H), 1.54 – 1.48 (m, 2H), 1.45 (s, 9H), 1.44 – 1.37 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.25, 172.01, 156.06, 139.65, 136.23, 130.55, 129.66, 52.12, 52.06, 40.49, 36.47, 36.07, 30.97, 30.07, 30.02, 28.52, 27.38, 17.23. ESI-TOF high-acc: m/z: 508.2910 ([MH]+, $C_{27}H_{41}NO_8$+, calc. 508.2905).

Trihydrazide Boc-amine (5)



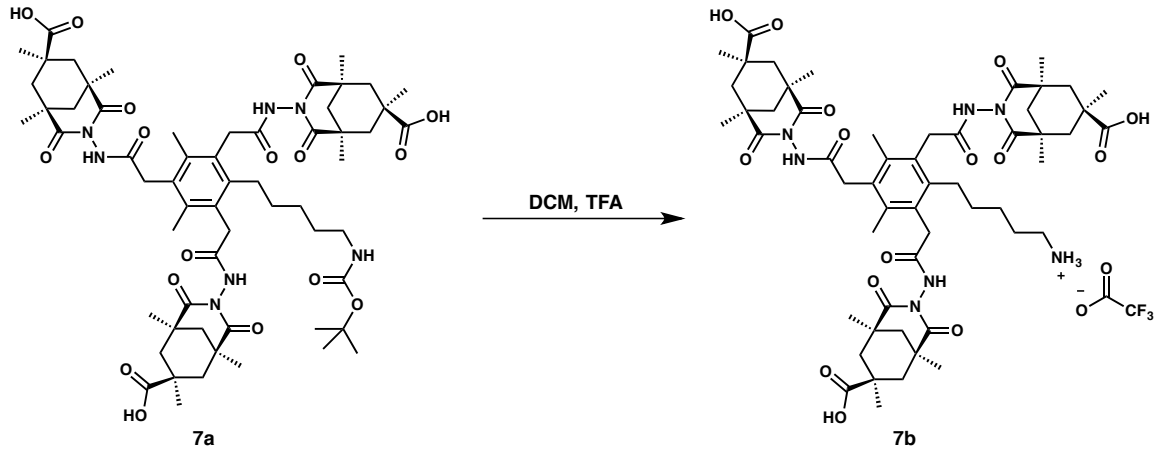
Trimethylester **4S** (8.0 g, 15.8 mmol) was added to a 500 mL round bottom flask with a stir bar. EtOH (275 mL) was added and the reaction mixture was warmed to 60° C to solubilize the starting material. Hydrazine (12.0 mL, 382 mmol) was added dropwise and the reaction was brought to reflux. After 24 hours additional hydrazine (12 mL) was added and the reaction mixture was refluxed for another 24 hours. The reaction mixture was then cooled to room temperature and the solvent was removed under vacuum. The resulting white solid was triturated in hot EtOH (50 mL), cooled to room temperature, and filtered to give **5** (7.435 g, 93% yield) as a pure white solid. ^{1}H NMR (600 MHz, DMSO-d6) δ 8.84 (s, 1H), 8.80 (s, 2H), 6.77 (t, *J* = 5.8 Hz, 1H), 4.17 (bs, 6H), 3.45 (two overlapping singlets, 6H), 2.90 (q, *J* = 6.3 Hz, 2H), 2.48 (s, 2H), 2.10 (s, 6H), 1.37 (s, 9H), 1.36 – 1.26 (m, 6H). ^{13}C NMR (151 MHz, DMSO-d6) δ 169.88, 169.58, 155.60, 139.11, 135.36, 130.74, 129.78, 77.36, 35.60, 35.18, 30.41, 29.77, 29.44, 28.31, 26.92, 16.77. ESI-TOF high-acc: m/z: 508.3244 ([MH]+, $C_{24}H_{41}N_7O_5$+, calc. 508.3242).

N-boc Kemp Ligand (6)



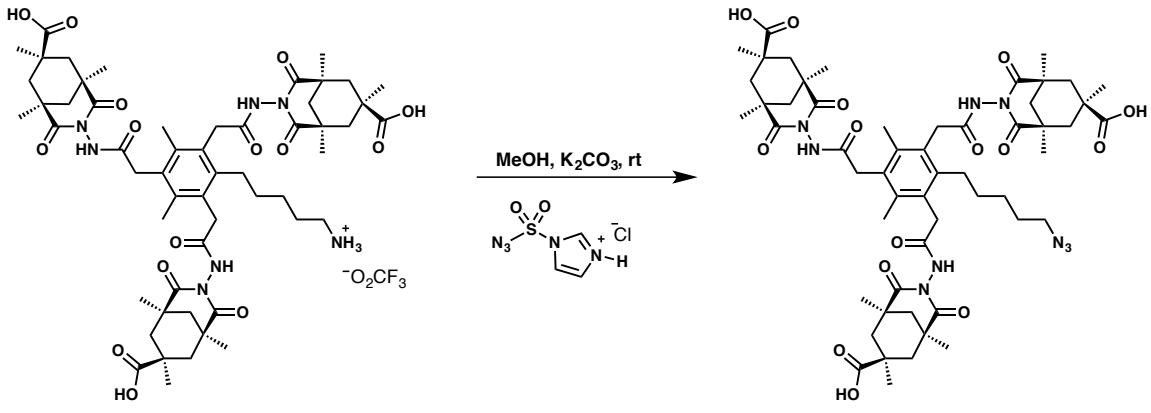
N-boc trihydrazide **5** (2.108 g, 4.15 mmol), Kemp's anhydride acid chloride **6** (3.33 g, 12.87 mmol), and a catalytic amount of DMAP (0.025 g) were added to a 500 mL round-bottom flask with stir bar. Dry pyridine (200 mL) was added to the reaction mixture, put under an argon atmosphere, and heated to 90° C overnight. After 17 hours, the reaction mixture was concentrated to dryness under reduced pressure. The residue was then dissolved in DCM (~300 mL) and washed with 10% HCl (~250 mL). The organics were washed with 2 M NaOH (1 × 250 mL). The base layer was then washed with DCM (2 × 250 mL), separated from the organics, and acidified with 2 M HCl, which caused a white precipitate to form. The precipitate mixture was cooled in an ice bath and filtered. The resulting white solid was dried under vacuum in a desiccator overnight to give **7a** (4.342 g, 89% yield) as an off white solid, which was used without further purification. ^{1}H NMR (600 MHz, CD_3OD) δ 3.89 (two overlapping singlets, 6H), 3.07 (t, *J* = 6.5 Hz, 2H), 2.69 (s, 2H), 2.56 (d, *J* = 13.6 Hz, 6H), 2.33 (s, 6H), 2.12 (dd, *J* = 13.4, 8.4 Hz, 3H), 1.60 – 1.42 (m, 19H), 1.33 (d, *J* = 13.5 Hz, 6H), 1.27 – 1.23 (m, 18H), 1.23 – 1.20 (m, 8H). ^{13}C NMR (151 MHz, CD_3OD) δ 179.50, 179.40, 175.54, 172.72, 172.54, 158.42, 142.00, 138.47, 131.30, 130.09, 79.75, 44.80, 43.08, 42.70, 42.67, 41.78, 41.29, 36.11, 36.05, 31.95, 31.05, 30.57, 30.54, 30.41, 28.87, 28.15, 25.49. ESI-TOF high-acc: m/z: 1174.5908 ([MH]+, $C_{60}H_{83}N_7O_{17}$+, calc. 1174.5918).

Kemp Ligand TFA Salt (7b)



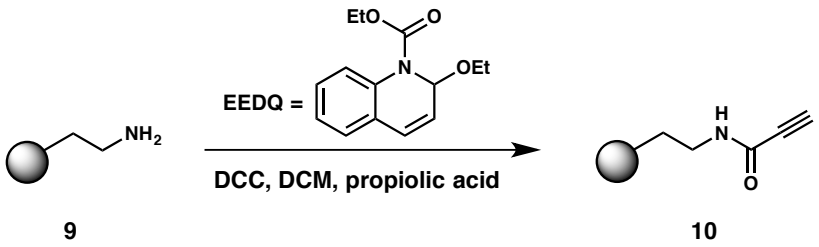
N-boc uranyl ligand **7a** (4.0 g, 3.4 mmol) was added to a 500 mL round-bottom flask and dissolved in 250 mL DCM containing 5 % TFA (12.5 mL). The reaction mixture was stirred at room temperature for 3 hours. The solvents were removed under vacuum to give **7b** (4.007 g, 99% yield) as a pure off white foam, which was used without further purification. ^{1}H NMR (600 MHz, CD_3OD) δ 3.89 (two overlapping singlets 6H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.71 (s, 2H), 2.60 – 2.51 (m, 6H), 2.34 (s, 6H), 2.14 – 2.06 (m, 3H), 1.75 (t, *J* = 7.5 Hz, 2H), 1.57 (bs, 5H), 1.52 – 1.45 (m, 3H), 1.35 (d, *J* = 13.3 Hz, 6H), 1.28 – 1.21 (m, 26H). ^{13}C NMR (151 MHz, CD_3OD) δ 179.69, 179.50, 175.79, 175.69, 172.94, 172.68, 141.69, 138.70, 131.72, 130.24, 44.90, 44.86, 43.22, 42.80, 41.89, 41.87, 40.78, 36.13, 36.01, 31.90, 30.62, 30.55, 27.99, 27.54, 25.49, 17.53. ESI-TOF high-acc: m/z: 1074.80 ([MH]+, $C_{55}H_{76}N_7O_{15}$+, calc. 1074.54).

Kemp Ligand Azide (8)



TFA salt **7b** (4.0 g, 3.36 mmol) was dissolved in MeOH (250 mL) and K_2CO_3 (2.791 g, 20.2 mmol) and $CuSO_4 \bullet 5H_2O$ (0.168 g, 0.673 mmol) were added. To the stirring suspension, imidazole-1-sulfonyl azide hydrochloride (1.42 g, 6.73 mmol) was added, the reaction was capped, and stirred for 19 hours at room temperature. The volatiles were removed under reduced pressure, the residue was suspended in 200 mL 1M HCl and extracted with DCM (3 × 150 mL). The organics were combined, dried over $MgSO_4$, and concentrated under reduced pressure to give **8** (3.37 g, 91% yield) as a pale yellow solid, which was used without further purification. Analytically pure samples of **8** can be obtained by silica gel column chromatography using 4% MeOH in DCM as the eluent. Iodine was used to help visualize **8** on TLC. ^{1}H NMR (600 MHz, CD_3OD) δ 3.88 (s, 6H), 2.74 – 2.67 (m, 2H), 2.56 (d, *J* = 13.5 Hz, 6H), 2.33 (s, 6H), 2.16 – 2.08 (m, 3H), 1.72 – 1.65 (m, 2H), 1.59 – 1.50 (m, 5H), 1.48 (d, *J* = 13.2 Hz, 4H), 1.35 – 1.28 (m, 9H), 1.24 (overlapping peaks, 15H), 1.22 (overlapping peaks, 9H). ^{13}C NMR (151 MHz, CD_3OD) δ 179.36, 175.58, 175.55, 172.70, 172.53, 142.02, 138.54, 131.39, 130.17, 52.51, 44.87, 43.17, 42.73, 41.84, 36.17, 32.09, 30.99, 30.57, 30.44, 29.70, 28.30, 25.58, 25.49, 17.53. ESI-TOF high-acc: m/z: 1100.5282 ([MH]+, $C_{55}H_{73}N_9O_{15}$+, calc. 1100.5299).

Alkyne Resin (10)

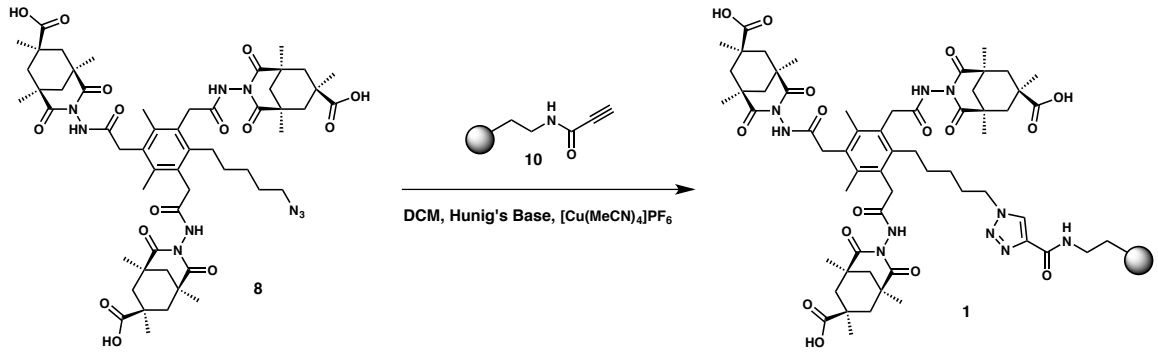


9 **10**

Resin **9** was purchased from Peptides International (TentaGel HL-NH_2 Resin; RTH-9337-PI, 0.48 meq/g).

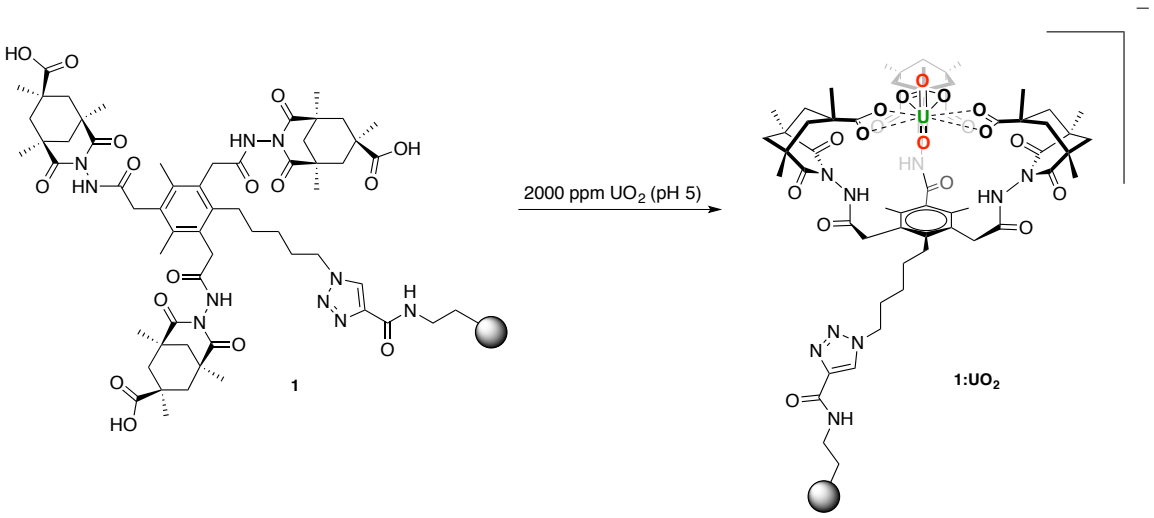
Primary amine TentaGel resin **9** (2.50 g, ~0.48 mmol/g) was suspended in DCM (90 mL), stirred gently, and cooled to -10° C in a salt/ice bath. Once the reaction mixture was cool, propiolic acid (0.222 mL, 3.6 mmol) was added and allowed to stir for 10 minutes. After this period, peptide coupling reagent *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ) was added. The reaction mixture was maintained between 0° C and -10° C for 4 hours before being allowed to warm to room temperature overnight (14 hours at room temperature, 18 hours total). The resin was collected by filtration with a glass frit and washed successively with DCM (3 × 150 mL), DMF (3 × 150 mL), MeOH (3 × 150 mL), and H_2O (3 × 150 mL). After the washes the resin was dried under vacuum for 24 hours to give **10** as pale yellow colored beads that were somewhat sticky (2.478 g resin after the reaction). The resin was analyzed with IR and Elemental Analysis.

Kemp Ligand Resin (1)



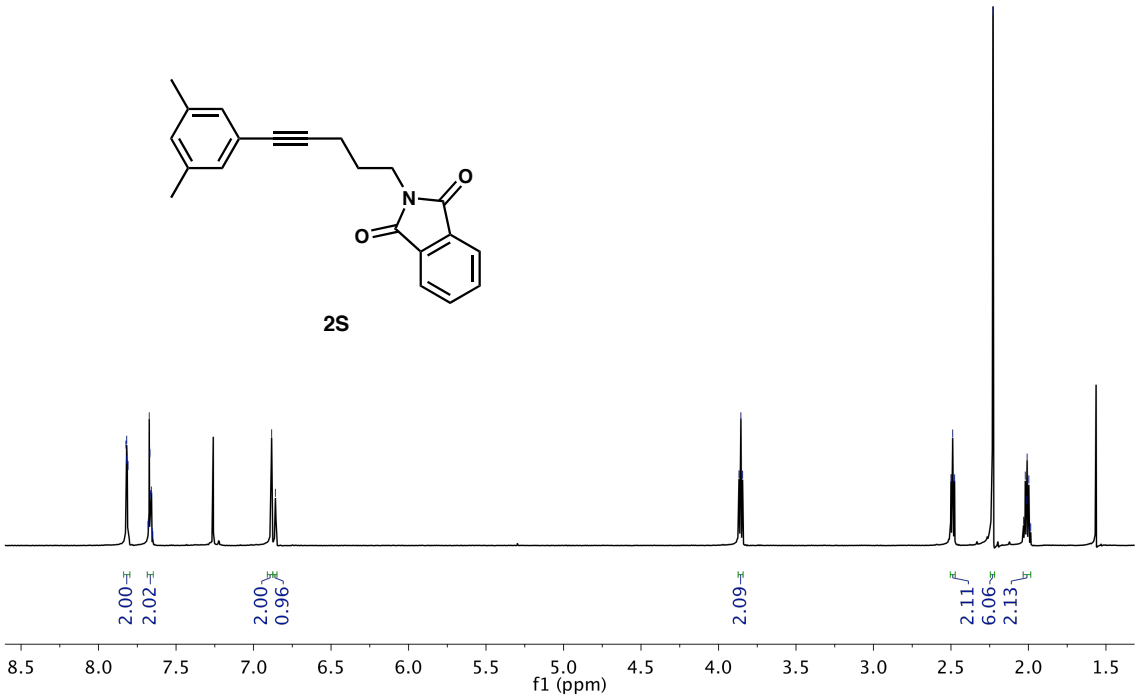
Alkyne resin **10** (1.650 g, 0.792 mmol) was added to a round bottom flask followed by azide **8** (1.749 g, 1.59 mmol) and DCM (100 mL). The suspension was stirred gently and Hünig's base (6.9 mL, 39.6 mmol) was added dropwise followed by the addition of $[Cu(MeCN)_4]PF_6$ (0.059 g, 0.159 mmol). The reaction mixture was capped and stirred for 20 hours. Methanol (50 mL) was then added to the mixture to dissolve any fine particulates that formed during the reaction. The resin was collected by filtration with a glass frit and washed with DCM (150 mL). Excess azide **8** was recovered by combining the filtrate and the DCM wash. The organics were evaporated under reduced pressure, dissolved in DCM (200 mL) and washed twice with 1 M HCl. The organics were then dried over $MgSO_4$ and evaporated under reduced pressure to recover **8** (1.28 g, 1.1 mmol) as an off white solid. The resin was then washed successively with DCM (3 × 150 mL), DMF (3 × 150 mL), MeOH (3 × 150 mL), 0.5 M HCl (3 × 150 mL), and H_2O (3 × 150 mL). After the washes the resin was dried under vacuum for 24 hours to give **1** (1.934 g resin, ~0.22 mmol/g) as tan colored beads that were free-flowing when dry.

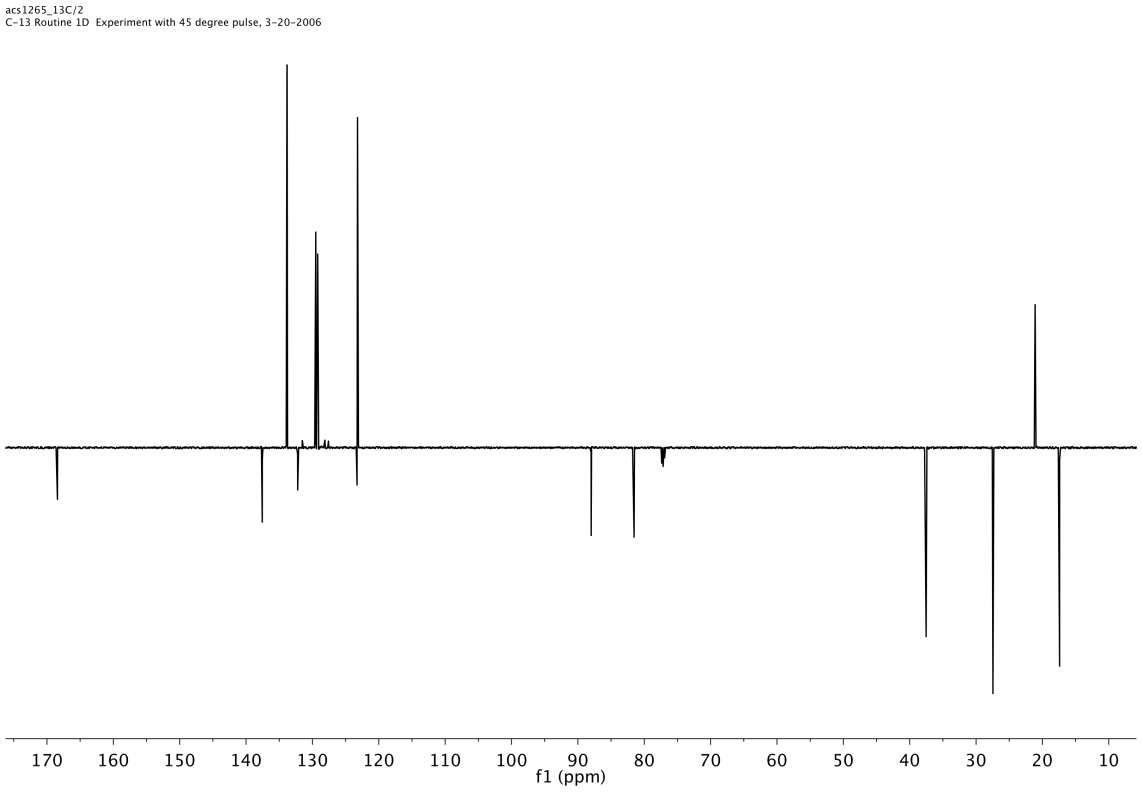
Kemp Resin Uranyl Complex 1:UO_2

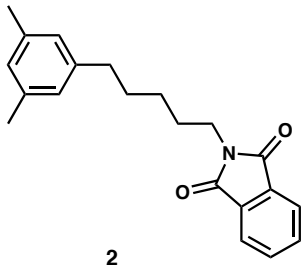


Kemp Resin **1** (0.075 g) was added to a Poly-Prep® chromatography column (Bio-Rad, catalog #731-1550) and 7 mL of 2000 ppm Uranium stock solution was added. The column was capped and placed on a nutating mixer (Fisher Scientific, catalog #260100F) to agitate the mixture for a period of 18 hours. After this period, the solution was collected by passing it through the frit at the bottom of the column. Another 7 mL of 2000 ppm Uranium stock solution was added, the column was capped, and agitated again for 18 hours. At this time the solution was removed as before and the resin was washed with deionized H_2O (3 × 15 mL), and dried under vacuum. An IR spectrum of **1:UO_2** was obtained showing the uranyl ν_3 antisymmetric stretch at 914 cm^{-1} (See IR Spectra).

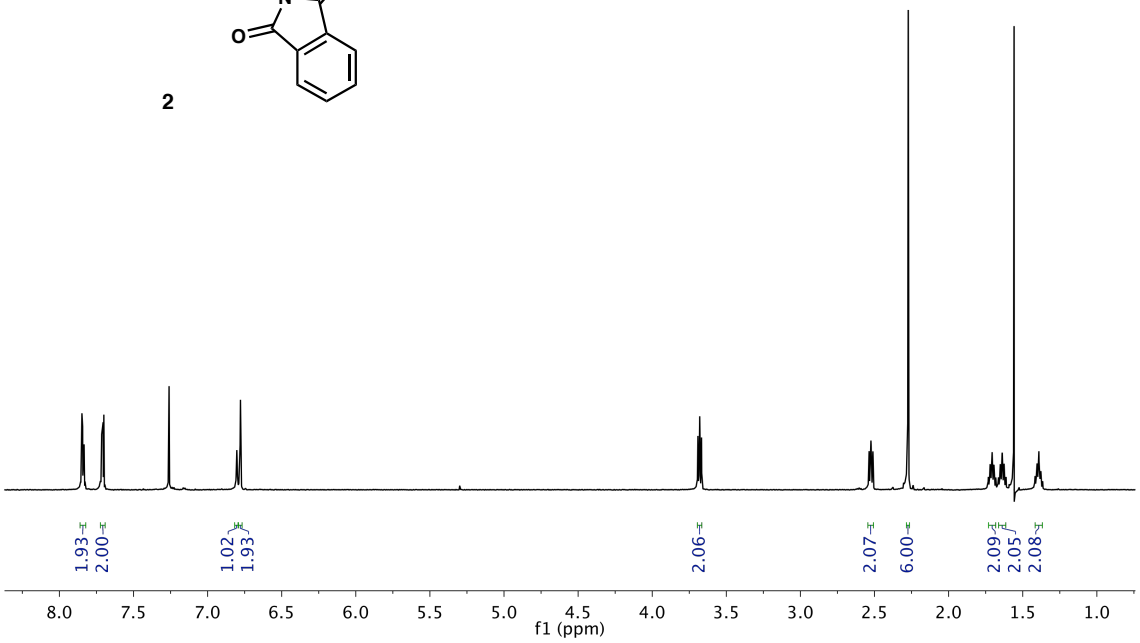
NMR Spectra

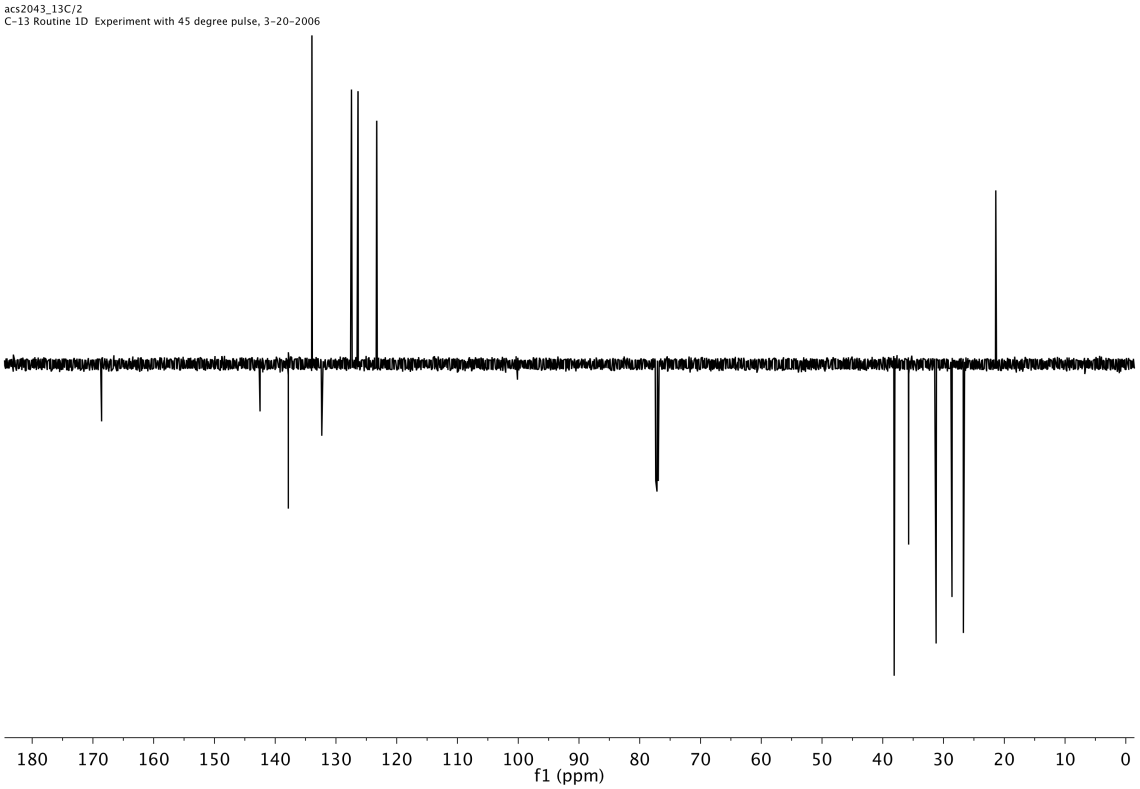


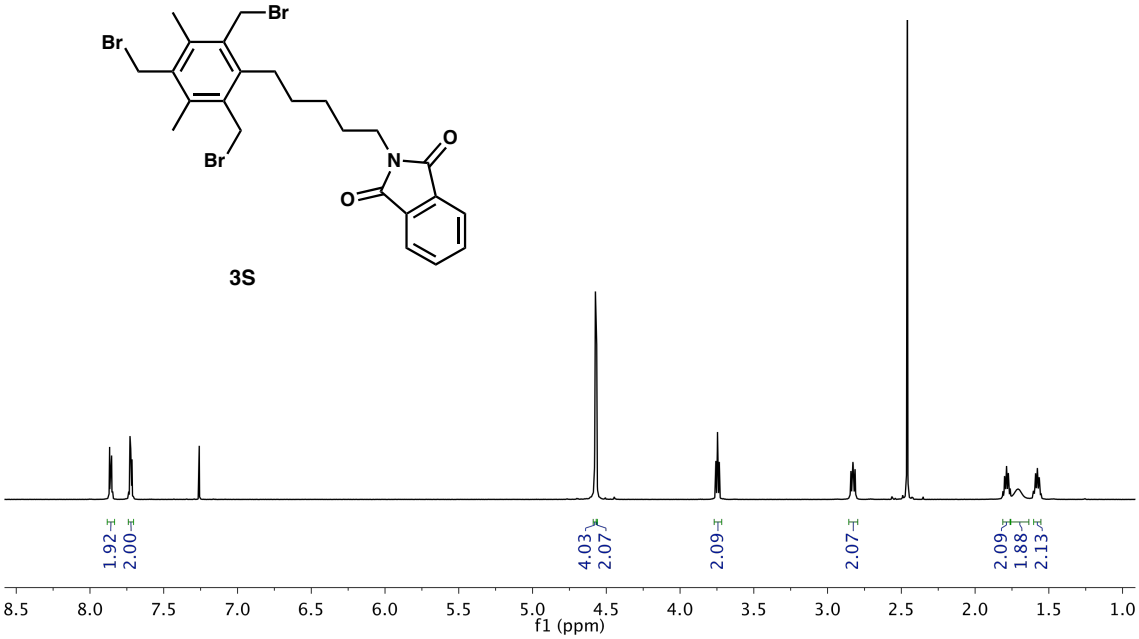




2







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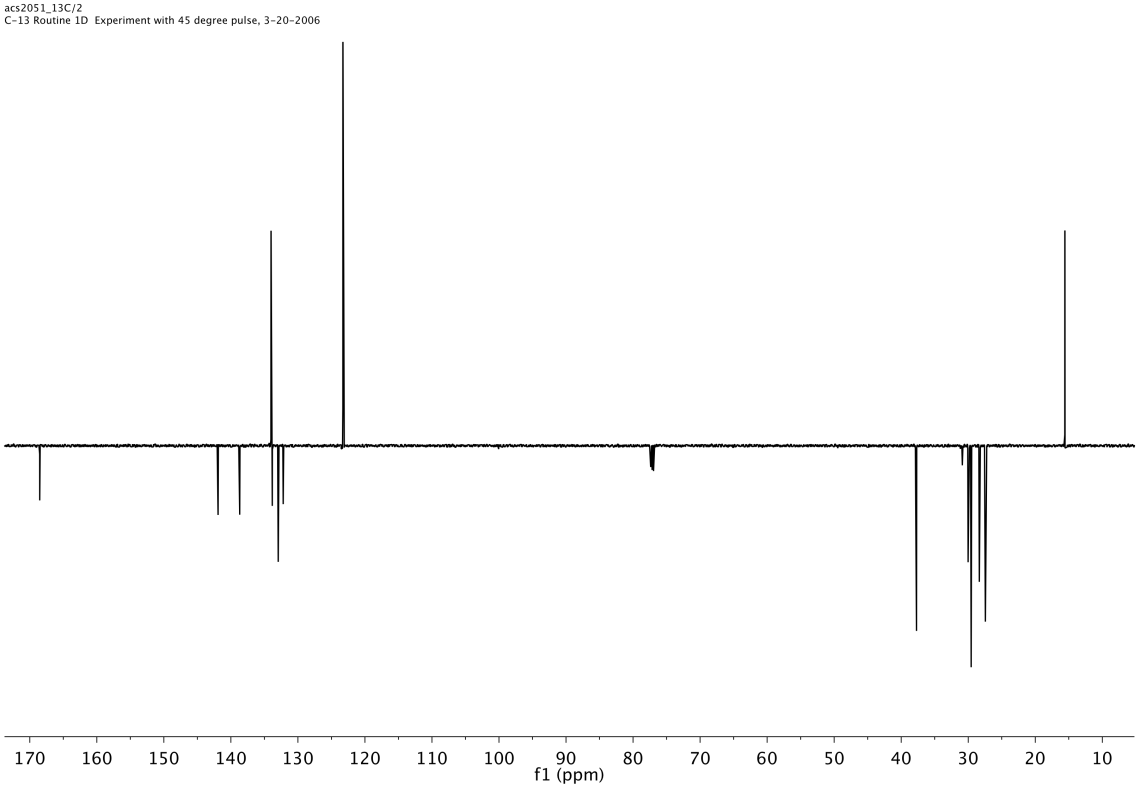

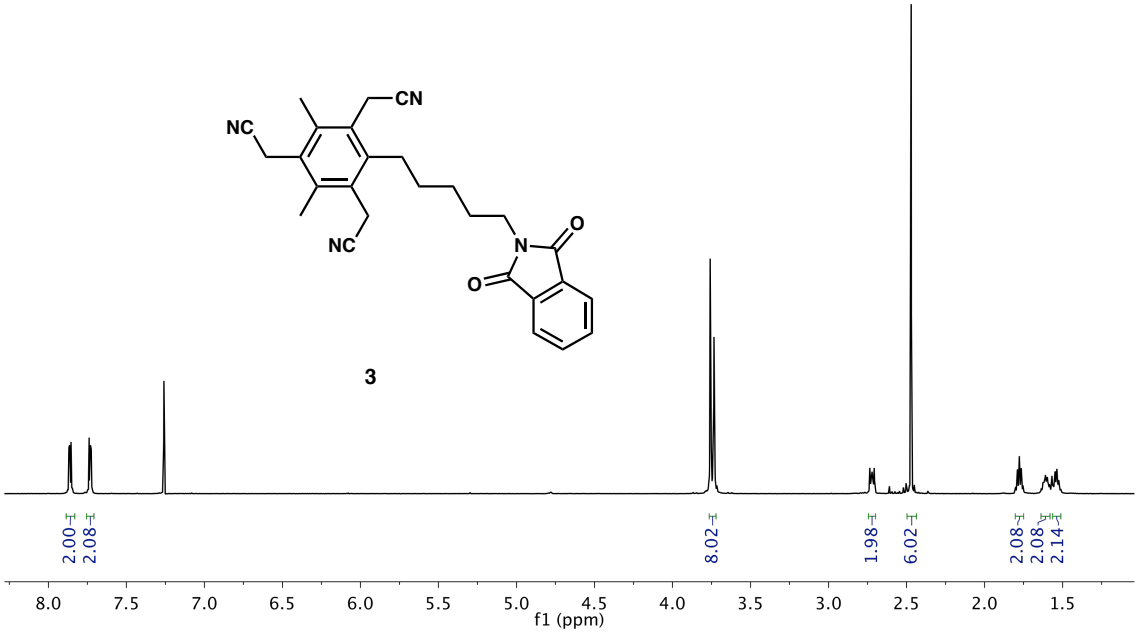

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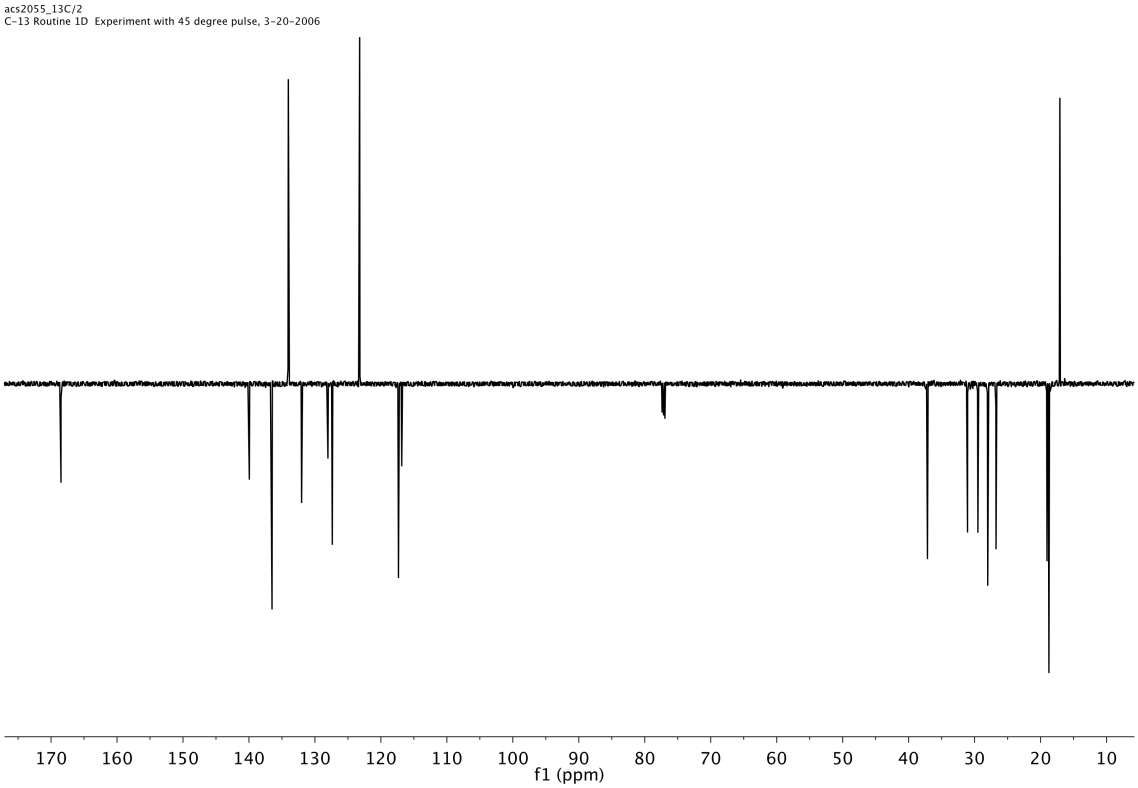

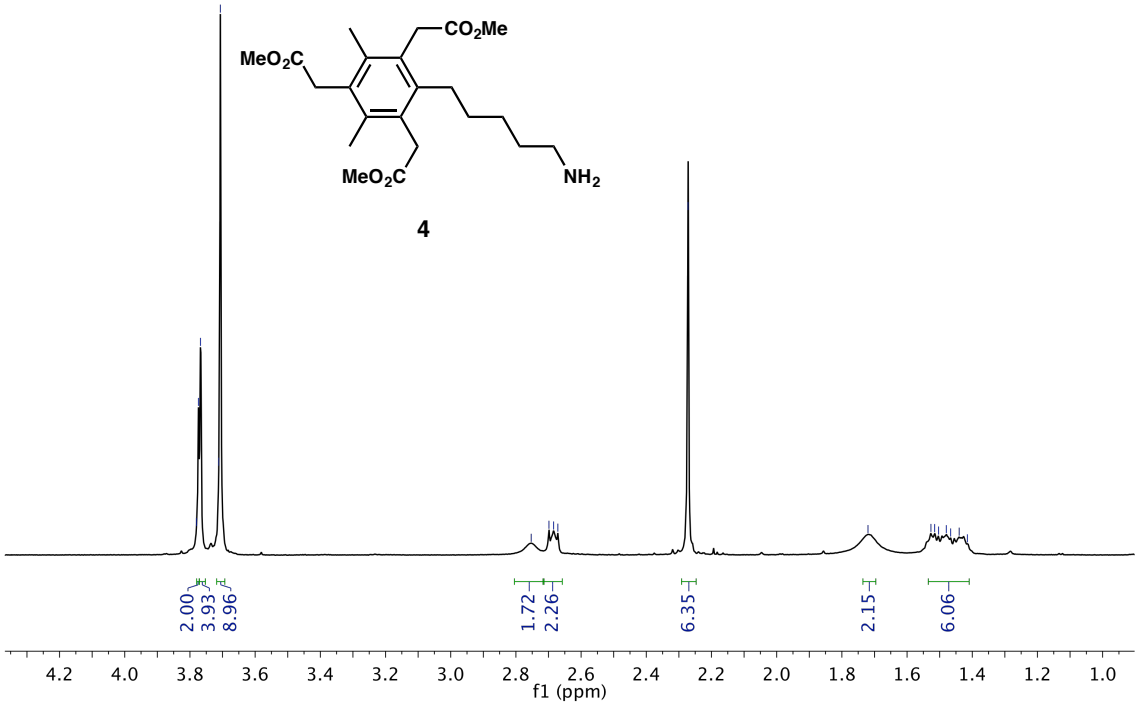

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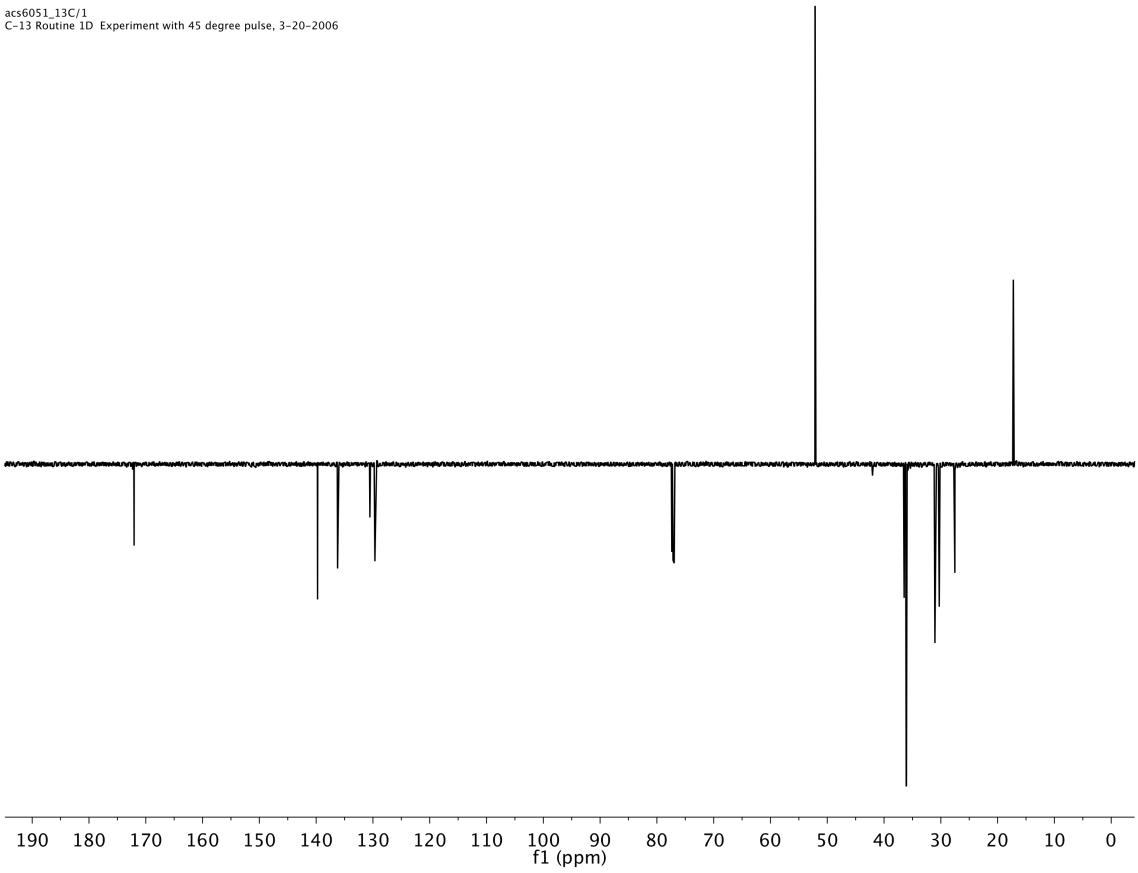

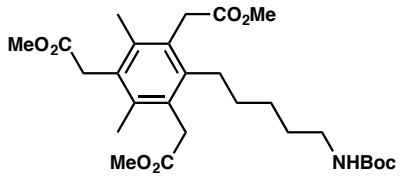

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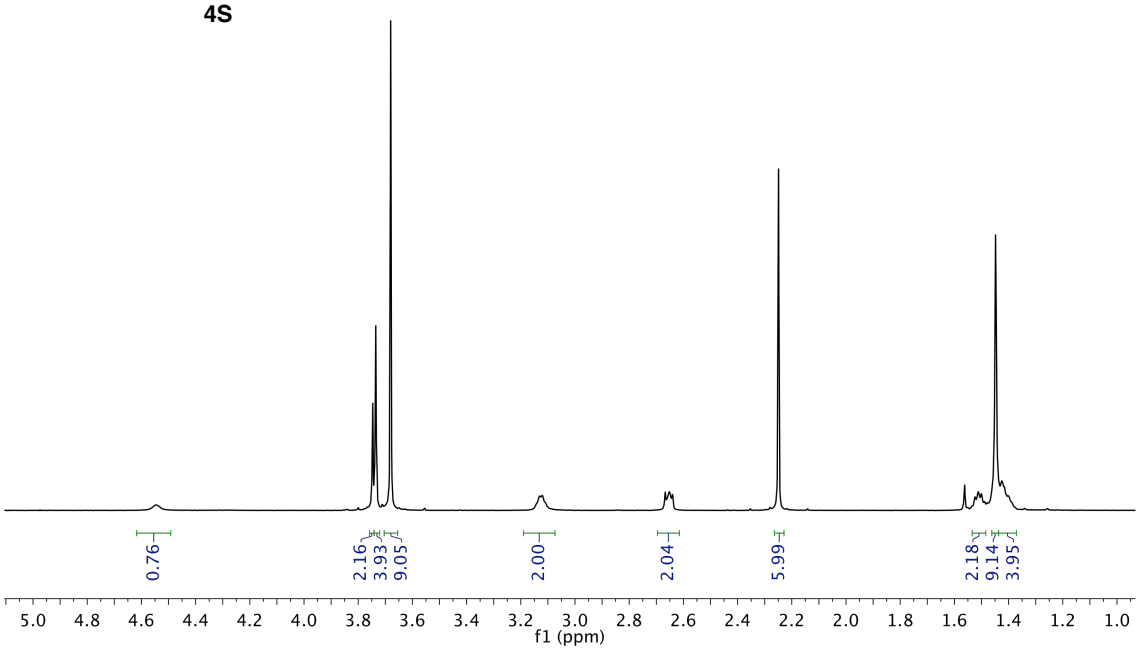

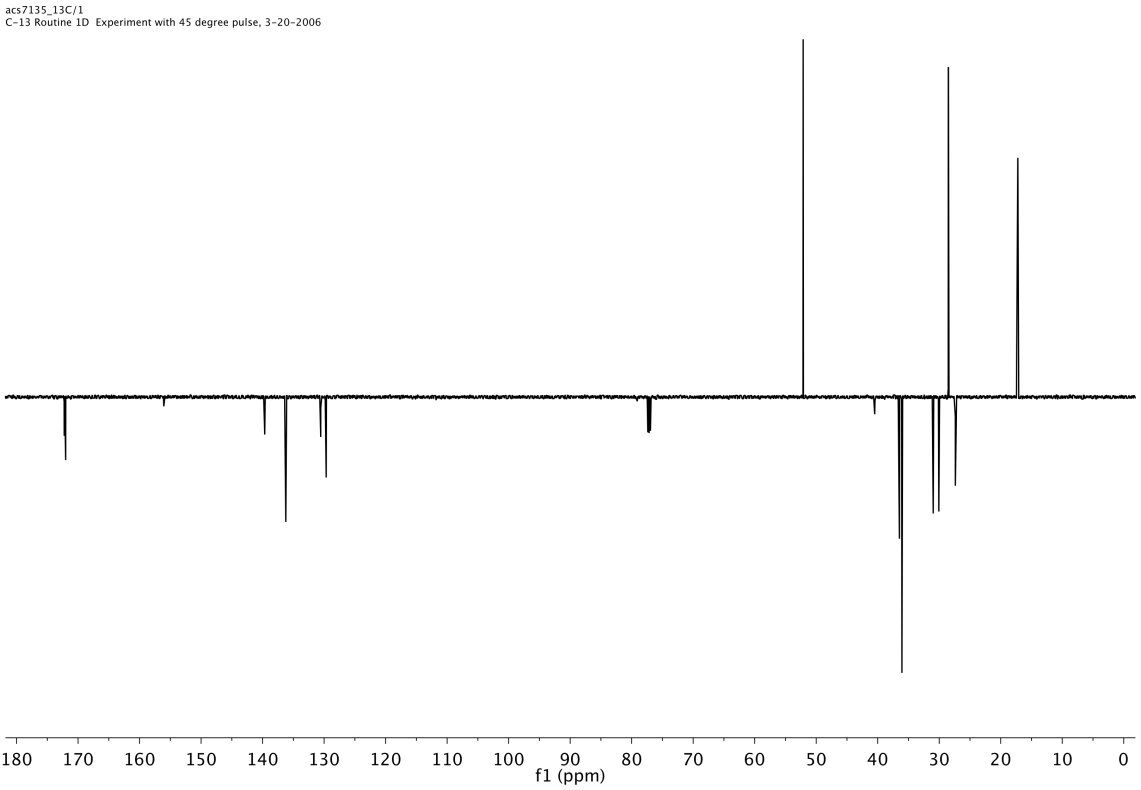

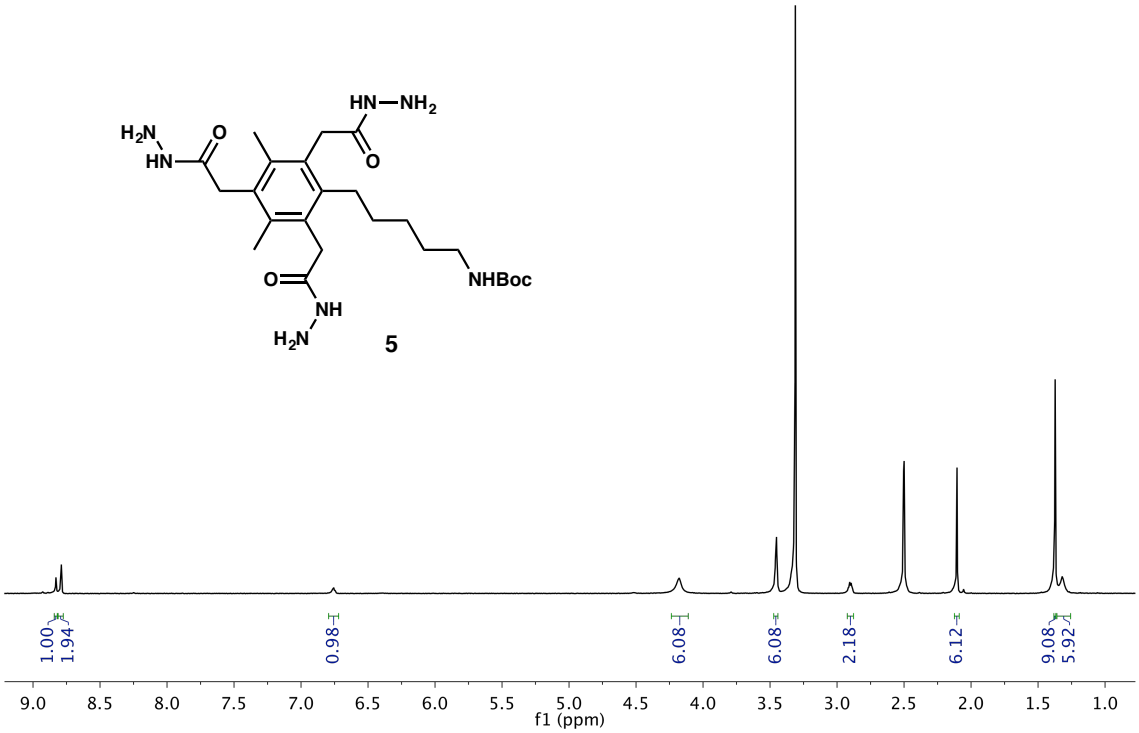

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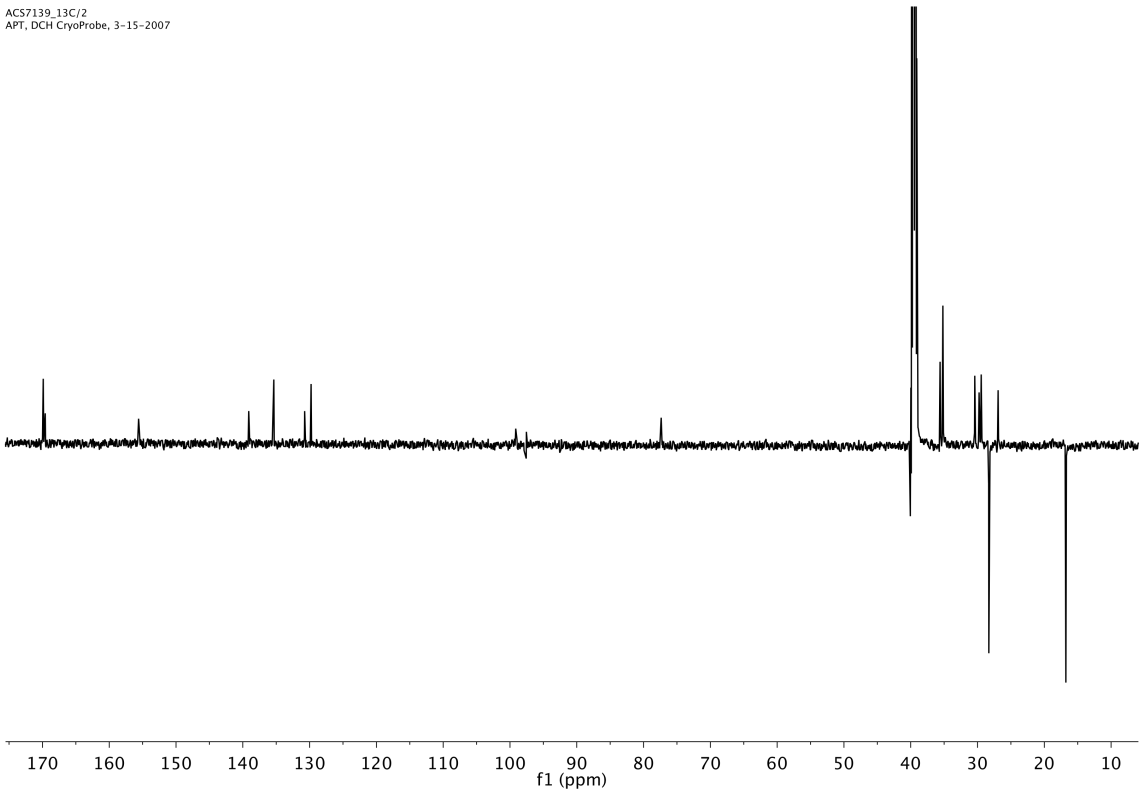
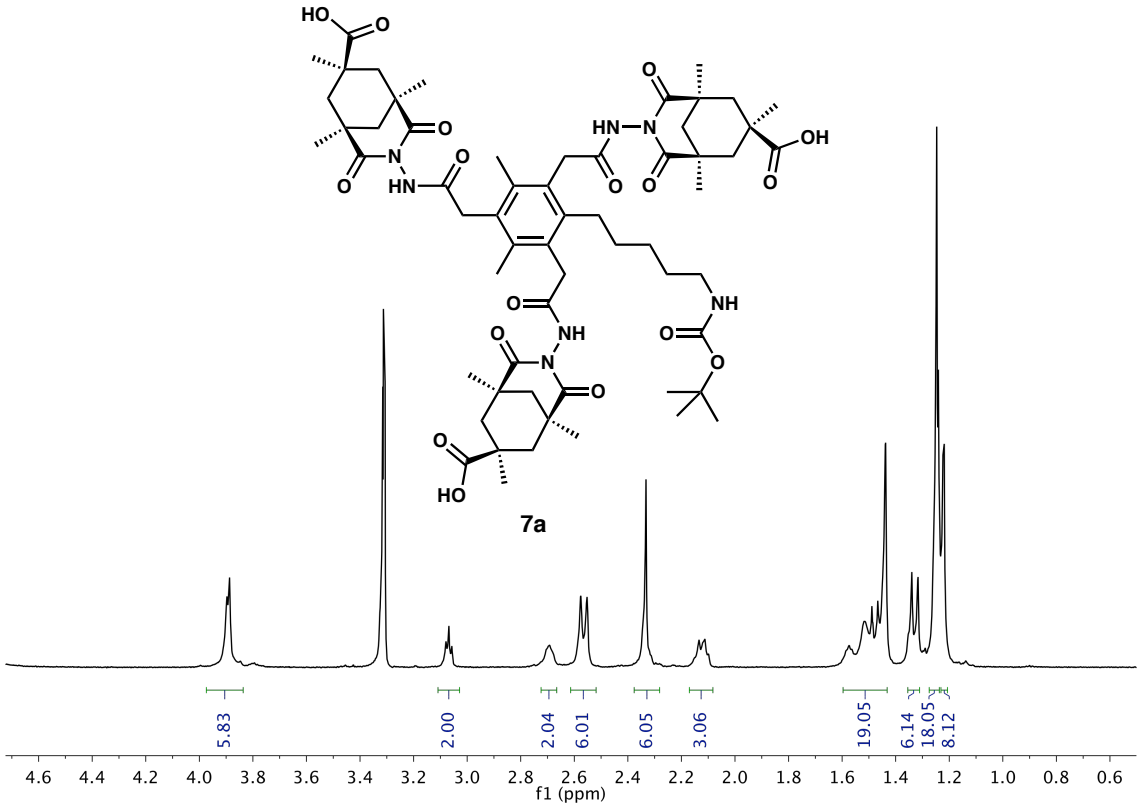
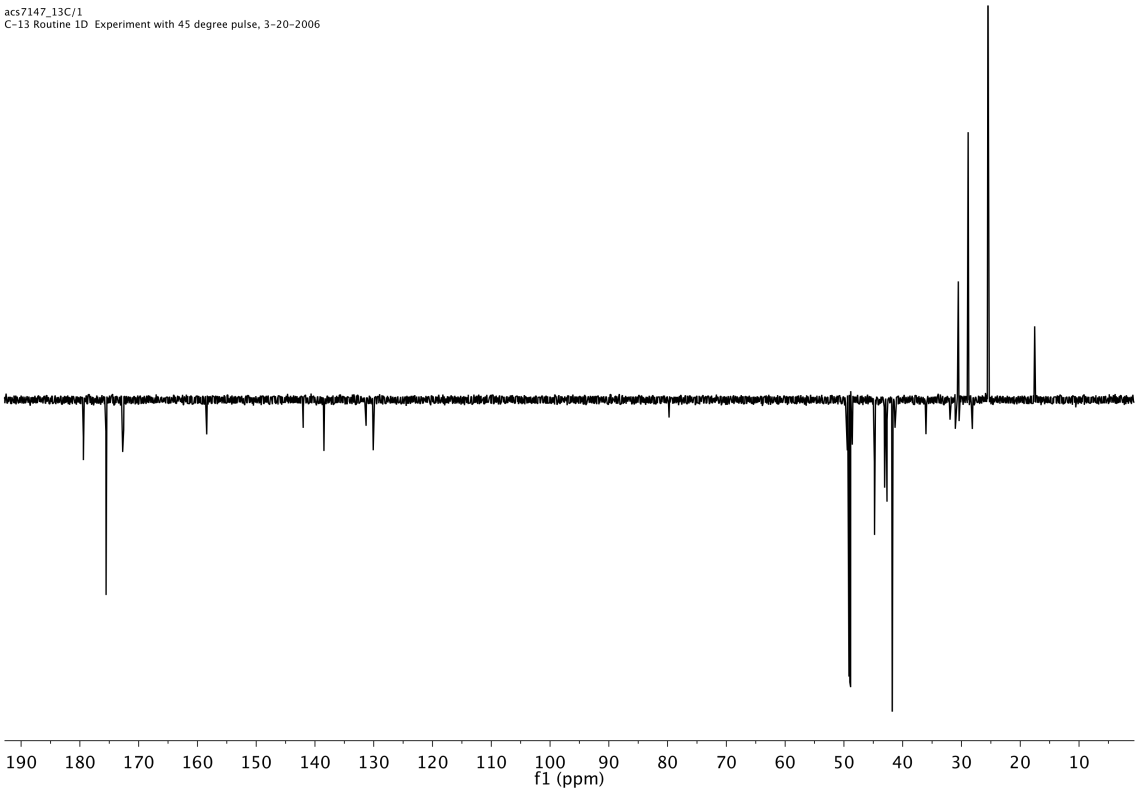
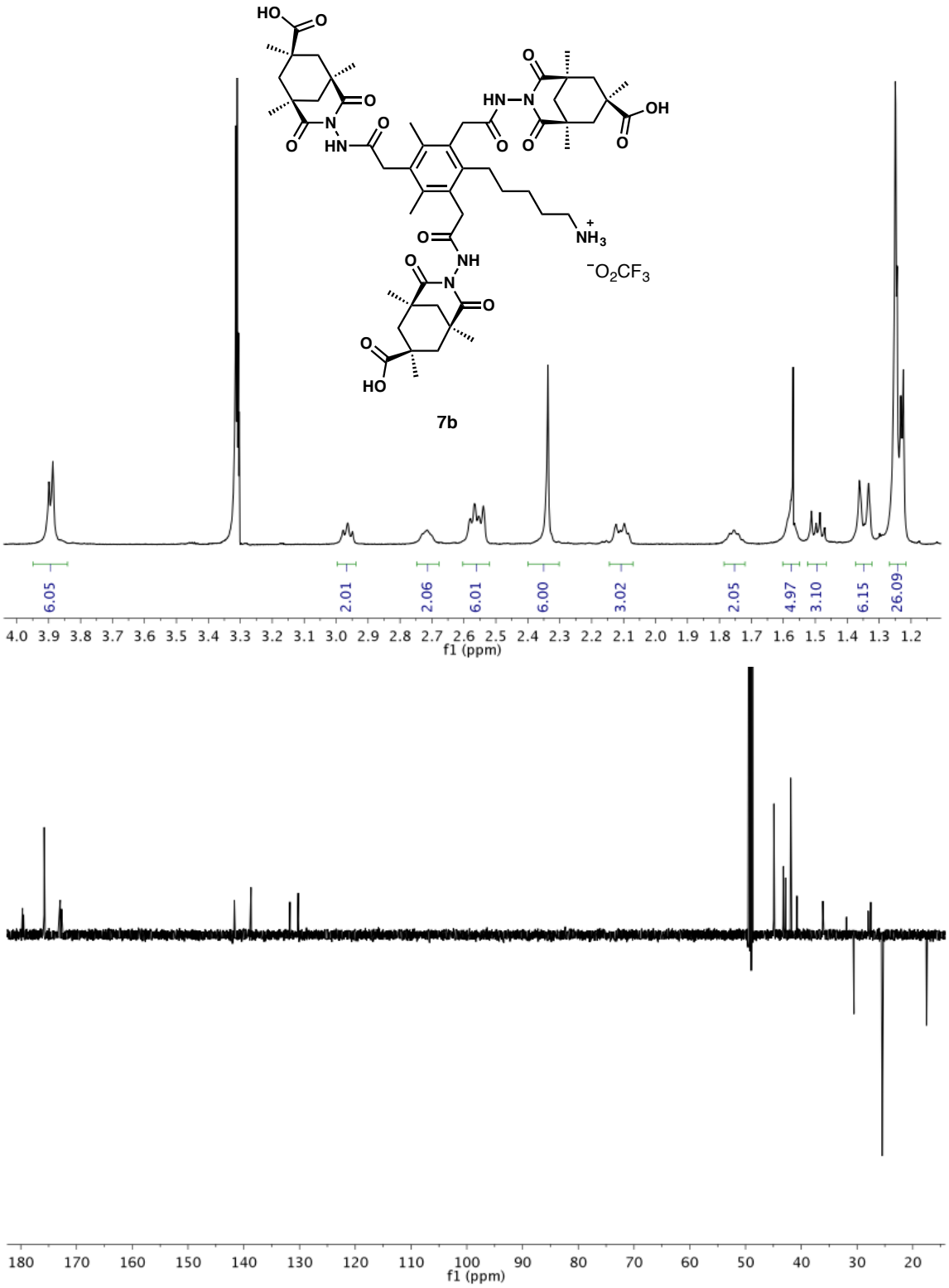


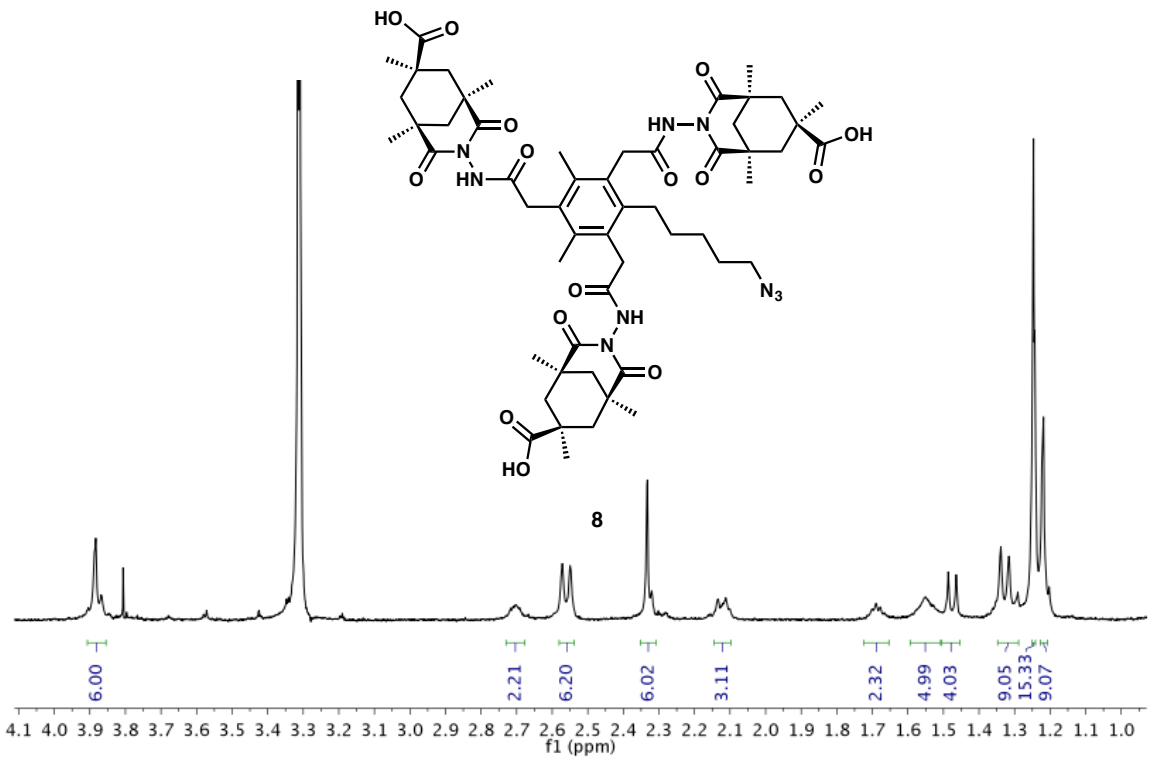


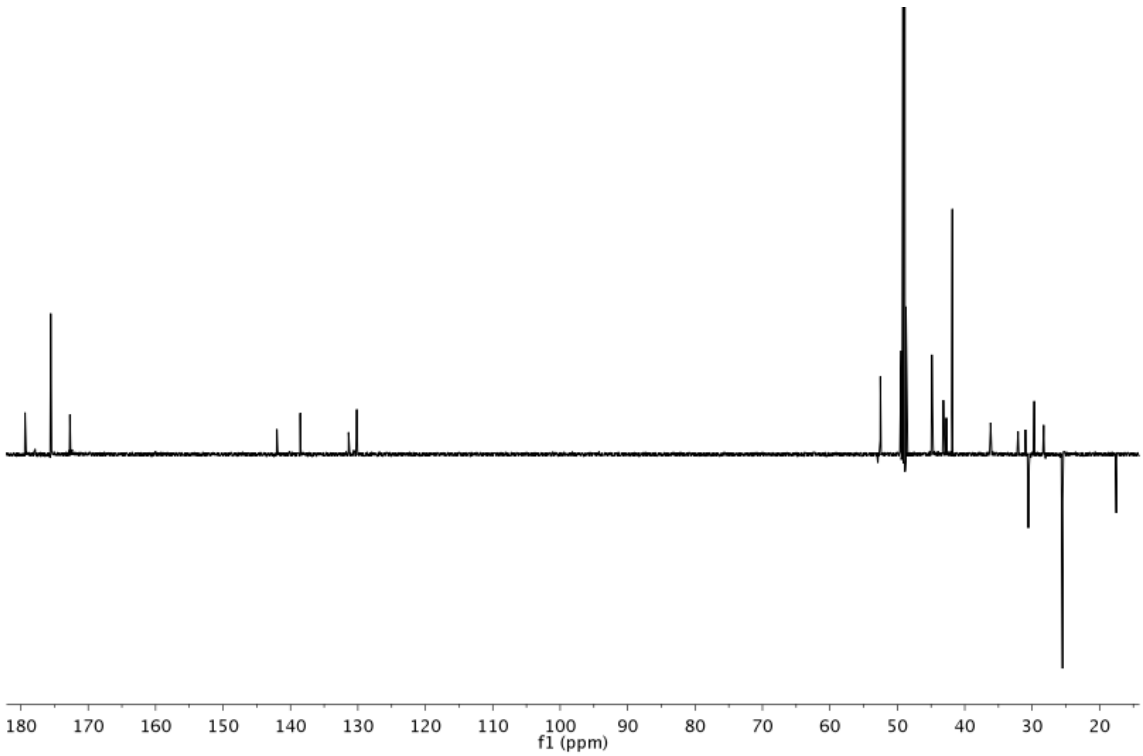
7a



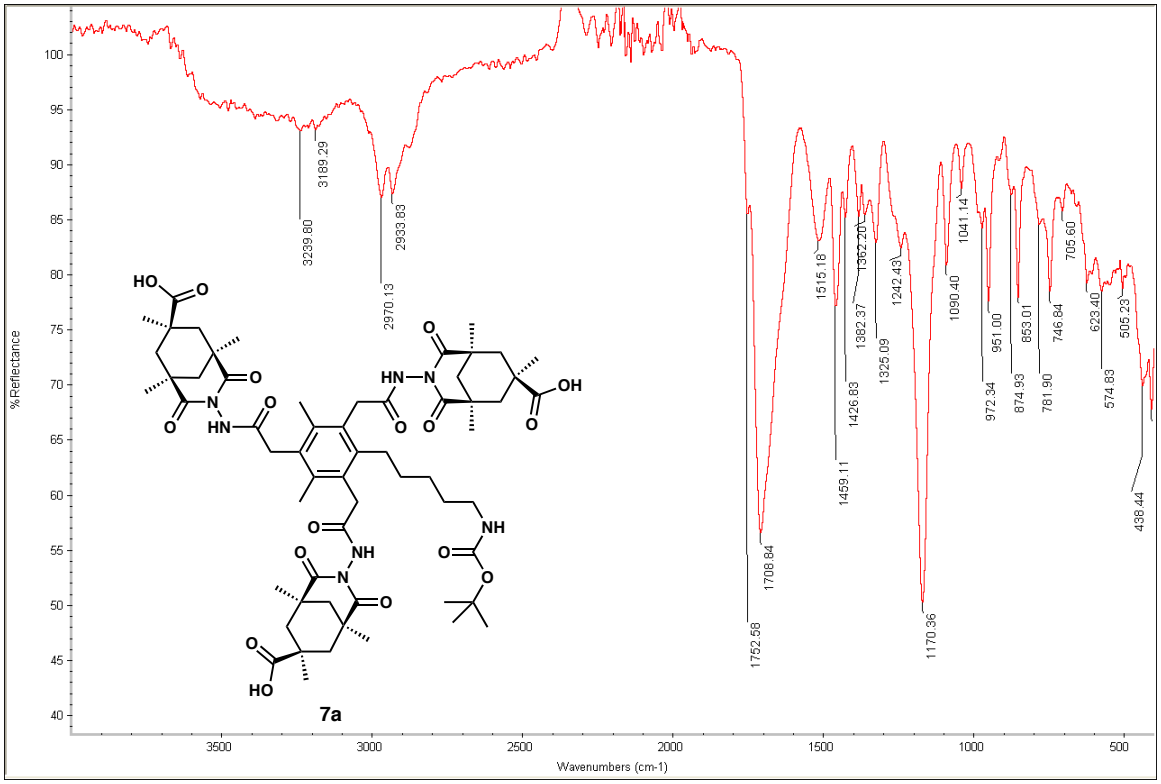


7b

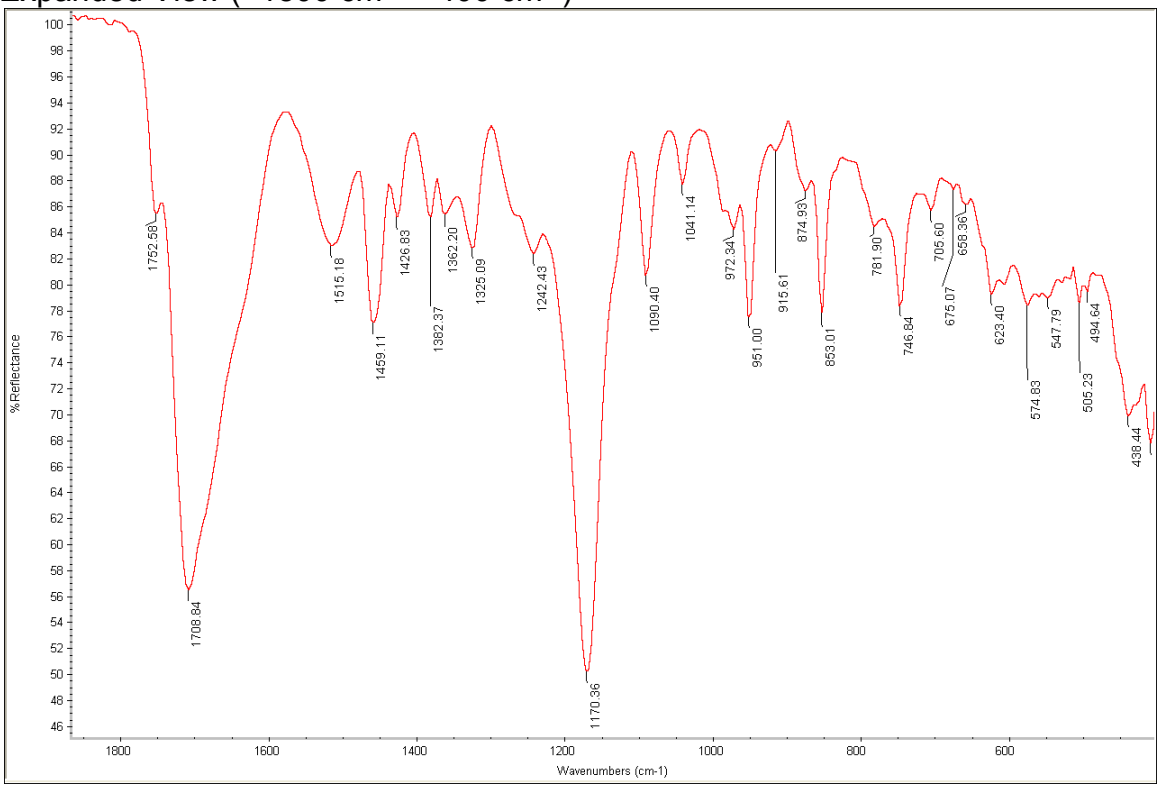


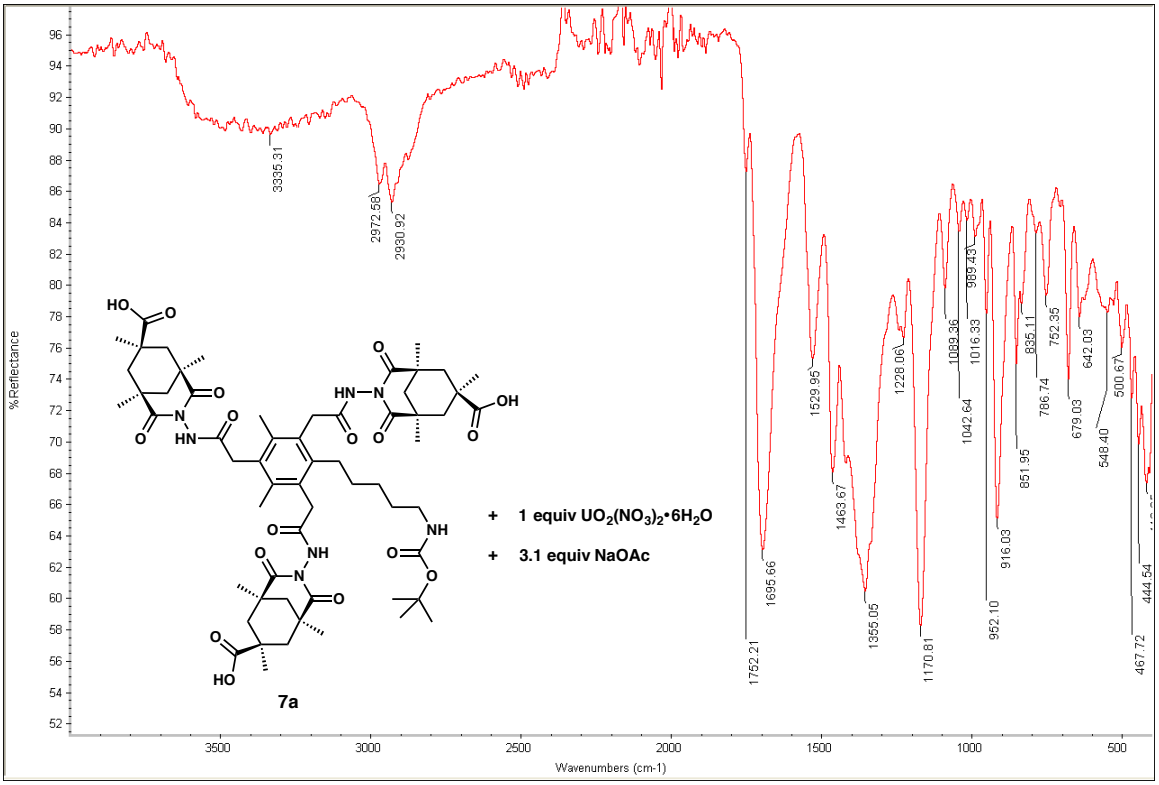


IR Spectra

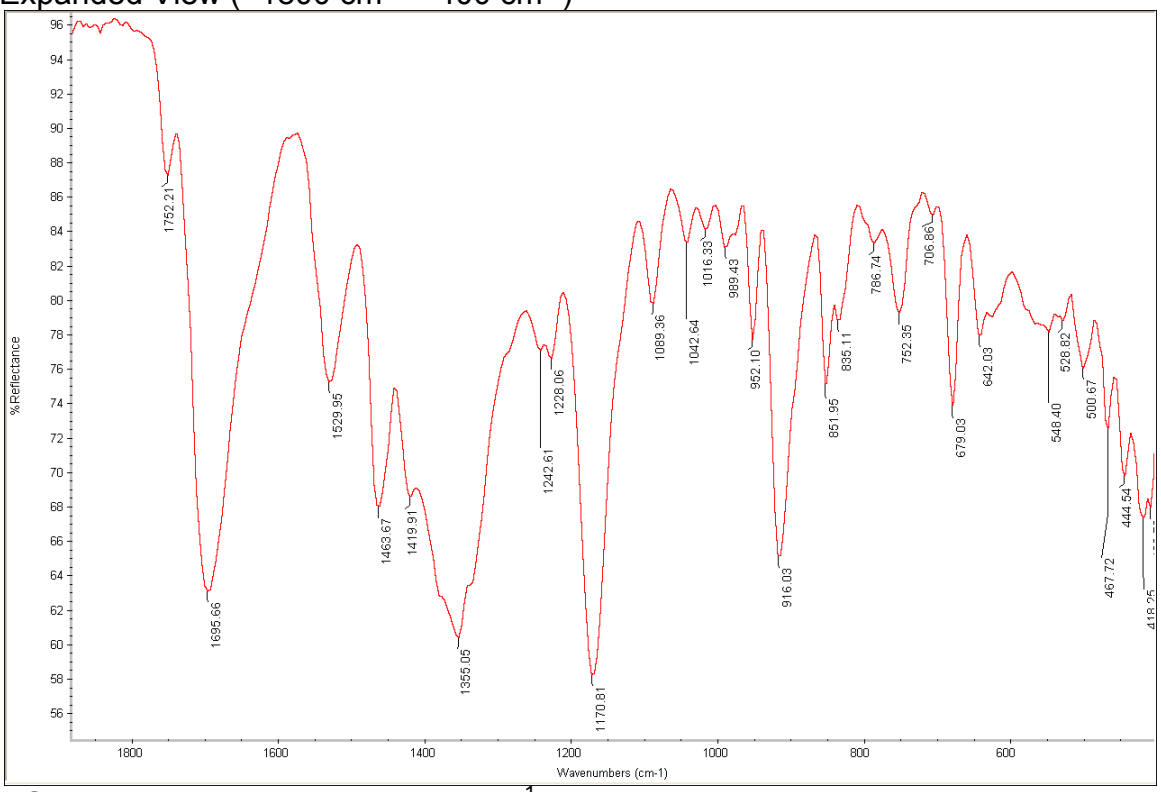


Expanded View (~1800 cm^{-1} – 400 cm^{-1})

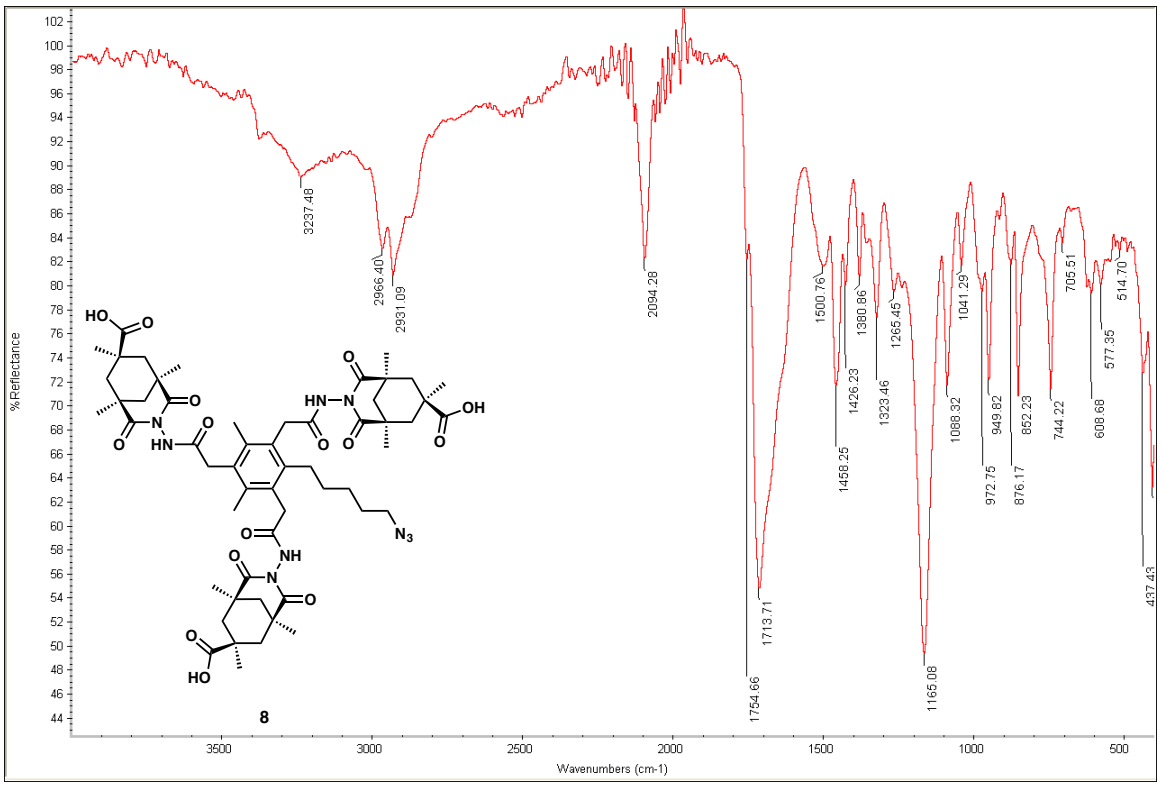




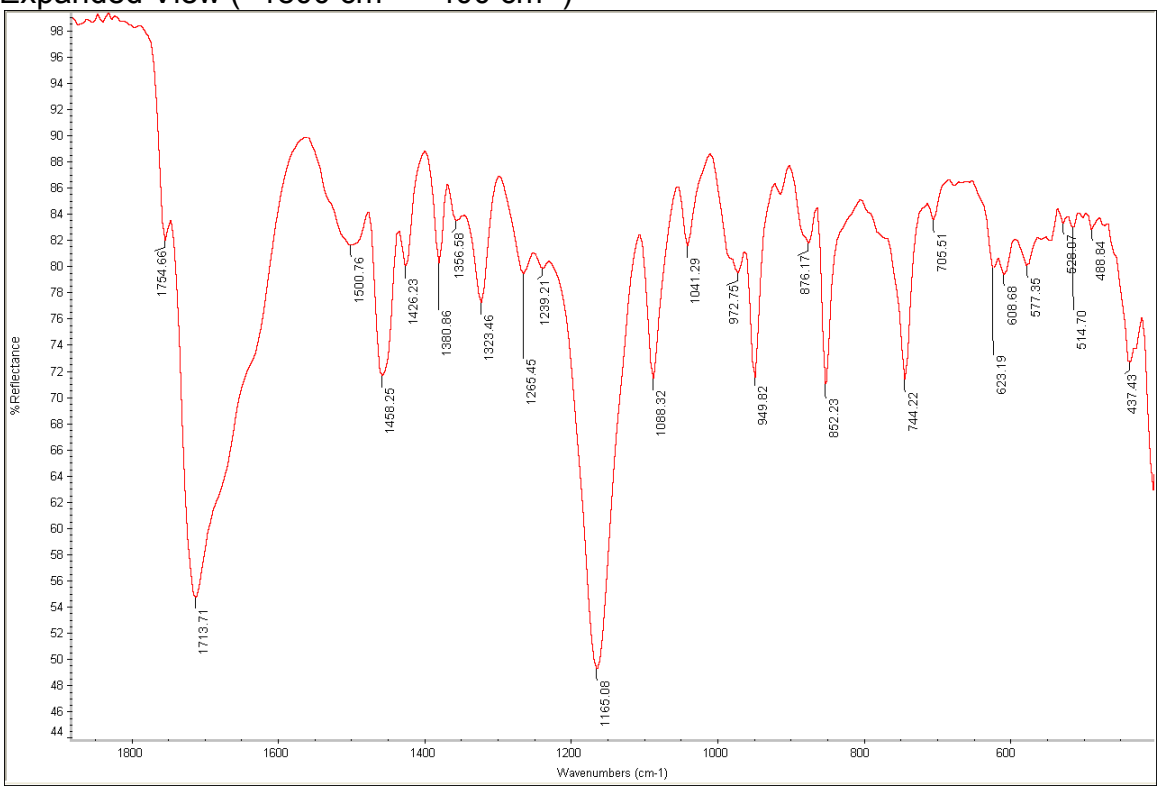
Expanded View (~1800 cm^{-1} − 400 cm^{-1})

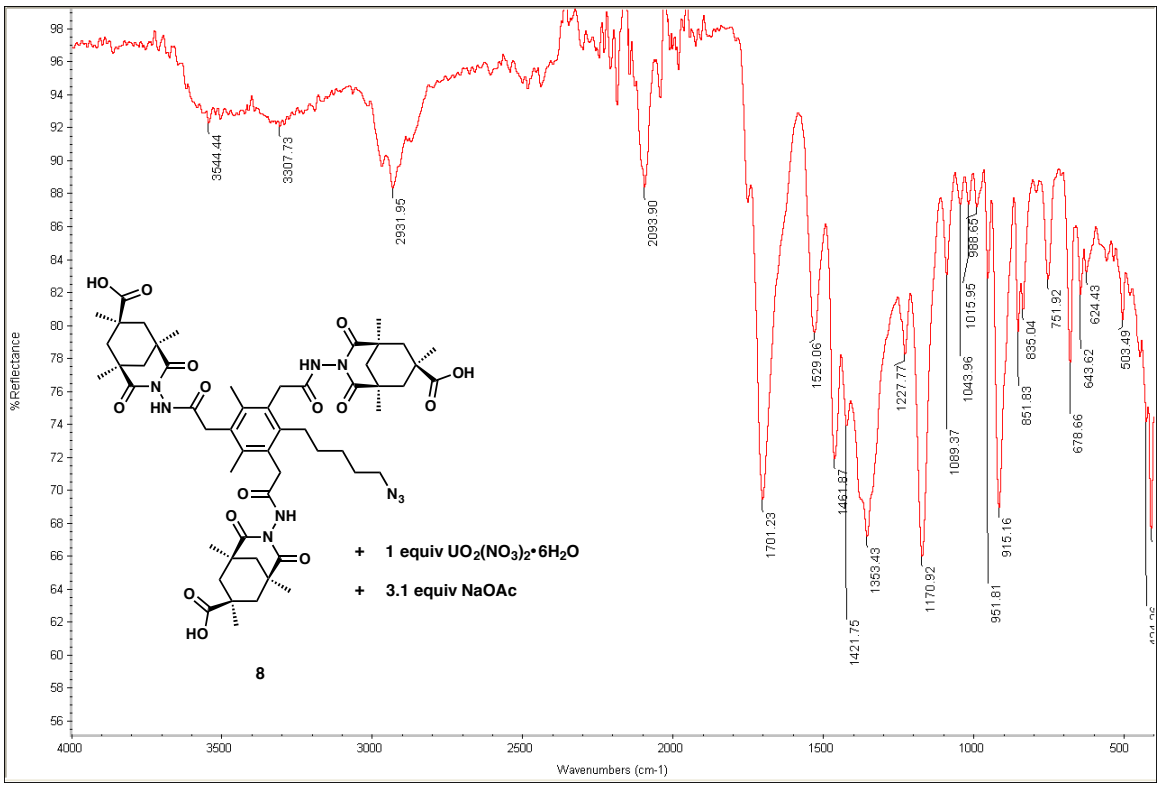


UO_2 asymmetric stretch (ν_3): 916 cm^{-1}
UO_2 symmetric stretch (ν_1): 835 cm^{-1}

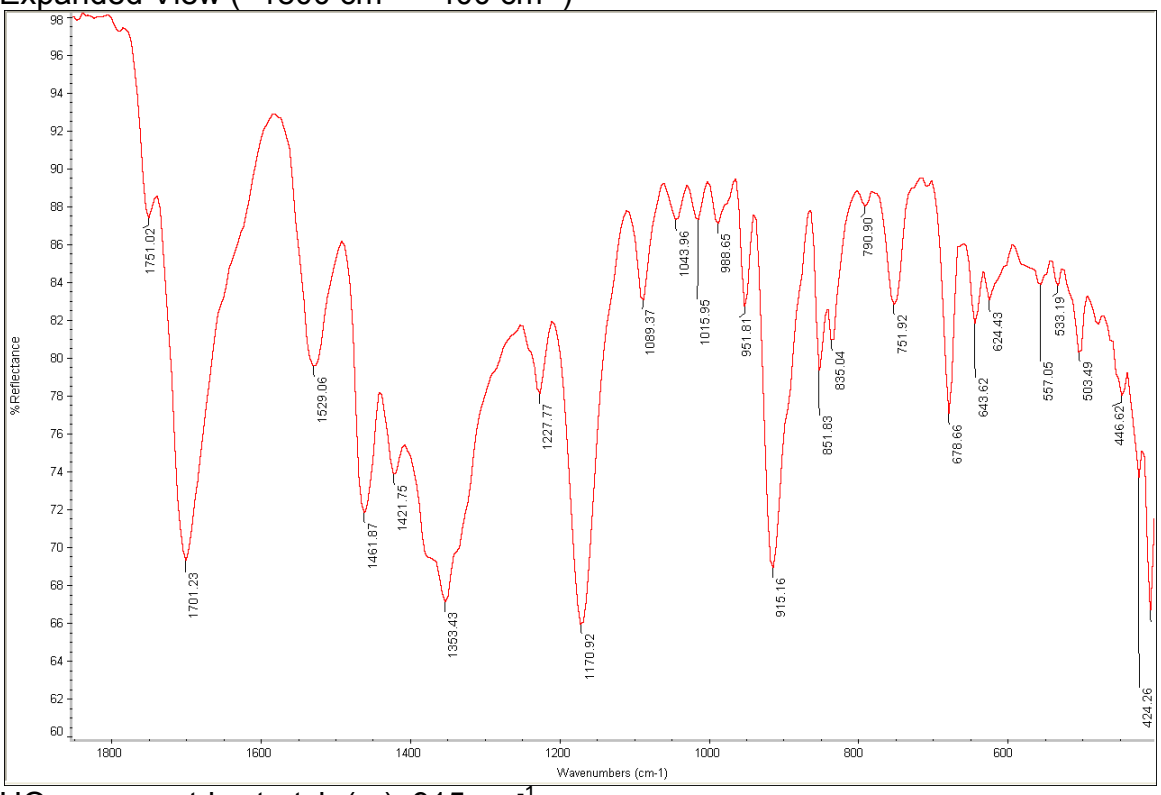


Expanded View (~1800 cm^{-1} − 400 cm^{-1})

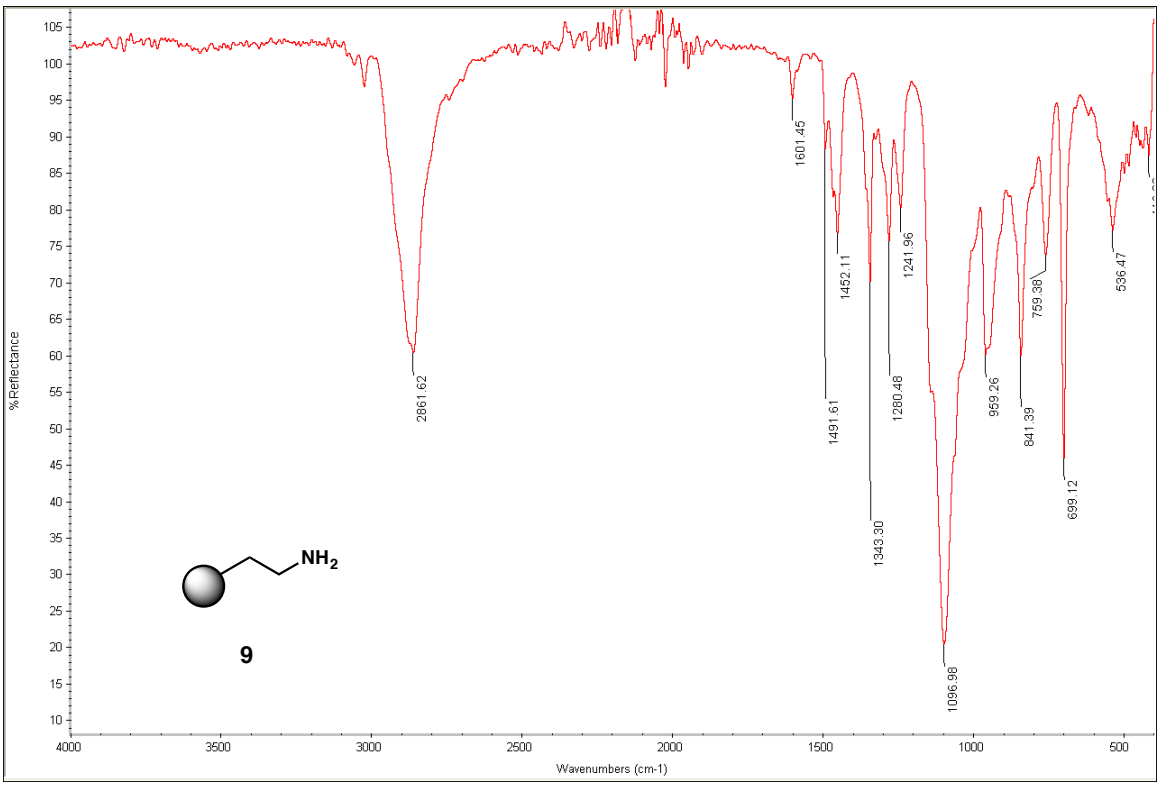




Expanded View (~1800 cm^{-1} – 400 cm^{-1})



UO_2 asymmetric stretch (v_3): 915 cm^{-1}
UO_2 symmetric stretch (v_1): 835 cm^{-1}


%Reflectance
Wavenumbers (cm-1)
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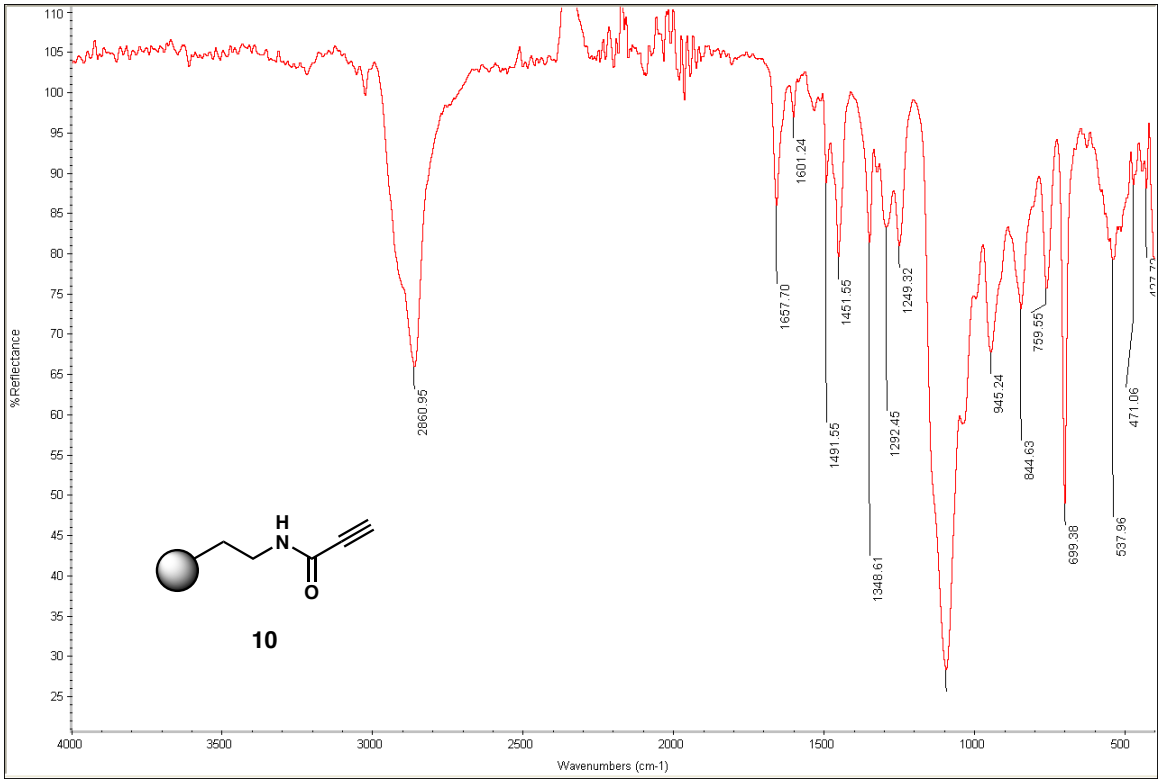
1601.45
1491.61
1452.11
1343.30
1280.48
1241.96
1096.98
959.26
841.39
759.38
699.12
536.47
NH2
9


%Reflectance
Wavenumbers (cm-1)
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1657.70
1601.24
1491.55
1451.55
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1292.45
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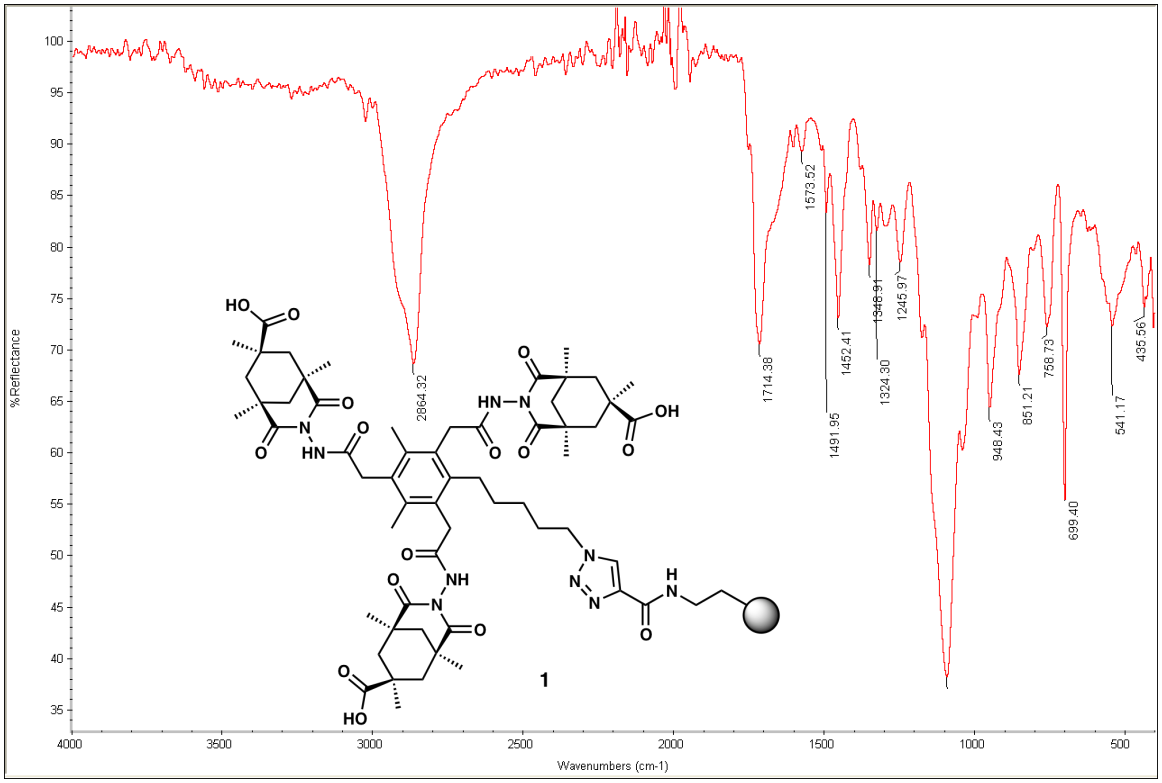
699.38
537.96
471.06
H
N
O

10


%Reflectance
Wavenumbers (cm-1)
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1714.38
1573.52
1491.95
1452.41
1348.91
1324.30
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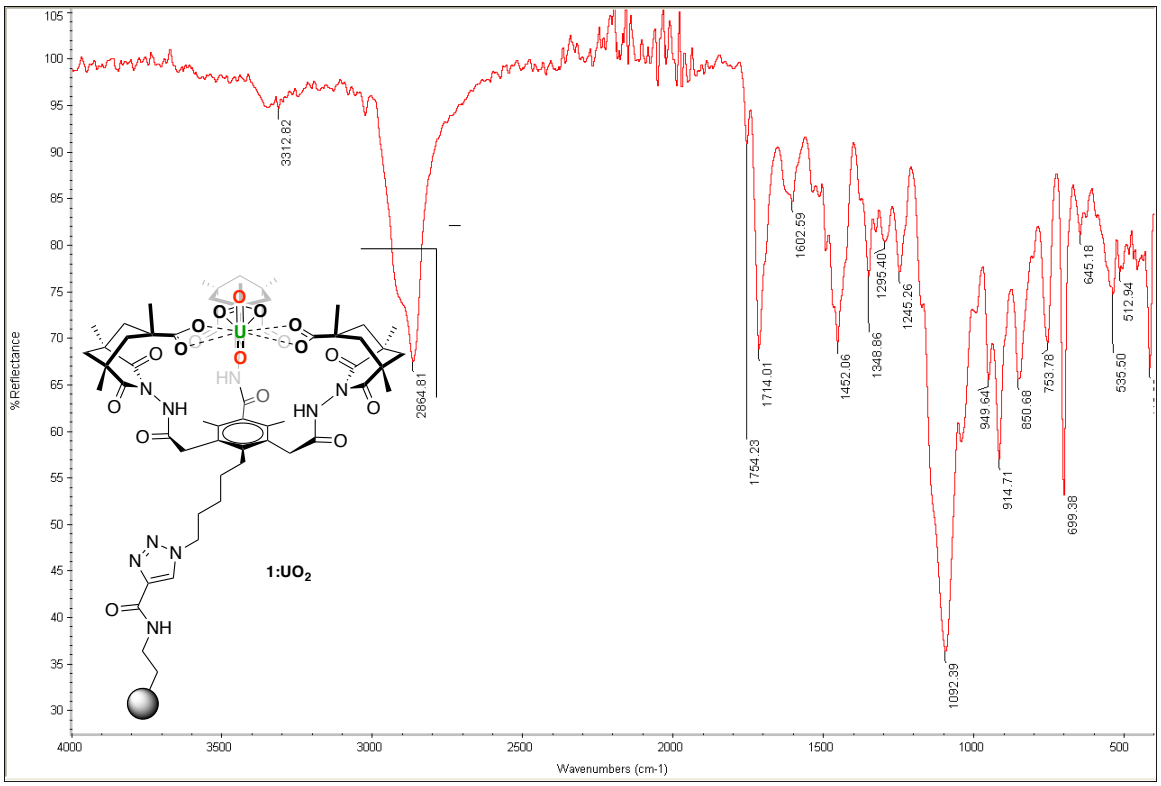
851.21
758.73
699.40
541.17
435.56
1

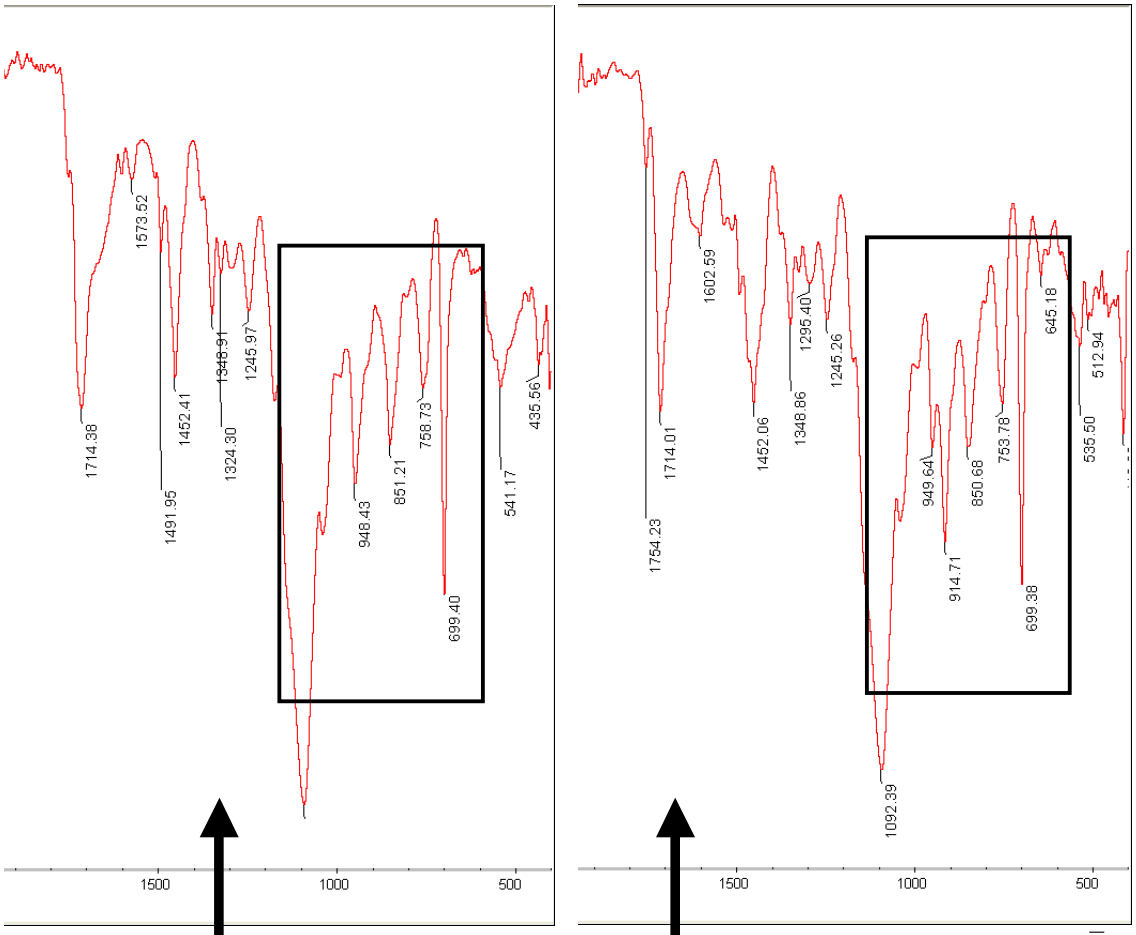


General note on IR:

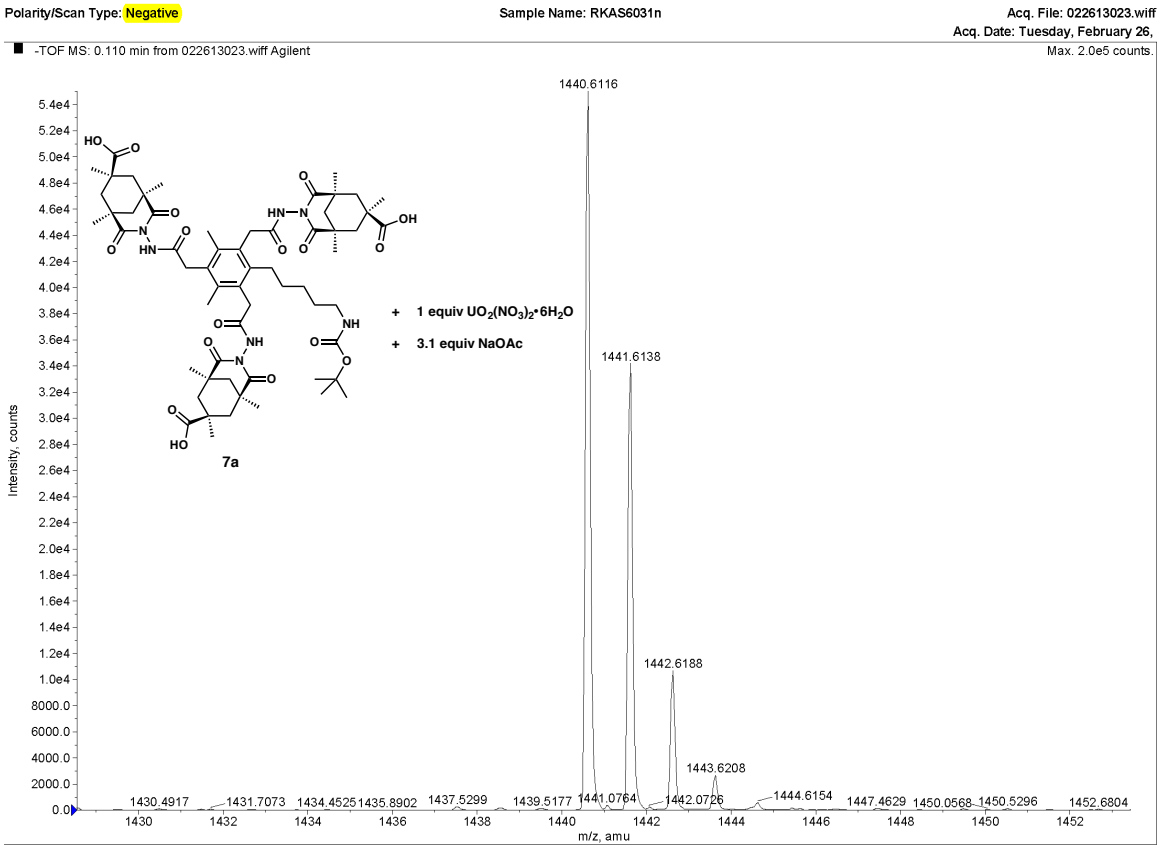
All IR spectra were acquired on a Nicolet 380 FT-IR from Thermo Scientific equipped with a Smart Orbit Diamond ATR accessory.

EZ-OMNIC software was used to process the spectra.

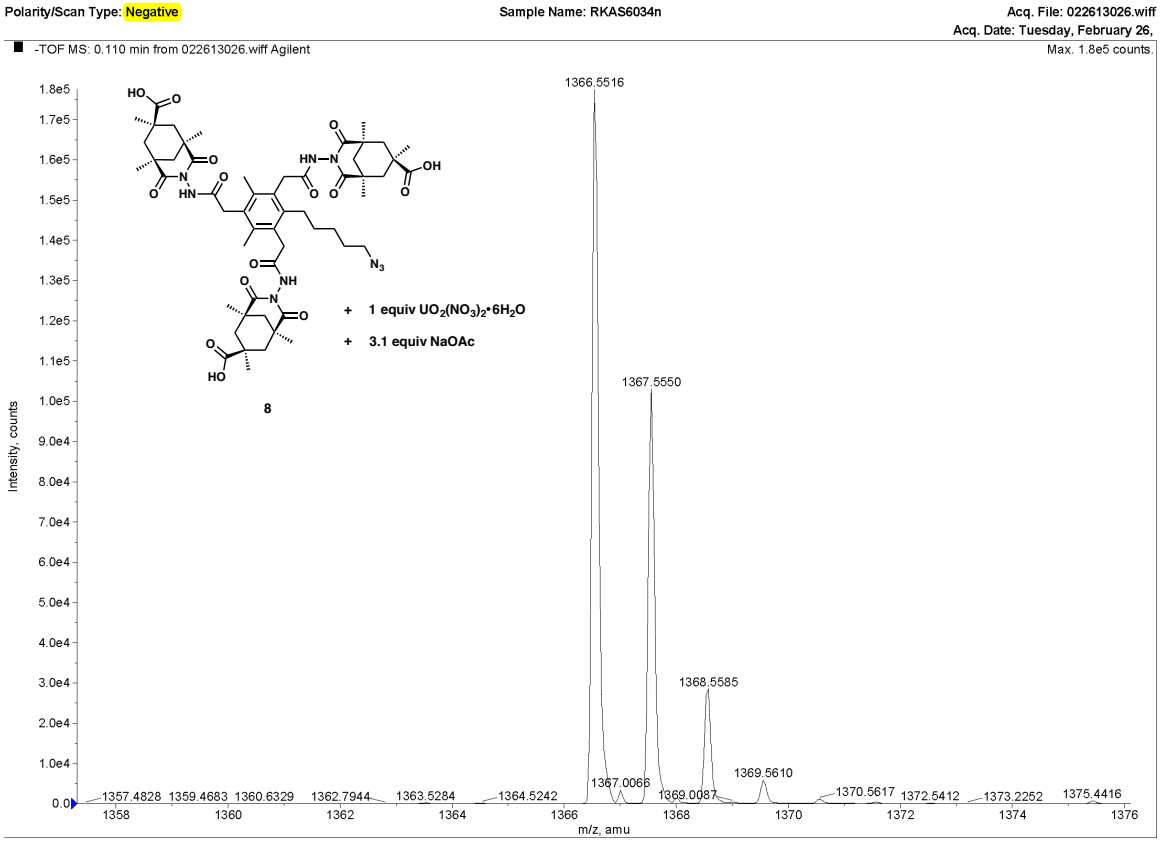
Range: (30,000 − 200 cm^{-1})



High-Resolution Mass Spectra of 6:U and 8:U

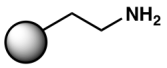
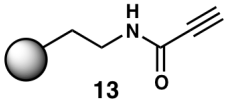
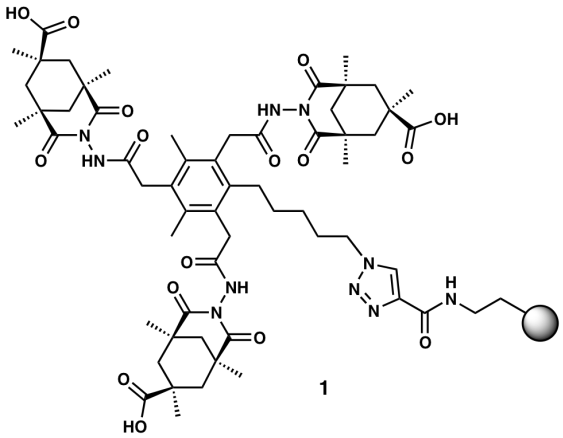


ESI-TOF high-acc: m/z: 1440.6116 ([**7a**-3H+UO_2]-, $C_{60}H_{80}N_7O_{19}U_1$, calc. 1440.6022)



ESI-TOF high-acc: m/z: 1366.5516 ([**8**-3H+UO_2]-, $C_{55}H_{71}N_9O_{17}U_1$, calc. 1366.5403)

Elemental Analysis

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)
 **12**	66.30	8.90	0.79
12 duplicate	66.33	8.90	0.83
 **13**	65.69	9.04	0.88
13 duplicate	65.73	9.05	0.83
 **1**	64.65	8.68	2.52
1 duplicate	64.63	8.63	2.58

Elemental analysis was carried out by:
NuMega Resonance Labs, Inc.
11526 Sorrento Valley Road, Suite B-2
San Diego, CA 92121
Phone: 858-793-6057
Fax: 858-793-2607

^{1}H NMR Solution Studies of Ligands 7a and 8 with the Uranyl Ion:

Experimental Setup

A uranyl solution was prepared by dissolving 0.258 g $UO_2(NO_3)_2$•$6H_2O$ in 1 mL methanol-d_4. This solution was used throughout the ^{1}H NMR experiments.

A sodium acetate solution was prepared by dissolving 0.221 g NaOAc in 3 mL methanol-d_4. This solution was used throughout the ^{1}H NMR experiments.

All spectra were carried out in methanol-d_4.

^{1}H NMR of 7a and UO_2

A sample of **7a** (3.7 mg) was dissolved in 0.5 mL methanol-d_4. The sodium acetate solution and uranyl solutions were added and details are reported on the spectra in Figure S1.

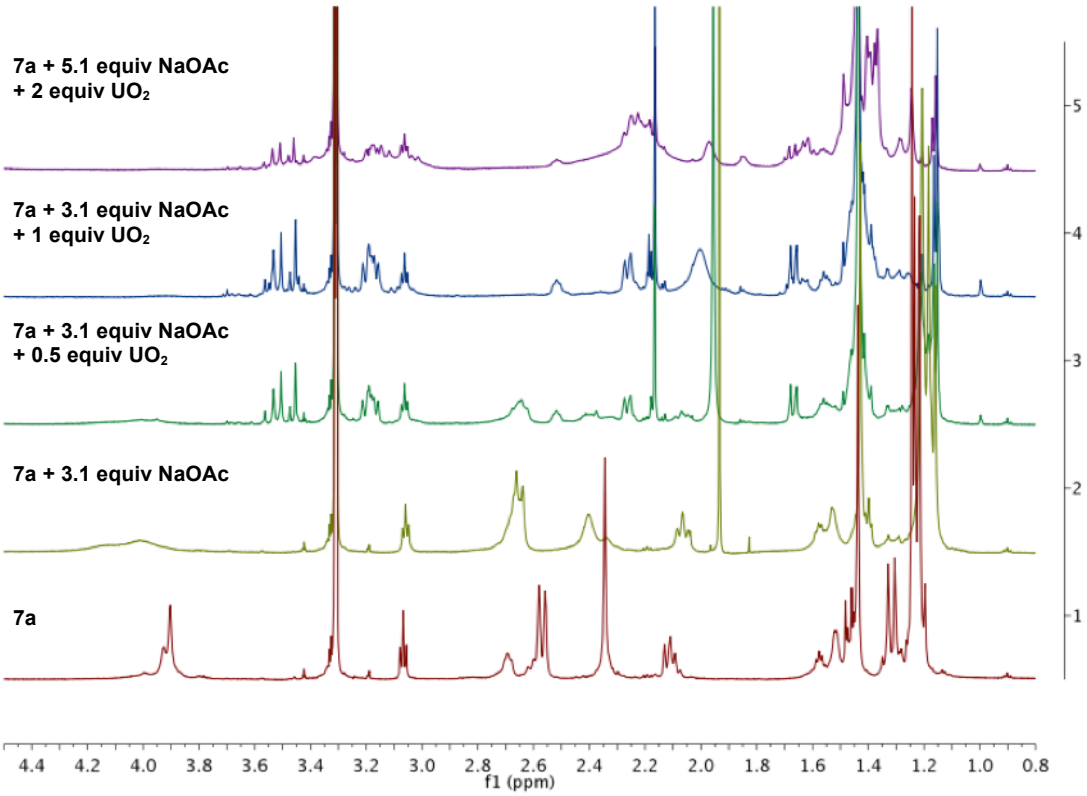


Figure S1. ^{1}H NMR spectra of **7a**, uranyl ion, and sodium acetate.

In Figure S1 spectrum 1 is **7a** in methanol-d_4. Spectrum 2 shows the addition of NaOAc. Spectrum 3 shows the addition of 0.5 equiv uranyl ion to the solution.

Both deprotonated **7a** and the **7a:U** complex appear in the spectrum 3. Spectrum 4 shows the addition of 1 equiv uranyl ion, giving the **7a:U** complex. Spectrum 5 shows the addition of additional NaOAc and uranyl ion. An additional 2 equiv of NaOAc is needed to keep the signals sharp when an additional equiv of uranyl ion is added. The signals for **7a:U** persist after the addition of excess uranyl ion suggesting the species that is formed is a 1:1 complex.

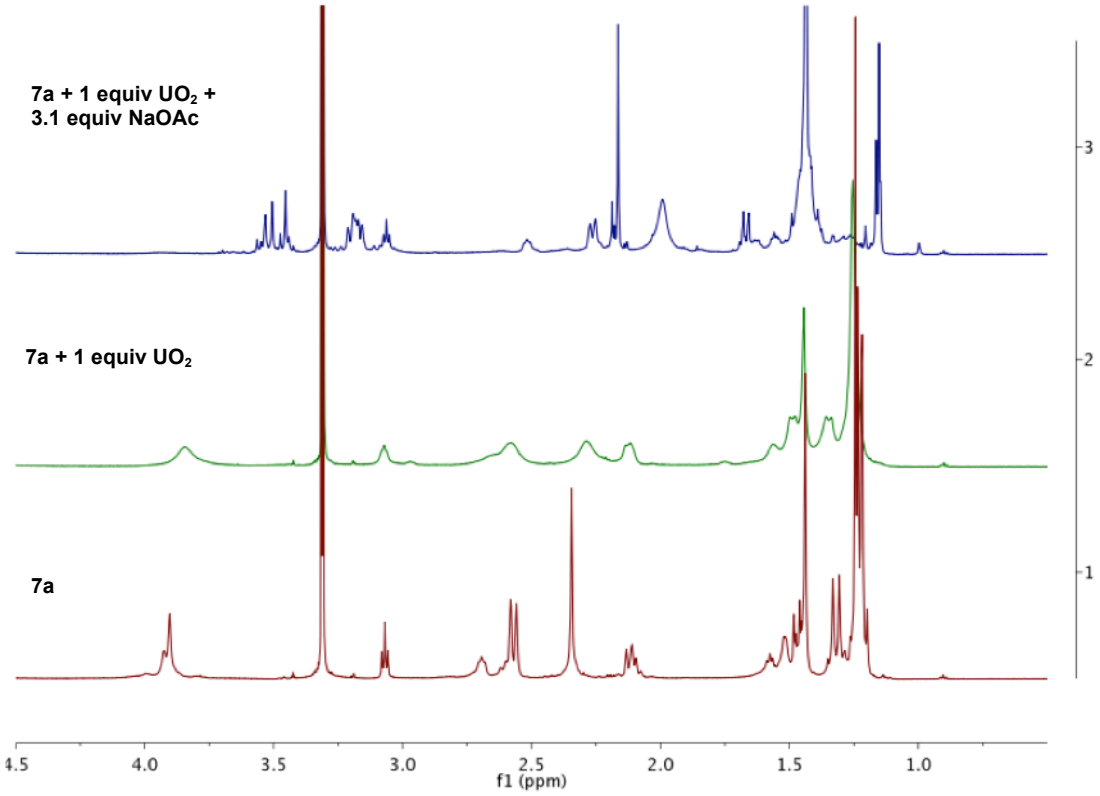


Figure S2. ^{1}H NMR spectra of **7a** adding the uranyl ion before addition of the sodium acetate.

In Figure S2 spectrum 1 shows **7a** in methanol-d_4. Spectrum 2 shows the addition of 1 equiv UO_2. Before the addition of base the spectrum is broad and unresolved. Spectrum 3 shows the addition of 3.1 equiv NaOAc. After the addition of base, the signals become sharp and resolved showing complex **7a:U**. This solution was dried under vacuum and their IR spectrum was measured (See IR section). High-resolution mass spec data was also obtained for this complex (See Mass Spec section).

^{1}H NMR of 8 and UO_2

A sample of **8** (4.0 mg) was dissolved in 0.5 mL methanol-d_4. The sodium acetate solution and uranyl solutions were added and details are reported on the spectra in Figure S3.

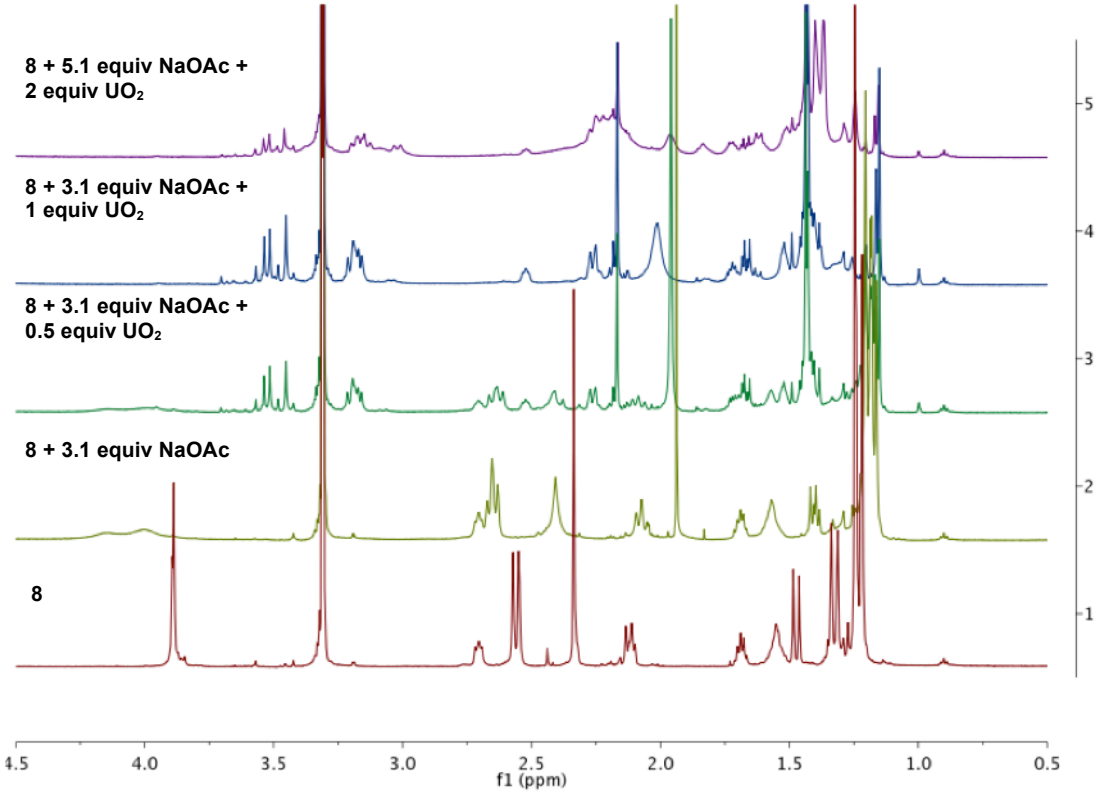


Figure S3. ^{1}H NMR spectra of **8**, uranyl ion, and sodium acetate.

Ligand **8** behaves the same as **7a**. In Figure S3 spectrum 1 is **8** in methanol-d_4. Spectrum 2 shows the addition of NaOAc. Spectrum 3 shows the addition of 0.5 equiv uranyl ion to the solution. Both deprotonated **8** and the **8:U** complex appear in the spectrum 3. Spectrum 4 shows the addition of 1 equiv uranyl ion, giving the **8:U** complex. Spectrum 5 shows the addition of additional NaOAc and uranyl ion. An additional 2 equiv of NaOAc is needed to keep the signals sharp when an additional equiv of uranyl ion is added. The signals for **8:U** persist after the addition of excess uranyl ion, suggesting the species that is formed is a 1:1 complex.

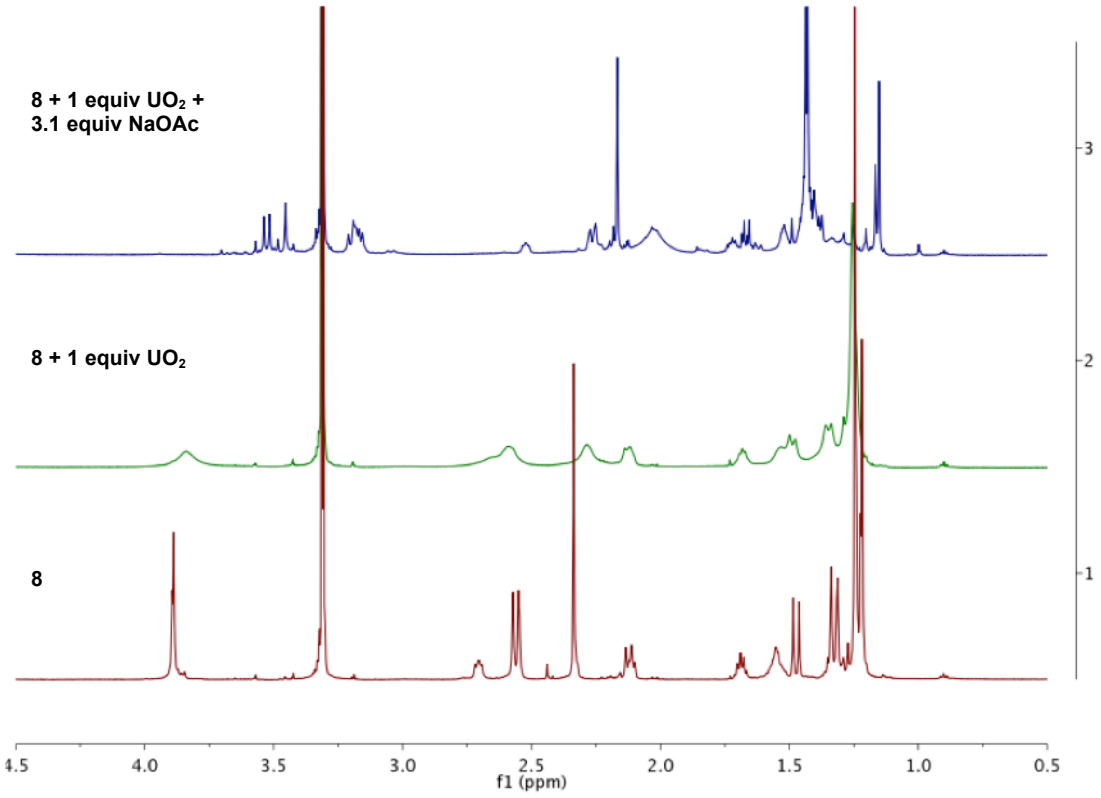


Figure S4. ^{1}H NMR spectra of **8** adding the uranyl ion before addition of the sodium acetate.

In Figure S4 spectrum 1 shows **8** in methanol-d_4. Spectrum 2 shows the addition of 1 equiv UO_2. Before the addition of base the spectrum is broad and unresolved. Spectrum 3 shows the addition of 3.1 equiv NaOAc. After the addition of base, the signals become sharp and resolved showing complex **8:U**. This solution was dried under vacuum and their IR spectrum was measured (See IR section). High-resolution mass spec data was also obtained for this complex (See Mass Spec section).

Preparation of Uranyl Stock Solutions:

Sodium Acetate/Acetic acid buffered solutions to pH 5:
A 2000 ppm Uranium stock solution was prepared by dissolving 422 mg $UO_2(NO_3)_2 \bullet 6H_2O$ in 100 mL aqueous acetate buffer with the pH adjusted to 5. This solution was used to prepare further solutions at lower concentrations (400 ppm and 400ppb).

A 400 ppm Uranium stock solution was prepared by adding 10 mL of the 2000ppm stock solution to a 50 mL volumetric flask and filling to the final volume with aqueous acetate buffer adjusted to pH 5.

A 400 ppb Uranium stock solution was prepared by adding 20 µL of the 2000 ppm stock solution to a 100 mL volumetric flask and filling to the final volume with aqueous acetate buffer adjusted to pH 5.

Seawater Solution:
A 400ppb Uranium stock solution was prepared by adding 20 µL of the 2000 ppm U stock solution to a 100 mL volumetric flask and filling to the final volume with water collected from the ocean (La Jolla, CA). Before addition to the volumetric flask, the seawater was through fluted filter paper to remove any debris.

A 400ppm Uranium solution using seawater was not prepared because at this pH and concentration yellow solids begin to form after a period of several hours.

Resin Amounts for Analysis:

Kemp resin **1**, is estimated to contain a functionality of 0.22 mmol/g. This estimation is made by mass balance of the copper mediated azide/alkyne cycloaddition reaction as described in the experimental section. An arbitrary amount of 0.030 g of resin **1** was used for every extraction experiment.

For direct comparison, an equimolar amount of 200-400 mesh Biotechnology Grade Chelex® 100 resin (0.022 g) was used in every extraction experiment. This equimolar amount was calculated from the *Chelex® 100 and Chelex® 20 Chelating Ion Exchange Resin Instruction Manual*.

Preparation of U standards to Calibrate the ICP-AES:

Blank: To a 25 mL volumetric flask was added 250 µL of a 1000 ppm Yttrium standard (Inorganic Ventures, catalog #CGY1-1) and the remainder of the volume was filled with 2% HNO_3.

100 ppb: To a 25 mL volumetric flask was added 250 µL of a 10 ppm Uranium standard (Inorganic Ventures, catalog #MSU-10PPM), 250 µL of a 1000 ppm Yttrium standard, and the remainder of the volume was filled with 2% HNO_3.

200 ppb: To a 25 mL volumetric flask was added 500 µL of a 10 ppm Uranium standard, 250 µL of a 1000 ppm Yttrium standard, and the remainder of the volume was filled with 2% HNO_3.

400 ppb: To a 50 mL volumetric flask was added 2 mL of a 10 ppm Uranium standard, 500 µL of a 1000 ppm Yttrium standard, and the remainder of the volume was filled with 2% HNO_3.

600 ppb: To a 50 mL volumetric flask was added 3 mL of a 10 ppm Uranium standard, 500 µL of a 1000 ppm Yttrium standard, and the remainder of the volume was filled with 2% HNO_3.

800 ppb: To a 25 mL volumetric flask was added 2 mL of a 10 ppm Uranium standard, 250 µL of a 1000 ppm Yttrium standard, and the remainder of the volume was filled with 2% HNO_3.

All analysis was completed on a Varian Vista AX CCD Simultaneous ICP-AES.
All measurements were made using the emission at 385.957 nm.

Extraction Experimental Details at 400ppm U:

Both Kemp Resin **1** and Chelex® 100 resins were treated in the same way. For a typical extraction experiment at 400 ppm uranium concentration, an appropriate amount of resin is added to a Poly-Prep® chromatography column (Bio-Rad, catalog #731-1550) and 1 mL 400 ppm Uranium stock solution is added. The column is capped and placed on a nutating mixer (Fisher Scientific, catalog #260100F) to agitate the mixture for a period of 18 hours. After this period, the solution was collected by passing it through the frit at the bottom of the column. The resin was then washed with deionized H_2O (3 × 15 mL). The Poly-Prep® chromatography column containing the resin was then placed under vacuum to dry.

To determine the amount of uranium extracted from the initial solution, 10 µL was removed from the collected sample and added to a 10 mL volumetric flask. To the volumetric flask was added 100 µL of a 1000 ppm Yttrium standard (Inorganic Ventures, catalog #CGY1-1) and the remainder of the volume was filled with 2% HNO_3. The prepared solution was analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (Table S1-S4).

Once the sample was dry, 1 mL 0.5 M HNO_3 was added to the Poly-Prep® chromatography column and agitated on the nutating mixer for a period of 18 hours. After this period, the acidic solution was collected by passing it though the frit at the bottom of the column. The resin was then washed with 0.5 M HNO_3 (2 × 15 mL), deionized H_2O (3 × 15 mL), and dried under vacuum.

To determine the amount of uranium recovered from the resin, 10 µL was removed from the acidic solution and added to a 10 mL volumetric flask. To the volumetric flask was added 100 µL 1000 ppm Yttrium standard and the remainder of the volume was filled with 2% HNO_3. The prepared solution was analyzed using ICP-AES (Table S1-S4).

% Extracted:
The percent extracted was calculated as: $(([U]_{initial}-[U]_{final})/[U]_{initial})*100$.

% Recovered:
The percent recovered was calculated as: $([U]_{final}/[U]_{initial})*100$.

Error:
Each experiment was performed three individual times and for each experiment three measurements were taken. The three measurements were averaged to give an average value for that particular experiment. The percentages from the three experiments were averaged to give a final value and the error is given from the standard deviation of the three individual experiments.

Extraction Experimental Details at 400ppb U:

Both Kemp Resin **1** and Chelex® 100 resins were treated in the same way. For a typical extraction experiment at 400 ppb uranium concentration, an appropriate amount of resin is added to a Poly-Prep® chromatography column (Bio-Rad, catalog #731-1550) and 7 mL 400 ppb Uranium stock solution is added. The column is capped and placed on a nutating mixer (Fisher Scientific, catalog #260100F) to agitate the mixture for a period of 18 hours. After this period, the solution was collected by passing it through the frit at the bottom of the column. The resin was then washed with deionized H_2O (3 × 15 mL). The Poly-Prep® chromatography column containing the resin was then placed under vacuum to dry.

A measurement of the uranium concentration was not determined at this point for two reasons. 1) The uranium concentration is too low to obtain reliable and accurate values. 2) Due to the low concentration, the sample would need to be analyzed without dilution with 2% HNO_3 and the high concentration of sodium in the sample (pH 5 sodium acetate buffer and seawater) bleaches out any observable measurement.

Once the sample was dry, 3 mL 0.5 M HNO_3 was added to the Poly-Prep® chromatography column and agitated on the nutating mixer for a period of 18 hours. After this period, the acidic solution was collected by passing it though the frit at the bottom of the column. The resin was then washed with 0.5 M HNO_3 (2 × 15 mL), deionized H_2O (3 × 15 mL), and dried under vacuum.

To determine the amount of uranium recovered from the resin, 2 mL was removed from the acidic solution and added to a 5 mL volumetric flask. To the volumetric flask was added 100 µL 1000 ppm Yttrium standard and the remainder of the volume was filled with 2% HNO_3. The prepared solution was analyzed using ICP-AES (Table S5-S12).

% Extracted:
Not measured/calculated due to the aforementioned difficulities.

% Recovered:
The percent recovered was calculated as: $([U]_{final}/[U]_{tot})*100$.
$[U]_{final}$ is the concentration of the final sample as treated above.
$[U]_{tot}$ is calculated as follows by assuming 100% of all available U was bound to the resin. The concentration (392.5 µg/1000 mL) was determined from adding 20 µL of a 2000 ppm U stock solution, 1 mL of a 1000 ppm Yttrium internal standard, and diluting to the final volume with 2% HNO_3 to give a 400ppb U stock solution.
7 mL*(392.5 µg/1000 mL) = 2.75 µg
2 mL*(2.75 µg/3 mL) = 1.83 µg
1.83 µg/0.005 L = 366 ppb = $[U]_{tot}$

Error:

Each experiment was performed three individual times and for each experiment three measurements were taken. The three measurements were averaged to give an average value for that particular experiment. The percentages from the three experiments were averaged to give a final value and the error is given from the standard deviation of the three individual experiments.

Recyclability of Kemp Resin 1 at 400 ppm (pH 5):

A single sample of Kemp Resin **1** (0.030 g) was added to a Poly-Prep® chromatography column and 1 mL 400 ppm Uranium stock solution is added. The column is capped and placed on a nutating mixer to agitate the mixture for a period of 18 hours. After this period, the solution was collected by passing it through the frit at the bottom of the column. The resin was then washed with deionized H_2O (3 × 15 mL).

To determine the amount of uranium extracted from the initial solution, 10 µL was removed from the collected sample and added to a 10 mL volumetric flask. To the volumetric flask was added 100 µL of a 1000 ppm Yttrium standard and the remainder of the volume was filled with 2% HNO_3. The prepared solution was analyzed using ICP-AES (Table S13 and Figure S5).

The resin was then regenerated by adding 3 mL 0.5 M HNO_3 to the Poly-Prep® chromatography column and placed on a nutating mixer to agitate the mixture for a period of 3 hours. The resin was then washed with 0.5 M HNO_3 (2 × 15 mL), deionized H_2O (3 × 15 mL), dried under vacuum, and used in the next experiemnt.

This process was repeated 15 times on the same sample to determine the stability of the resin **1** to the conditions of the experiment and if **1** is recyclable.

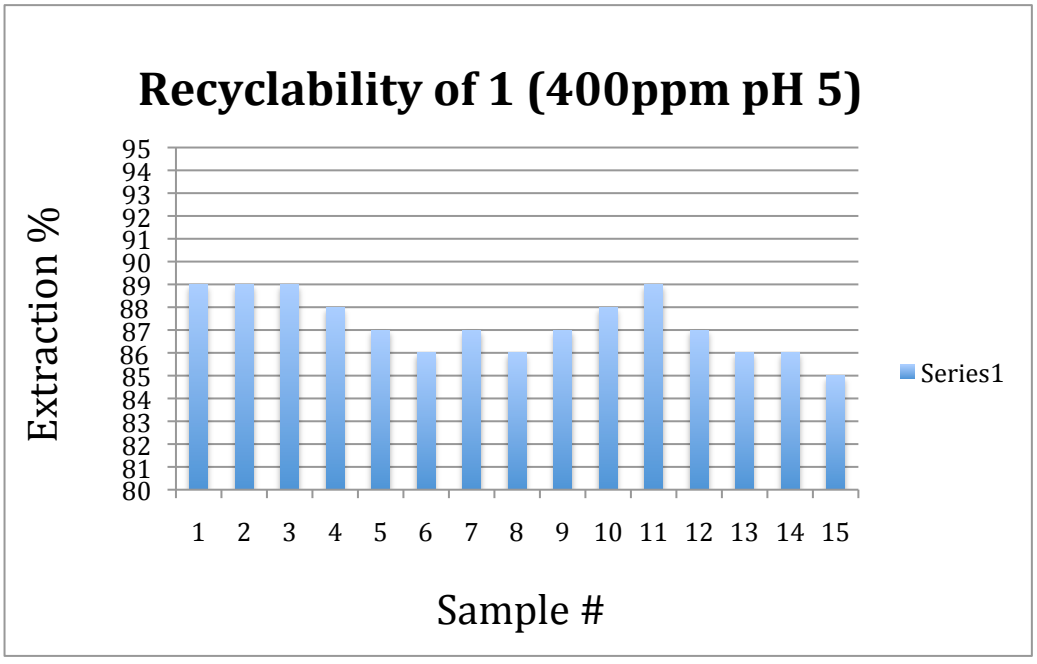


Figure S5. Recyclability experiment of Kemp Resin **1**.

Kemp Resin 1: Rate of U Extraction at 400 ppm (pH 5):

To determine the rate at which resin **1** is able to remove uranium from a solution buffered at pH 5 at 400 ppm, several 0.030 g samples of **1** were treated with 1 mL 400 ppm Uranium stock solution as described before. The solution was then removed at different time points and the percent extracted was calculated for each sample (Table S14 and Figure S6).

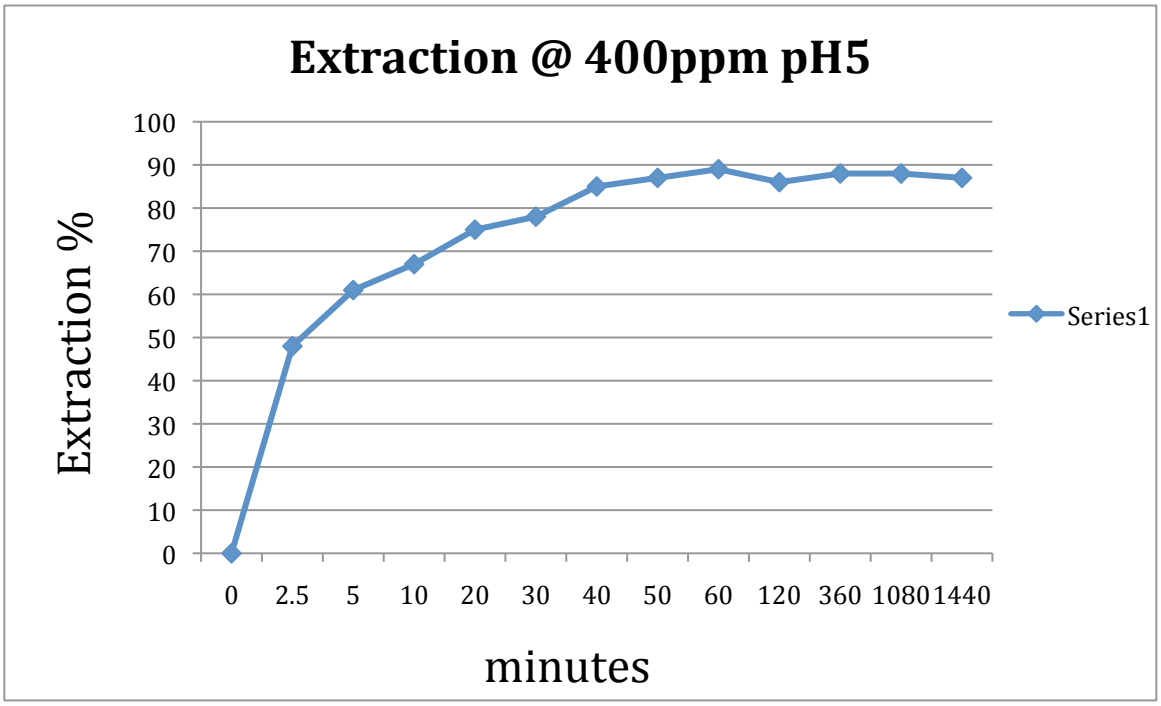
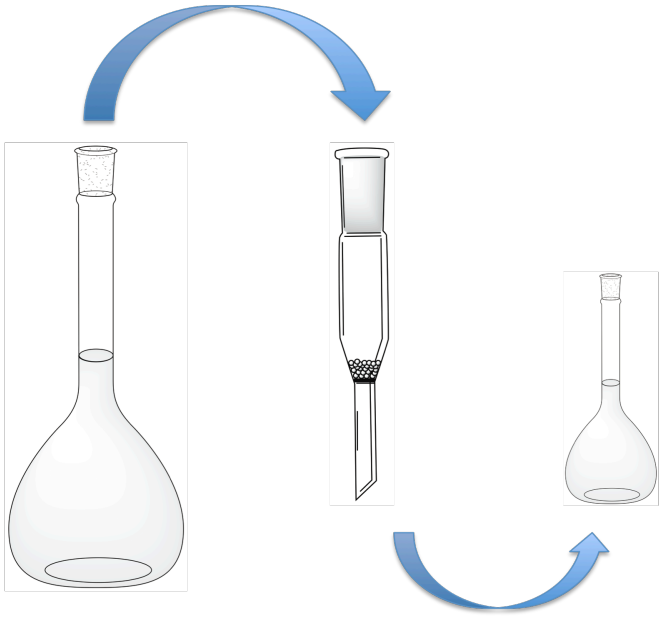


Figure S6. Rate of U uptake at 400 ppm (pH 5) by Kemp Resin **1**.

Schematic Representation of Uranyl Extraction Experimental Setup:

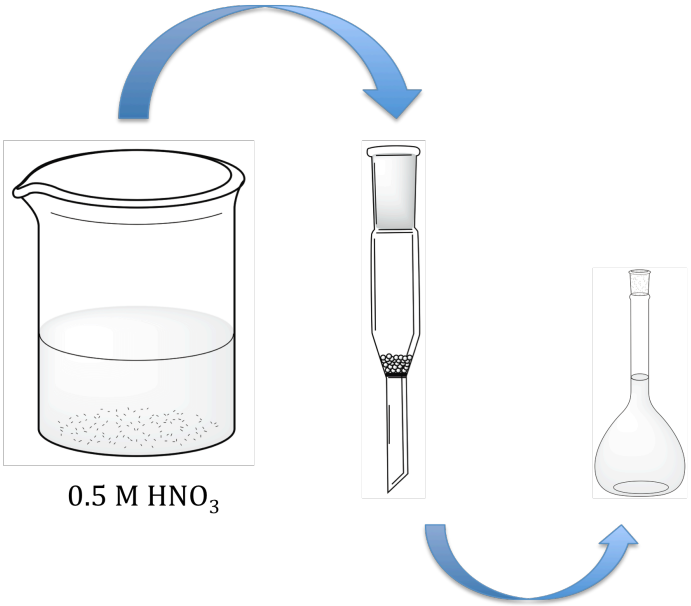
Extraction Experimental Setup



- Yttrium internal standard
- Samples adjusted to appropriate volume with 2% HNO_3

Schematic Representaion of Uranyl Recovery Experimental Setup:

U Recovery Experimental Setup



- Yttrium internal standard
- Samples adjusted to appropriate volume with 2% HNO_3

Extraction Data

Table S1. Kemp Resin **1** U Extraction/Recovery Data at 400 ppm (pH 5).

sample	385.957 (λ)	Average	% Recovered
400ppm	406.873	399.217	
	392.145		
	398.634		
Kemp Resin **1** ext (sample 1)	61.2425	54.0745	
	48.0129		
	52.9681		
Kemp Resin **1** ext (sample 2)	81.7111	71.6710	
	67.5145		
	65.7875		
Kemp Resin **1** ext (sample 3)	52.5886	59.4922	
	62.0357		
	63.8525		
Kemp Resin **1** digest (sample 1)	325.379	346.916	86.8990
	363.046		
	352.323		
Kemp Resin **1** digest (sample 2)	335.300	343.308	85.9953
	348.856		
	345.769		
Kemp Resin **1** digest (sample 3)	324.753	329.705	82.5878
	340.818		
	323.544		

Table S2. Kemp Resin **1** Final U Recovery Data at 400 ppm (pH 5).

	% Recovered	Error (Stdev)	% Recovery Average
Sample 1	87	2	85 ± 2
Sample 2	86		
Sample 3	83		

Table S3. Chelex® 100 U Extraction/Recovery Data at 400 ppm (pH 5).

Sample	U conc. (ppb)	Average	% Recovered
400ppm	393.278	399.643	
	399.264		
	406.387		
Chelex® 100 ext (sample 1)	19.1873	22.6334	
	25.8141		
	22.8988		
Chelex® 100 ext (sample 2)	5.21224	20.7818	
	19.2633		
	37.87		
Chelex® 100 ext (sample 3)	6.20062	14.39364	
	24.5789		
	12.4014		
Chelex® 100 digest (sample 1)	345.871	350.211	86.9388
	354.592		
	350.172		
Chelex® 100 digest (sample 2)	365.87	363.833	90.3202
	366.674		
	358.955		
Chelex® 100 digest (sample 3)	356.972	355.964	88.3667
	361.997		
	348.923		

Table S4. Chelex® 100 Final U Recovery Data at 400 ppm (pH 5).

	% Recovered	Error (Stdev)	% Recovery Average
Sample 1	87	2	88 ± 2
Sample 2	90		
Sample 3	88		

Table S5. Kemp Resin **1** U Recovery Data at 400 ppb (pH 5).

Sample	U conc. (ppb)	avg	% Recovered
400ppb stock	389.652	392.477	
	393.314		
	394.466		
Kemp Resin 1 digest (Sample 1)	266.916	274.217	74.8589
	274.254		
	281.482		
Kemp Resin 1 digest (Sample 2)	270.528	284.434	77.6480
	293.696		
	289.079		
Kemp Resin 1 digest (Sample 3)	275.345	289.666	79.0762
	290.421		
	303.232		

Table S6. Kemp Resin **1** Final U Recovery Data at 400 ppb (pH 5).

	% Recovered	Error (Stdev)	% Recovery average
Sample 1	75	2	77 ± 2
Sample 2	78		
Sample 3	79		

Table S7. Chelex® 100 U Recovery Data at 400 ppb (pH 5).

sample	U conc. (ppb)	avg	% Recovered
400ppb stock	389.652	392.477	
	393.314		
	394.466		
Chelex® 100 digest (sample 1)	341.634	347.895	94.9724
	359.385		
	342.668		
Chelex® 100 digest (sample 2)	364.605	347.799	94.9461
	346.975		
	331.818		
Chelex® 100 digest (sample 3)	364.723	357.340	97.5506
	346.205		
	361.092		

Table S8. Chelex® 100 Final U Recovery Data at 400 ppb (pH 5).

	% Recovered	Error (Stdev)	% Recovery average
Sample 1	95	2	96 ± 2
Sample 2	95		
Sample 3	98		

Table S9. Kemp Resin **1** U Recovery Data at 400 ppb (Seawater).

sample	U conc. (ppb)	avg	% Recovered
400ppb stock	389.652	392.477	
	393.314		
	394.466		
Kemp Resin **1** digest (Sample 1)	302.97	306.655	83.7142
	306.685		
	310.311		
Kemp Resin **1** digest (Sample 2)	298.332	298.969	81.6160
	300.774		
	297.803		
Kemp Resin **1** digest (Sample 3)	304.699	307.037	83.8183
	311.27		
	305.142		

Table S10. Kemp Resin **1** Final U Recovery Data at 400 ppb (Seawater).

	% Recovered	Error (Stdev)	% Recovery average
Sample 1	84	1	83 ± 1
Sample 2	82		
Sample 3	84		

Table S11. Chelex® 100 U Recovery Data at 400 ppb (Seawater).

sample	U conc. (ppb)	avg	% Recovered
400ppb stock	389.652	392.477	
	393.314		
	394.466		
Chelex® 100 digest (sample 1)	40.9069	34.1611	9.32568
	30.3409		
	31.2356		
Chelex® 100 digest (sample 2)	18.694	28.8204	7.86772
	40.8198		
	26.9475		
Chelex® 100 digest (sample 3)	44.7249	49.2668	13.4494
	57.3253		
	45.7502		

Table S12. Chelex® 100 Final U Recovery Data at 400 ppb (Seawater).

	% Recovered	Error (Stdev)	% Recovery average
Sample 1	9	3	10 ± 3
Sample 2	8		
Sample 3	14		

Table S13. Recyclability of Kemp Resin **1** at 400 ppm (pH 5).

Sample	U conc. (ppb)	Average	% Extracted	% Extracted
400ppm stock soln.	401.117	402.361		
	410.23			
	395.736			
1	48.4527	44.4911	88.9424	89
	42.2911			
	42.7297			
2	46.248	46.0576	88.5531	89
	47.8917			
	44.0331			
3	46.8733	45.6189	88.6621	89
	46.4934			
	43.49			
4	52.0012	47.2455	88.2579	88
	46.0045			
	43.7309			
5	54.1705	53.274	86.7596	87
	53.6636			
	51.9879			
6	57.6591	55.6434	86.1707	86
	55.5016			
	53.7697			
7	50.4863	51.9409	87.0909	87
	49.6798			
	55.6568			
8	55.584	58.3405	85.5004	86
	59.3778			
	60.0598			
9	53.1937	53.8330	86.6207	87
	53.5618			
	54.7435			
10	48.2676	50.1483	87.5364	88
	53.6048			
	48.5726			
11	44.341	43.7356	89.1302	89
	46.0573			
	40.8087			
12	54.8084	53.5847	86.6824	87
	56.812			
	49.1339			
13	54.816	56.6776	85.9137	86

	58.2729			
	56.9441			
14	55.1382	56.1992	86.0326	86
	55.0777			
	58.3819			
15	60.0316	59.0616	85.3212	85
	59.995			
	57.1582			

Resin **1** is recyclable and it extracted an average value of 87 ± 2%.

Table S14. Kemp Resin **1**, Rate of U extraction at 400 ppm (pH 5).

Sample	U conc. (ppb)	Average	% Extracted	% Extracted
400ppm (t=0)	401.117	402.361		
	410.23			
	395.736			
2.5 min	209.439	207.824	48.3487	48
	207.598			
	206.437			
5 min	158.463	156.569	61.0873	61
	153.85			
	157.395			
10 min	132.072	134.248	66.6348	67
	136.694			
	133.979			
20 min	105.552	102.701	74.4753	75
	106.202			
	96.3498			
30 min	88.5816	87.3126	78.2999	78
	86.6339			
	86.7223			
40 min	65.7027	59.6888	85.1653	85
	57.2959			
	56.0678			
50 min	57.6253	52.3064	87.0001	87
	48.9857			
	50.3084			
60 min	42.7099	46.0600	88.5525	89
	48.8468			
	46.6234			
2 hours	54.8632	57.5882	85.6874	86
	60.9165			
	56.9849			
6 hours	55.0784	48.0873	88.0487	88
	44.8017			
	44.3818			
18 hours	50.1663	49.8682	87.6061	88
	51.2479			
	48.1904			
24 hours	55.442	51.4046	87.2242	87
	44.0059			
	54.7661			

Attempt at Extracting UO_2 From Seawater at Natural Concentration (3.3 ppb)

Two samples of Kemp Resin **1** (0.300 g) and Chelex® 100 (0.220 g) were each added to a tea bag and closed with a rubber band. The newly sealed tea bag was then added to another tea bag with ~35 glass beads to act as a weight. The bag was then sealed with another rubber band and four lengths of string were tied to the top of the bag (Figure S7). The two samples of resin **1** were added to a water cooler (~19 L) of seawater that was collected in La Jolla shores (Figure S8). The two samples of Chelex® 100 were treated in an identical manner and added to another water cooler of seawater. A magnetic stir bar was added to each container and they were placed onto a stir plate to agitate the water. The samples were submerged for a period of 30 days and the resin was collected, washed with deionized water and dried under vacuum. The resin samples were then digested with 5 mL 0.5 M HNO_3. From the acidic solution, 4 mL were removed and added to a 5 mL volumetric flask with 50 µL of a 1000 ppm Yttrium standard and the remainder of the volume was filled with 2% HNO_3. The samples were analyzed with ICP-AES but unfortunately neither sample contained a detectable amount of uranium.

Figure S7. Resin added to tea bags for U extraction.

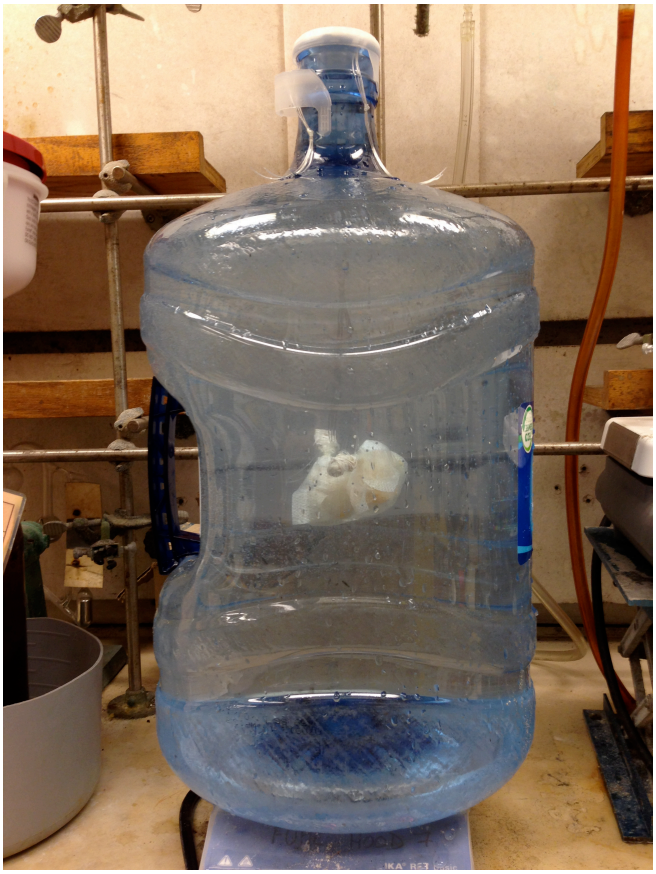


Figure S8. Tea bags containing resin added to seawater in water cooler.