Contents

1. General consideration

Unless stated otherwise all synthesis and manipulations were performed under aerobic conditions. $(CH_3)_2SAuCl$, Ag_2O, 1-methylbenzimidazole, 9-(chloromthyl)anthracene, pentrafluorophenol, and 4-(bromomethyl)benzoic aicd were obtained from Sigma Aldrich and used without further purification. ^1H and ^{13}C NMR spectra were obtained on Varian INOVA spectrometer (500 MHz), or a Mercury (400 MHz and 300 MHz for proton). Chemical shifts, reported in δ (ppm), were referenced on the solvent, on the TMS scale for ^1H and ^{13}C. The fluorescence spectra of compounds were measured using a HORIBA Jobin Yvon fluorescence spectrophotometer. Elemental analyses were performed at Complete Analysis Laboratory Inc., Parsippany, New Jersey.

2. DNA synthesis

All oligonucleotides were synthesized based on solid-phase phosphoramidite chemistry at a 1 μmol scale using the ABI3400 DNA/RNA synthesizer (Applied Biosystems, Foster City, CA).[1] Amine was directly coupled at the 5′-end of oligonucleotides with an extended coupling time. A ProStar HPLC (Varian, Walnut Creek, CA) instrument with a C18 column (Econosil, 5, 250 mm) from Alltech (Deerfield, IL) was used to purify all fabricated DNA. The collected sequences were vacuum-dried and quantified using a Cary Bio-300 UV spectrometer (Varian, Walnut Creek, CA).

3. Cell culture

CCRF-CEM (CCL-119, T-cell line, human ALL) and K562 (CCL-240, acute promyelocytic leukemia, CML) were cultured in RPMI 1640 medium (American

Type Culture Collection) with 10% fetal bovine serum (Invitrogen, Carlsbad, CA) and 0.5 mg/mL penicillin-streptomycin (American Type Culture Collection) at 37 °C under a 5% CO_2 atmosphere. Cells were washed before and after incubation with washing buffer [4.5 g/L glucose and 5 mM $MgCl_2$ in Dulbecco's PBS with calcium chloride and magnesium chloride (Sigma-Aldrich)]. Binding buffer was prepared by adding yeast tRNA (0.1 mg/mL; Sigma-Aldrich) and BSA (1 mg/mL; Fisher Scientific) to the washing buffer to reduce background binding. All reagents for buffer preparation and HPLC purification came from Fisher Scientific. Unless otherwise stated, all chemicals were used without further purification

4. General procedure for MTS assay

50 μL of 30000 freshly collected cells were seeded into each well of a 96-well plate, and then incubated with different concentration of the tested compound. After 4 h of incubation, the mixture was centrifuged and 80 μL of old media was removed from each well. Then, 200 uL of fresh media was added to each well for another 48 h incubation under at 37 °C in a 5% CO_2 atmosphere. After 48 h, the mixture in each well was centrifuged to remove 170 μL of the supernatant, and then each well was treated with 120 uL of MTS dye (MTS = 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium) diluted with fresh media with no phosphatidyserine. The assay was allotted 2 h at 37 °C for development. After incubation with the MTS dye, the 490 nm absorbance of each well was collected on a Tecan plate 110 reader. Each cell measurement had the treatment background subtracted before analysis. Cells in media and DMSO (0.01%) alone were used as a control. Each analysis was repeated for at least five times and the error bars represent

the standard deviation .Quantitative and statistical analyses were performed using the nonlinear dose response curve fitting in Origin 8.5 software.

5. General procedure for flow cytometry

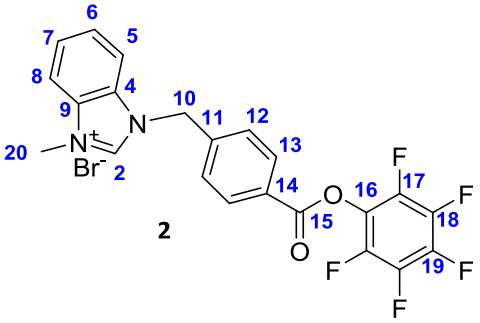
Cells were plated in a 35 mm cell culture dish (Corning Incorporated, Corning, NY, USA) and grown to around 80% confluency for 24 h before the experiments. Cells were washed twice with 1 mL PBS and then incubated with the sgc8c-drug conjugate and LIB-drug conjugate at the concentration of 400nM for 0.5 h at 4°C. After incubation, cells were washed with washing buffer three times, dispersed in 500 μL PBS, and finally subjected to flow cytometry analysis using a FACScan cytometer (Becton Dickinson Immunocytometry Systems, San Jose, CA, USA). Fluorescence was determined by counting 10,000 events, and data were analyzed with FlowJo software.

6. Confocal microscopy

All cellular fluorescent images were collected on a Leica TCS SP5 confocal microscope (Leica Microsystems Inc., Exton, PA) with a 63x oil immersion objective and Leica Confocal Software. CCRF-CEM cells and K562 cells were observed in DIC mode. Cells were treated with sgc8c-7 or LIB-7, respectively, in serum-free cell culture medium, incubated in a cell culture incubator for 4 h, followed by washing with Dulbecco's PBS. The resultant cells were then observed by confocal microscopy.

7. Synthesis procedure.

7.1 Synthesis of 2

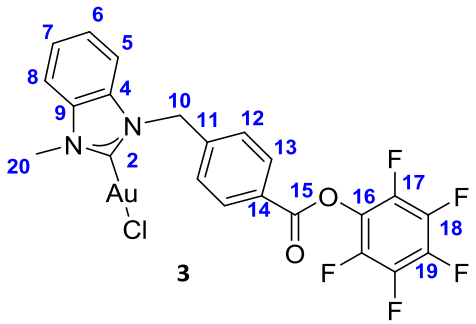


2

To the solution of 1-methylbenzimidazole (0.400 g, 3.03 mmol) in dry THF (10 mL) was added dropwise a solution of **1** (1.140 g, 3.00 mmol) dissolved in THF (10 mL). After complete addition, the mixture was refluxed for 24 h during which time a white precipitate formed. The solvent was decanted from the precipitate and the solid was washed with THF (3 x 10 mL) and then dried in vacuo to give a white solid (1.09 g, 78.0% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.74 (s, 1 H, C_2H), 8.17 (s, 2 H, HC_{13}), 7.76 (s, 1 H, HC_8), 7.70 (s, 2 H, HC_{12}), 7.65 (s, 1 H, HC_7), 7.59 (s, 1 H, HC_6), 7.56 (s, 1 H, HC_5), 6.13 (s, 2 H, $C_{10}H_2$), 4.30 (s, 3 H, $C_{20}H_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 162.02 (C_{15}), 144.09 (C_2), 139.86 (C_{11}), 132.35 (C_9), 131.80 (C_4), 129.04 (C_{13}), 127.87 (C_{14})，127.63 (C_{12})，127.65 (C_6, C_7), 113.68 (C_8), 113.16 (C_5), 51.06 (C_{10}), 34.27 (C_{20}) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –152.45 (d, $^{3}J_{FF}$ = 19.1 Hz, 2F, $C_{17}F$), 157.57 (t, $^{3}J_{FF}$ = 23.2 Hz, 1 F, $C_{19}F$), 162.12 (dd, $^{3}J_{F,F}$ = 19.1, 23.2 Hz, 2F, $C_{18}F$) ppm. Elemental analysis calcd. (%)

for $C_{22}H_{14}BrF_5N_2O_2$ (512.02 g/mol): C: 51.48, H: 2.75, N: 5.46; Found: C: 51.17, H: 2.59, N: 5.32.

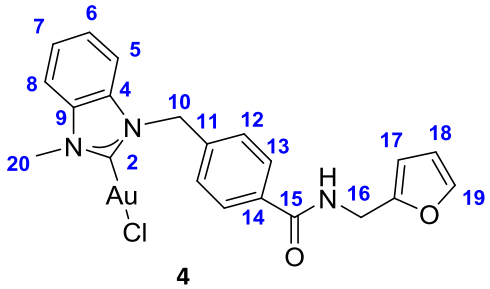
7.2 Synthesis of 3



Inside an argon filled glovebox, ligand **2** (0.308 g, 0.601 mmol, 1 equiv.) and Ag_2O (0.100 g, 0.420 mmol, 0.7 equiv.) were dissolved in DCM (10 mL) and stirred for 2 d to provide the NHC–Ag complex in situ. To the reaction mixture was added $(CH_3)_2SAuCl$ (0.177g, 0.601 mmol, 1 equiv.) and stirred for 1 h. Then, the reaction vial was brought out of the glovebox, and the reaction mixture was filtered through Celite® in the air. The filtrate was collected and reduced under vacuum to 1 mL of solution. Diethyl ether was added to precipitate a pale yellow powder. The solid was collected by filtration and dried under vacuum for 2 h to provide complex **3** (0.203g, Yield = 50.8%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 2 H, *H*C$_{13}$), 7.54 (s, 1 H, *H*C$_8$), 7.53 (s, 2 H, *H*C$_{12}$), 7.49 (s, 1 H, *H*C$_7$), 7.41 (s, 1 H, *H*C$_6$), 7.33 (s, 1 H, *H*C$_5$), 5.84 (s, 2 H, C$_{10}$*H*$_2$), 4.13 (s, 3 H, C$_{20}$*H*$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 179.6 (*C*$_2$), 161.9 (*C*$_{15}$), 141.5 (*C*$_{11}$), 136.1 (*C*$_{17}$F), 134.4 (*C*$_{19}$F), 134.1 (*C*$_9$), 132.7 (*C*$_{18}$F), 132.7 (*C*$_4$), 131.5(*C*$_{13}$), 127.7 (*C*$_{12}$), 127.2 (*C*$_{14}$), 125.1 (*C*$_7$), 125.0 (*C*$_6$), 119.9 (*C*$_{16}$), 116.6 (*C*$_8$), 111.7 (*C*$_5$), 52.3 (*C*$_{10}$), 35.4 (*C*$_{20}$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –152.77 (t, $^3J_{FF}$ = 19.1 Hz, 2 F, C$_{17}$*F*), –158.05 (t, $^3J_{FF}$ = 23.2 Hz, 1 F, C$_{19}$*F*), –162.55 (dd, $^3J_{FF}$ = 19.1, 23.2 Hz, 2 F, C$_{18}$*F*) ppm. Elemental analysis

calcd. (%) for $C_{22}H_{13}AuClF_5N_2O_2$ (664.03 g mol^{-1}): C: 39.75; H: 1.97; N: 4.21, Found: C: 39.89; H: 2.10 N: 4.42.

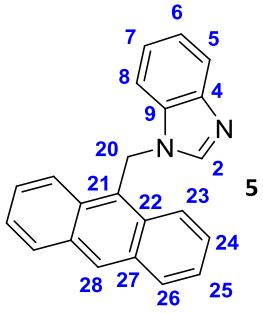
7.3 Synthesis of 4



4

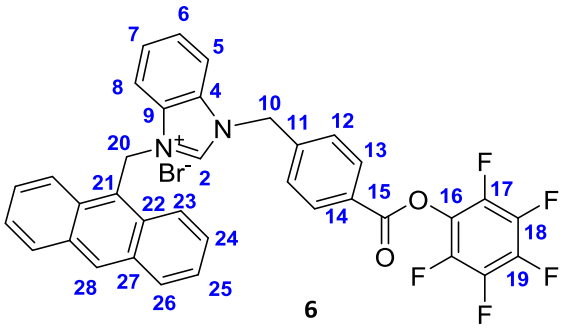
A 20 ml vial was charged with a stir bar, complex **3** (0.120 g, 0.180 mmol, 1 equiv.) and 5 ml of THF. Then, 0.020 g of furfurylamine (0.206 mmol, 1.15 equiv) and 0.018 mg of triethylamine (0.180 mmol, 1 equiv) were added. The mixture was stirred for 6 hours, then filtrated through Celite. The filtrate was concentrated and diethyl ether was added to precipitate the product. The solids were collected by filtration (0.093g, Yield = 89.4%). ^{1}H NMR (300 MHz, DMSO): δ = 8.93 (t, $^3J_{HH}$ = 5.8 Hz, 1H, *H*N), 7.80 (m, 2H, *H*C_{13})， 7.68 (s, 1H, *H*C_8), 7.66 (m, 1H, *H*C_7), 7.52 (dd, $^3J_{HH}$ = 2.0, 0.7 Hz, 1H, *H*C_{19}), 7.45-7.40 (m, 4H, *H*Ar), 6.34 (dd, $^3J_{HH}$ = 3.3, 2.0 Hz 1H, *H*C_{18}), 6.25 (dd, $^3J_{HH}$ = 3.3, 0.7 Hz 1H, *H*C_{17}, 5.78 (s, 2H, $C_{10}H_2$), 4.41(d, 2H, $^3J_{HH}$ = 5.8 Hz, $C_{16}H_2$), 4.04 (s, 3H, $C_{20}H_3$) ppm. . $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 179.16 (C_2), 166.50 (C_{15}), 151.03 (C_{19}), 142.28 (*C*-Ar), 138.03 (*C*-Ar), 134.47(*C*-Ar), 134.02 (*C*-Ar), 132.69 (*C*-Ar), 130.28(*C*-Ar), 127.81 (*C*-Ar), 127.48 (*C*-Ar), 125.0 (C_6), 119.9 (C_{16}), 116.6 (C_8), 111.7 (C_5), 52.3 (C_{10}), 35.4 (C_{20}) ppm. DART-MS (positive ion) $[M/Z]^+$ calcd for $C_{21}H_{19}AuClN_3O_2$ 578.0897; Found: 578.0897.

7.4 Synthesis of 5



A mixture of benzimidazole (0.354g, 3.00 mmol), tetrabutylammonium bromide (TBAB) (0.096g, 0.300 mmol), THF (10 mL) and 50% aqueous K_2CO_3 (10 mL) was stirred. 9-(chloromethyl)anthracene (0.678 g, 3.00 mmol) was added in portions. The mixture was heated to 70 °C for 40 h. After cooling the reaction to room temperature the mixture was extracted with DCM. The organic layer was dried with Na_2SO_4. The solvent was removed in vacuo to give compound **5** as yellow solid. (0.700g, Yield = 76.1%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, C_2H), 8.14 (m, 5 H, $HC_{23,}$ $HC_{26,}$ HC_{28}), 7.84 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, HC_8), 7.74 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, HC_5), 7.55 (m, 4 H, $HC_{24,}$ HC_{25}), 7.45 (t, $^3J_{HH}$ = 7.0Hz, 1 H, HC_7), 7.37 (t, $^3J_{HH}$ = 7.0 Hz, 1 H, HC_6), 6.21 (s, 2 H, $C_{20}H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 143.93 (C_2), 142.14 (*C*-Ar), 134.18 (*C*-Ar), 131.40 (*C*-Ar), 129.69 (*C*-Ar), 129.48 (*C*-Ar), 127.52 (*C*-Ar), 125.38 (*C*-Ar), 122.92(*C*-Ar), 122.41 (*C*-Ar), 120.50 (*C*-Ar), 109.49(*C*-Ar), 41.34 (C_{20}) ppm. DART-MS (positive ion) $[M/Z]^+$ calcd for $C_{22}H_{16}N_2$ 309.1381; Found: 309.1381.

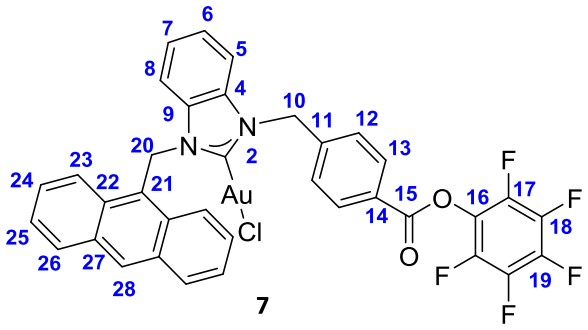
7.5 Synthesis of 6



6

To a solution of **5** (0.500g, 1.60 mmol) in dry THF (10 mL) was added dropwise a solution of **1** (0.610mg, 1.60 mmol) in THF (10 mL). After complete addition, the mixture was refluxed for 24 h during which a yellow precipitate formed. The solids was collected by filtration and washed with THF (3×10 mL). The crude product was dried in vacuo to give a yellow solid (504 mg, 51% yield). ^{1}H NMR (300 MHz, DMSO): δ =9.32 (s, 1 H, C_2H), 8.94 (s, 1 H, HC_{28}), 8.44 (d, $^{3}J_{HH}$ = 7.6 Hz, 2 H, HC_{13}), 8.37 (m, 1 H, HC_{Ar}), 8.29 (d, $^{3}J_{HH}$ = 7.6 Hz, 2 H, HC_{12}), 8.13 (m, 2 H, HC_{Ar}), 7.90 (m, 1 H, *H*Ar), 7.80 (m, 1 H, *H*Ar),7.68 (m, 6 H, *H*Ar), 7.52 (m, 2 H, *H*Ar), 6.80 (s, 2H, $C_{20}H$), 5.78 (s, 2H, $C_{10}H$) ppm. ^{13}C{^{1}H} NMR (DMSO, 125 MHz): δ = 162.16 (C_2), 142.45 (C_{15}), 142.25 (*C*-Ar), 132.44 (*C*-Ar), 131.65 (*C*-Ar), 131.56(*C*-Ar), 131.51 (*C*-Ar), 131.34 (*C*-Ar), 131.03 (*C*-Ar), 129.96 (*C*-Ar), 128.93 (*C*-Ar), 128.36 (*C*-Ar), 127.67 (*C*-Ar), 127.45 (*C*-Ar), 126.33 (*C*-Ar), 126.14 (*C*-Ar), 123.93(*C*-Ar), 122.38(*C*-Ar), 114.99 (*C*-Ar), 114.39 (*C*-Ar), 49.70 (C_{20}), 44.25 (C_{10}) ppm.^{19}F NMR (DMSO, 282 MHz): δ = –152.38 (t, $^{3}J_{FF}$ = 19.1 Hz, 2F, $C_{17}F$), –157.53 (t, $^{3}J_{FF}$ = 23.2 Hz, 1F, $C_{19}F$),–162.09 (dd, $^{3}J_{FF}$ = 19.1, 23.2 Hz, 2F, $C_{18}F$) ppm. DART-MS (positive ion) $[M/Z]^{+}$ calcd for $C_{36}H_{22}BrF_5N_2O_2$ 609.1596; Found: 609.1612.

7.6 Synthesis of 7



Inside an argon filled glovebox, solid ligand **6** (0.100 g, 0.164 mmol, 1 equiv.) and Ag_2O (0.027 g, 0.115 mmol, 0.7 equiv.) were dissolved in DCM (5 mL) and stirred for 2 d to provide the NHC–Ag complex *in situ*. To the reaction mixture was added $(CH_3)_2SAuCl$ (0.050 g, 0.164 mmol, 1 equiv.) and stirred for 1 h. Then, the reaction mixture was filtered through Celite®. The filtrate was collected and reduced under vacuum to 0.5 ml of solution. Diethyl ether was added to precipitate a pale yellow powder. The solid was collected by filtration and dried under vacuum for 2 h to provide the NHC–Au complex **7** (0.098 g, Yield = 71.1%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (s, 1H, *H*C$_{28}$), 8.50 (d, $^3J_{HH}$ = 9.0 Hz, 2H, *H*C$_{13}$), 8.50 (d, $^3J_{HH}$ = 9.0 Hz, 2H, *H*C$_{13}$), 8.18 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*C$_{23}$) 8.13 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*C$_{26}$), 7.61 (m, 4H, *H*C$_{23,}$ *H*C$_{25}$), 7.46 (d, $^3J_{HH}$ = 9.0 Hz, 2H, *H*C$_{12}$),7.15 (m, 2H, *H*Ar), 6.84 (m, 1H, *H*Ar), 6.84 (s, 1H, *H*C$_{20}$), 6.58 (m, 1H, *H*Ar), 5.92 (s, 2H, C$_{10}$*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 180.55 (*C*$_2$), 161.9 (*C*$_{15}$), 141.5 (*C*-Ar), 133.48 (*C*-Ar), 133.00 (*C*-Ar), 131.45(*C*-Ar), 131.32 (*C*-Ar), 131.32 (*C*-Ar), 131.21 (*C*-Ar), 130.93 (*C*-Ar), 130.32 (*C*-Ar), 129.95 (*C*-Ar), 128.47 (*C*-Ar), 127.68 (*C*-Ar), 127.41 (*C*-Ar), 127.10 (*C*-Ar), 126.95(*C*-Ar), 125.75(*C*-Ar), 125.38 (*C*-Ar), 124.79

(*C*-Ar), 124.67 (*C*-Ar), 123.26 (*C*-Ar), 122.06 (*C*-Ar), 113.01 (*C*-Ar), 111.50 (*C*-Ar), 52.36 (C_{20}), 47.93 (C_{10}) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –152.32 (t, $^3J_{FF}$ = 19.1 Hz, 2F, $C_{17}F$), –157.66 (t, $^3J_{FF}$ = 23.2 Hz, 1F, $C_{19}F$),–162.15 (dd, $^3J_{FF}$ = 19.1, 23.2 Hz, 2F, $C_{18}F$) ppm. DART-MS (positive ion, for M = $C_{36}H_{22}AuClF_5N_2O_2$). $[M+NH_4]^+$ calcd for 858.1210; Found: 858.1236. Elemental analysis calcd. (%) for $C_{36}H_{21}AuClF_5N_2O$ (840.09 g/mol): C: 51.42, H: 2.52, 3.33; Found: C: 51.60, H: 2.39, N: 3.19.

7.7 Synthesis of sgc8c-NHC-Au conjugates sgc8c-3 and sgc8c-7.

In a 2 ml test tube, 0.1 μmol (1 equiv.) of aptamer on solid supporting beads were suspended in a 500 μL THF solution of complex **3** (or **7**) (10 μmol, 100 equiv.). 1.4 μL of trimethylamine (100 equiv) was slowly added and completely mixed. The mixture was shaken at room temperature for 18 h, after which it was centrifuged for 30 minutes at 4,000 rpm. The supernatant was decanted and only the solids part (crude DNA products on the beads) were collected and transferred to a new test tube with cap. Then the crude DNA product were mixed with 3 mL AMA (Ammonium Hydroxide, methylamine 50:50) and incubated at 65˚ for 30 minutes. Wait until the deprotection solution cools down, transfer the supernatant (leaving all the cpg beads behind) into a plastic centrifuge tube. 250 μL of 3M NaCl solution and 6000 μL of cold ethanol were added to the tube, then the mixture was vortexed and DNA slowly precipitated. Centrifuge the mixture for 30 minutes at 4,000 rpm and discard the supernatant. 400 μL 0.1 M TEAA (triehtylamine acetate) was added to the same tube to dissolve (with the help of pipette tip) the solids left from last step. After all the DNA dissolved, transfer the solution to an Eppendorf tube for HPLC purification.

HPLC condition: Eluent A: 0.1M TEAA aqueous solution; Eluent B: acetonitrile. Low pressure gradient by varying B concentration from 10% (min 4) to 66 % (min 42:15), and then to 100 % (min 47:37). The flow rate was kept at 1 ml/min, and temperature was maintained at room temperature.

8. NMR Spectroscopic data for complexes 2-7 and stability test of 7.

8.1 NMR spectra of 2

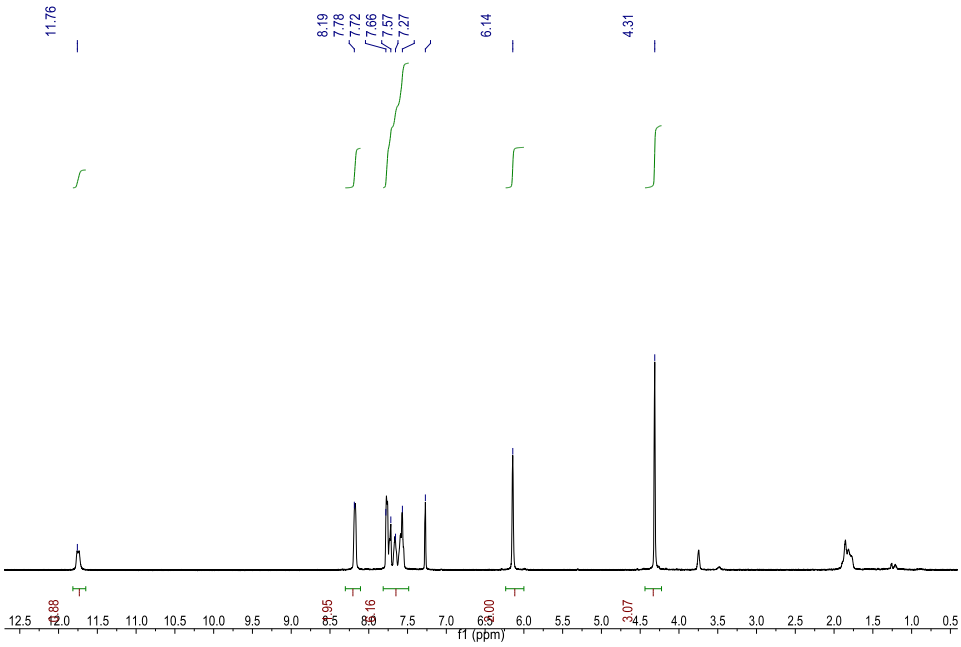


Figure S 1. ^{1}H NMR spectrum of **2** in $CDCl_3$

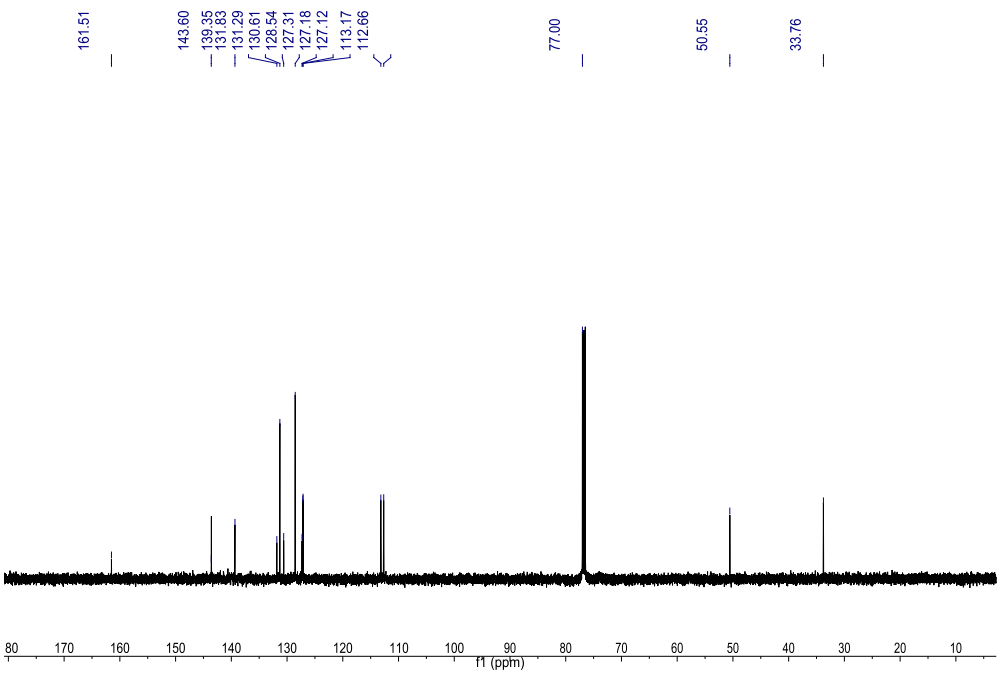


Figure S 2. $^{13}C\{1H\}$ NMR spectrum of **2** in CDCl3.

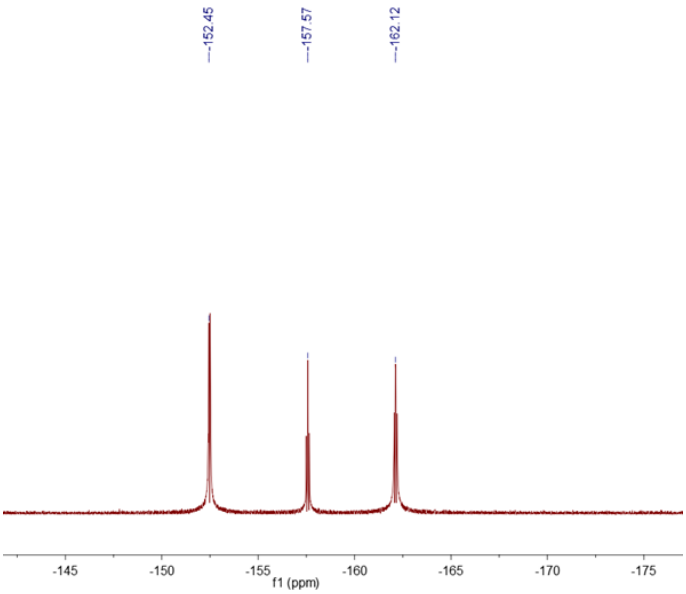


Figure S 3. ^{19}F NMR spectrum of **2** in $CDCl_3$

8.2 NMR spectra of 3

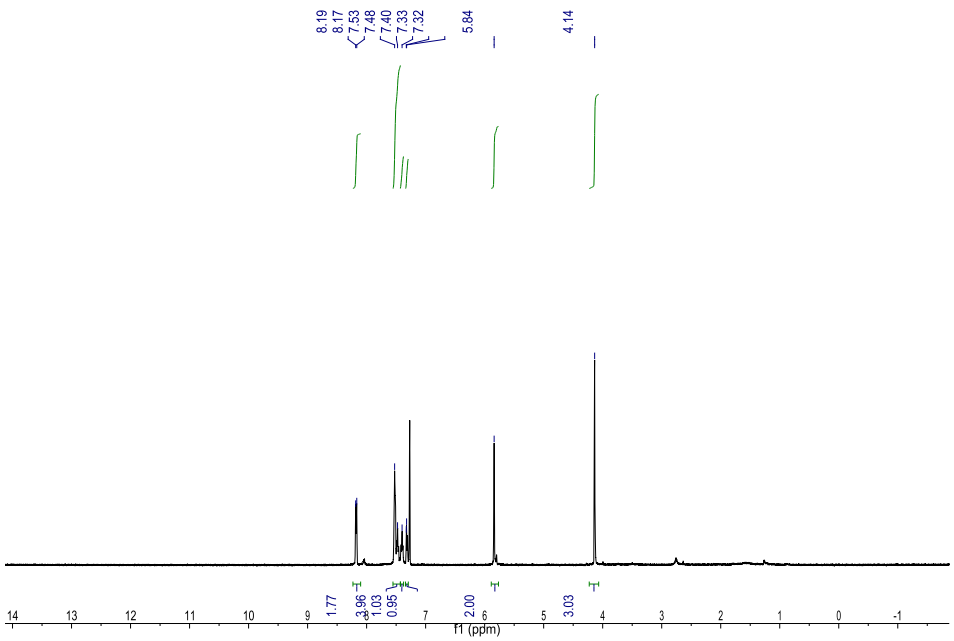


Figure S 4. ^{1}H NMR spectrum of **3** in $CDCl_3$

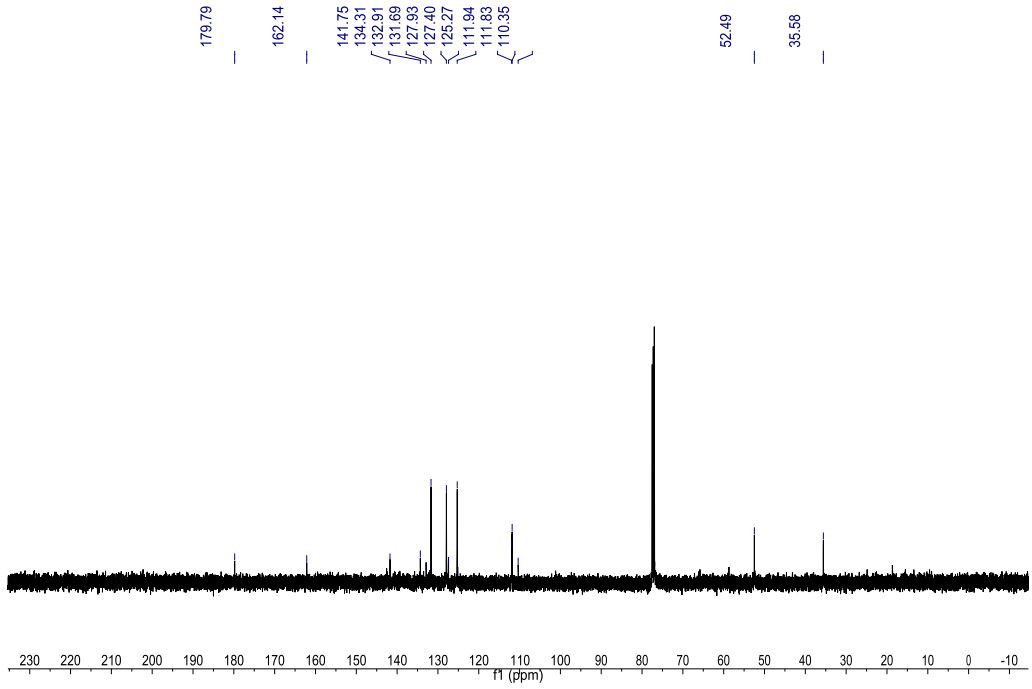


Figure S 5. $^{13}C\{1H\}$ NMR spectrum of **3** in $CDCl_3$

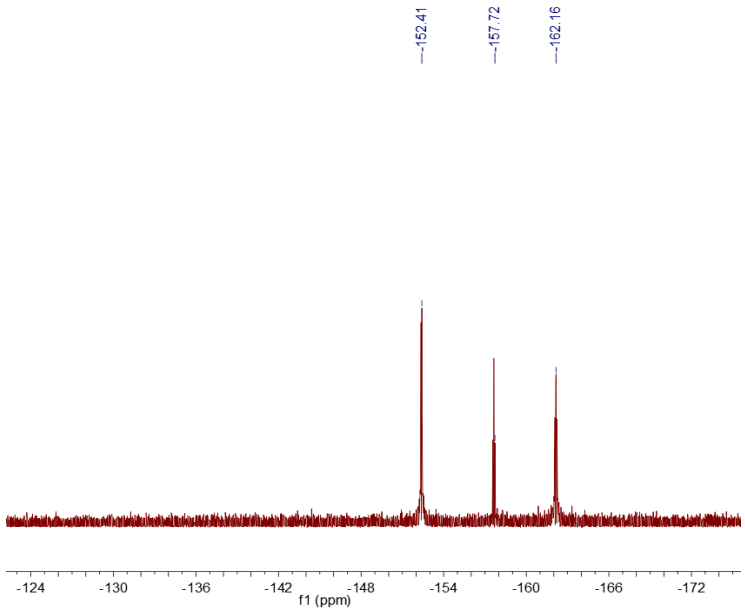


Figure S 6. ^{19}F NMR spectrum of **3**in $CDCl_3$

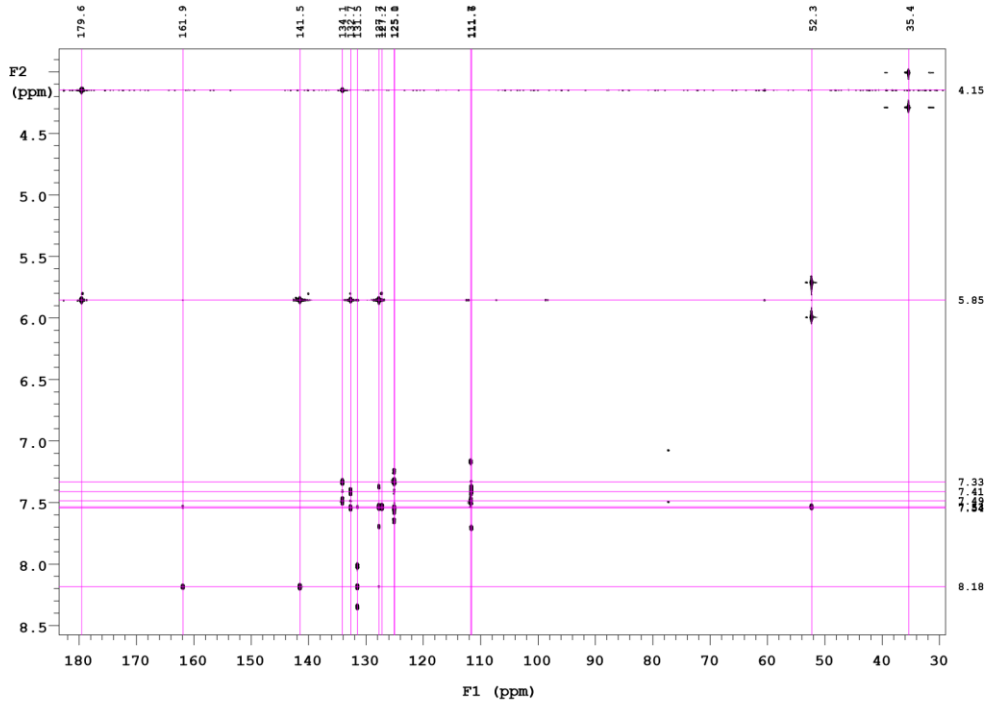


Figure S 7. ^{1}H-^{13}C gHBMC spectrum of **3** in $CDCl_3$

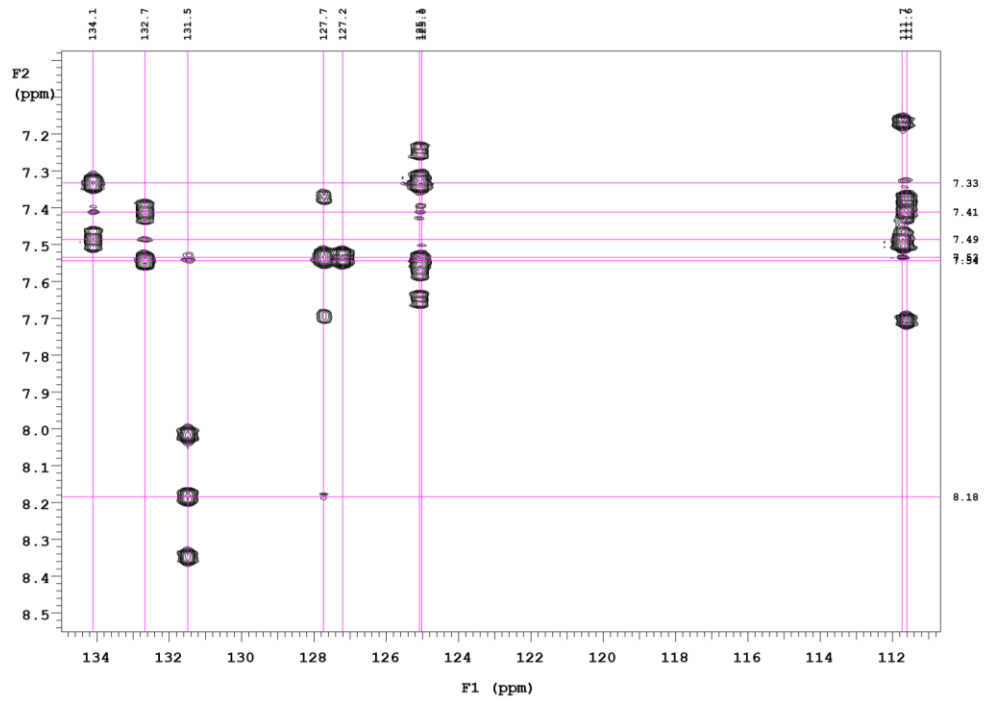


Figure S 8. ^{1}H-^{13}C gHBMC spectrum of **3** in $CDCl_3$

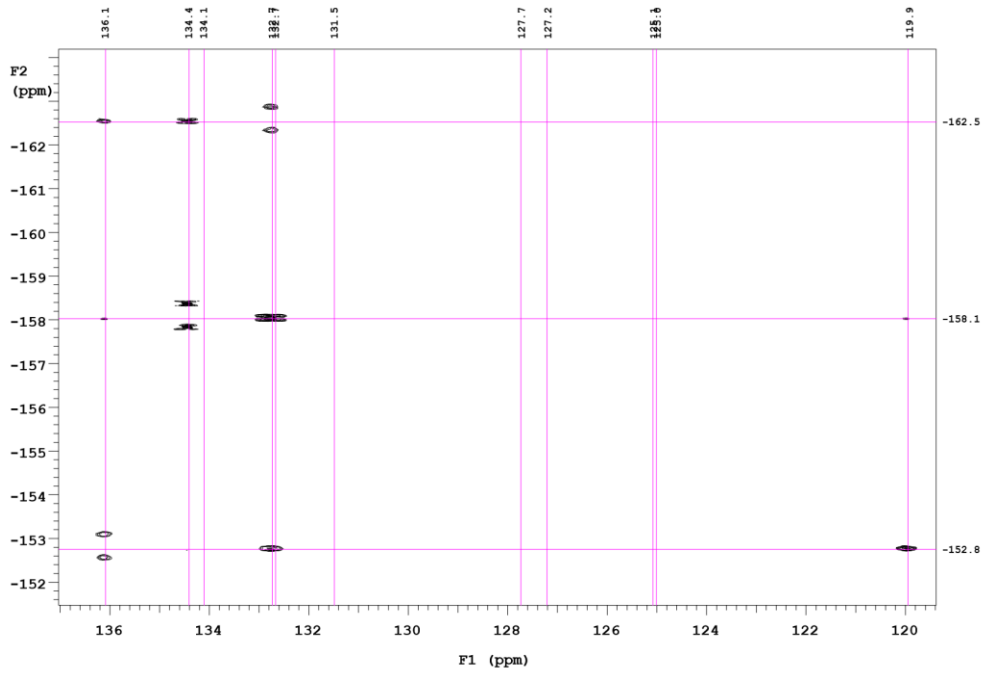


Figure S 9. ^{19}F-^{13}C gHBMC spectrum of **3** in $CDCl_3$

8.3 NMR spectrum of 4

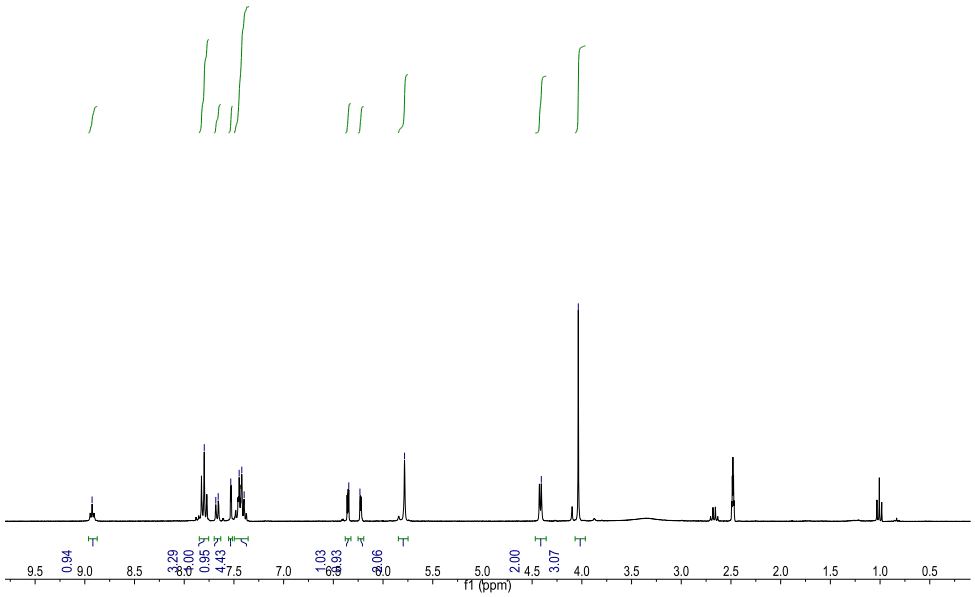


Figure S 10. ^{1}H NMR spectrum of **4** in DMSO.

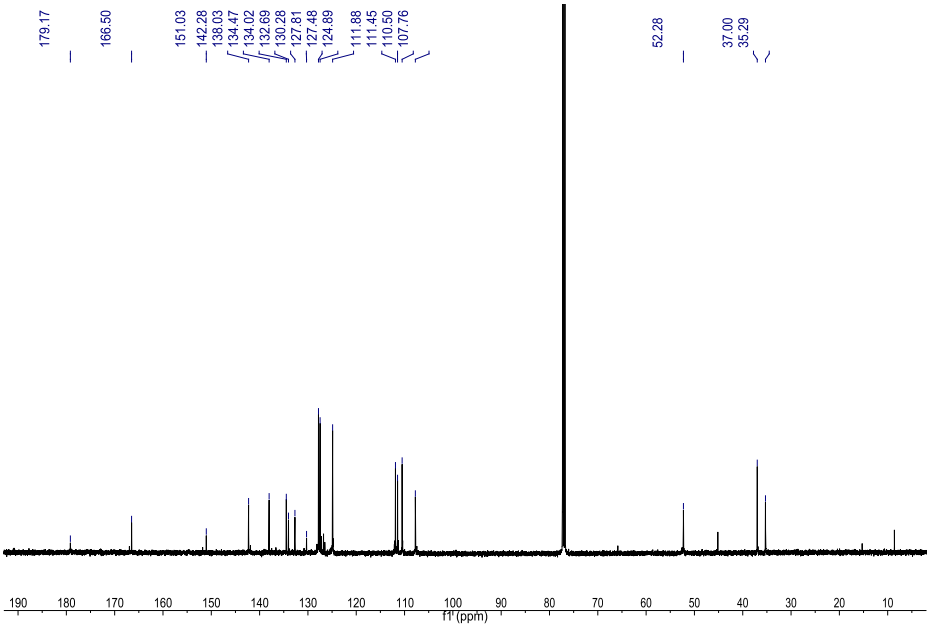


Figure S 11

Figure S 11. $^{13}C\{1H\}$ NMR spectrum of **4** in $CDCl_3$

8.4 NMR spectra of 5

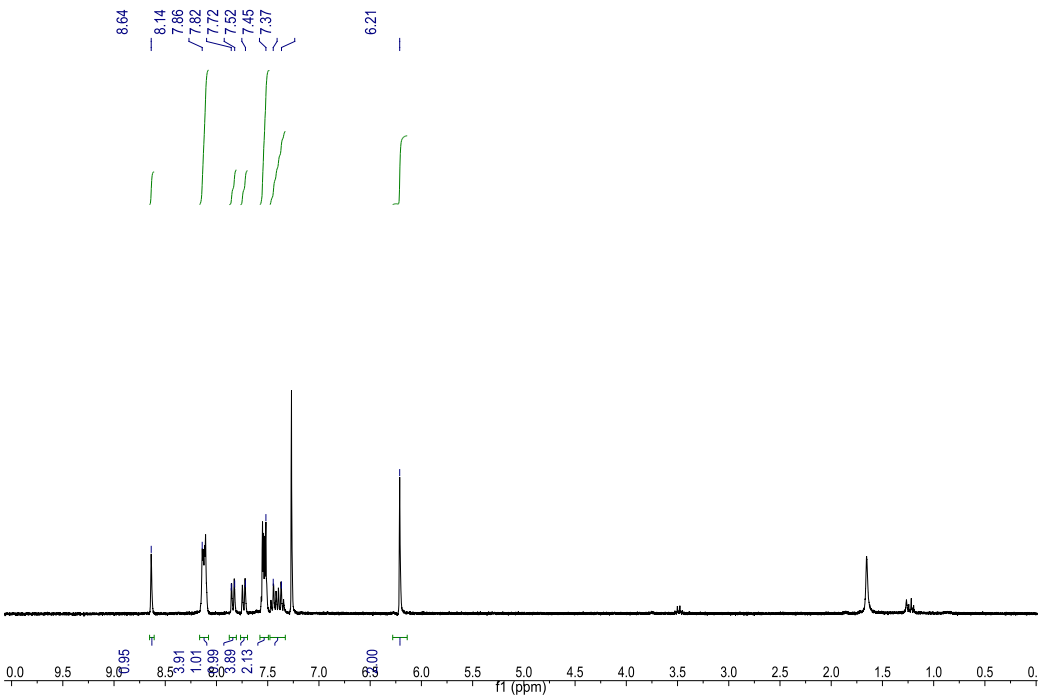


Figure S 12. ^{1}H NMR spectrum of **5** in $CDCl_3$

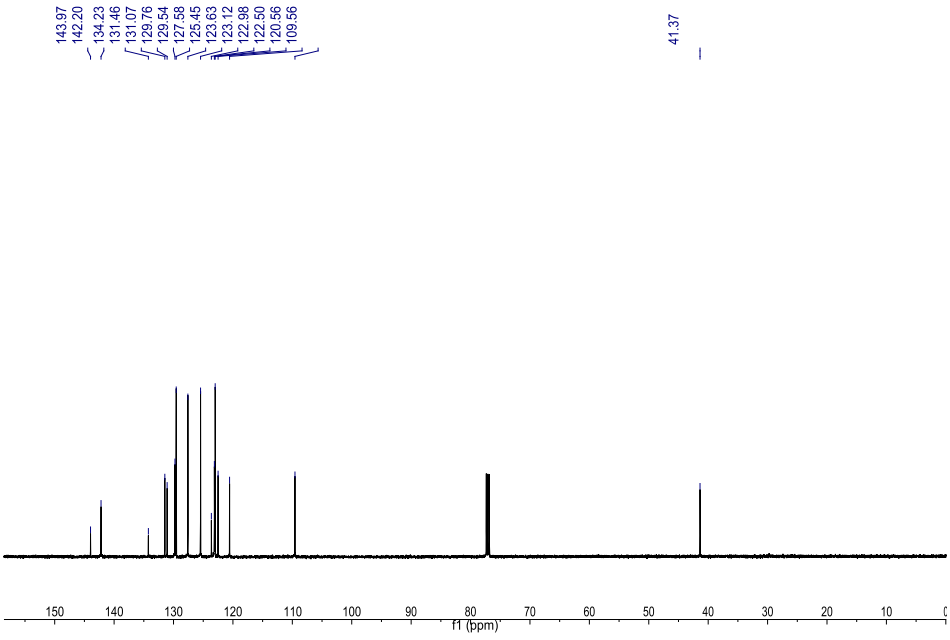


Figure S 13. $^{13}C\{1H\}$ NMR spectrum of **5** in $CDCl_3$

8.5 NMR spectra of 6

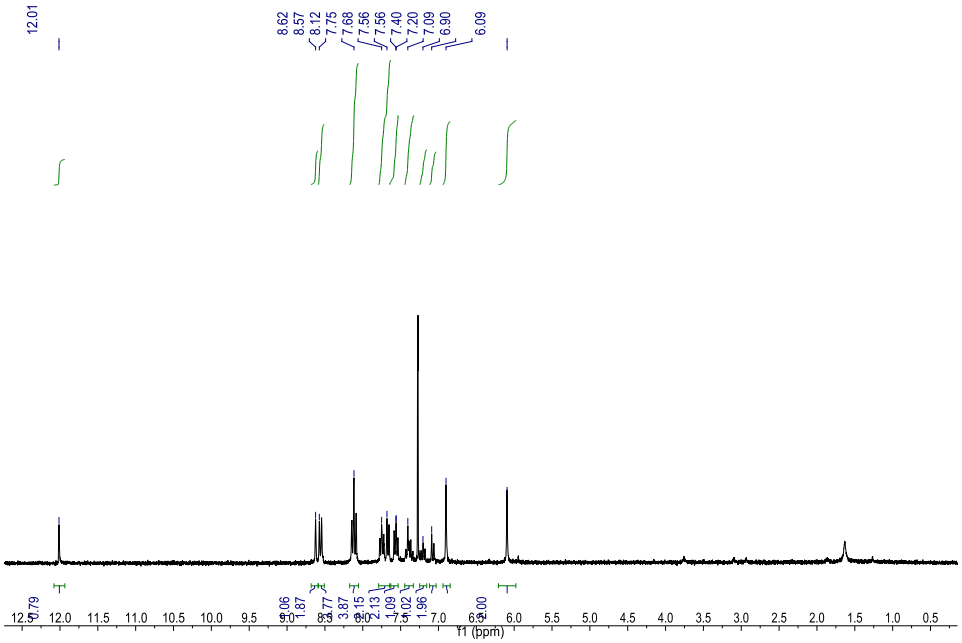


Figure S 14. ^{1}H NMR spectrum of **6** in $CDCl_3$

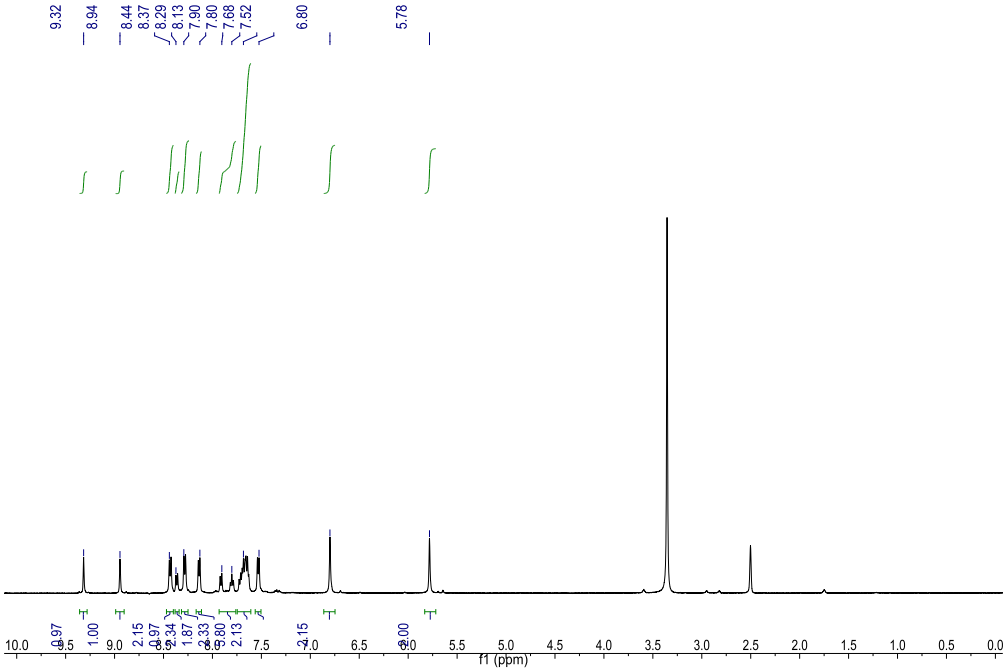


Figure S 15. ^{1}H NMR spectrum of **6** in DMSO.

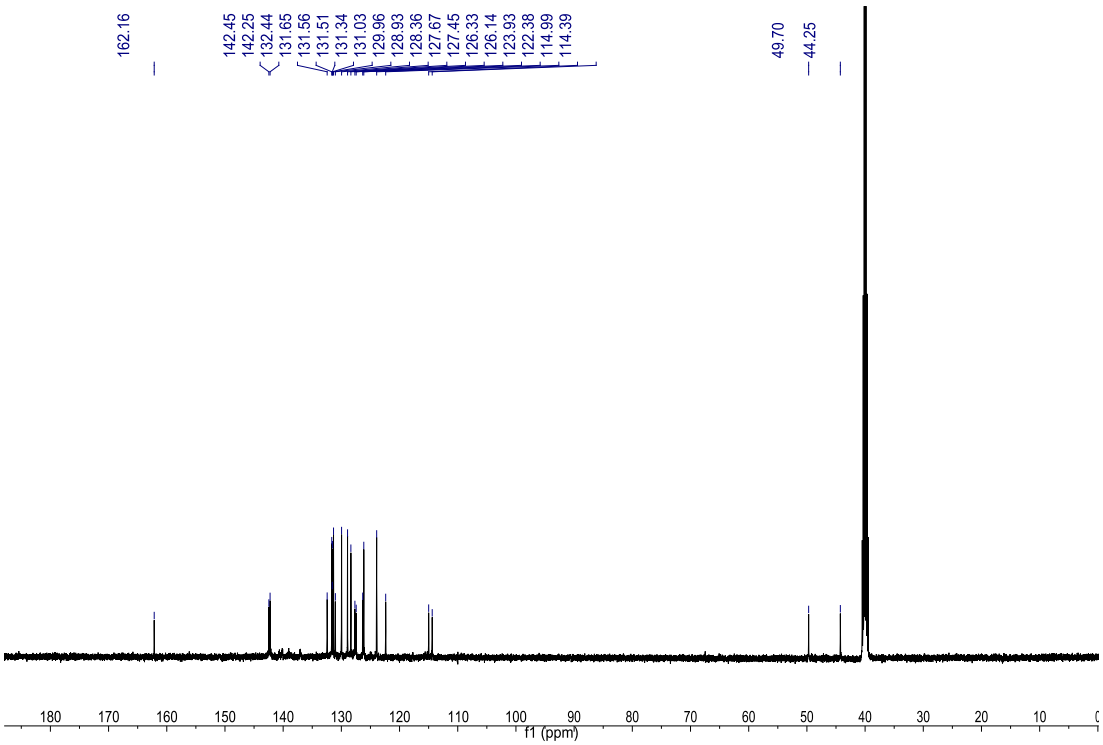


Figure S 16. $^{13}C\{1H\}$ NMR spectrum of **6** in DMSO.

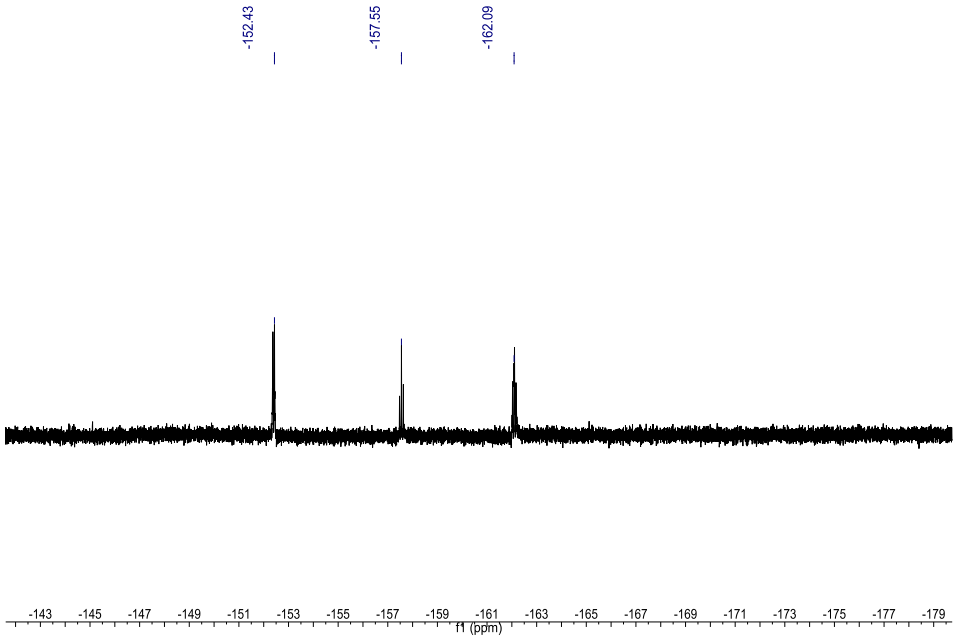


Figure S 17. ^{19}F NMR spectrum of **6** in DMSO.

8.6 NMR spectra of 7

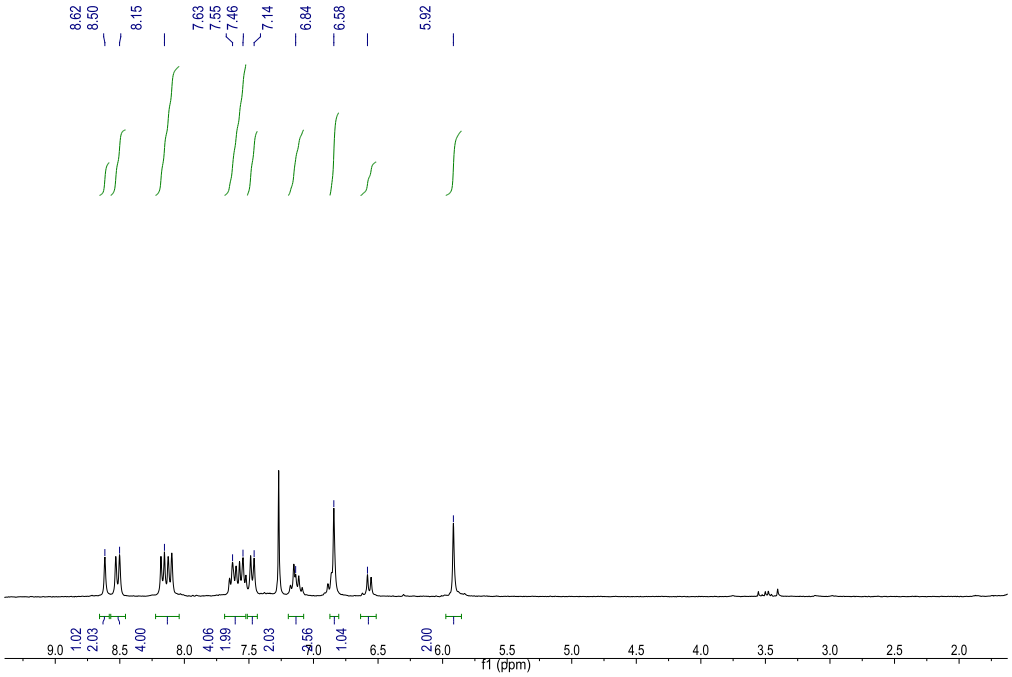


Figure S 18. ^{1}H NMR spectrum of **7** in $CDCl_3$

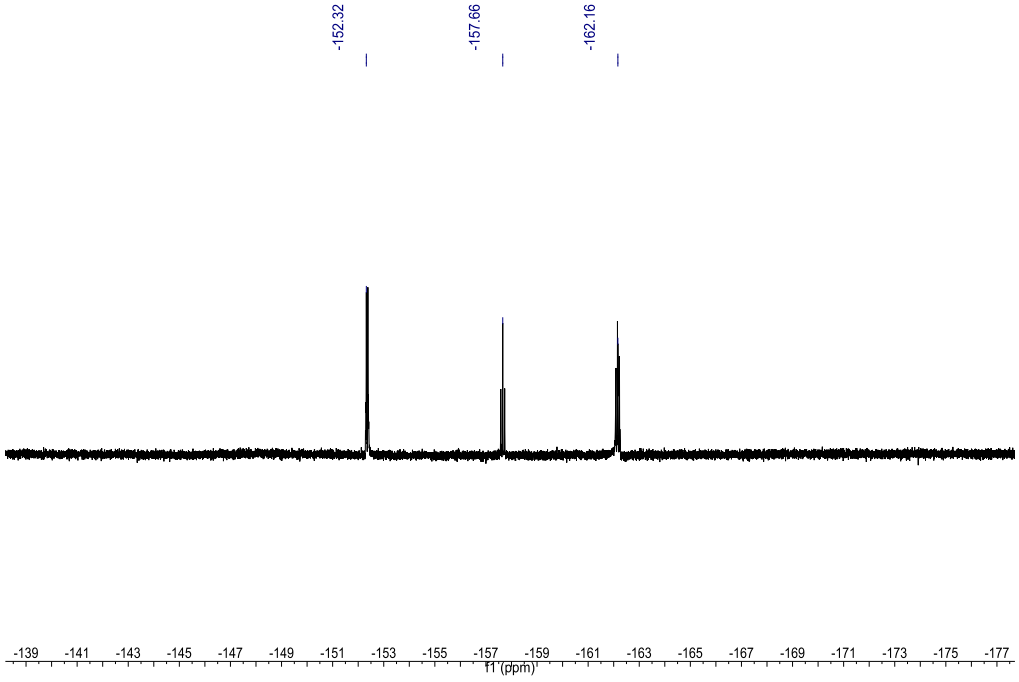


Figure S 19. ^{19}F NMR spectrum of **7** in $CDCl_3$

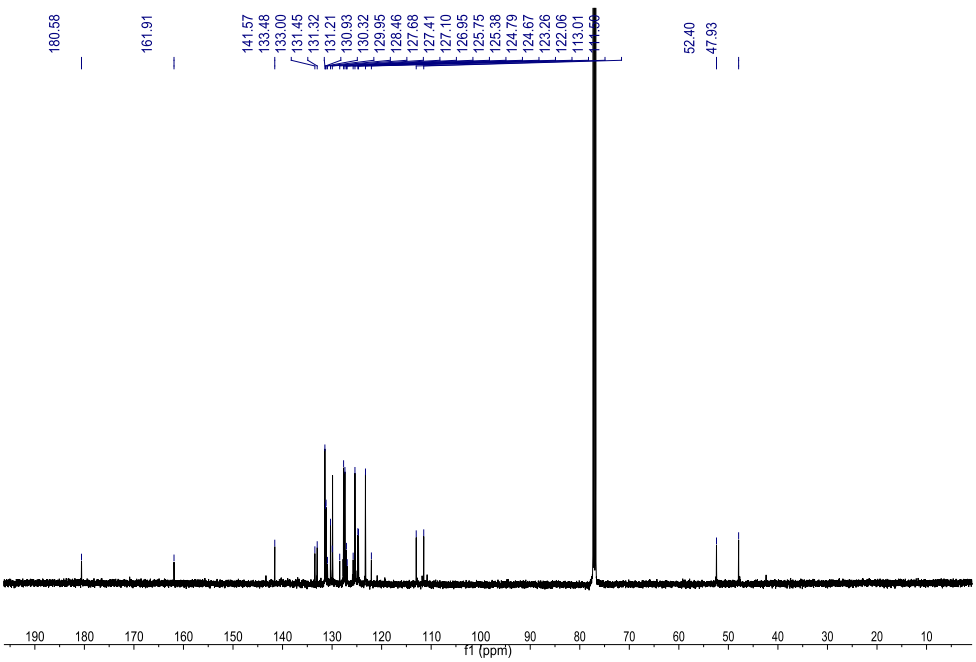


Figure S 20. $^{13}C\{1H\}$ NMR spectrum of **7** in $CDCl_3$.

8.7 NMR spectra of leftover complex 7 after conjugation with aptamer.

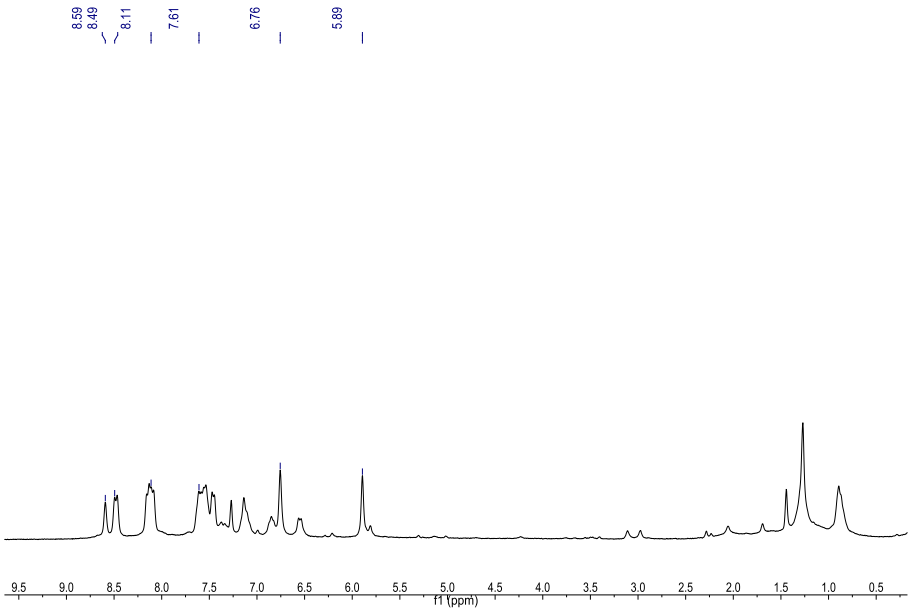


Figure S 21. ^{1}H NMR spectrum of leftover **7** after conjugation with aptamer. The residue peaks from 0-3 ppm come from the reagent used during the reaction.

9. **Mass spectrometry data of complexes 3-7.**

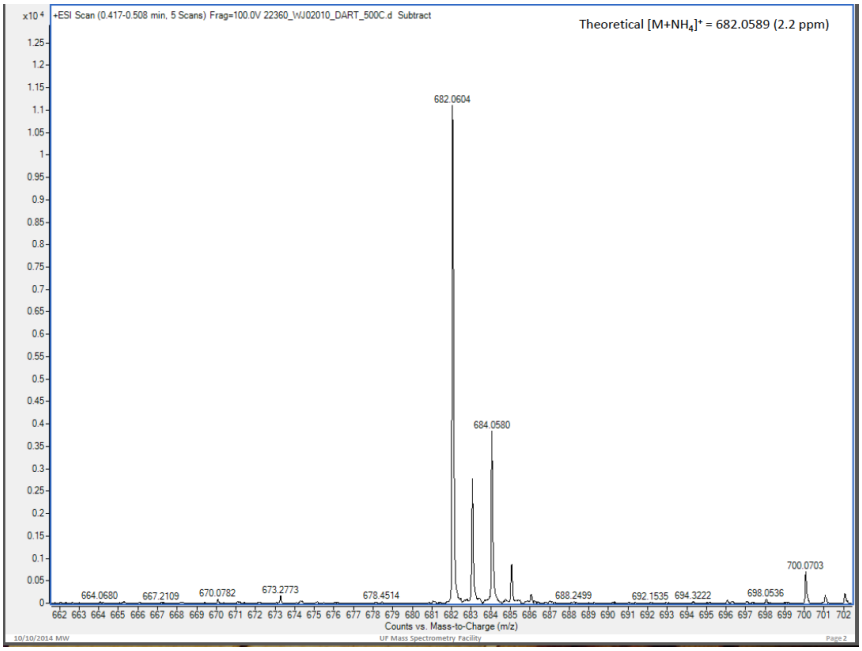


Figure S 22. HRMS (DART-MS) of **3**; [M/Z]+ calcd for $C_{22}H_{13}AuClF_5N_2O_2$ 682.0589; Found: 682.0604.

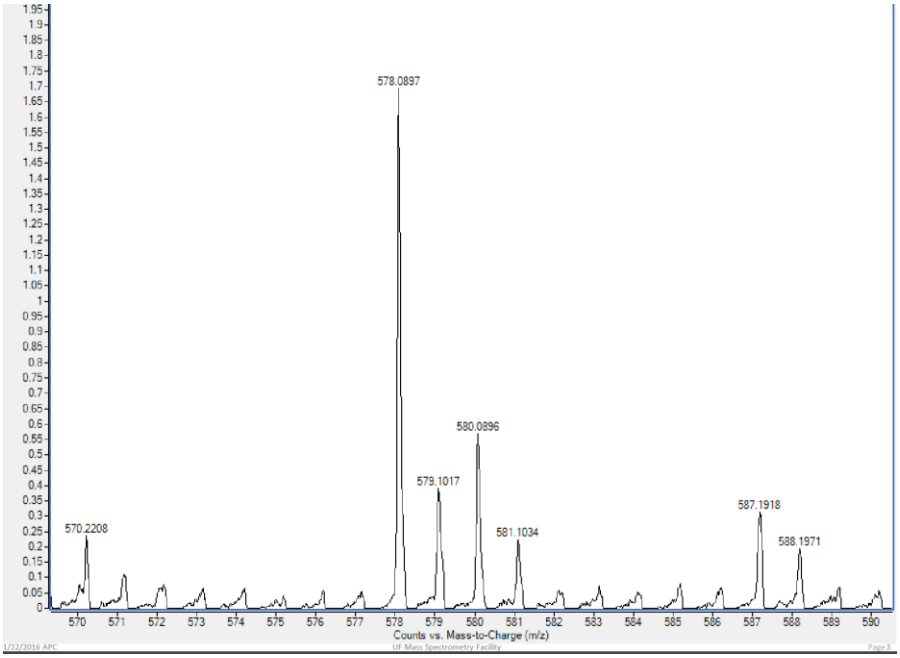


Figure S 23. HRMS (DART-MS) of **4**; [M+H]+ calcd for $C_{21}H_{19}AuClN_3O_2$ 578.0897; Found: 578.0897.

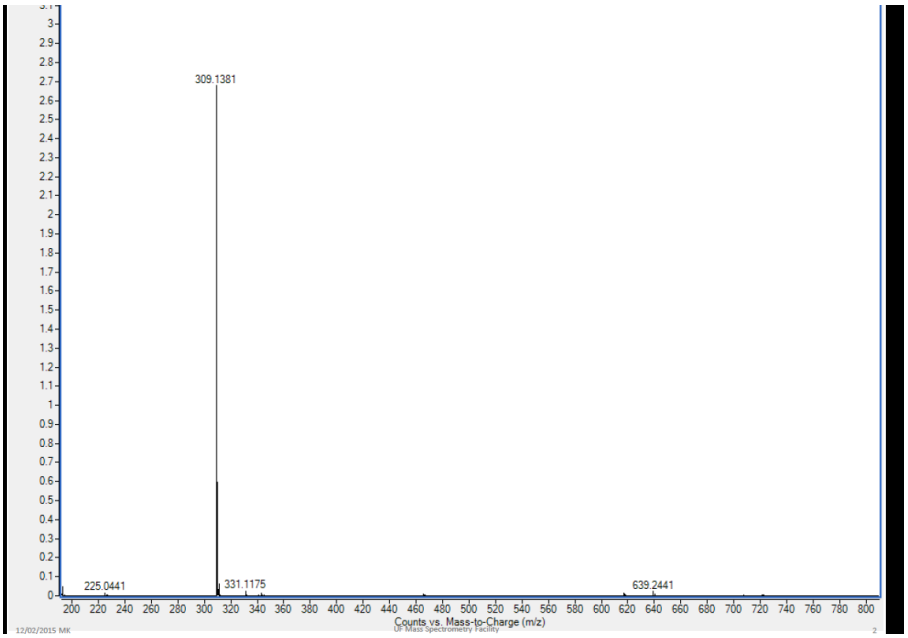


Figure S 24. HRMS (DART-MS) of **5**; $[M/Z]^+$ calcd for $C_{22}H_{16}N_2$ 309.1381; Found: 309.1381.

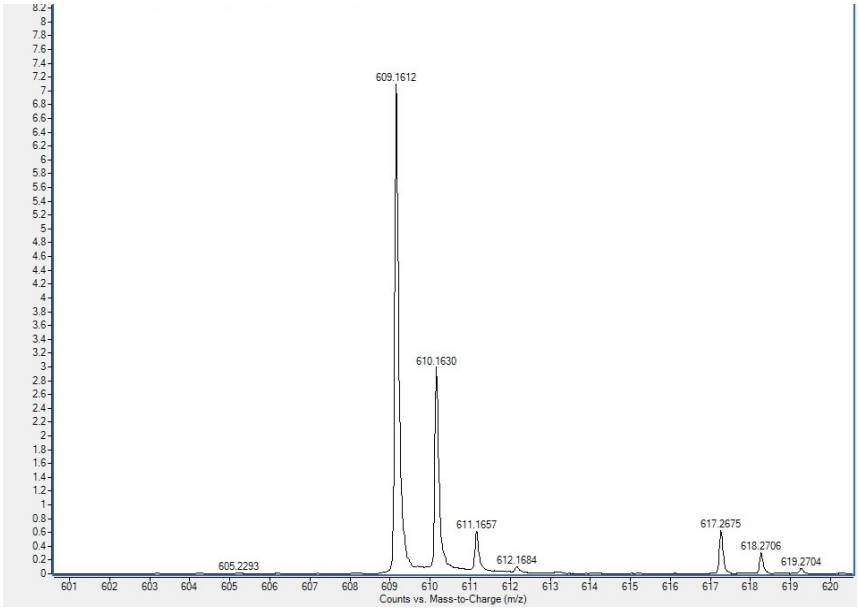


Figure S 25. HRMS (DART-MS) of **6**; $[M/Z]^+$ calcd for $C_{36}H_{22}F_5N_2O_2$ 609.1596; Found: 609.1612.

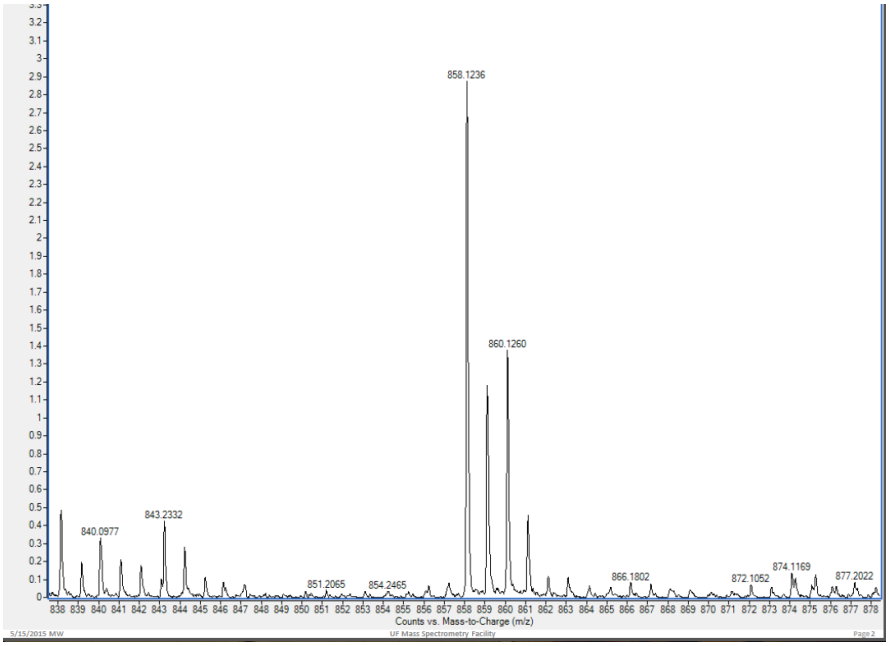


Figure S 26. HRMS (DART-MS) of **7**; $[M+NH_4]^+$ calcd for $C_{36}H_{21}AuClF_5N_2O_2$ 858.1210; Found: 858.1236.

10. MTS assay of complexes 2, 3, 7, sgc8c-3 and sgc8c-7

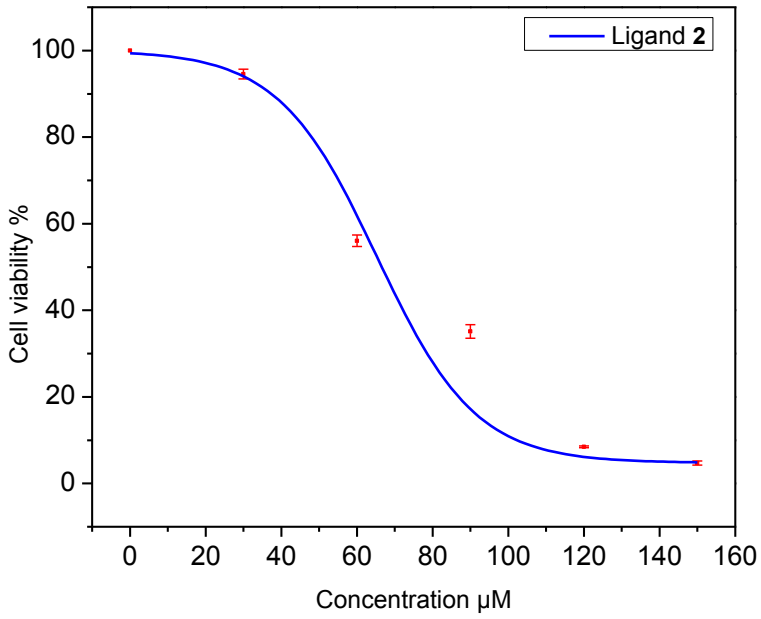


Figure S 27. MTS assay of complex **2** with CCRF-CEM cell line.

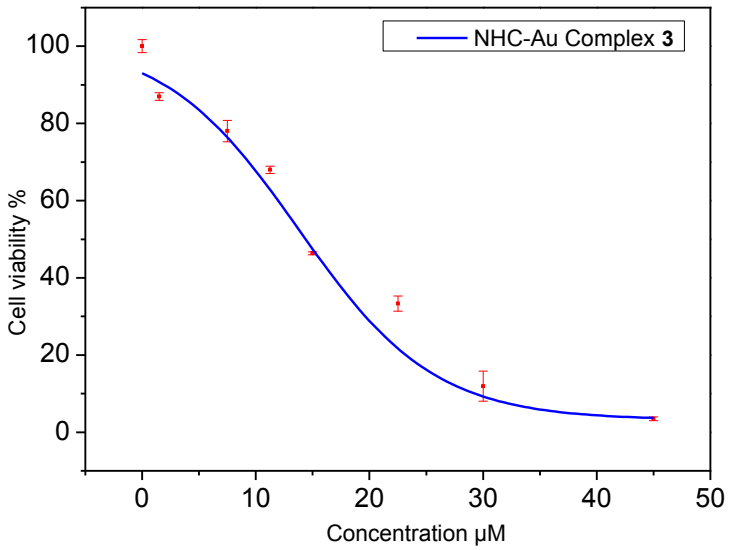


Figure S 28. MTS assay of complex **3** with CCRF-CEM cell line.

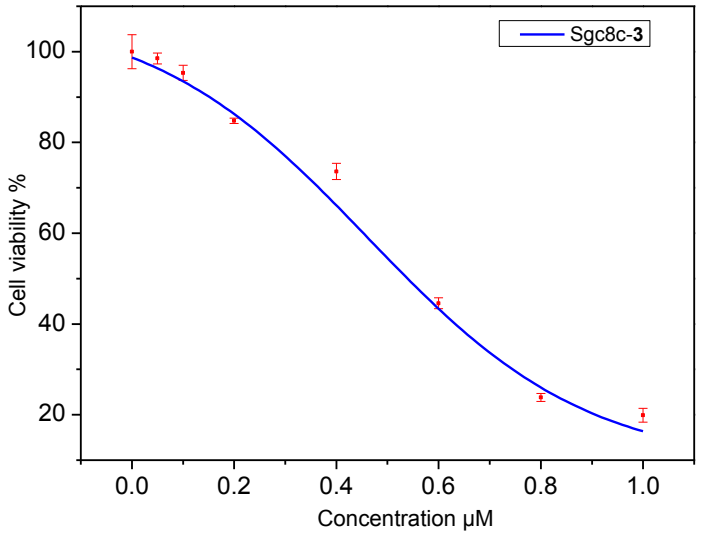


Figure S 29. MTS assay of **sgc8c-3** with CCRF-CEM cell line.

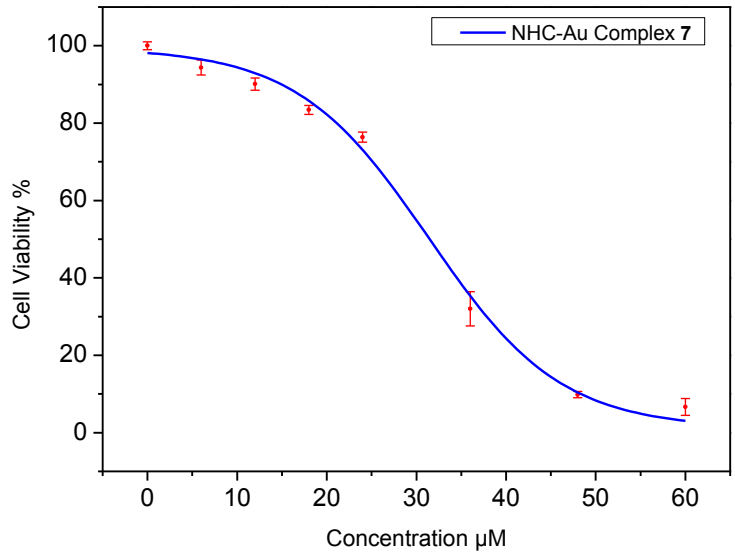


Figure S 30. MTS assay of complex **7** with CCRF-CEM cell line.

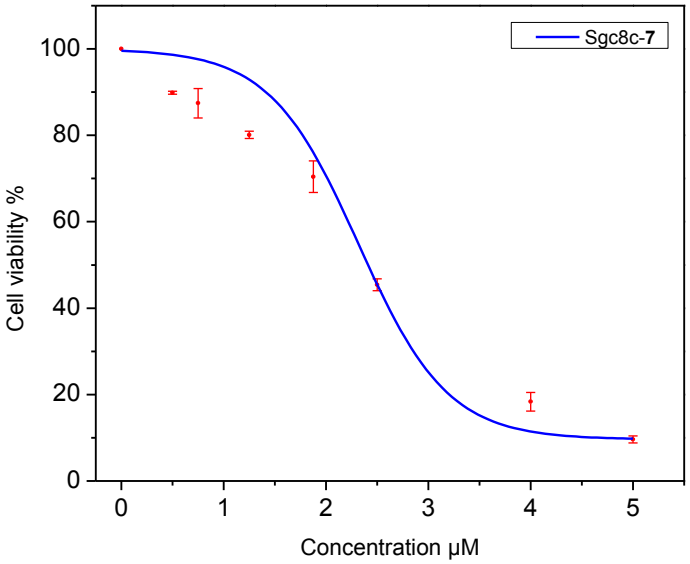


Figure S 31. MTS assay of complex **sgc8c-7** with CCRF-CEM cell line.

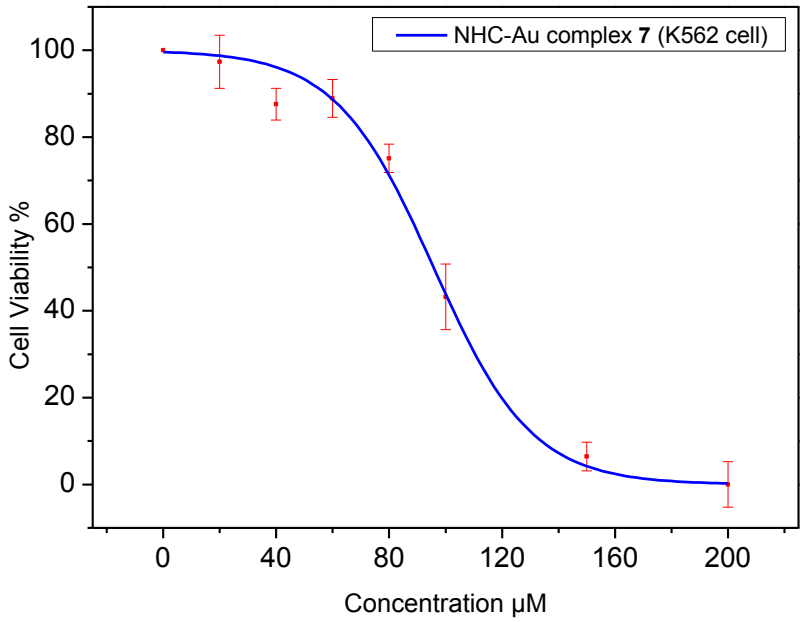


Figure S 32. MTS assay of complex **7** with K562 cell line.

11. Paper figures.

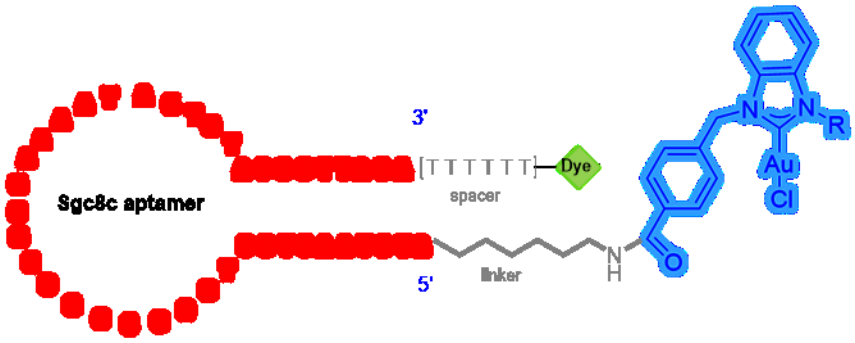


Figure S 33. Design of the aptamer-NHC-Au(I) conjugate

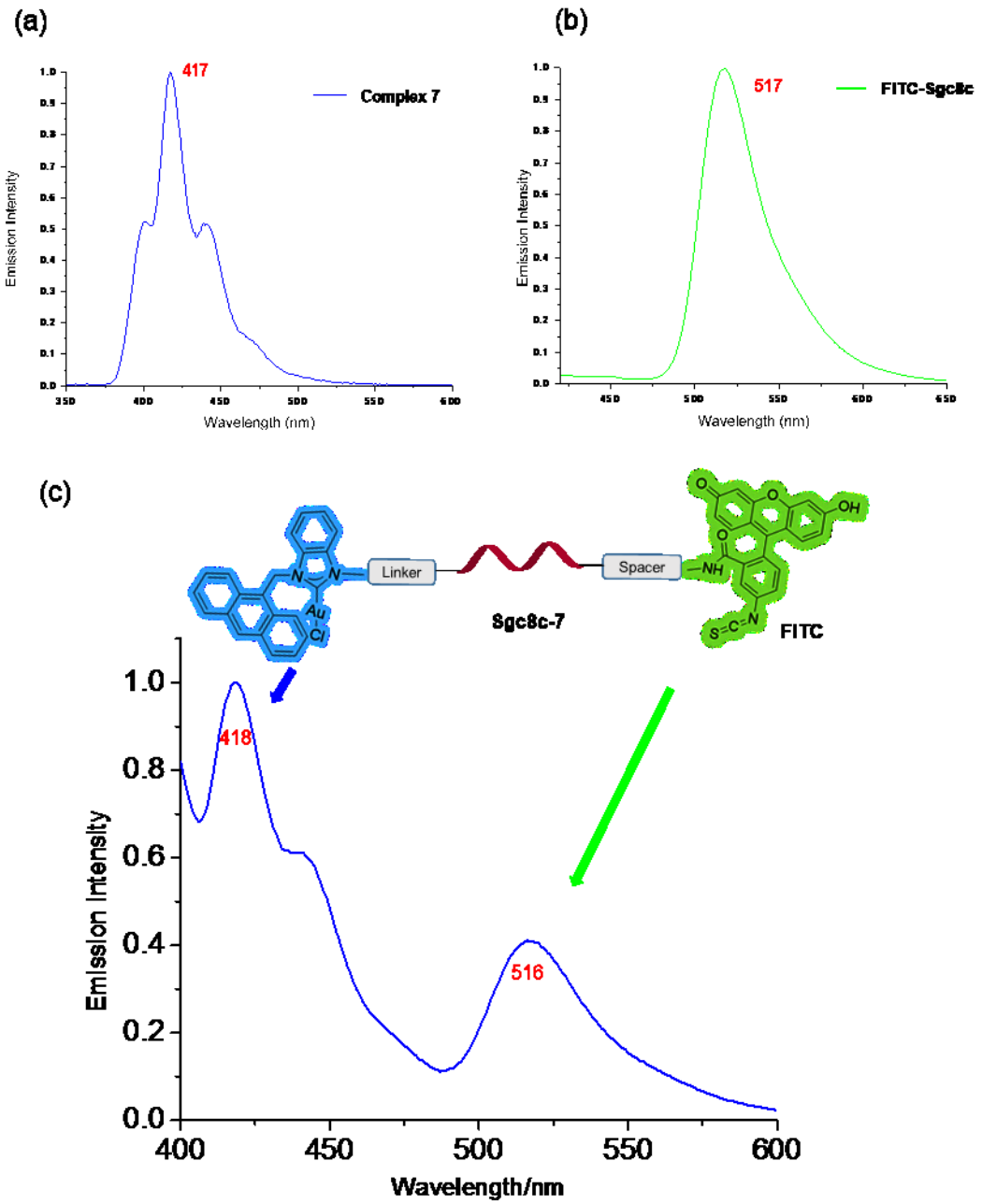


Figure S 34. (a) The emission spectrum of complex **7** (acetonitrile/H2O=1:1); (b) The emission spectrum of complex FITC-sgc8c (acetonitrile/H2O=1:1); (c) The emission spectrum of HPLC-separated aptamer-drug conjugate sgc8c-7 exhibiting both the emission of the NHC-Au(I) and FITC-aptamer fragments (acetonitrile:H2O=1:1).

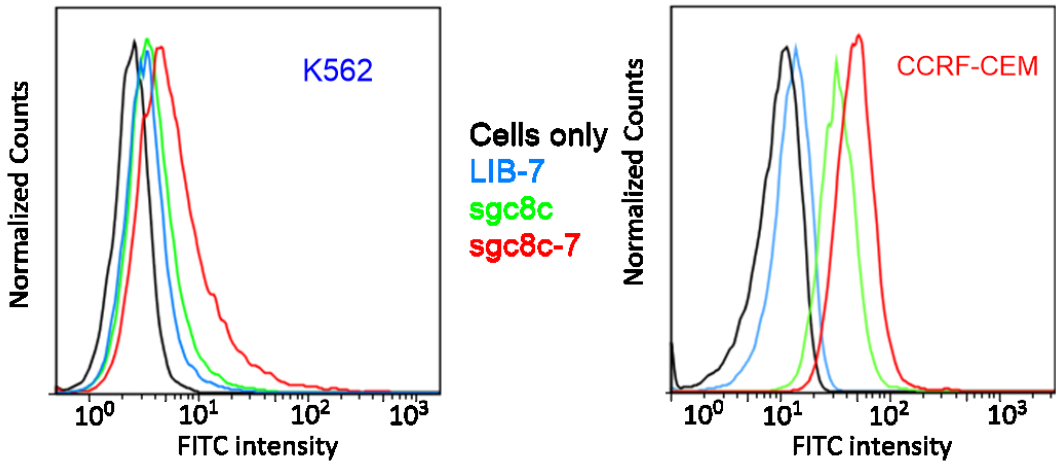


Figure S 35. Flow cytometry assays of conjugate **sgc8c-7** with the K562 cell line (left)and the CCRF-CEM cell line (right). Random aptamer sequences conjugated to **7** to create **LIB-7** were used as negative control and do not exhibit any fluorescence intensity change. The aptamer sgc8c and the conjugate **sgc8c-7**, which can target CCRF-CEM cells exhibit fluorescence intensity increases.

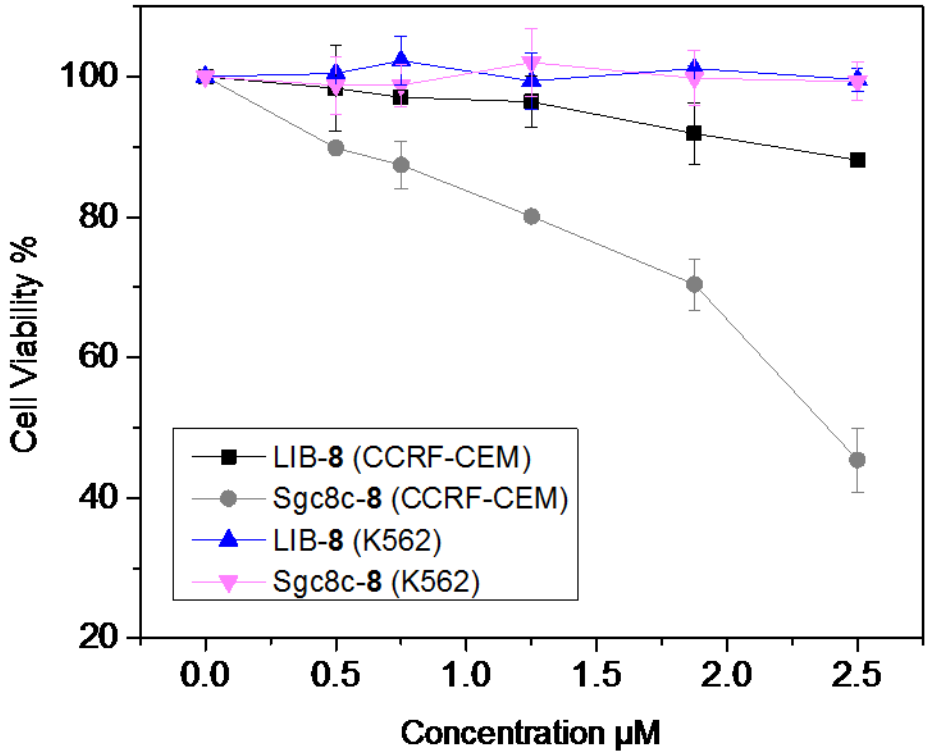


Figure S 36. MTS cell proliferation assay results demonstrating the specific cytotoxicity of **sgc8c-7** towards CCRF-CEM cells.

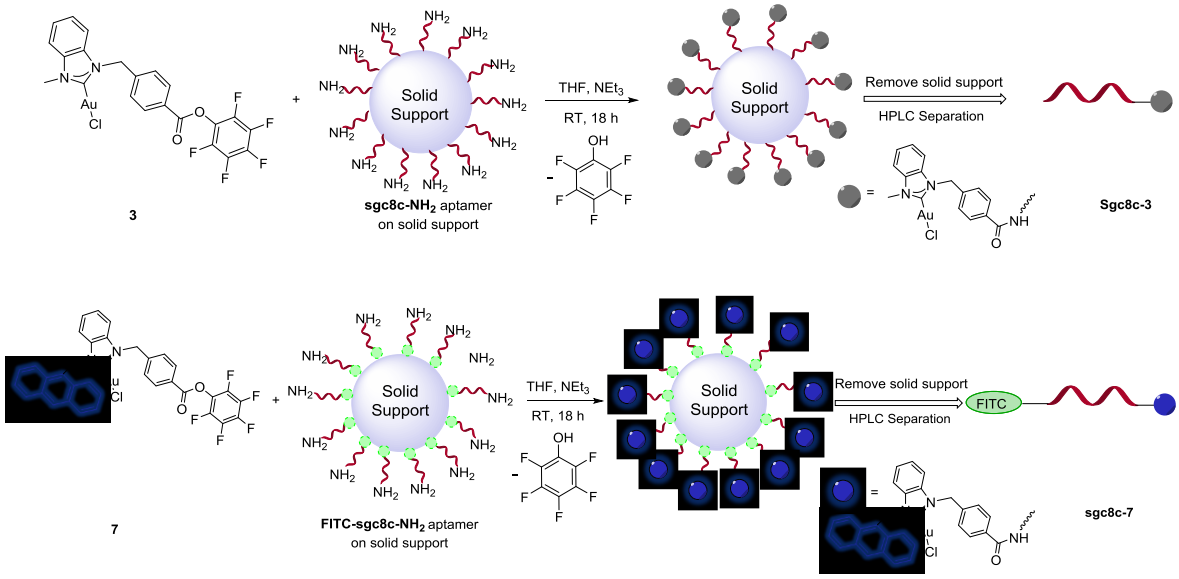


Figure S 37. Synthesis strategy of aptamer-NHC-Au conjugations **sgc8c-3** and **sgc8c-7**.

REFERENCE

1. Xiao, Z.; Shangguan, D.; Cao, Z.; Fang, X.; Tan, W., *Chemistry-a European Journal* **2008,** *14*, 1769-1775.