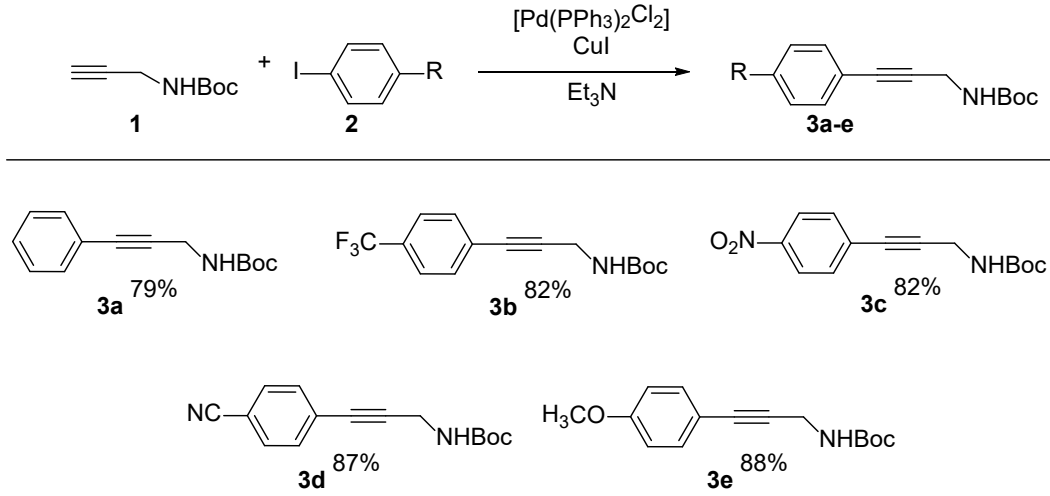
Appendix

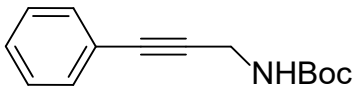
Experimental Procedures

Sonogashira Coupling Reactions



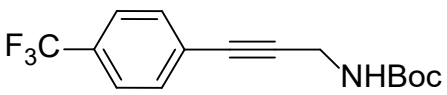
Reagents and conditions: iodoaryl compound (1.04 equiv.), $[Pd(PPh_3)_2Cl_2]$ (2.0 mol%), CuI (2.3 mol%), triethyl amine (2.07 equiv.), acetonitrile. rt, 1 h.

General procedure: To a microwave vial equipped with a stirring bar, the iodoaryl compound (1.04 equiv.) and triethylamine (2.07 equiv.) were added to a degassed solution of *N*-Boc propargylamine in dry acetonitrile (1 mol•L^{-1}) under a nitrogen atmosphere. Copper iodide (2.3 mol%) and bis(triphenylphosphine)palladium(II) dichloride (2.0 mol%) were subsequently added. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 1 h. Then the solution was transferred to a one-neck flask and concentrated on a rotary evaporator. The crude residue was finally purified by flash chromatography on silica gel (10:1 pentane/ethyl acetate). The alkynes were obtained according to the reported literature.[1]



***tert*-Butyl (3-phenylprop-2-yn-1-yl)carbamate (3a)**

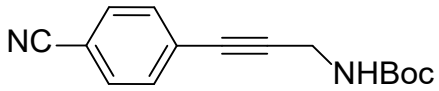
Following the general procedure, the title compound was obtained as a white powder (551 mg, 2.38 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 4.82 (s, 1H), 4.15 (d, J = 4.0 Hz, 2H), 1.47 (s, 9H).[1]



***tert*-Butyl (3-(4-cyanophenyl)prop-2-yn-1-yl)carbamate (3b)**

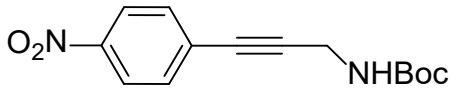
Following the general procedure, the crude residue was finally purified by flash

chromatography on silica gel (8:1 pentane/ethyl acetate). The title compound was obtained as a white powder (245 mg, 0.82 mmol, 82%).



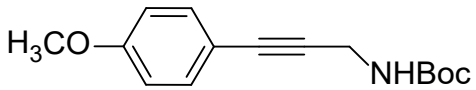
***tert*-Butyl (3-(4-cyanophenyl)prop-2-yn-1-yl)carbamate (3c)**

Following the general procedure, the crude residue was finally purified by flash chromatography on silica gel (8:1 Pentane/Ethyl Acetate). The title compound was obtained as a white powder (222 mg, 0.87 mmol, 87%).



***tert*-Butyl (3-(4-nitrophenyl)prop-2-yn-1-yl)carbamate (3d)**

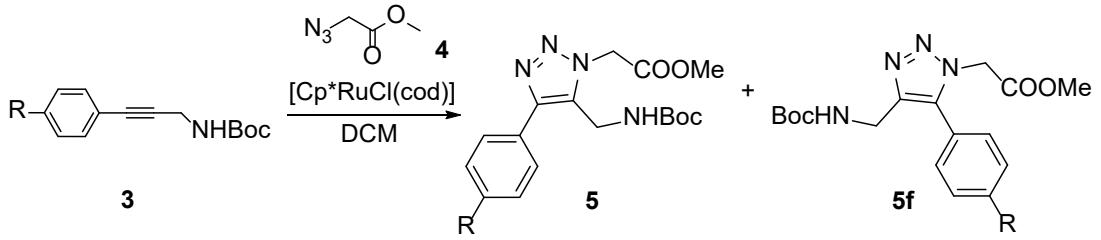
Following the general procedure, the crude residue was finally purified by flash chromatography on silica gel (8:1 Pentane/Ethyl acetate). The title compound was obtained as a yellow powder (486 mg, 1.76 mmol, 88%).

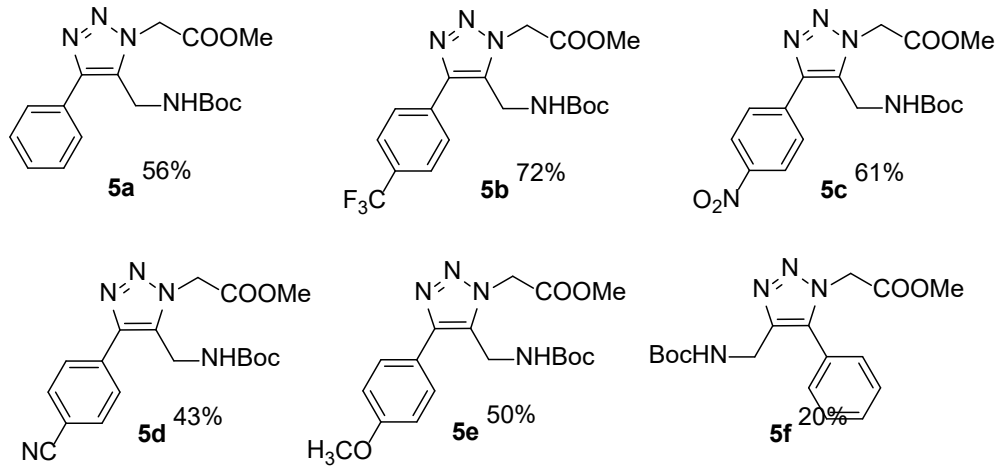


***tert*-Butyl (3-(4-methoxyphenyl)prop-2-yn-1-yl)carbamate (3e)**

Following the general procedure, the title compound was obtained as a white powder (429 mg, 1.64 mmol, 82%).

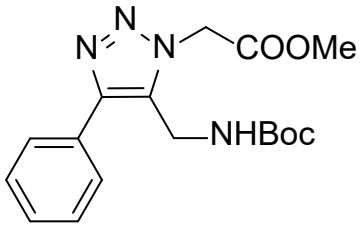
Ruthenium-Catalyze Azide Alkyne Cycloaddition (RuAAC) Reactions





Reagents and conditions: Azide (1 equiv.), [Cp* RuCl(cod)] (5 mol%), DCM, rt, 30 min

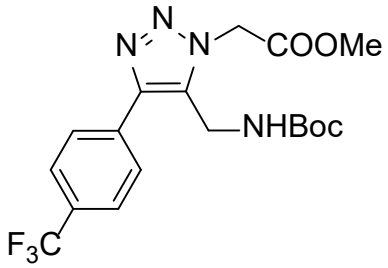
General procedure: To a microwave vial equipped with a stirring bar, The azide (1 equiv.) was added to a degassed solution of the alkyne in dry dichloromethane (0.5 mol•L^{-1}). $Cp^*RuCl(COD)$ (5 mol%) was subsequently added. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min. Then the solution was transferred to a one-neck flask and concentrated on a rotary evaporator. The crude residue was finally purified by flash chromatography on silica gel (1:1 pentane/ethyl acetate).



Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (5a)

Following the general procedure, the title compound was obtained as a white powder (427 mg, 1.35 mmol, 56%).

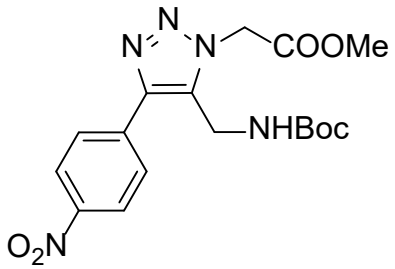
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 6.6 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 5.38 (s, 2H), 4.90 (s, 1H), 4.55 (d, J = 6.0 Hz, 2H), 3.83 (s, 3H), 1.43 (s, 9H).



Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)acetate (5b)

Following the general procedure, the title compound was obtained as a white powder (297 mg, 0.72 mmol, 72%).

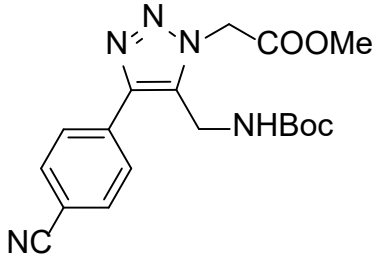
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 5.39 (s, 2H), 4.93 (s, 1H), 4.56 (d, *J* = 6.0 Hz, 2H), 3.85 (s, 3H), 1.43 (s, 9H).



Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-nitrophenyl)-1H-1,2,3-triazol-1-yl)acetate (5c)

Following the general procedure, the title compound was obtained as a white powder (154 mg, 0.41 mmol, 61%).

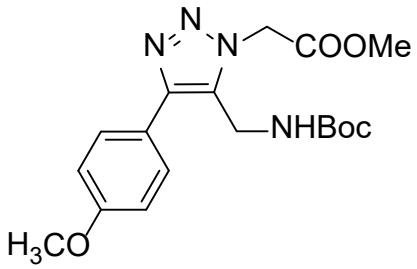
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 5.40 (s, 2H), 5.04 (s, 1H), 4.57 (d, *J* = 5.9 Hz, 2H), 3.86 (s, 3H), 1.44 (s, 9H).



Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-cyanophenyl)-1H-1,2,3-triazol-1-yl)acetate (5d)

Following the general procedure, the title compound was obtained as a white powder (443 mg, 1.08 mmol, 43%).

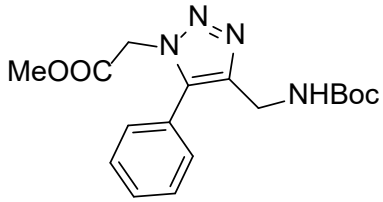
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 2H), 5.40 (s, 2H), 5.01 (br s, 1H), 4.58 (d, *J* = 5.9 Hz, 2H), 3.86 (s, 3H), 1.44 (s, 9H).



Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)acetate (5e)

Following the general procedure, the title compound was obtained as a white powder (372 mg, 0.99 mmol, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 5.35 (s, 1H), 4.51 (d, *J* = 6.0 Hz, 1H), 3.85 (s, 2H), 3.82 (s, 2H), 1.43 (s, 5H).

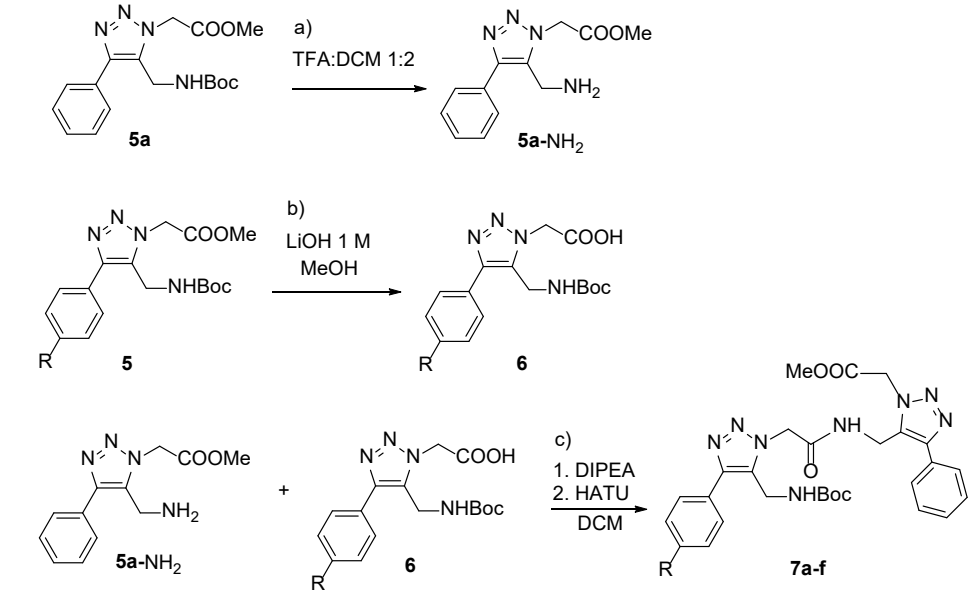


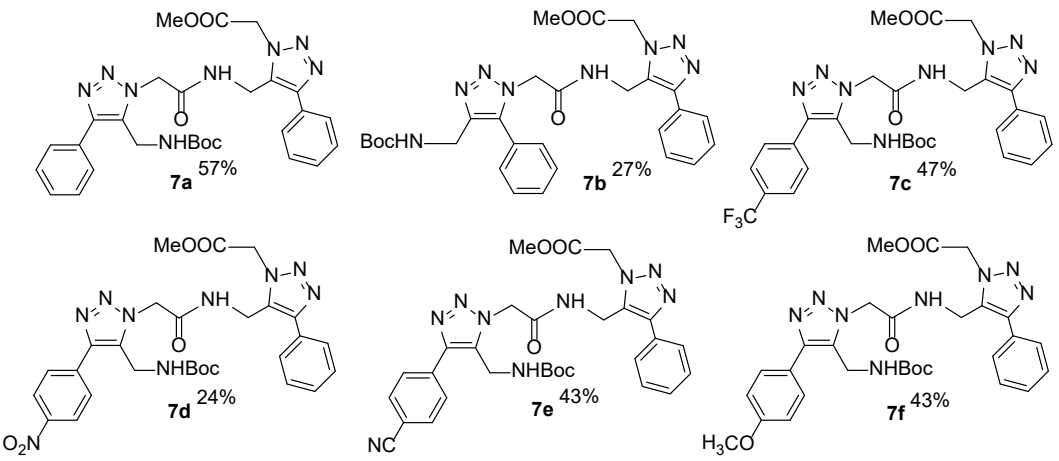
Methyl 2-(4-(((tert-butoxycarbonyl)amino)methyl)-5-phenyl-1H-1,2,3-triazol-1-yl)acetate (7a)

Following the general procedure, the title compound was obtained as a brown oil.
(117 mg, 0.33 mmol, 20%).

1H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 3H), 7.32 (dd, *J* = 6.6, 3.0 Hz, 2H), 5.16 (br s, 1H), 5.02 (s, 2H), 4.37 (d, *J* = 5.2 Hz, 2H), 3.74 (s, 3H), 1.40 (s, 9H).

Synthesis of triazole dimers





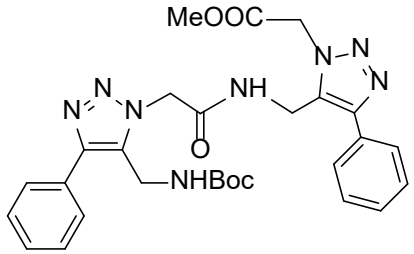
Reagents and conditions: a) TFA (11.6 equiv.), DCM, rt, 1 h; b) LiOH 1 M (1.56 equiv.), MeOH, 1 h; c) DIPEA (4.00 equiv.), HATU (1.05 equiv.), DCM, rt, 5 h.

General procedure for Boc-deprotection: To a microwave vial equipped with a stirring bar, trifluoroacetic acid (11.6 equiv.) was added to a solution of the triazole **5** in DCM (0.60 mol•L^{-1}). The reaction mixture was stirred in the open air at room temperature for 1 h and the progress was followed by TLC (1:1 pentane/ethyl acetate). The reaction mixture was then condensed under a stream of nitrogen and the salt was used directly in the amide coupling reaction.

General procedure for ester hydrolysis: To a microwave vial equipped with a stirring bar, 1 M lithium hydroxide (1.56 equiv.) was added to a solution of the triazole **5** in methanol (0.25 mol•L^{-1}). The reaction mixture was stirred in the open air at room temperature for 1 h and the progress was followed by TLC (1:1 pentane/ethyl acetate). Deionized water (10 mL) was added and 1 M HCl (1.56 equiv.) was then added dropwise with stirring. The reaction mixture was extracted with ethyl acetate (4*30 mL).

The combined organic layers were dried over dry magnesium sulfate and concentrated on a rotary evaporator. The product was used directly in the next step.

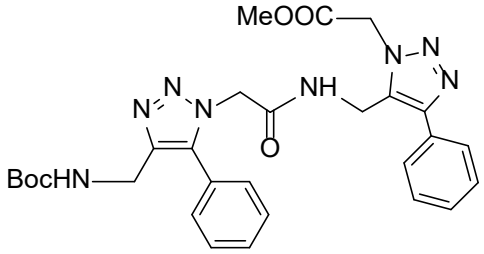
General procedure for the amide coupling: To a microwave vial equipped with a stirring bar, DIPEA (4 equiv.) was added to a solution of the acid while keeping the nitrogen flow on to maintain an inert atmosphere. HATU (1.05 equiv.) was then added. The amine was added at the end and the reaction was stirred at room temperature for 6 h, where it was determined complete by TLC. Deionized water (10 mL) was added and 1 M HCl (4 equiv.) was then added dropwise with stirring. The reaction mixture was washed with deionized water (3*10 mL) and extracted with ethyl acetate (4*20 mL). The combined organic layers were dried over dry magnesium sulfate and concentrated on a rotary evaporator. The crude residue was finally purified by flash chromatography on silica gel (1:5 pentane/ethyl acetate).



Methyl 2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (7a)

Following the general procedure, the title compound was obtained as a white powder (198 mg, 0.34 mmol, 57%).

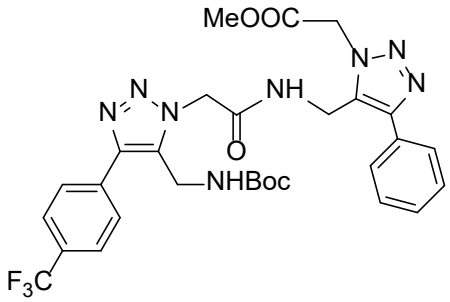
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.61 (m, 4H), 7.45 – 7.36 (m, 6H), 5.35 (s, 2H), 5.16 (m, 3H), 4.70 (br s, 2H), 4.47 (br s, 2H), 3.73 (s, 3H), 1.40 (s, 9H).



Methyl 2-(5-((2-(4-(((*tert*-butoxycarbonyl)amino)methyl)-5-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (7b)

Following the general procedure, the title compound was obtained as a white powder (67 mg, 0.12 mmol, 27%).

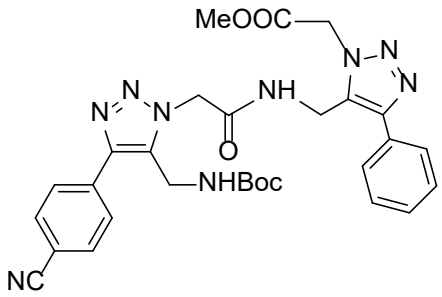
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.71 – 7.62 (m, 2H), 7.45 (m, 2.2 Hz, 3H), 7.42 – 7.36 (m, 2H), 7.31 (m, 3H), 5.97 (br s, 1H), 5.21 (s, 2H), 4.93 (s, 2H), 4.52 (d, J = 5.6 Hz, 2H), 4.48 (d, J = 5.4 Hz, 2H), 3.69 (s, 3H), 1.39 (s, 9H).



Methyl 2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (7c)

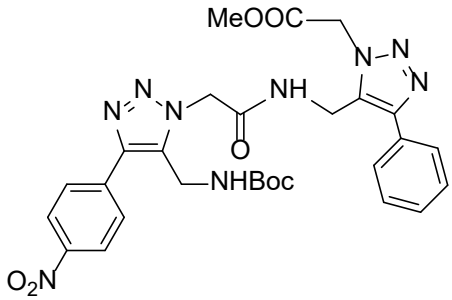
Following the general procedure, the title compound was obtained as a white powder (214 mg, 0.34 mmol, 47%).

^{1}H NMR (600 MHz, DMSO) δ 9.07 (t, J = 5.5 Hz, 1H), 8.09 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.81 (m, *J* = 8.4, 6.8 Hz, 4H), 7.51 (m, *J* = 7.7 Hz, 3H), 5.52 (s, 2H), 5.28 (s, 2H), 4.59 (d, *J* = 5.6 Hz, 2H), 4.39 (d, *J* = 5.6 Hz, 2H), 3.73 (s, 3H), 1.33 (s, 9H).



Methyl 2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-cyanophenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (7d)

Following the general procedure, the title compound was obtained as a white powder (126 mg, 0.21 mmol, 43%).^{1}H NMR data to be added.

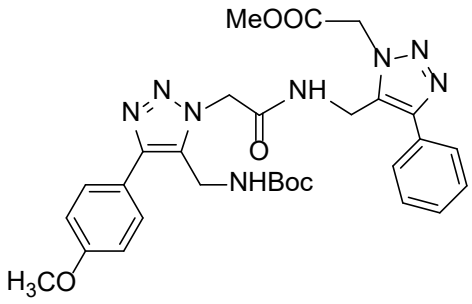


Methyl 2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-nitrophenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (7e)

Following the general procedure, the title compound was obtained as a white powder (77 mg, 0.12 mmol, 24%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.71 – 7.58 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 (m, *J* = 7.4 Hz, 2H), 5.48 (s, 1H), 5.32 (s,

2H), 5.16 (s, 2H), 4.70 (d, *J* = 5.6 Hz, 2H), 4.50 (d, *J* = 5.9 Hz, 2H), 3.76 (s, 3H), 1.42 (s, 9H).

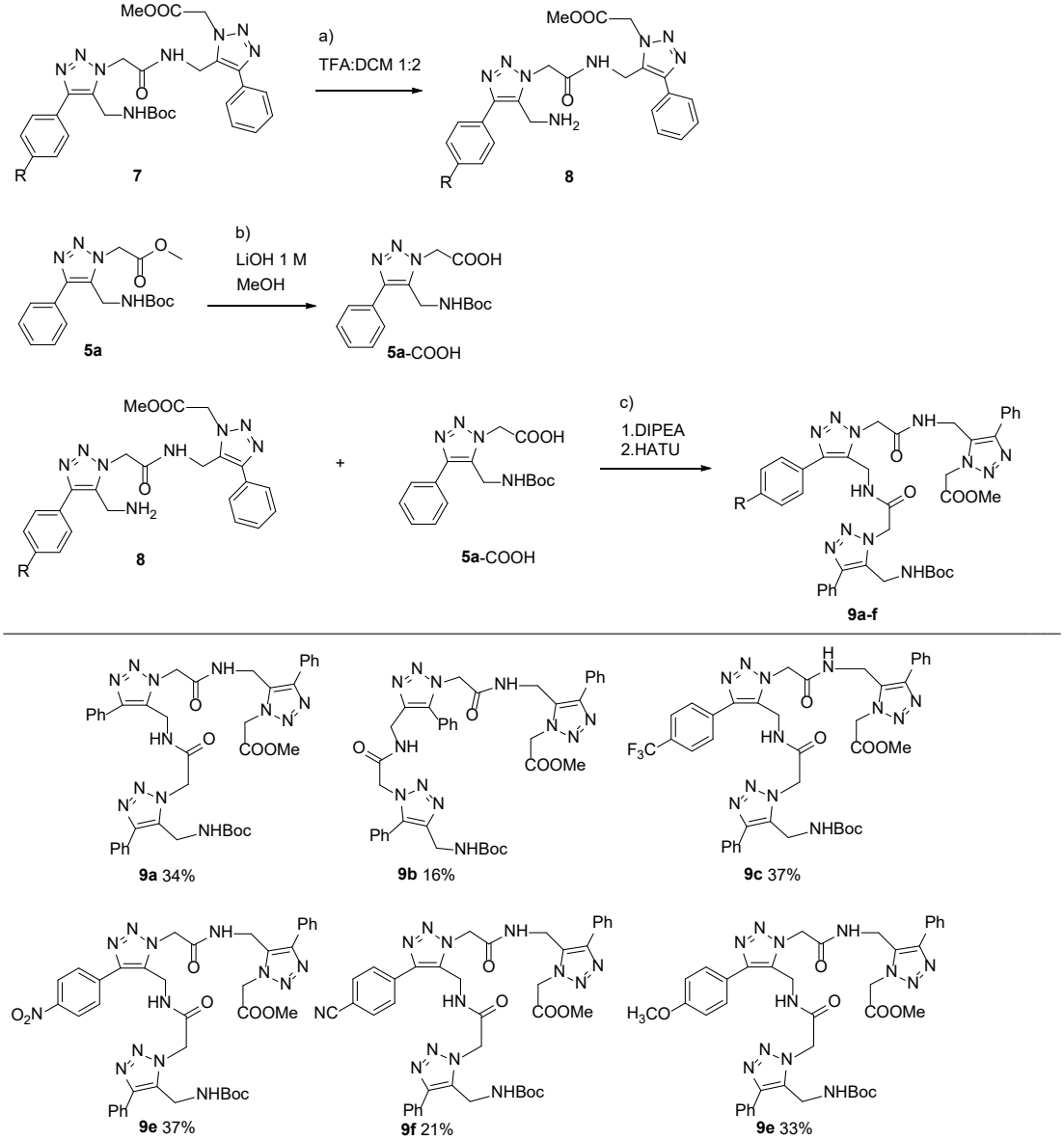


Methyl 2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (7f)

Following the general procedure, the title compound was obtained as a white powder (127 mg, 0.215 mmol, 43%).

^{1}H NMR (600 MHz, DMSO) δ 9.04 (t, *J* = 5.6 Hz, 1H), 7.79 (d, *J* = 1.2 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.52 (s, 2H), 5.22 (s, 2H), 4.58 (d, *J* = 5.5 Hz, 2H), 4.31 (d, *J* = 5.5 Hz, 2H), 3.81 (s, 3H), 3.73 (s, 3H), 1.36 (s, 9H).

Synthesis of triazole trimers



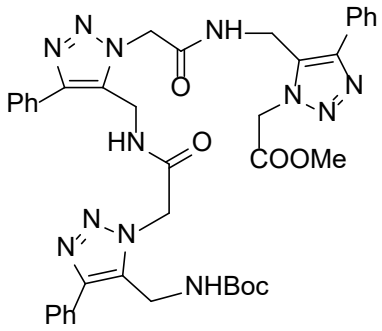
Reagents and conditions: a) TFA (11.6 equiv.), DCM, rt, 1 h; b) LiOH 1 M (1.56 equiv.), MeOH, 1 h; c) DIPEA (4.00 equiv.), HATU (1.05 equiv.), DCM, rt, 5 h.

General procedure for Boc-deprotection: To a microwave vial equipped with a stirring bar, trifluoroacetic acid (11.6 equiv.) was added to a solution of the triazole dimer **7** in DCM (0.60 mol•L^{-1}). The reaction mixture was stirred in the open air at room temperature for 1 h. TLC results were checked with the solvent system (1:5 pentane/ethyl acetate). The reaction mixture was then condensed under a stream of nitrogen and the salt was used directly in the amide coupling reaction.

General procedure for ester hydrolysis: To a microwave vial equipped with a stirring bar, 1 M lithium hydroxide (1.56 equiv.) was added to a solution of the triazole **5** in methanol (0•25 mol•L^{-1}). The reaction mixture was stirred in the open air at room temperature for 1 h. TLC results were checked with the solvent system (1:1 pentane/ethyl acetate). Deionized water (5 mL) was added and 1 M HCl (1.56 equiv.)

was then added dropwise with stirring. The reaction mixture was extracted with ethyl acetate (4*15 mL). Organic layers were dried over dry magnesium sulfate and concentrated on a rotary evaporator.

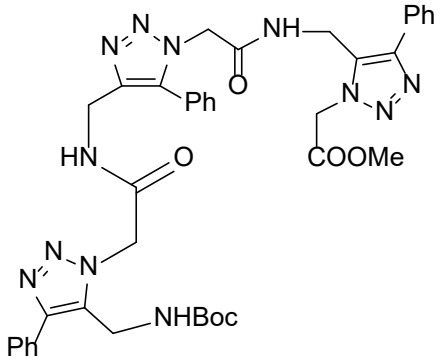
General procedure for the amide coupling: To a microwave vial equipped with a stirring bar, DIPEA (4 equiv.) was added to a solution of the acid while keeping the nitrogen flow on to maintain an inert atmosphere. HATU (1.05 equiv.) was added then. The amine was then added and the reaction was stirred at room temperature for 6 h, when it was determined complete by TLC. Deionized water (10 mL) was added and 1 M HCl (4 equiv.) was then added dropwise with stirring. The reaction mixture was washed with deionized water (3*5 mL) and extracted with ethyl acetate (4*15 mL). The combined organic layers were dried over dry magnesium sulfate and concentrated on a rotary evaporator. The crude residue was finally purified by flash chromatography on silica gel (10:1 dichloromethane/methanol).



Methyl 2-(5-((2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (9a)

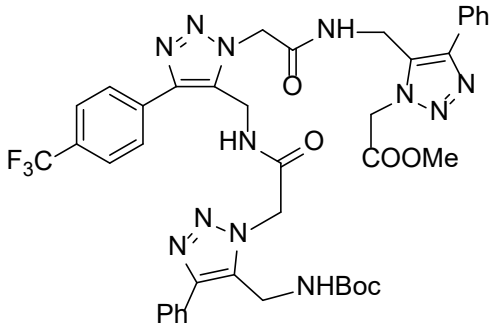
Following the general procedure, the title compound was obtained as a white powder (58 mg, 0.074 mmol, 34%).

^{1}H NMR (600 MHz, DMSO) δ 9.06 (t, *J* = 5.6 Hz, 1H), 9.01 (t, *J* = 5.4 Hz, 1H), 7.82 – 7.72 (m, 5H), 7.54 – 7.36 (m, 10H), 5.50 (s, 2H), 5.25 (s, 4H), 4.59 (d, *J* = 5.5 Hz, 2H), 4.55 (d, *J* = 5.3 Hz, 2H), 4.33 (d, *J* = 5.5 Hz, 2H), 3.70 (s, 3H), 1.33 (s, 9H).

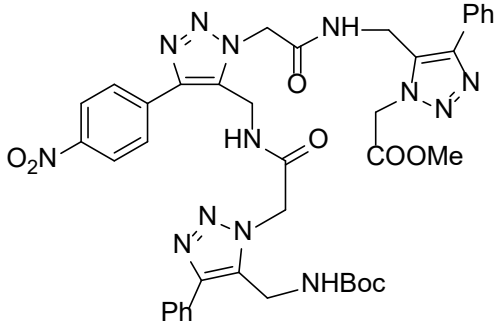


Methyl 2-(5-((2-(4-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-5-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (9b)

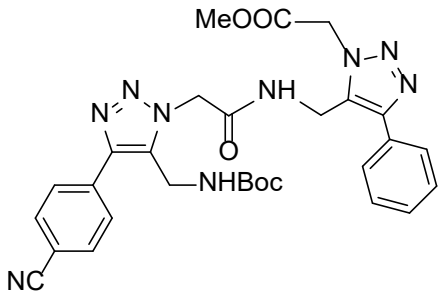
Following the general procedure, the title compound was obtained as a white powder (15 mg, 0.020 mmol, 16%).
^{1}H NMR (600 MHz, MeOD) δ 7.79 – 7.60 (m, 4H), 7.55 – 7.30 (m, 11H), 5.40 (s, 2H), 5.24 (s, 2H), 4.97 (s, 2H), 4.58 (s, 2H), 4.49 (s, 2H), 4.39 (s, 2H), 3.79 (s, 3H), 1.40 (s, 9H).



Methyl 2-(5-((2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (9c)
Following the general procedure, the title compound was obtained as a white powder (46 mg, 0.055 mmol, 37%).
^{1}H NMR (600 MHz, DMSO) δ 9.07 (m, 2H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.81 – 7.76 (m, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.35 (m, 7H), 5.50 (s, 2H), 5.28 (s, 2H), 5.24 (s, 2H), 4.59 (d, *J* = 5.3 Hz, 4H), 4.32 (d, *J* = 5.5 Hz, 2H), 3.69 (s, 3H), 1.31 (s, 9H).



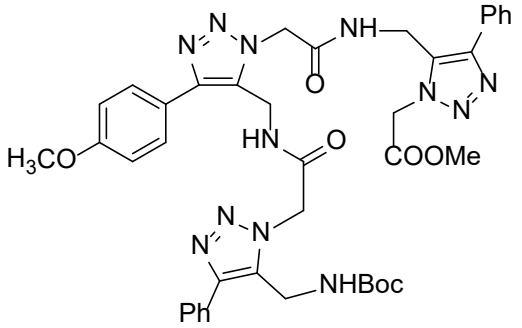
Methyl 2-(5-((2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-(4-nitrophenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (9d)
Following the general procedure, the title compound was obtained as a white powder (49 mg, 0.060 mmol, 50%).
^{1}H NMR (600 MHz, DMSO) δ 9.13 – 9.05 (m, 2H), 8.34 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.79 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.36 (m, 7H), 5.51 (s, 2H), 5.31 (s, 2H), 5.23 (s, 2H), 4.62 (d, *J* = 5.3 Hz, 2H), 4.60 (d, *J* = 5.5 Hz, 2H), 4.30 (d, *J* = 5.5 Hz, 2H), 3.70 (s, 3H), 1.32 (s, 9H).



Methyl 2-(5-((2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (9e)

Following the general procedure, the title compound was obtained as a white powder (35 mg, 0.044 mmol, 21%).

^{1}H NMR (600 MHz, DMSO) δ 9.08 (m, 2H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.14 – 8.04 (m, 2H), 7.83 – 7.76 (m, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.36 (m, 6H), 5.50 (s, 2H), 5.30 (s, 2H), 5.23 (s, 2H), 4.62 (d, *J* = 5.3 Hz, 2H), 4.60 (d, *J* = 5.5 Hz, 2H), 4.30 (d, *J* = 5.5 Hz, 2H), 3.70 (s, 3H), 1.32 (s, 9H).

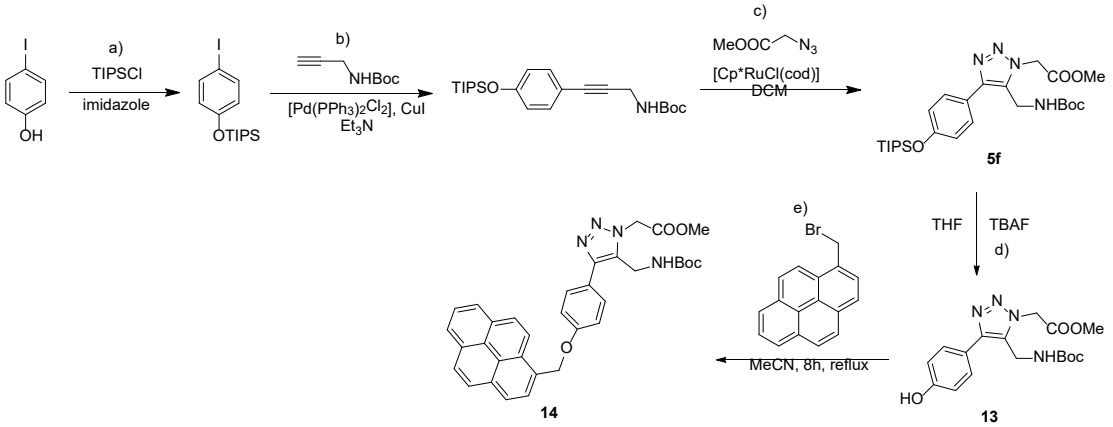


Methyl 2-(5-((2-(5-((2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)acetamido)methyl)-4-phenyl-1H-1,2,3-triazol-1-yl)acetate (9f)

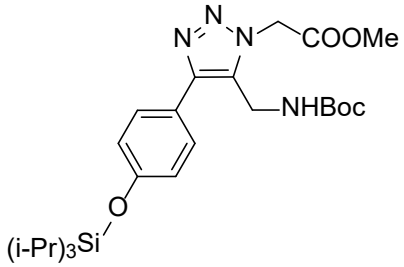
Following the general procedure, the title compound was obtained as a white powder (53 mg, 0.066 mmol, 33%).

^{1}H NMR (600 MHz, DMSO) δ 9.04 (d, *J* = 5.6 Hz, 1H), 8.98 (s, 1H), 8.06 – 7.63 (m, 6H), 7.61 – 7.27 (m, 6H), 7.04 (d, *J* = 8.8 Hz, 2H), 5.49 (s, 2H), 5.23 (d, *J* = 14.5 Hz, 2H), 4.58 (d, *J* = 5.4 Hz, 2H), 4.51 (d, *J* = 5.2 Hz, 2H), 4.33 (d, *J* = 5.4 Hz, 2H), 3.80 (s, 2H), 3.69 (s, 3H), 1.32 (s, 9H).

Synthesis of triazole-pyrene derivative 14



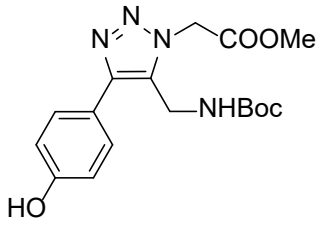
Reagents and conditions: a) TIPSCl (1.00 equiv.), imidazole (2.27 equiv), DCM, rt, 16 h, 68%; b) iodoaryl compound (1.00 equiv.), $[Pd(PPh_3)_2Cl_2]$ (2.0 mol%), CuI (2.3 mol%), triethyl amine (2.07 equiv.), acetonitrile, r.t., 1 h, 70%; c) Azide (1.00 equiv.), [Cp*RuCl(cod)] (5.0 mol%), DCM, r.t., 30 min, 56%; d) TBAF(1.5 equiv.), THF, r.t., 30 min, 22%; e) K_2CO_3 (1.0 equiv.), KI (1.1 equiv.), 1-(bromomethyl)pyrene (1.0 equiv.), MeCN, 80 °C, 12 h, 10%.



Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-((triisopropylsilyl)oxy)phenyl)-1H-1,2,3-triazol-1-yl)acetate (5f)

To a microwave vial equipped with a stirring bar, the azide (290 mg, 2.52 mmol) was added to a degassed solution of the alkyne in dry dichloromethane (0.5 mol•L^{-1}). $Cp^*CRuCl(COD)$ (48 mg, 0.13 mmol) was subsequently added. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 30 min. Then the reaction flask was removed, transferred to a one-neck flask, and concentrated on a rotary evaporator. The crude residue was finally purified by flash chromatography on silica gel (1:1 pentane/ethyl acetate). The title compound was obtained as a yellow gel (762 mg, 1.47 mmol).

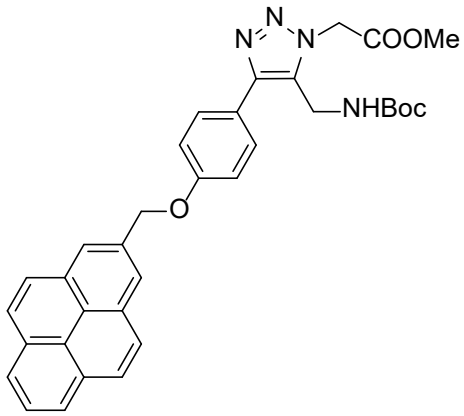
^{1}H NMR (600 MHz, CDCl3) δ 7.53 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.35 (s, 2H), 4.51 (d, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 1.43 (s, 9H), 1.32 – 1.23 (m, 3H), 1.11 (d, *J* = 7.5 Hz, 18H).



Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-hydroxyphenyl)-1H-1,2,3-triazol-1-yl)acetate (13)

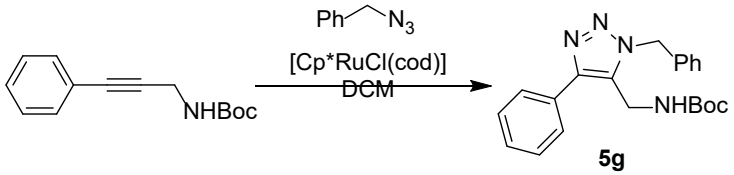
To a microwave vial equipped with a stirring bar, TBAF (0.75 mmol, 1 M in THF) was added to a solution of the triazole (259 mg, 0.5 mmol) in THF (2 ml), and the reaction

was stirred at room temperature for 30 min. 50 ml water was added and the mixture was extracted with DCM (3*30 ml). The combined organic layers were dried over magnesium sulfate and the solvent was evaporated and the crude residue was finally purified by flash chromatography on silica gel (1:1 pentane/ethyl acetate). The title compound was obtained as a white powder (40 mg, 0.11 mmol, 22%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.36 (s, 2H), 4.50 (d, *J* = 5.9 Hz, 2H), 3.83 (s, 3H), 1.44 (s, 9H).



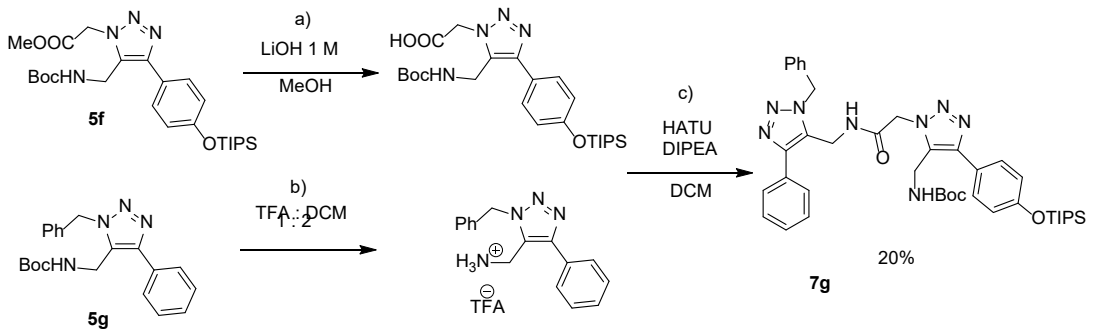
Methyl 2-(5-(((*tert*-butoxycarbonyl)amino)methyl)-4-(4-(pyren-2-ylmethoxy)phenyl)-1H-1,2,3-triazol-1-yl)acetate (14)
To a stirred solution of 1-(bromomethyl)pyrene (32 mg, 0.1 mmol) in 17 ml acetonitrile at room temperature, **14** (28 mg, 0.1 mmol), K_2CO_3 (37 mg, 0.27 mmol) and KI (17 mg, 0.1 mmol) were slowly added. After 8 h reflux, all the volatile was removed, and the residue was partitioned between water and EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (1:1 pentane/ethyl acetate). The titled compound was obtained as a yellow gel (5 mg, 0.01 mmol, 10%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.2 Hz, 1H), 8.27 – 7.98 (m, 8H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 5.81 (s, 2H), 5.37 (s, 2H), 4.90 (s, 1H), 4.52 (d, *J* = 6.0 Hz, 2H), 3.83 (s, 3H), 1.43 (s, 9H).

Synthesis of monomer 5g and dimer 7g



Reagents and conditions: Azide (1.0 equiv.), [Cp*RuCl(cod)] (5 mol%), DCM, rt, 30 min, 57%.

***tert*-butyl ((1-benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)methyl)carbamate (5g)**
RuAAC conditions employed for **5g** are the same ones as the ones employed for the other monomers (**5a-f**). Following the general procedure, compound **5g** was obtained as a white solid (346 mg, 0.94 mmol 57%).^{1}H NMR (600 MHz, chloroform-*d*) δ 7.66 (d, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.29 (m, 6H), 5.69 (s, 2H), 4.54 – 4.45 (m, 3H), 1.41 (s, 9H).



Reagents and conditions: a) TFA (11.6 equiv.), DCM, r.t., 1 h; b) LiOH 1 M (1.56 equiv.), MeOH, r.t., 1 h; c) DIPEA (4.00 equiv.), HATU (1.05 equiv.), DCM, r.t., 5 h.

***tert*-Butyl ((1-(2- (((1 -benzyl-4- phenyl- 1*H*- 1,2,3-triazol-5- yl) methyl) amino)-2-oxoethyl) -4- (4- ((triisopropylsilyl) oxy)phenyl)- 1*H*-1,2,3-triazol-5 yl) methyl) carbamate (7g)**

Coupling conditions employed for **7g** are the same ones as the ones employed for the other dimers (**7a-f**). Following the general procedure, compound **7g** was obtained as a white solid (296.5 mg, 0.39 mmol, 20%). ^{1}H NMR (600 MHz, DMSO) δ 8.10 (t, *J* = 5.2 Hz, 1H), 6.84 (d, *J* = 6.9 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.57 (t, *J* = 7.7 Hz, 2H), 6.51 – 6.41 (m, 5H), 6.33 (d, *J* = 7.3 Hz, 2H), 6.02 (d, *J* = 8.7 Hz, 2H), 4.77 (s, 2H), 4.20 (s, 2H), 3.64 (d, *J* = 5.2 Hz, 2H), 3.35 (d, *J* = 5.5 Hz, 2H), 0.43 (s, 9H), 0.35 (hept, *J* = 7.5 Hz, 3H), 0.16 (d, *J* = 7.5 Hz, 18H).

NMR spectra

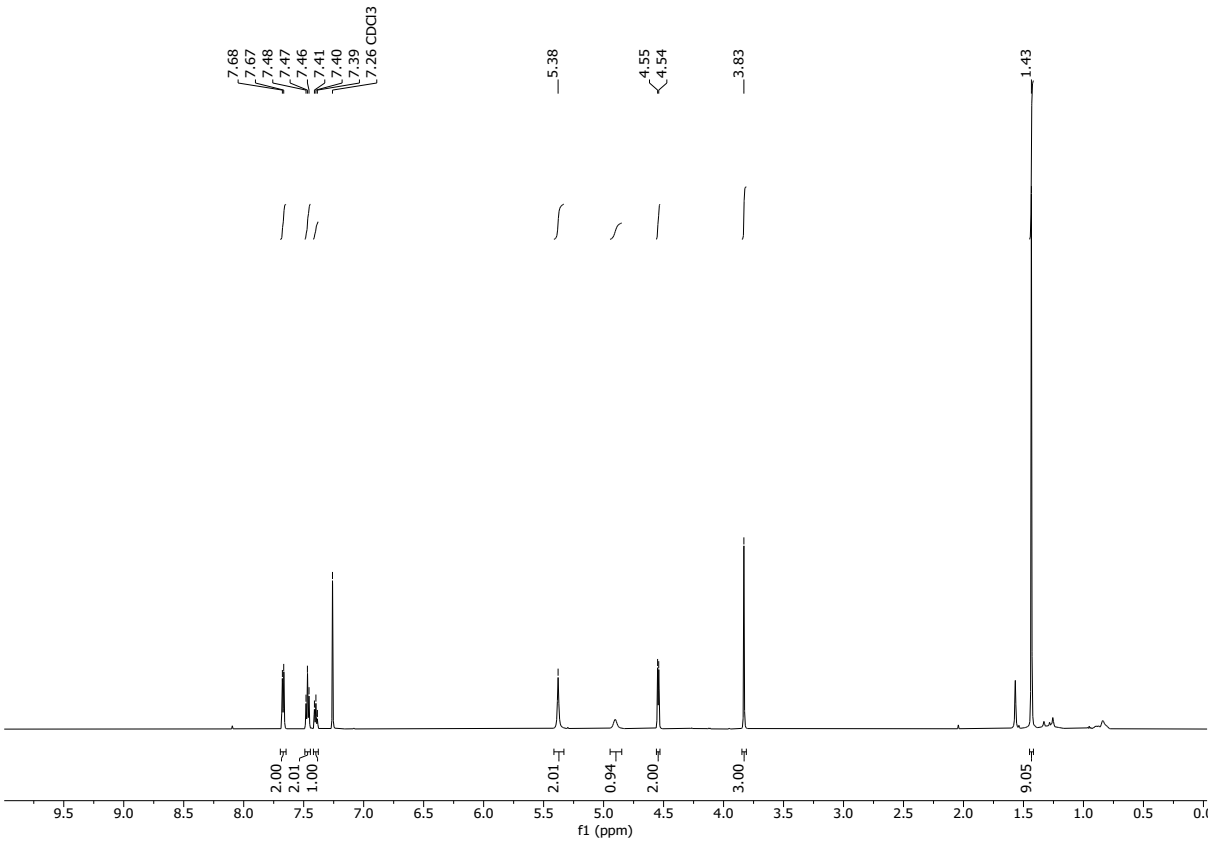


Figure S1. [1]H NMR spectra of **5a** in chloroform-*d*

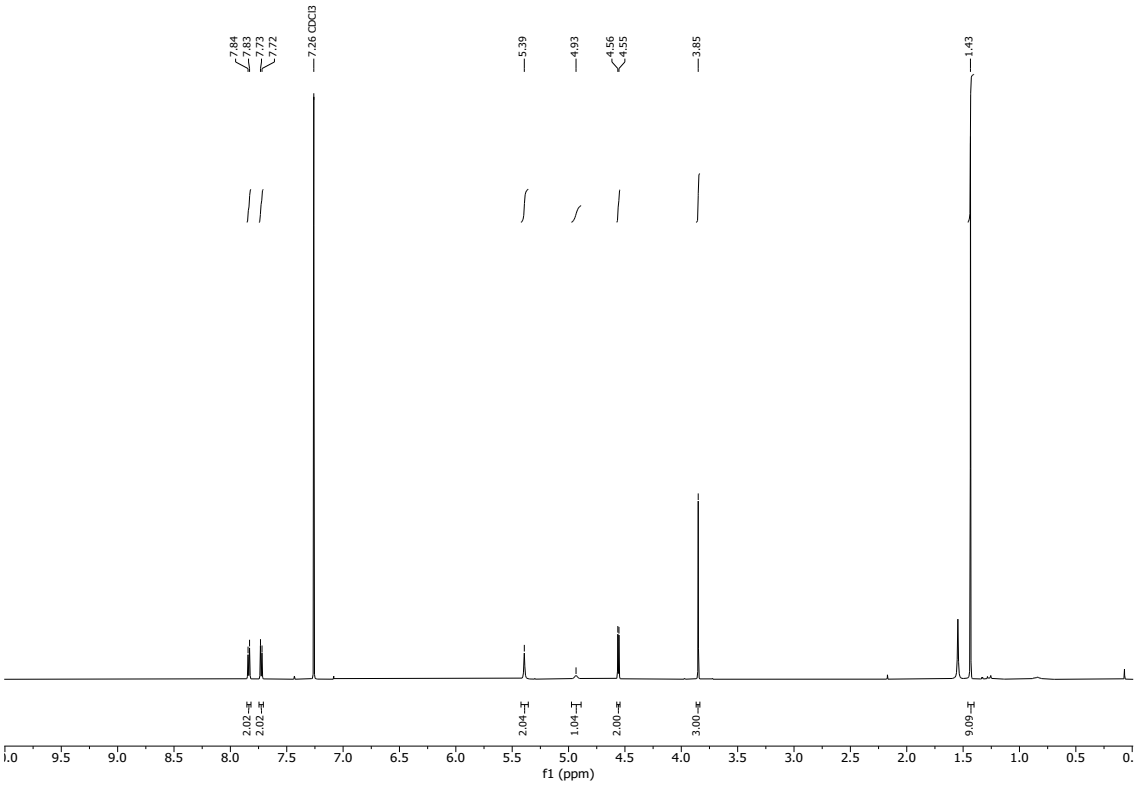


Figure S2. [1]H NMR spectra of **5b** in chloroform-*d*

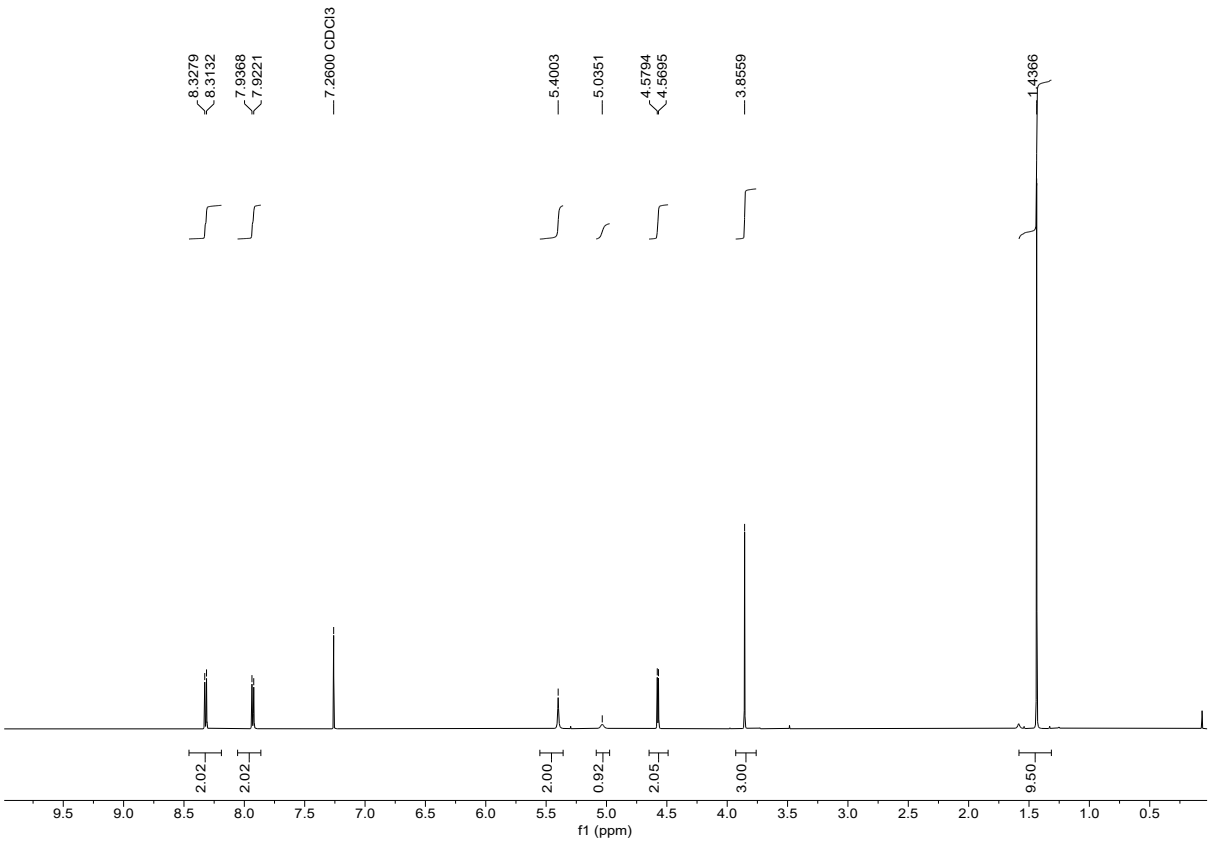


Figure S3. [1]H NMR spectra of **5c** in chloroform-*d*

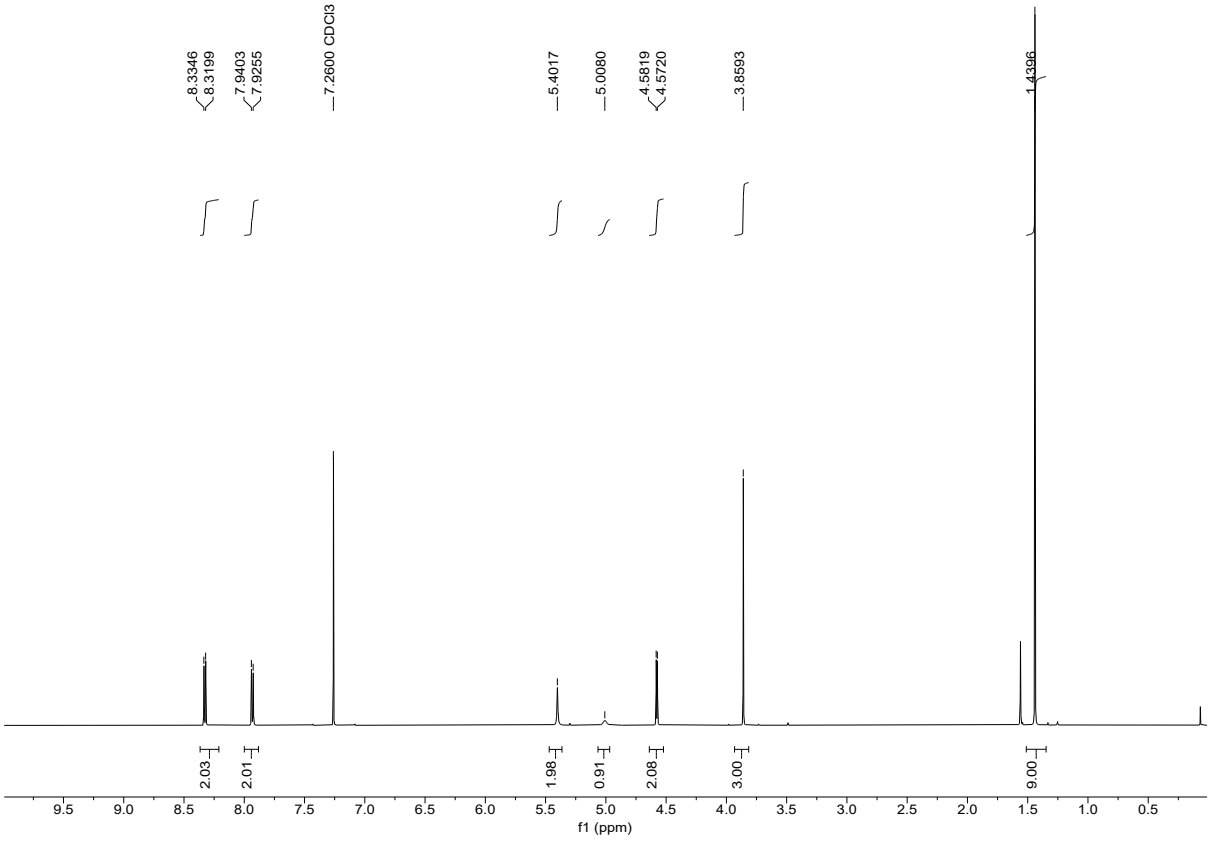


Figure S4. [1]H NMR spectra of **5d** in chloroform-*d*

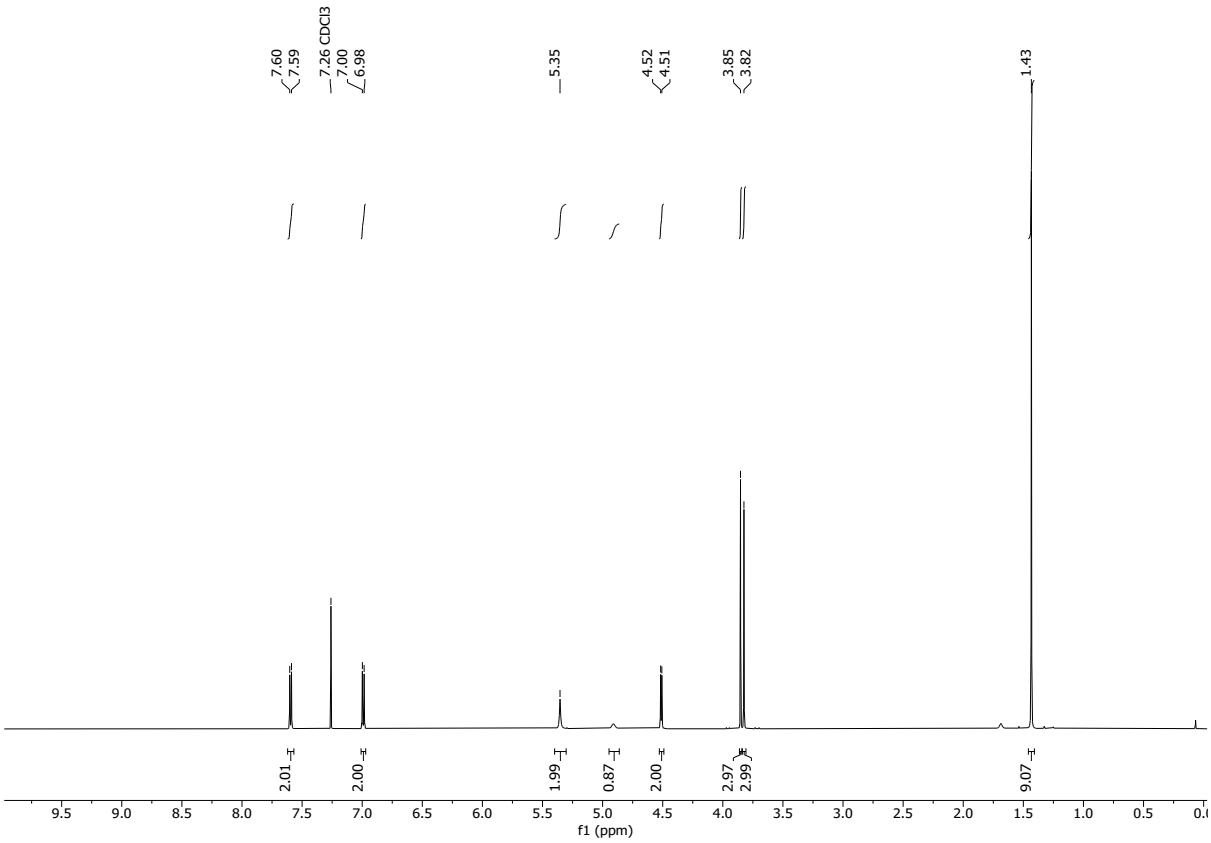


Figure S5. ^{1}H NMR spectra of **5e** in chloroform-*d*

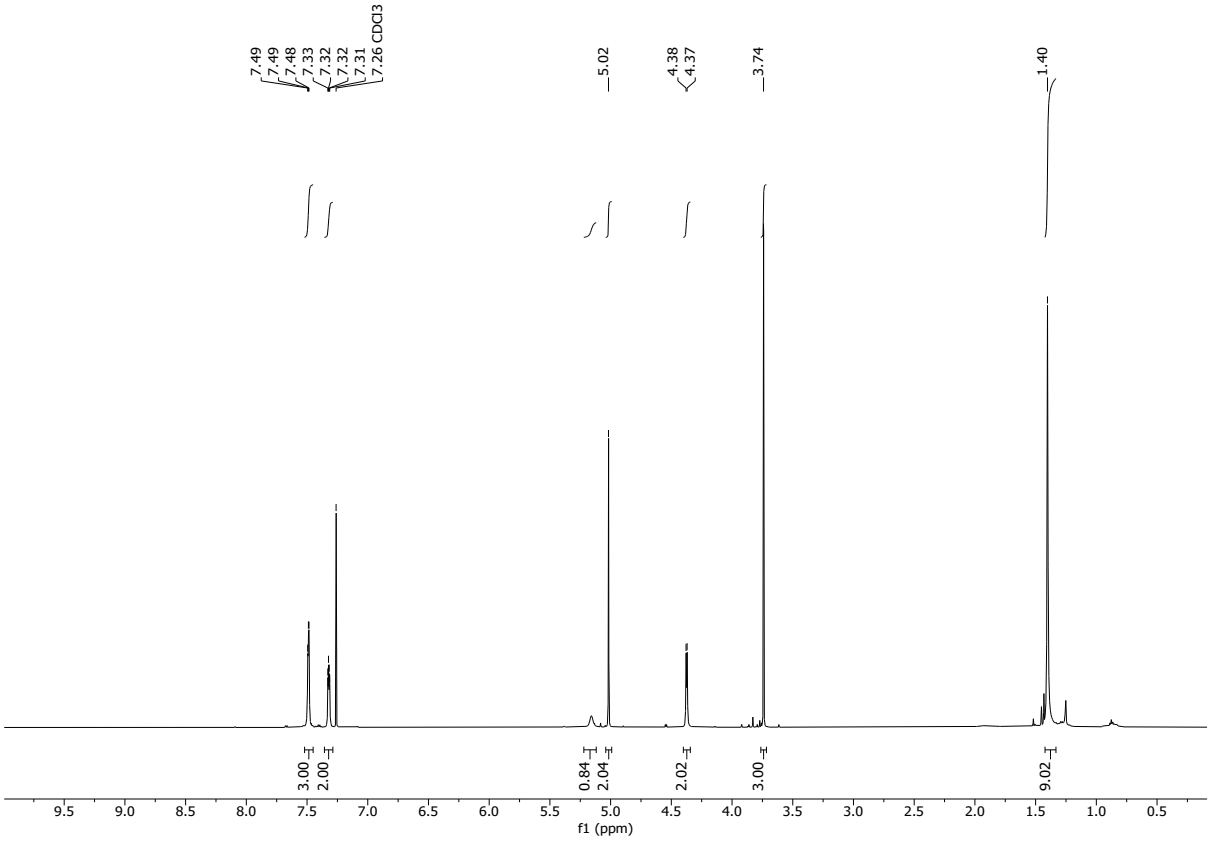


Figure S6. ^{1}H NMR spectra of **5f** in chloroform-*d*

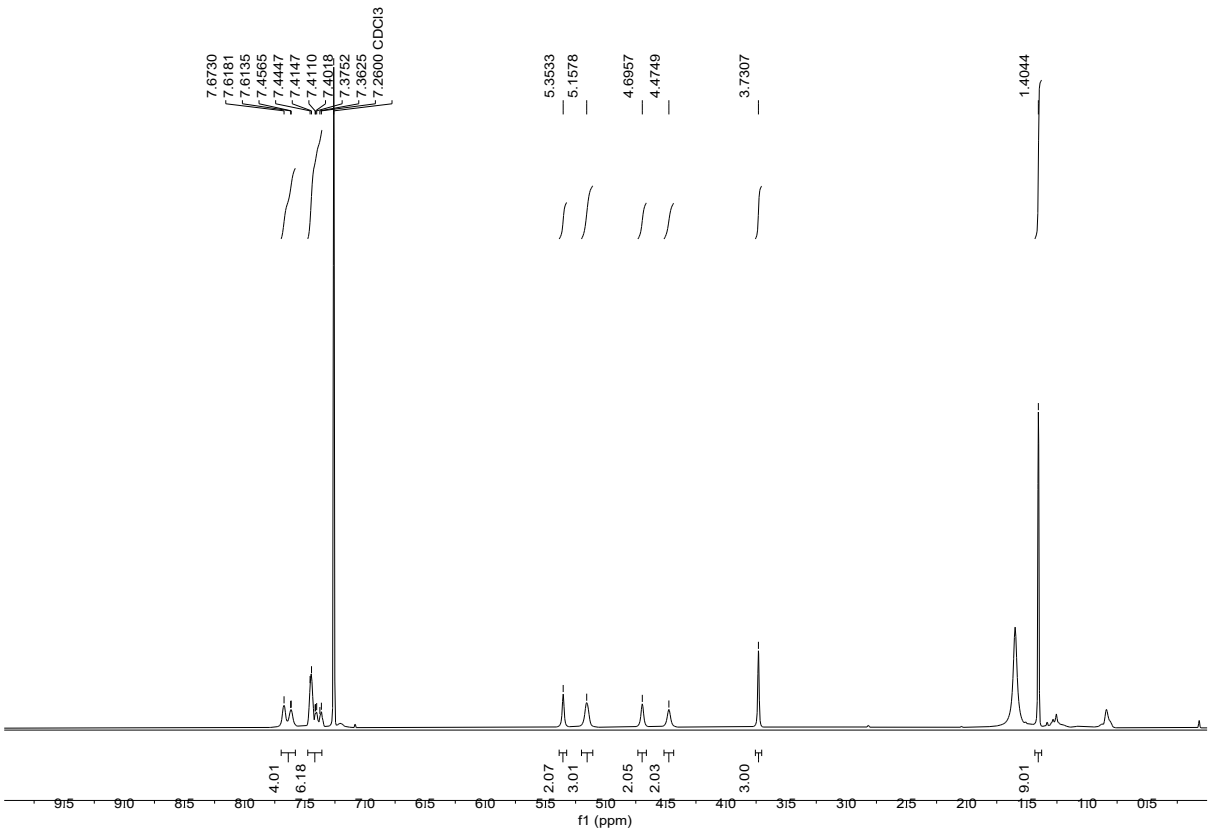


Figure S7. ^{1}H NMR spectra of **7a** in chloroform-*d*

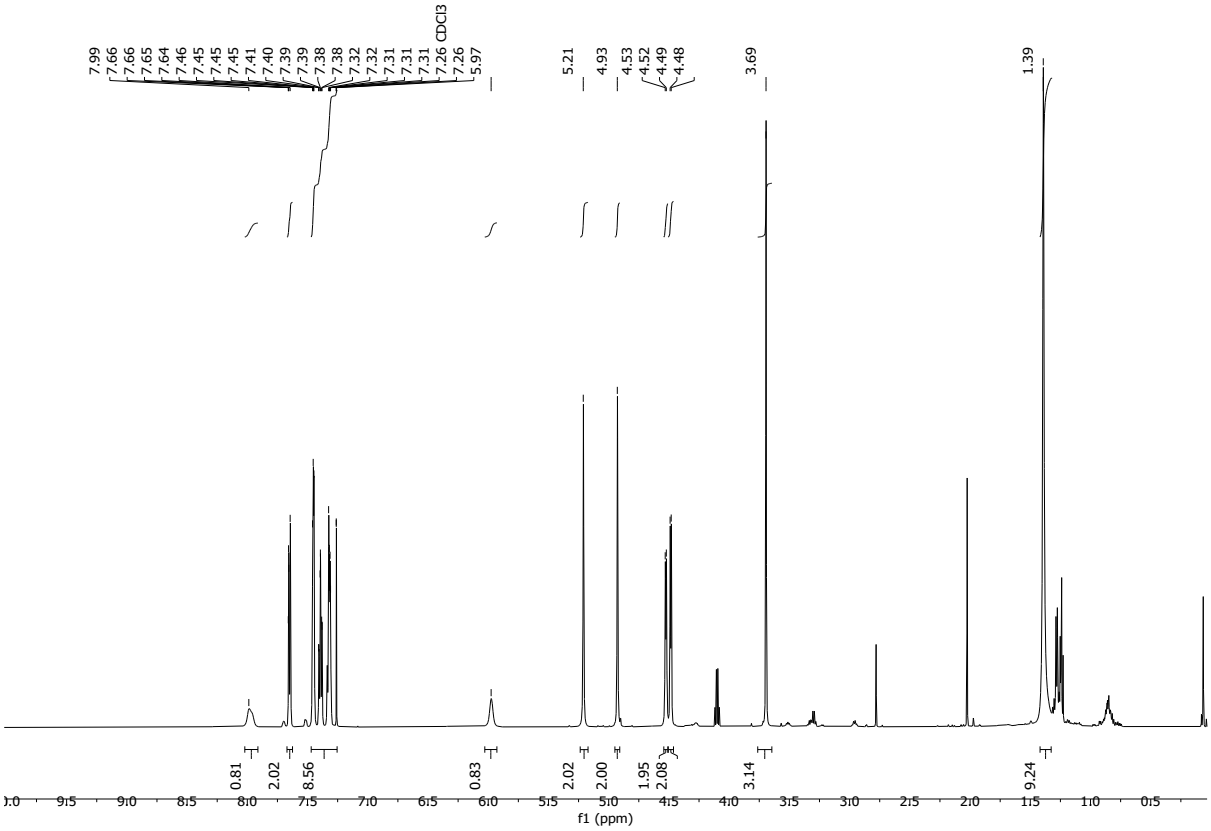


Figure S8. ^{1}H NMR spectra of **7b** in chloroform-d

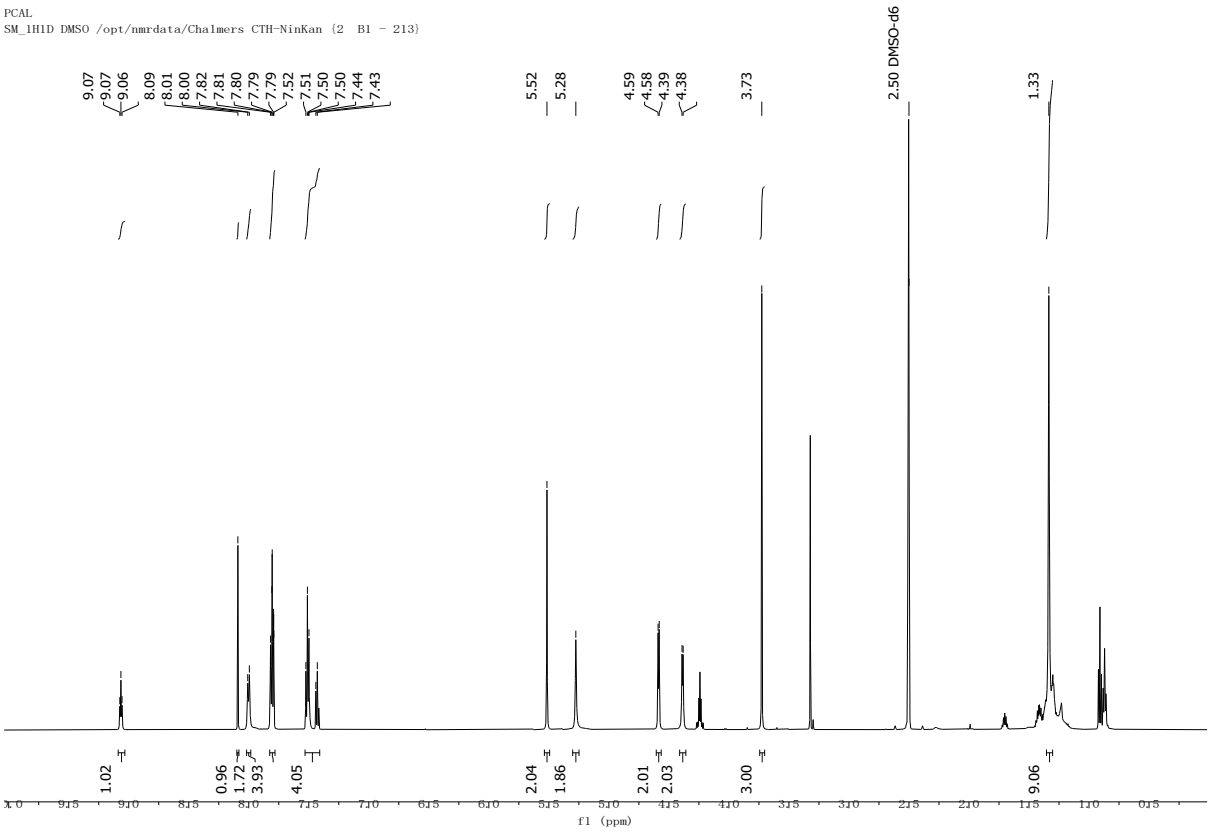


Figure S9. ^{1}H NMR spectra of **7c** in DMSO-d_6

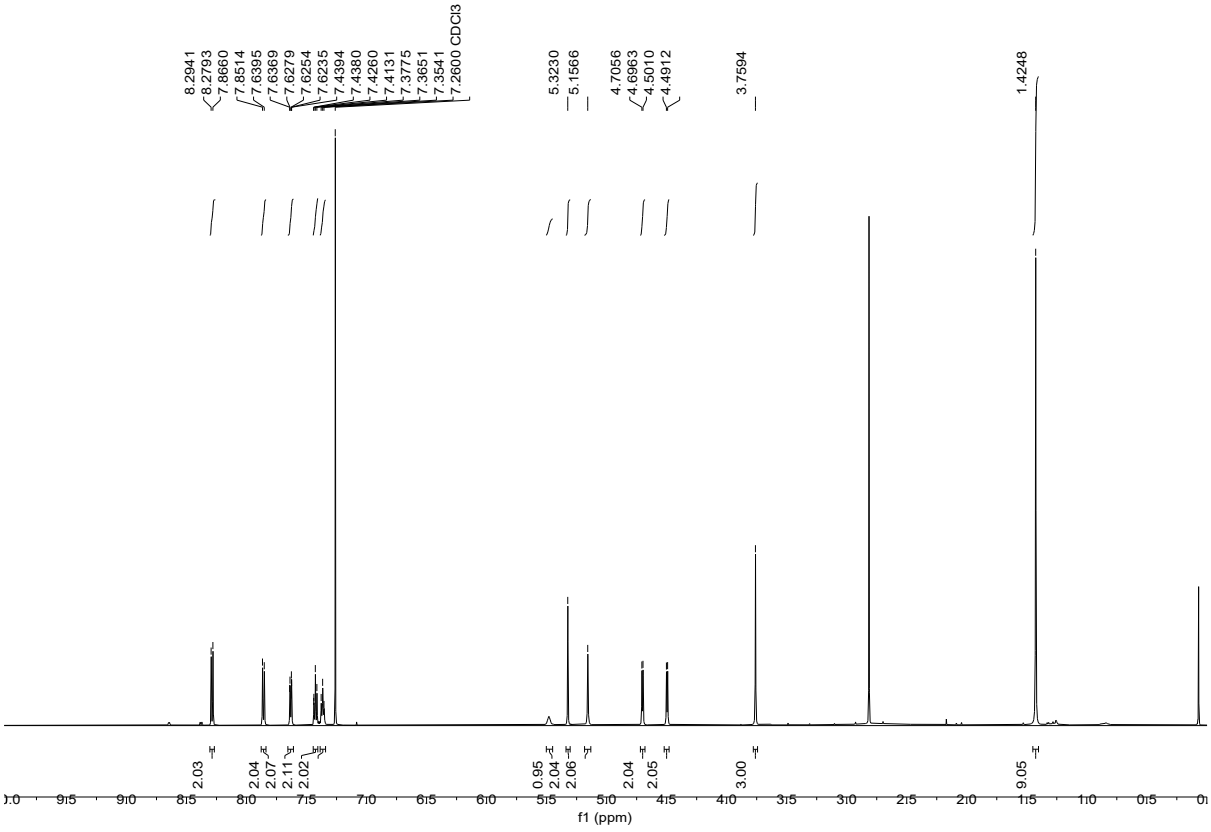


Figure S10. ^{1}H NMR spectra of **7d** in DMSO-d_6

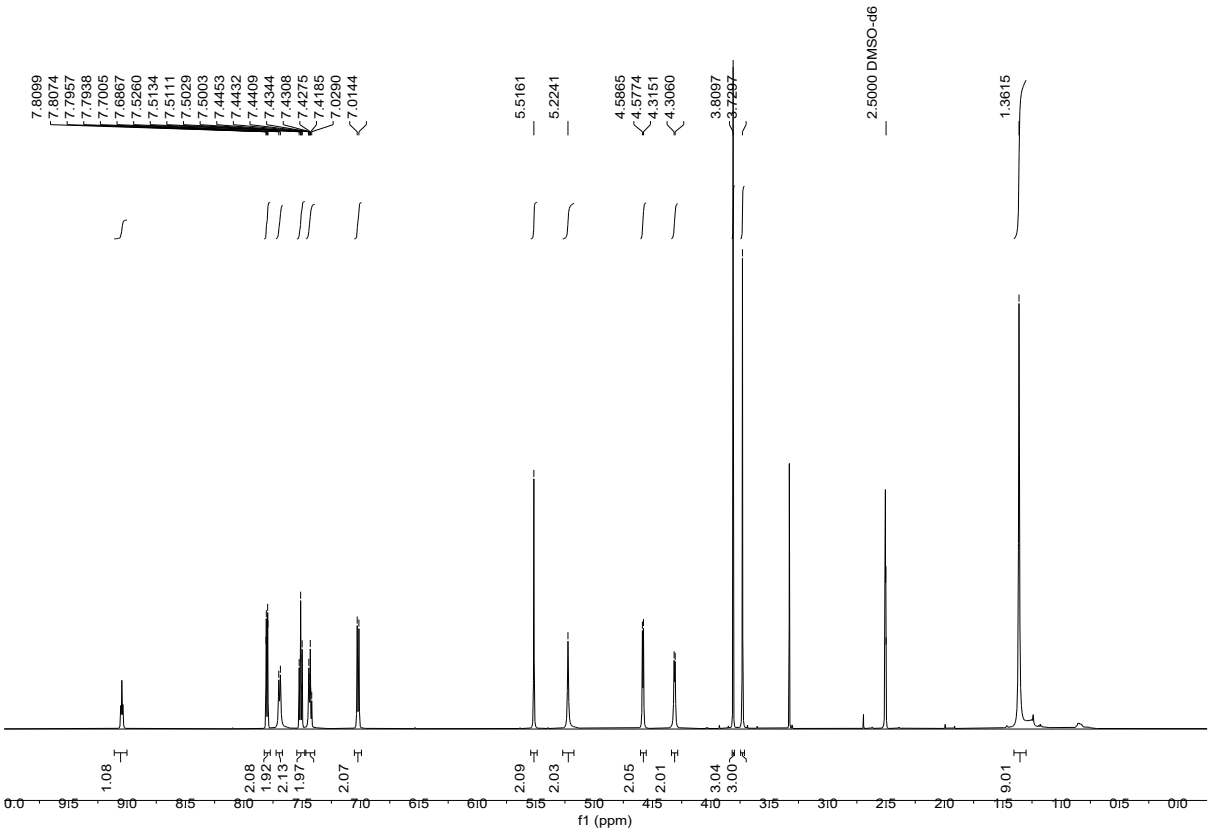


Figure S11. ^{1}H NMR spectra of **7f** in DMSO-d_6

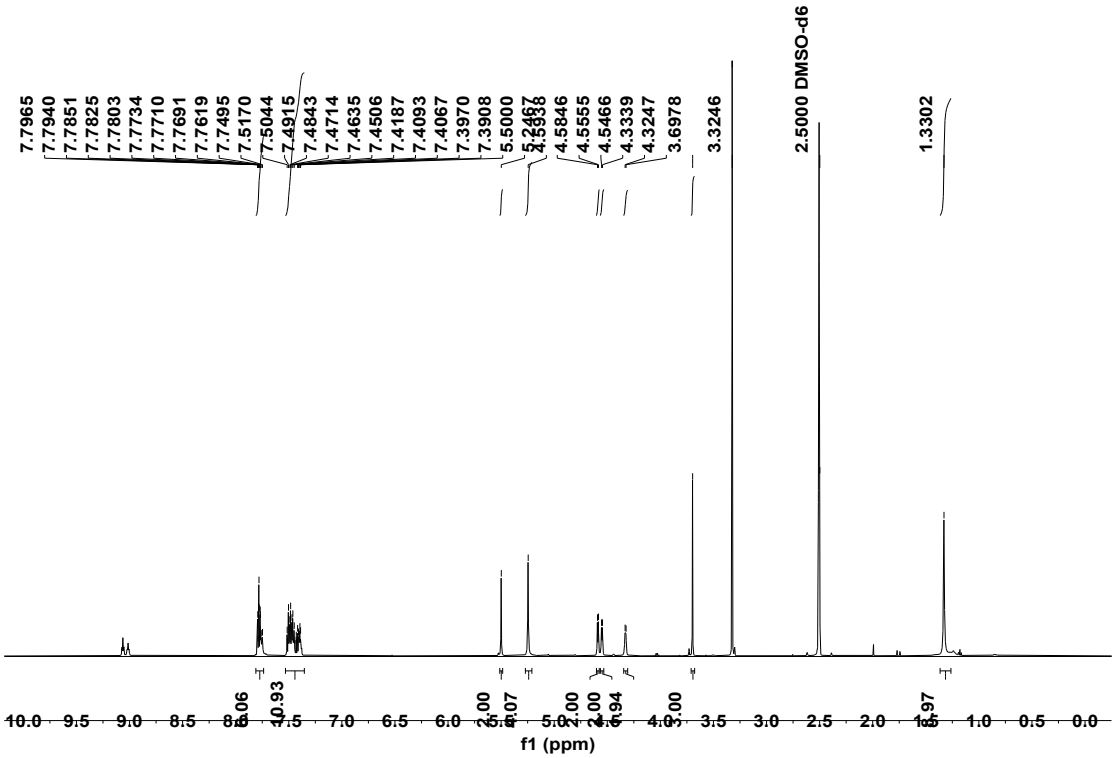


Figure S12. ^{1}H NMR spectra of **9a** in DMSO-d_6

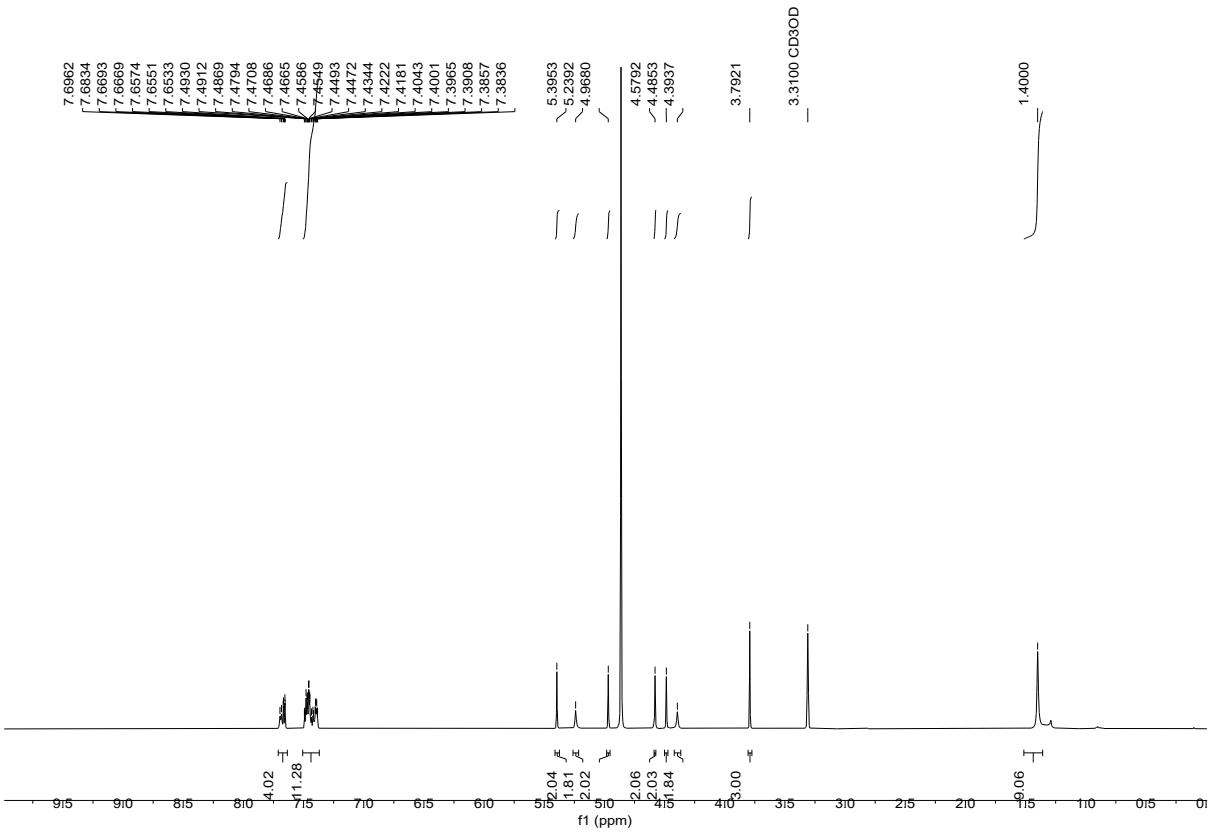


Figure S13. ^{1}H NMR spectra of **9b** in CD_3OD-d_4

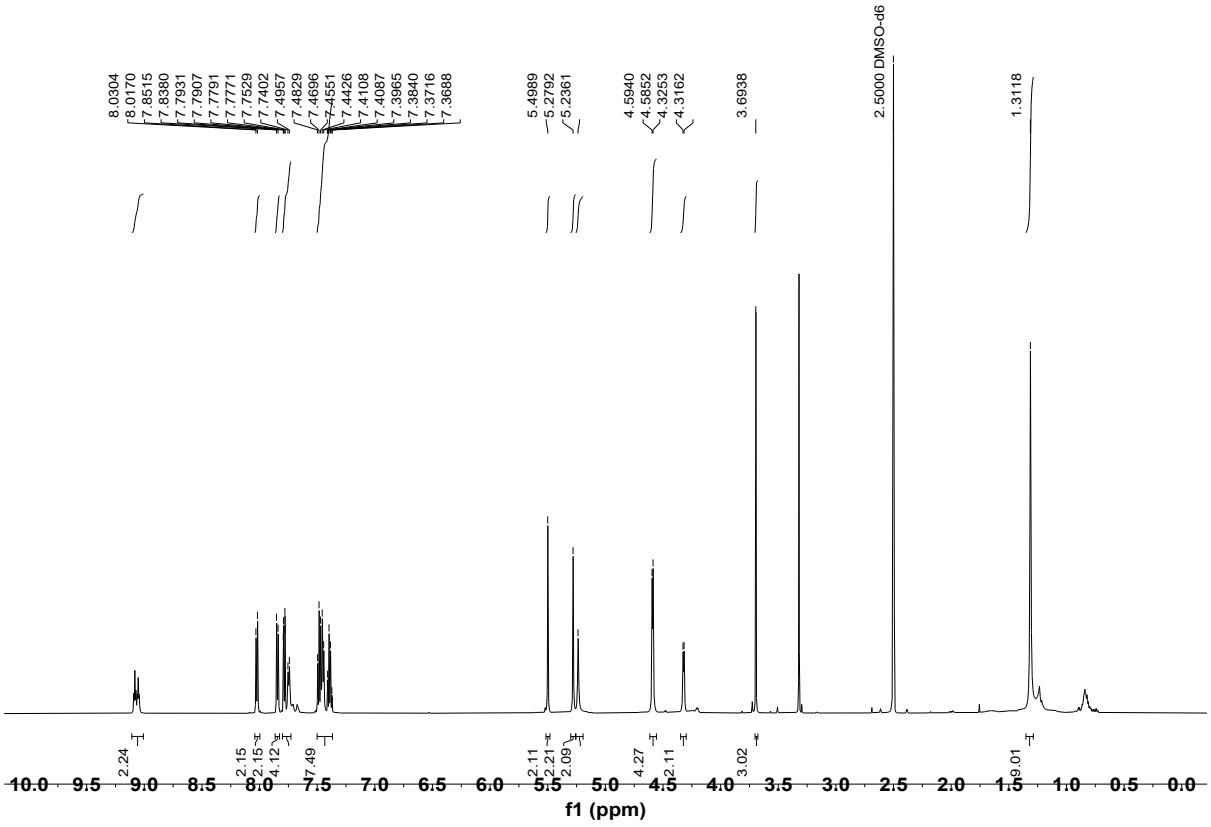


Figure S14. ^{1}H NMR spectra of **9c** in DMSO-d_6

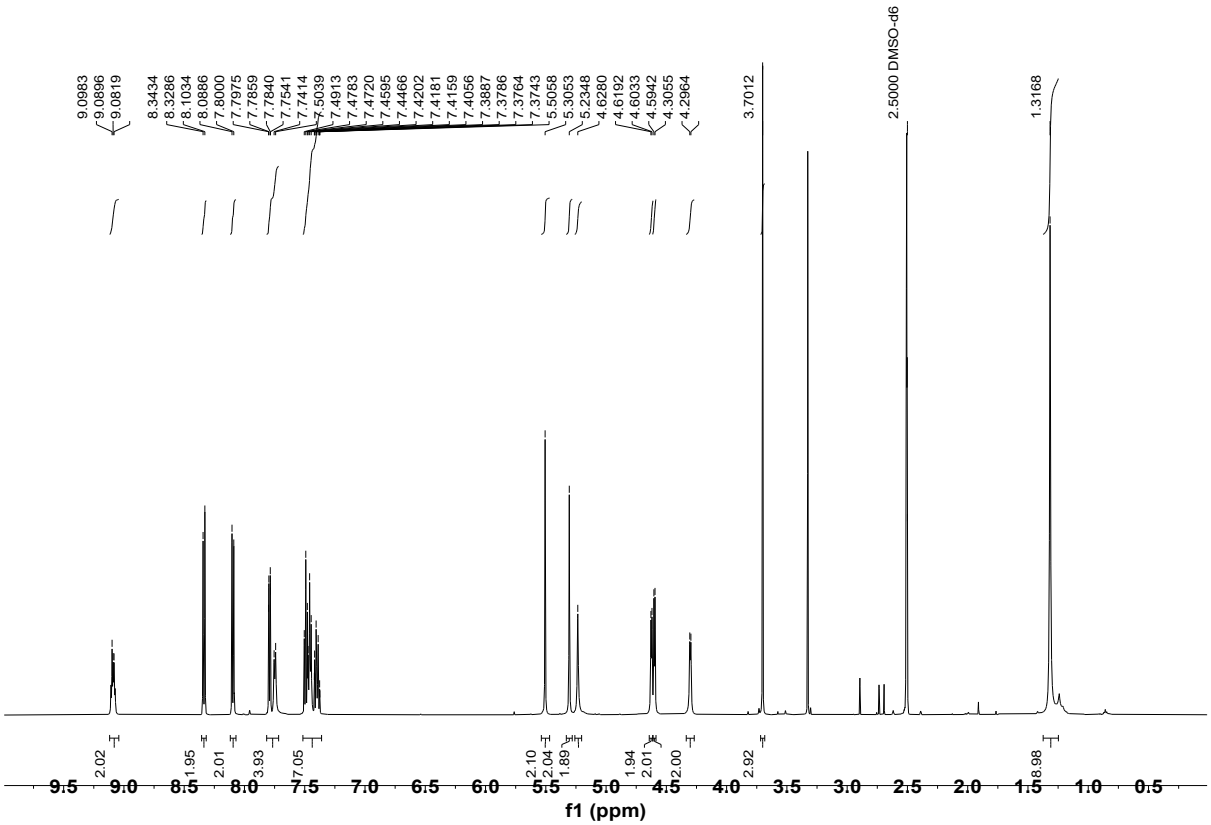


Figure S15. ^{1}H NMR spectra of **9d** in DMSO-d_6

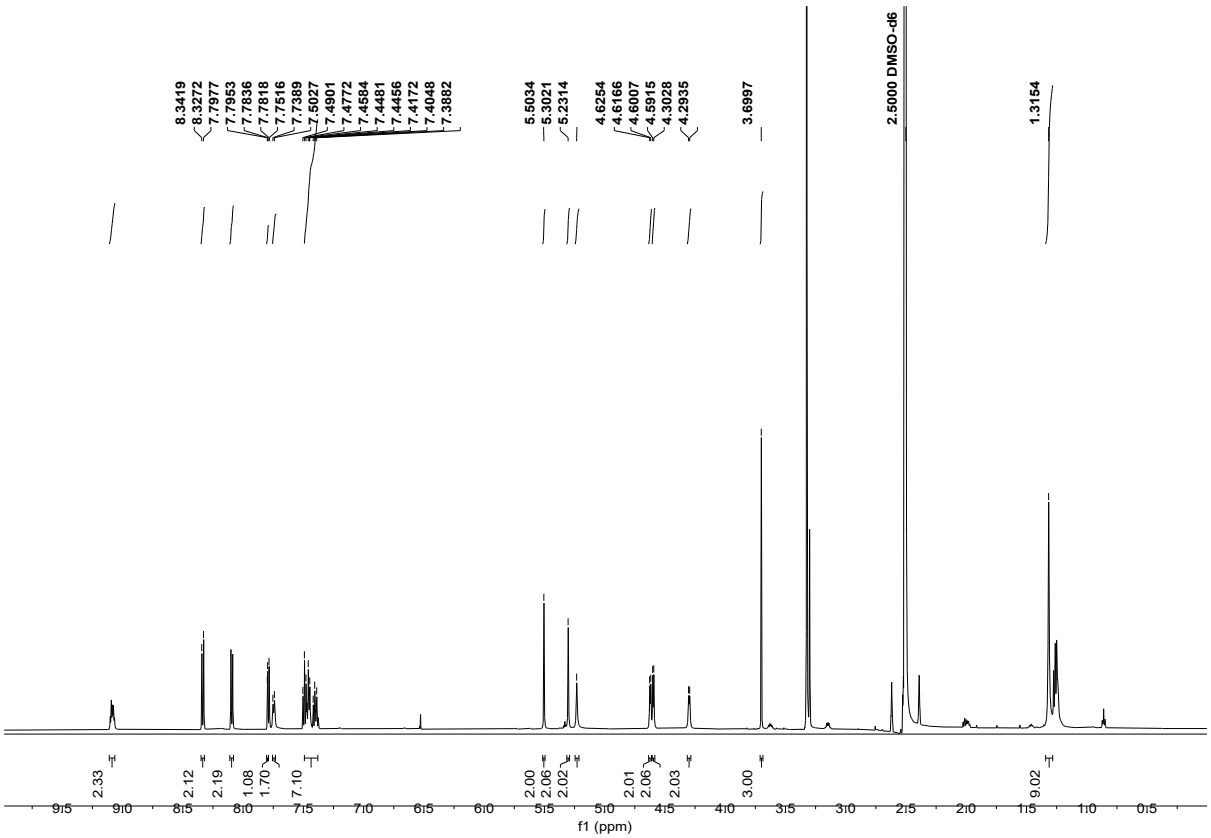


Figure S16. ^{1}H NMR spectra of **9e** in DMSO-d_6

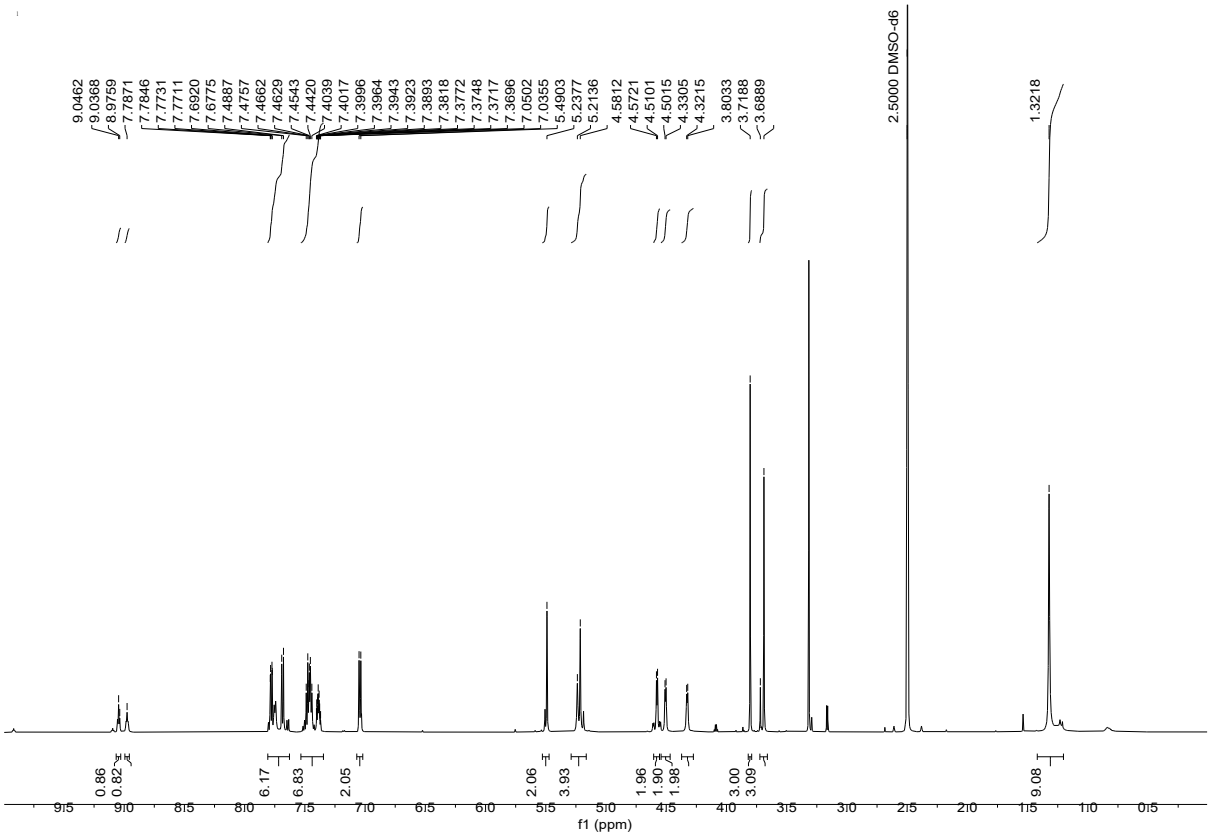


Figure S17. [1]H NMR spectra of **9f** in DMSO-d_6

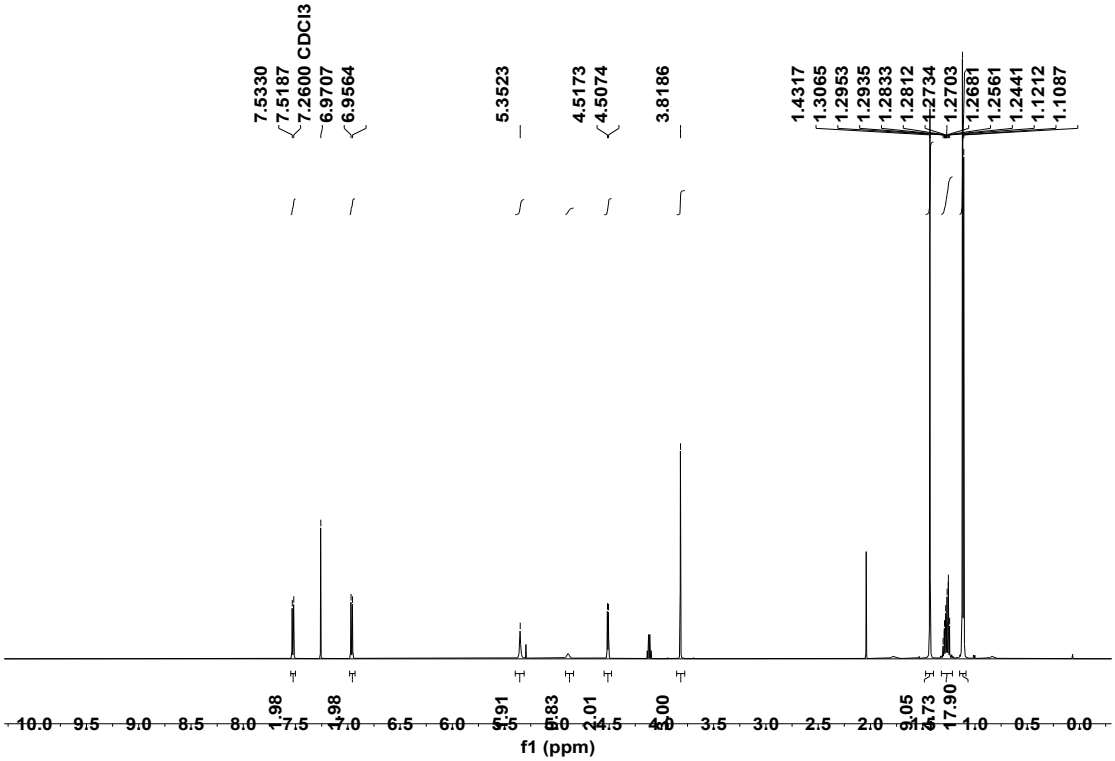


Figure S18. [1]H NMR spectra of **5f** in chloroform-*d*

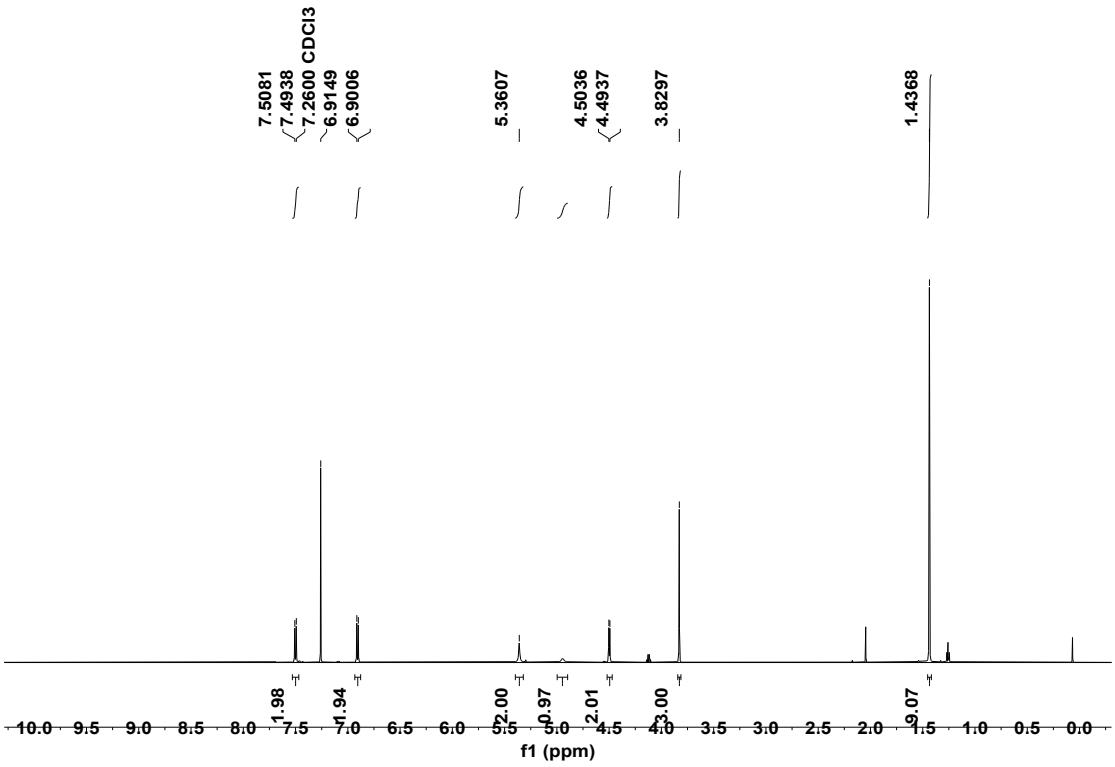


Figure S19. ^{1}H NMR spectra of **13** in chloroform-*d*

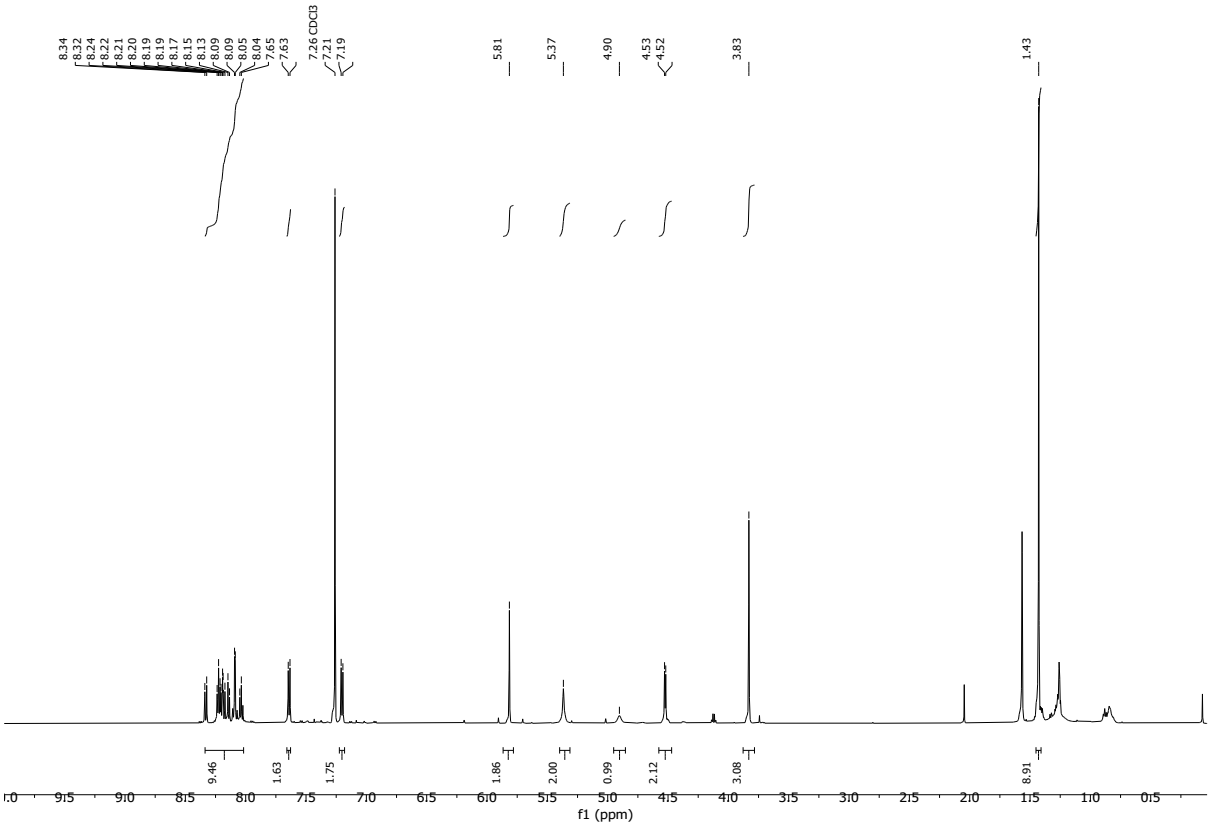


Figure S20. ^{1}H NMR spectra of **14** in chloroform-*d*

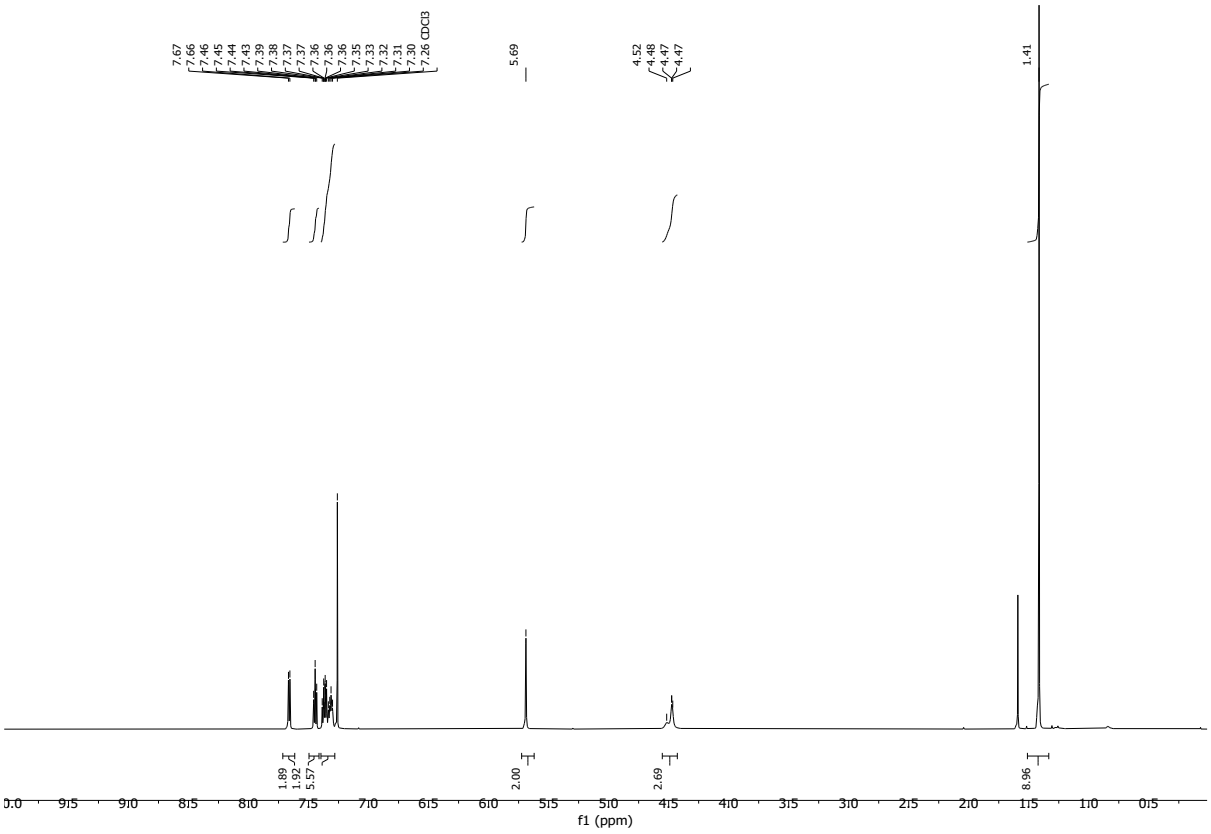


Figure S21. [1]H NMR spectra of **5g** in chloroform-*d*

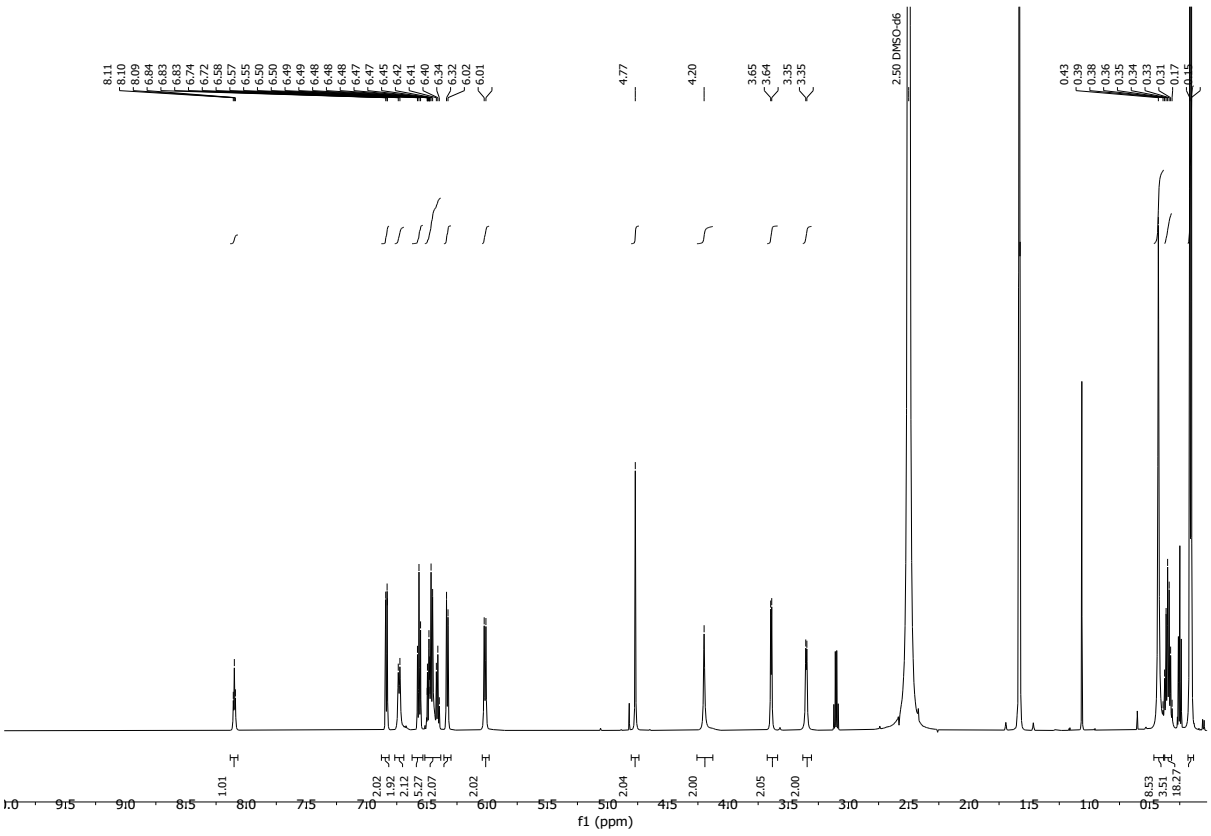


Figure S22. [1]H NMR spectra of **7g** in chloroform-*d*

Reference

(1) Jouha, J.; Buttard, F.; Lorion, M.; Berthonneau, C.; Khouili, M.; Hiebel, M.-A.; Guillaumet, G.; Brière, J.-F.; Suzenet, F. Domino Aza-Michael-ih-Diels–Alder Reaction to Various 3-Vinyl-1, 2, 4-triazines: Access to Polysubstituted Tetrahydro-1, 6-naphthyridines. *Organic letters* **2017**, *19*, 4770.