Supplementary Information

Ion Transport and Membrane Channel Formation Using a Peptidomimetic in Droplet Interface Bilayers

Raj Paul,[a,b] Debasish Dutta,[a] Mark I. Wallace,[*b] Jyotirmayee Dash[*a]

[a]School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India, email: ocjd@iacs.res.in
[b]Department of Chemistry, King's College London, London, United Kingdom, email: mark.wallace@kcl.ac.uk

Experimental techniques

Materials or reagents

1,2-diphytanoyl-sn-glycero-3-phosphocholine (DPhPC) (Avanti Polar Lipids, Alabama, USA), hexadecane, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), NaCl, KCl, $CaCl_2$ ethylenediaminetetraacetic acid (EDTA), agarose (low gelling temperature), and Fluo-8 (ABD Bioquest) were used as received without further purification.

General protocol of Droplet Interface Bilayer (DIB) preparation

A 0.75% (w/v) ultra-low gelling temperature agarose solution was homogenized at 90 °C, and 150 µl of the solution was spun onto a plasma-cleaned coverslip (Menzel-Gläzer, ThermoFisher Scientific). The coverslip was attached to the underside of a custom-made poly(methyl methacrylate) device featuring 16 wells, each 1 mm in diameter. A 1.4% (w/v) agarose solution containing 1 M KCl (or 0.66 M $CaCl_2$ for oSCR experiments), buffered with 10 mM Tris-HCl at pH 8, was introduced into the device to hydrate the substrate agarose without covering it. Wells were filled with hexadecane containing DPhPC at 9.5 mg/ml, and the device was left undisturbed for 30 minutes to facilitate monolayer formation. Simultaneously, aqueous droplets (~100 nl) were incubated in the same lipid-in-oil solution to form monolayers. The droplets, containing 1 M KCl, 10 mM Tris-HCl, 10 mM EDTA, 0.25 mM Fluo-8H, and 1 µM **TBP2**, were transferred into the wells, where they sank onto the substrate to form bilayers at the droplet-agarose interface. Ag/AgCl electrodes were positioned in the droplets and the agarose substrate (serving as the ground). The DIB system, electrodes, and patch clamp amplifier head stage were housed in a custom-built Faraday cage. Electrical currents were recorded using an Axopatch 200B patch clamp amplifier (Axon Instruments) and analyzed with Windows Electrophysiology Disk Recorder (WinEDR) or Clampfit 10.2 software.

Electrophysiological recordings via DIBs

Electrical measurements were conducted in the presence of **TBP2** at various applied voltages, ranging from -180 mV to +150 mV, in 10 mM HEPES and either 1 M NaCl, KCl, or CaCl2 (pH 7.4). To conduct these measurements, a 50 µm diameter Ag/AgCl wire electrode coated with a small volume of agarose was carefully inserted into the droplet using a micromanipulator. A corresponding ground electrode was embedded in the rehydrating agarose, ensuring electrical contact with the underside of the bilayer. The experimental setup was enclosed within a Faraday cage and positioned on an inverted microscope. After

applying voltage potential, the resulting electrical current was recorded using a patch clamp amplifier, Axopatch 200B from Axon Instruments. Data were digitized (Ni-DAQ system from National Instruments, USA) and subsequently processed, including a 2 kHz low pass filter, using WinEDR V3.9.7 (University of Strathclyde, UK) or Clampfit 10.6 software for further analysis.

Total internal reflection fluorescence (TIRF) microscopic imaging

Subtractive micromilling (Modela MDX-40A, Roland DG, Japan) was employed to fabricate the arrayed well devices in which the droplet interface bilayers were formed. Black Polyoxymethylene resin (Delrin) substrate material was used to prevent transmission of scattered laser light to neighbouring droplet bilayers in the array. Optical interrogation of the bilayer array was made with a custom built wide-field total internal reflection fluorescence (TIRF) microscope. 100 mW 473 nm laser (Shanghai Dream Lasers Technology, Shanghai, China), attenuated to 5mW, was expanded and collimated to achieve a beam width of 30 mm. Total internal reflection at the glass coverslip - agarose interface was achieved by transmission of the laser light into a BK7 glass dove prism (30 x 127.1 mm 45 degree) (Thorlabs, Germany), mounted on an x/y/z translatable stage (Thorlabs, Germany), onto which the DIB Array device was centered with refractive index matched immersion oil (n= 1.518) (Immersol 518F, Ziess) optically interfacing the upper prism surface with the glass coverslip. The angle of entry of the laser into the prism was modulated with a periscope assembly. The effective evanescent field penetration depth of 100 nm afforded high signal to noise fluorescence measurements at the upper surface of the agarose support. This produced a TIRF interrogated area of 1.5 cm^2 at the DIB Array with a laser power density of 0.67 mW cm^{-2}. Imaging of the entire DIB Array was achieved with a CCD camera (iXon+, Andor Technology, 512 x 512 pixels), 545 +/- 75 nm emission filter (Chroma) and focusing lens. Data capture was automated by LabView (National Instruments, USA) together with TTL control of the laser. Operating at 30 second capture intervals, images of the fluorescence response of the array were generated from the mean pixel intensity of 25 consecutive frames (20 ms) during one second of laser exposure.

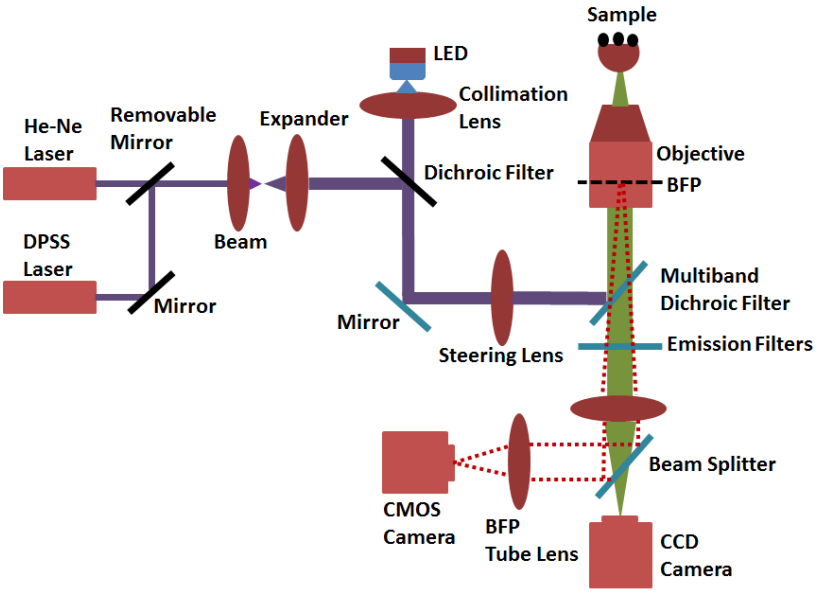


Fig. S1. Schematic representation of Total Internal Reflection Fluorescence (TIRF) microscopy set-up.

Data Processing. The acquired 8-bit monochrome time course images were analyzed using ImageJ to determine the mean pixel intensity fluorescence response of each droplet bilayer in the array. For **TBP2** droplets, DIB fluorescence intensity data at each time point was normalized to the maximal measured response at Fluo-8 dye saturation, following subtraction of the background pixel response.

Determination of approximate pore size in the DIBs

The estimated pore size via the DIBs was calculated based on the current measurement using the Hille equation as follows:[2]

$$1/g = l\rho / [\pi(d/2)^2] + \rho/d$$

where l is the ion channel length (34 Å) and ρ the resistivity of the recording solution [ρ = 18 Ωcm for 1 M NaCl]. The conductance value (g) of **TBP2** for transporting Na^+ via the droplet interface bilayers was calculated to be ~0.11 nS. membrane The pore conductance obtained from the slope of the *I-V* curve was converted into the diameter *d* using the Hille equation. The approximate pore size via the DIBs was determined to be ~3.9 Å.

Compound Synthesis

General information

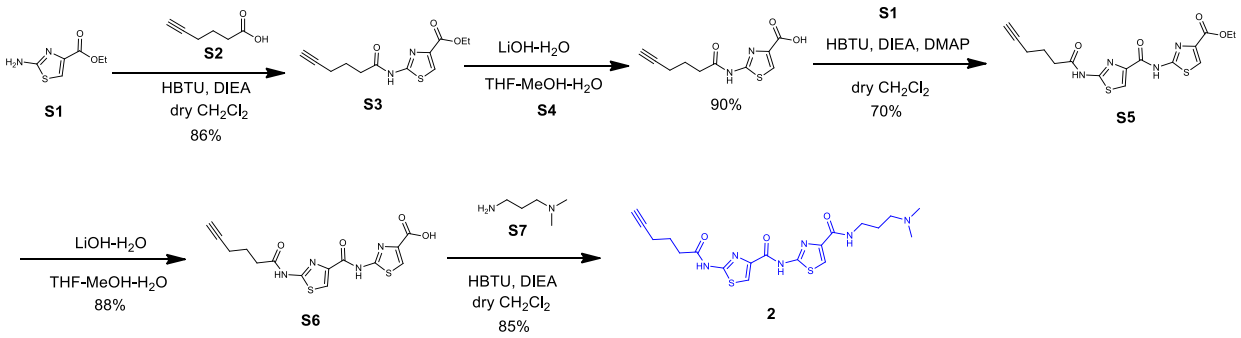
All experiments were carried out under an inert atmosphere of argon in flame-dried flasks. Solvents were dried using standard procedures. All starting materials were obtained from commercial suppliers and used as received. Products were purified by flash chromatography on silica gel (100-200 mesh, Merck). Unless otherwise stated, yields refer to analytical pure samples. Melting points were measured with BÜCHI Melting point B-545 and are uncorrected. NMR spectra were recorded in $CDCl_3$ unless otherwise stated. **^{1}H NMR** spectra were recorded at 500 MHz using Brüker AVANCE 500 MHz and JEOL 400 MHz instruments at 298 K. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard ($CDCl_3$: δ 7.26 ppm). Data is reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), and coupling constants (Hz). **^{13}C NMR** spectra were recorded on either a JEOL-400 (100 MHz), or a Brüker AVANCE 500 MHz (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.16 ppm). Infrared (FTIR) spectra (ν_{max}) are recorded on a Perkin Elmer spectrophotometer Spectrum RX1 using KBr disk techniques for solid compounds and as a thin film (neat) for liquid samples and are reported in cm^{-1}. **HRMS** analyses were performed with Q-TOF YA263 high resolution (Water Corporation) instruments by +ve mode electrospray ionization.

Synthesis of thiazole based peptidomimetics[2]

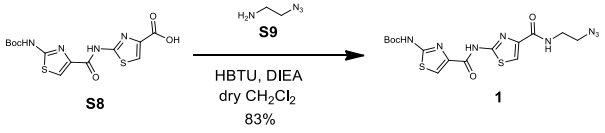
Dimeric thiazole peptidomimetic was synthesized using Cu(I) catalyzed azide–alkyne cycloaddition as depicted in Scheme S1. Bis-thiazole acid **S6** was prepared in four steps from ethyl 2-aminothiazole-4-carboxylate **S1** and 5-hexynoic acid **S2** by stepwise amide coupling using HBTU (hexafluorophosphate benzotriazole tetramethyl uronium) as a coupling reagent and followed by ester hydrolysis using LiOH. The amide coupling between ethyl 2-aminothiazole-4-carboxylate **S1** and 5-hexynoic acid **S2** was carried out using HBTU in presence of DIPEA (di-isopropyl-ethyl amine) as a base to afford thiazole derivative **S3** which upon ester hydrolysis using LiOH provided the corresponding acid **S4**. Thiazole acid **S4** was next coupled with **S1** using HBTU in the presence of DIPEA and a catalytic amount of DMAP (4-(dimethylamino)pyridine) to provide thiazole peptide **S5** which underwent ester hydrolysis to provide the acid **S6**. The amine side chain was incorporated by amide coupling of **S6** with 3-(dimethylamino)-1-propylamine **S7** resulting in bis-thiazole alkyne **2**.

The thiazole azide **1** was synthesized by the coupling between Boc protected thiazole acid S**8** and 2-azidoethylamine **S9**. The cycloaddition reaction between alkyne functionalized bis-thiazole peptide **2** and azido functionalized bis-thiazole peptide **1** was carried out in the presence of copper sulphate and sodium ascorbate to provide the desired thiazole peptide **TBP1** and subsequent Boc-deprotection provided the dimeric thiazole dipeptide **TBP2** in high overall yield.

i) Synthesis of thiazole alkyne:



ii) Synthesis of thiazole azide:



iii) Synthesis of dimeric thiazole peptide TBP2:

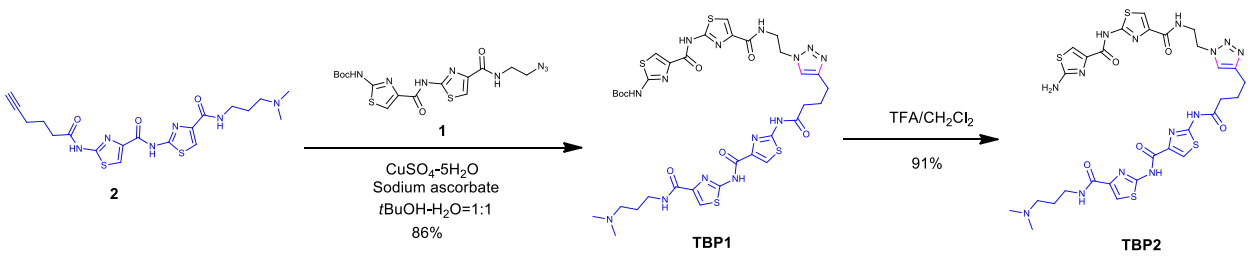


Fig. S2. Synthesis of dimeric thiazole compounds.

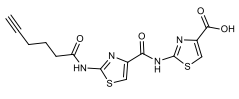
Synthesis of thiazole peptide S3: To a stirred solution of thiazole amine **S1** (2.0 gm, 11.61 mmol) in dry CH_2Cl_2, DIEA (6.07 mL, 34.81 mmol) was added to it followed by the addition of 5-hexynoic acid **S2** (1.28 mL, 11.61 mmol). After stirring for 15 minutes at 0 °C, HBTU (6.6 gm, 17.41 mmol) was added. The reaction was allowed to stir for 24 hours at room temperature. Subsequently, the reaction mixture was concentrated and the residue was dissolved in ethylacetate (3×10 mL). The ethylacetate layer was successively washed with 1(N) HCl solution (3×10 mL), saturated $NaHCO_3$ solution (3×10 mL) and brine. After drying with Na_2SO_4 and filtration, the solvents were removed under vacuum. The residue was purified by column chromatography to furnish the desired compound **S3** (2.66 gm, 86 %) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$): 10.87 (s, 1H), 7.82 (s, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H), 2.28 (td, *J* = 6.8, 2.5 Hz, 2H), 1.94 – 1.90 (m, 3H, merged with CH_2 peak), 1.37 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.4, 161.3, 159.1, 141.1, 122.2, 83.0, 69.6, 61.6, 34.7, 23.5, 17.9, 14.4; HRMS (ESI) calcd for $C_{12}H_{14}N_2O_3SNa$ $[M+Na]^+$: 289.0623; Found: 289.0626.

Synthesis of thiazole acid S4: Using general procedure **GP-1**, LiOH-H_2O (1.18 g, 28.16 mmol) and thiazole peptide **S3** (2.5 g, 9.39 mmol) in THF/MeOH/H_2O (20 mL) were stirred for 4 h to provide the corresponding thiazole acid **S4** (2.01 g, 90%) as a white solid; ^{1}H NMR (400 MHz, DMSO-d_6): 12.80 (s, 1H), 12.43 (s, 1H), 7.94 (s, 1H), 2.81 (t, *J* = 2.8 Hz, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.21 (td, *J* = 7.2, 2.8 Hz, 2H), 1.81 – 1.73 (m, 2H); 13C NMR (100 MHz, DMSO-d_6): 171.2, 162.3, 157.7, 141.9, 122.0, 83.6, 71.7, 33.6, 23.3, 17.2; HRMS (ESI) calcd for $C_{10}H_{10}N_2O_3SNa$ $[M+Na]^+$: 261.0310; Found: 261.0311.

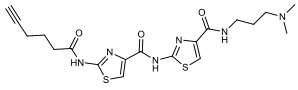
Synthesis of thiazole peptide S5: To a stirred solution of thiazole amine **S1** (1.08 gm, 6.29 mmol) in dry CH_2Cl_2, DIEA (3.29 mL, 18.87 mmol) and DMAP (154 mg, 1.26 mmol) were added followed by the addition of thiazole acid **S4** (1.5 gm, 6.29 mmol). After stirring for 15 minutes at 0 °C, HBTU (3.75 gm, 9.435 mmol) was added. The reaction was allowed to stir for 24 hours at room temperature. The reaction mixture was then concentrated and the residue was dissolved in ethylacetate. The ethylacetate layer was successively washed with 1(N) HCl solution (3×10 mL), saturated $NaHCO_3$ solution (3×10 mL) and brine. After drying with Na_2SO_4 and filtration, the solvents were removed under vacuum and purified by column chromatography to provide the desired compound **S5** (1.72 gm, 70 %) as a white solid; ^{1}H NMR (500 MHz, DMSO-d_6): 12.5 brs, 2H), 8.31 (s, 1H), 8.10 (s, 1H), 4.29 (q, *J* = 6.8 Hz, 2H), 2.81 (t, *J* = 2.7 Hz, 1H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.24-2.21

(m, 2H), 1.82 – 1.76 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): 171.4, 160.9, 159.4, 158.0, 141.9, 141.2, 123.2, 120.6, 83.7, 71.7, 60.6, 33.7, 23.3, 17.2, 14.2; HRMS (ESI) calcd for $C_{16}H_{17}N_4O_4S_2$ $[M+H]^+$: 393.0686; Found: 393.0693.

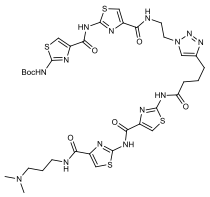
Synthesis of thiazole acid S6: Using general procedure **GP-1**, thiazole peptide **S5** (1.5 g, 3.822 mmol) was stirred for 4 h in THF/MeOH/H_2O (20 mL) with LiOH-H_2O (482 mg, 11.47 mmol), , providing the corresponding thiazole acid **S6** (1.22 g, 88%) as a white solid; ^{1}H NMR (500 MHz, DMSO-d_6): 13.86 (s, 1H), 13.00 (s, 1H), 8.35 (s, 1H), 7.52 (s, 1H), 2.83 (t, *J* = 2.7 Hz, 1H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.29 (td, *J* = 7.2, 2.7 Hz, 2H), 1.91 – 1.85 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): 171.2, 165.1, 158.8, 157.3, 156.9, 150.3, 141.6, 119.1, 114.7, 83.7, 71.5, 33.8, 23.4, 17.3; HRMS (ESI) calcd for $C_{14}H_{13}N_4O_4S_2$ $[M+H]^+$: 365.0373; Found: 365.0373.



Synthesis of thiazole peptide 2: To a stirred solution of thiazole acid **S6** (1.0 gm, 2.744 mmol) in dry CH_2Cl_2, DIEA (1.43 mL, 8.23 mmol) was added to it followed by the addition of amine **S7** (0.41 mL, 3.29 mmol). After stirring for 15 minutes at 0 °C, HBTU (1.56 gm, 4.12 mmol) was added. The reaction was stirred overnight at room temperature. After completion of the reaction, the reaction mixture was diluted with dichloromethane and the dichloromethane layer was successively washed with saturated $NaHCO_3$ solution (3×10 mL) and brine. After drying with Na_2SO_4 and filtration, the solvents were removed under vacuum and purified by column chromatography, provided the desired compound **2** (1.05 gm, 85 %) as an off-white solid; ^{1}H NMR (400 MHz, $CDCl_3$): 8.47 (t, *J* = 6.0 Hz, 1H), 7.82 (s, 1H), 7.78 (s, 1H), 3.58 (q, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.41-2.37 (m, 2H), 2.32 (t, *J* = 6.8 Hz, 2H), 2.07-2.01 (m, 9H, merged with one CH_2 and two CH_3 peaks), 1.81-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.7, 164.1, 159.0, 158.7, 158.6, 145.2, 141.6, 121.1, 118.4, 83.4, 69.5, 56.8, 45.3, 38.0, 34.7, 27.1, 23.8, 18.1; HRMS (ESI) calcd for $C_{19}H_{25}N_6O_3S_2$ $[M+Na]^+$: 449.1424; Found: 449.1425.



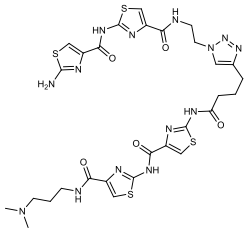
Synthesis of thiazole peptide 1: To a stirred solution of thiazole acid **S8** (500 mg, 1.35 mmol) in dry CH_2Cl_2, DIEA (0.7 mL, 4.05 mmol) was added to it followed by the addition of azido amine **S9** (581 mg, 6.75 mmol). After stirring for 15 minutes at 0 ° C, HBTU (767.5 mg, 2.025 mmol) was added. The reaction was stirred overnight at room temperature. The reaction mixture was subsequently diluted with dichloromethane. The dichloromethane layer was successively washed with saturated $NaHCO_3$ solution (3×10 mL) and brine. After drying with Na_2SO_4 and filtration, the solvents were removed under vacuum and purified by column chromatography to obtain the desired compound **1** (509 mg, 86 %) as a white solid; ^{1}H NMR (500 MHz, $CDCl_3$): 10.25 (s, 1H), 9.38 (s_{br}, 1H), 7.95 (s, 1H), 7.85 (s, 1H), 7.82 (s, 1H), 3.68 (q, *J* = 5.5 Hz, 2H), 3.57 (t, *J* = 5.5 Hz, 2H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.5, 160.3, 158.6, 157.4, 152.6, 144.3, 142.1, 120.4, 118.9, 83.5, 51.1, 38.8, 28.3.



Synthesis of triazole containing thiazole peptide TBP1: Alkyne **2** (100 mg, 0.223 mmol) was dissolved in a 1:1 mixture of *t*BuOH/H_2O (3 mL). Copper(II) sulphate pentahydrate (5.6 mg, 0.0223 mmol) and sodium ascorbate (8.5 mg, 0.0446 mmol) were added and the solution was stirred for 10 min. The azide **1** (117 mg, 0.2675 mmol) was added and the mixture was then allowed to stir for overnight. After completion of the reaction, the reaction mixture was concentrated. The crude product was purified by column

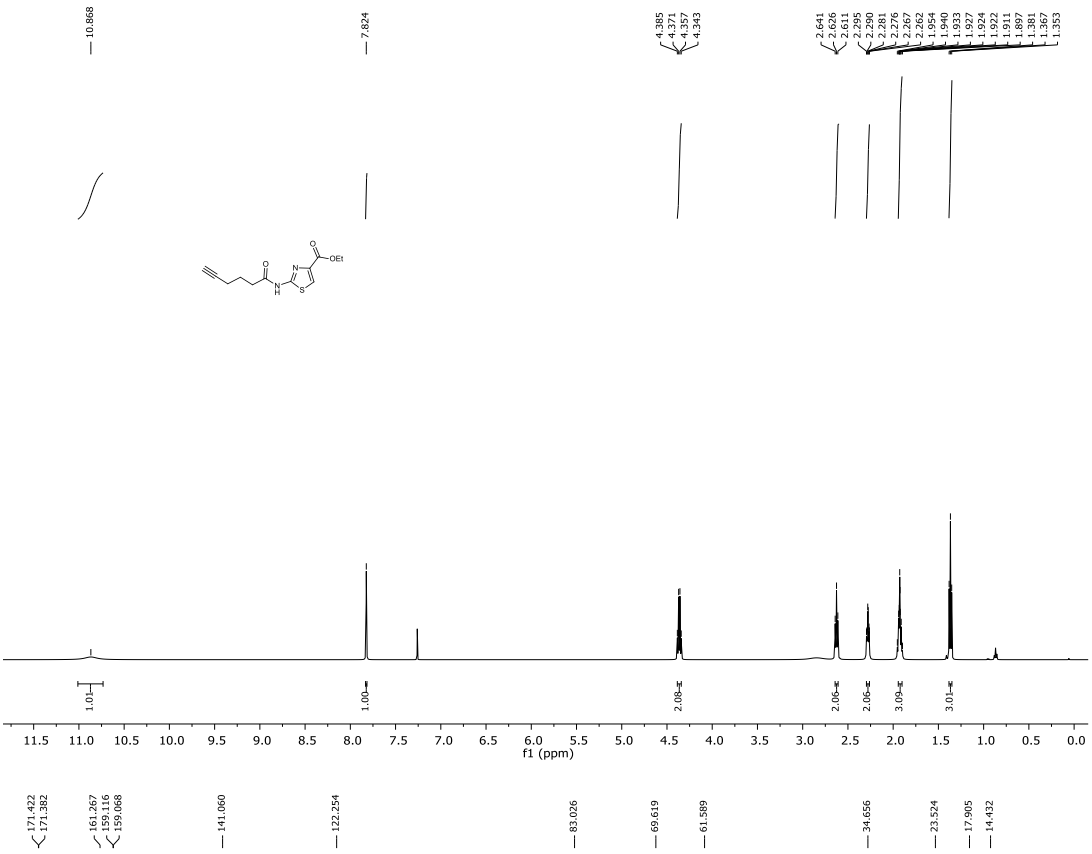
chromatography to provide the desired peptide **TBP1** (170 mg, 86%) as an off-white solid; ^{1}H NMR (400 MHz, DMSO-d_6): 8.27 (t, *J* = 6.0 Hz, 1H), 8.21 (s, 1H), 8.16 (s, 1H), 8.09 (t, *J* = 6.0 Hz, 1H), 7.89 (s, 1H), 7.84 (s, 1H), 7.81 (s, 1H), 5.75 (s, CH_2Cl_2), 4.51 (t, *J* = 6.1 Hz, 2H), 3.72 (q, *J* = 6.0 Hz, 2H), 3.29 (q, *J* = 6.8 Hz, 2H), 2.67 (t, *J*= 7.56 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H, merged), 2.31 (t, *J* = 7.2 Hz, 2H), 2.18 (s, 6H), 1.97 – 1.89 (m, 2H), 1.69-1.62 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): 171.8, 160.9, 160.6, 160.2, 159.3, 159.2, 158.1, 157.6, 157.5, 153.0, 146.0, 144.9, 144.3, 142.4, 142.1, 122.3, 120.4, 120.3, 118.2, 117.5, 81.8, 56.7, 54.8 (CH_2Cl_2 peak), 48.6, 44.9, 37.1, 34.2, 31.1, 27.8, 26.9, 24.4, 24.3; HRMS (ESI) calcd for $C_{34}H_{43}N_{14}O_7S_4$ $[M+H]^+$: 887.2316; Found: 887.2 .

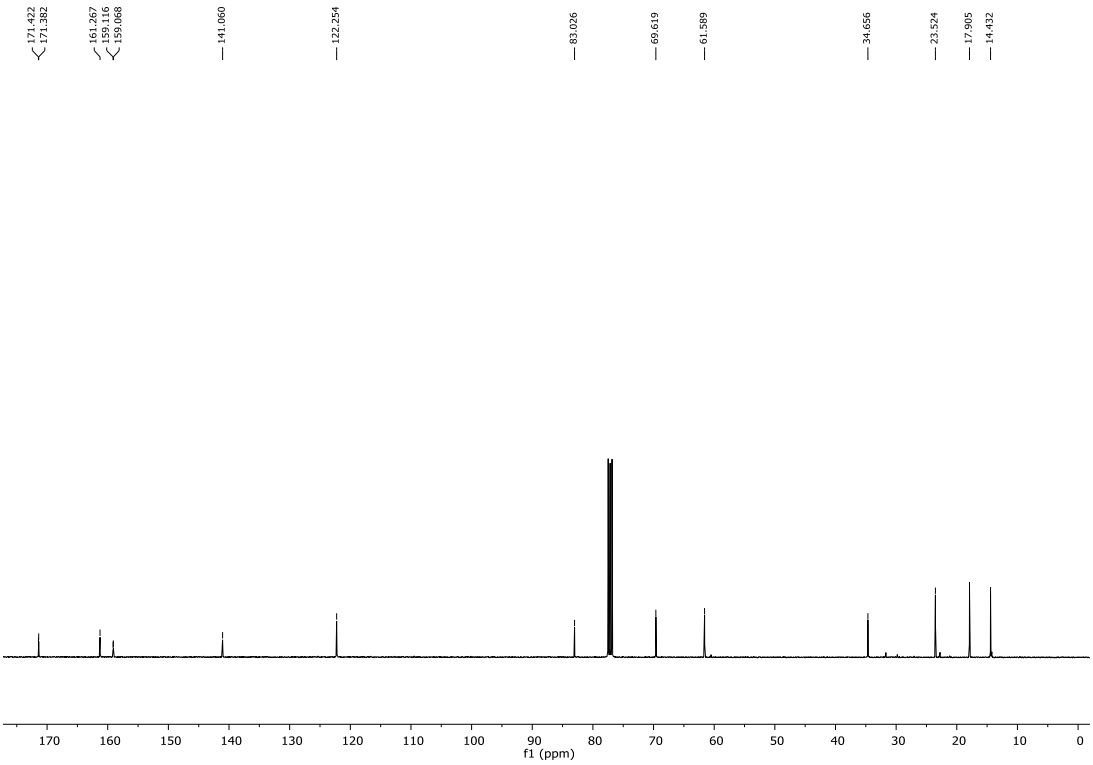
Synthesis of thiazole peptide TBP2: Boc protected thiazole peptide **TBP1** (100 mg, 0.113 mmol) was dissolved in CH_2Cl_2 (1 mL) and cooled to 0 °C. 1 mL Trifluoroacetic acid (equal amount as the solvent) was added and the solution was warmed to room temperature. The reaction mixture was stirred for about 3-4 hours at room temperature until starting material was fully consumed. The reaction was monitored by TLC. After completion of the reaction, the solvent was removed in vacuo and the residue was washed with ether. The solid residue was dried under vacuum to provide the corresponding amine free triazole containing thiazole peptide **TBP2** as a TFA salt (92.4 mg, 91%, white solid); ^{1}H NMR (400 MHz, DMSO-d_6): 12.37 (s, 1H), 11.65 (s, 1H), 11.15 (s, 1H), 9.58 (s, 1H), 8.34 (t, *J* = 6.0 Hz, 1H), 8.24 (s, 1H), 7.89 (s, 1H), 7.87 (s, 1H), 7.84 (s, 1H), 7.68 (s, 1H), 4.50 (t, *J* = 6.4 Hz, 2H), 3.71 (q, *J* = 6.0 Hz, 2H), 3.34 (q, *J* = 6.4 Hz, 2H), 3.11 – 3.05 (m, 2H), 2.78 (d, *J* = 4.4 Hz, 6H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H, merged with DMSO-d_6 peak), 1.97 – 1.81 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): 171.8, 168.7, 161.0, 160.8, 159.0, 158.4, 158.3 (q, *J* = 35.7 Hz), 158.2, 158.16 , 157.2, 157.0, 146.0, 144.6, 144.3, 141.7, 122.3, 120.7, 118.3, 118.1, 115.7 (q, *J* = 290.2 Hz), 115.3, 54.7, 48.6, 42.3, 35.9, 34.2, 24.5, 24.4, 24.3; peaks for trifluoroacetate salt were observed at 158.3 (q, *J* = 35.7 Hz), 115.7 (q, *J* = 290.2 Hz) in ^{13}C NMR; HRMS (ESI) calcd for $C_{29}H_{35}N_{14}O_5S_4$ $[M+H]^+$: 787.1792; Found: 787.1798.



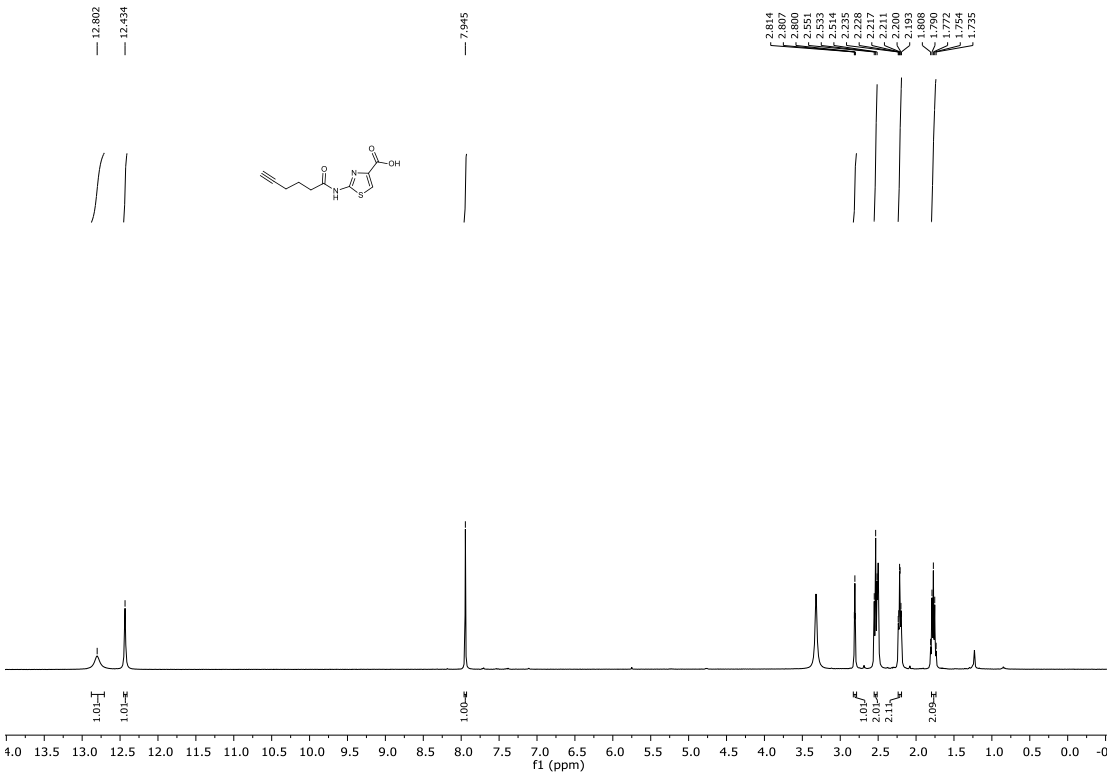
NMR spectra of compounds

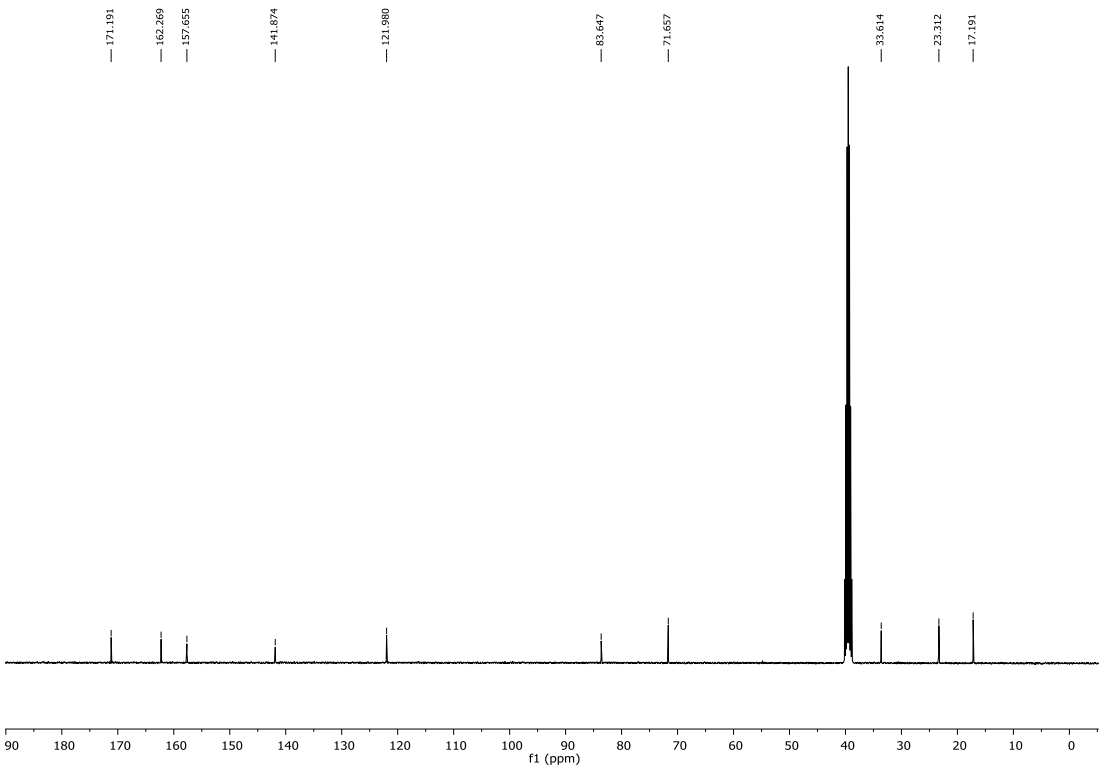
^{1}H and ^{13}C NMR of compound S3:



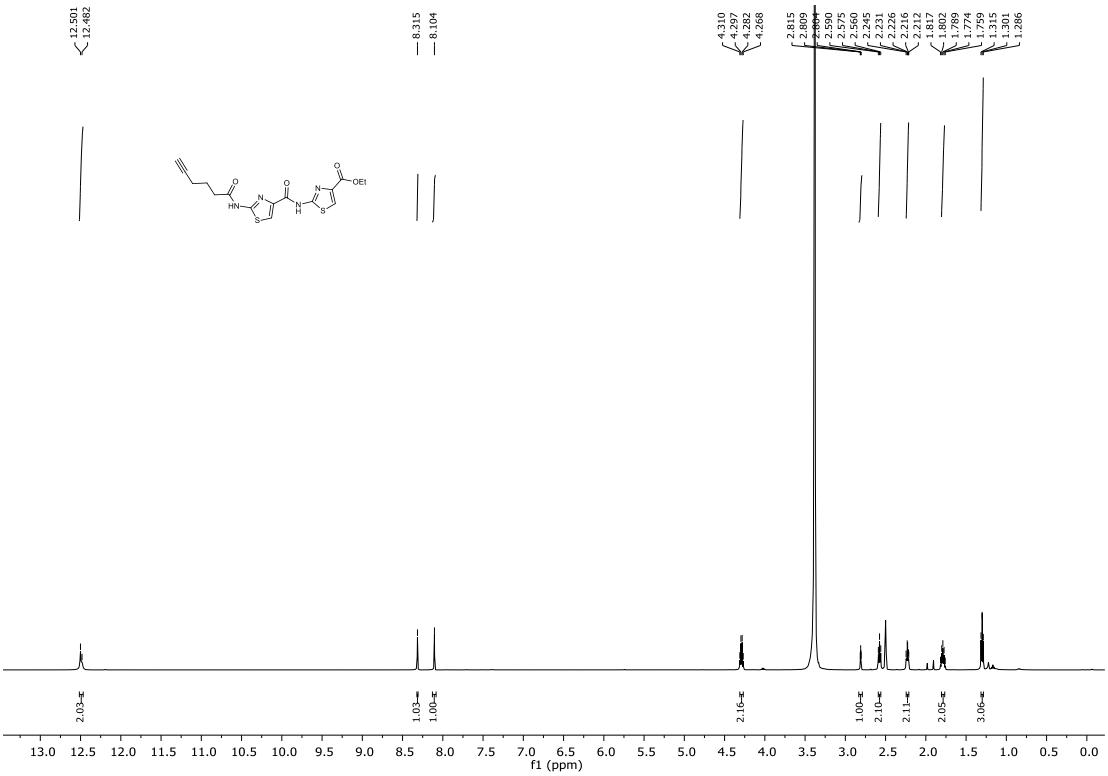


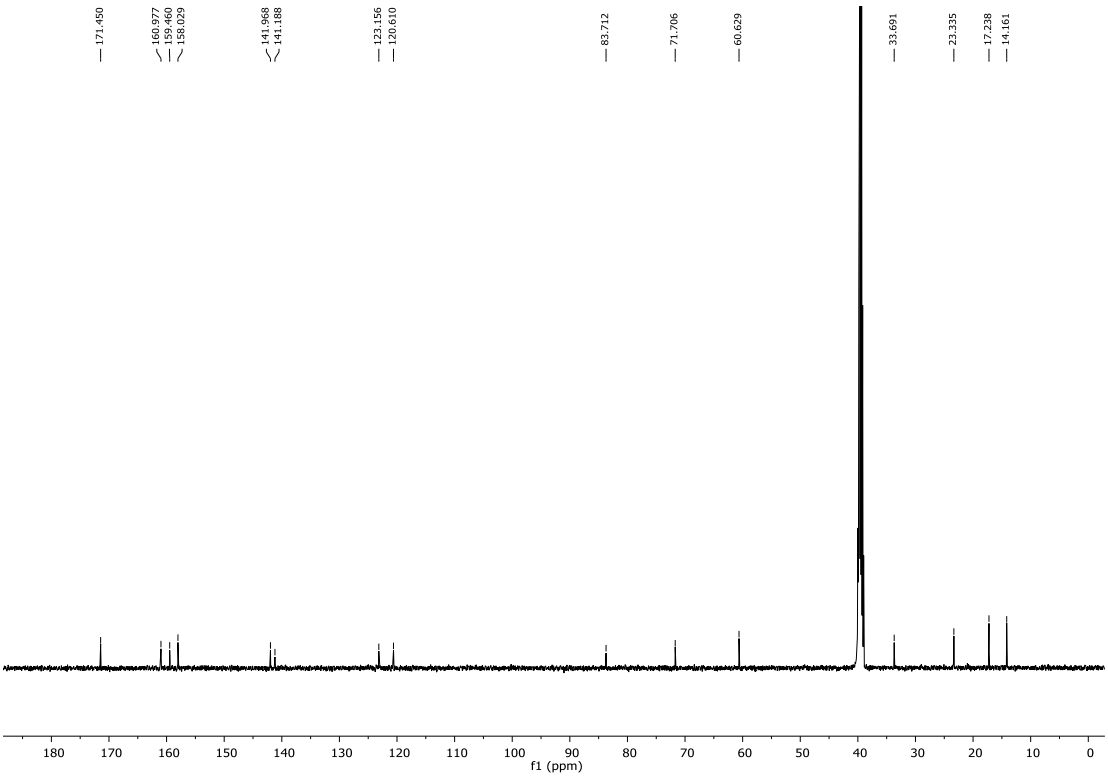
^{1}H and ^{13}C NMR of compound S4:



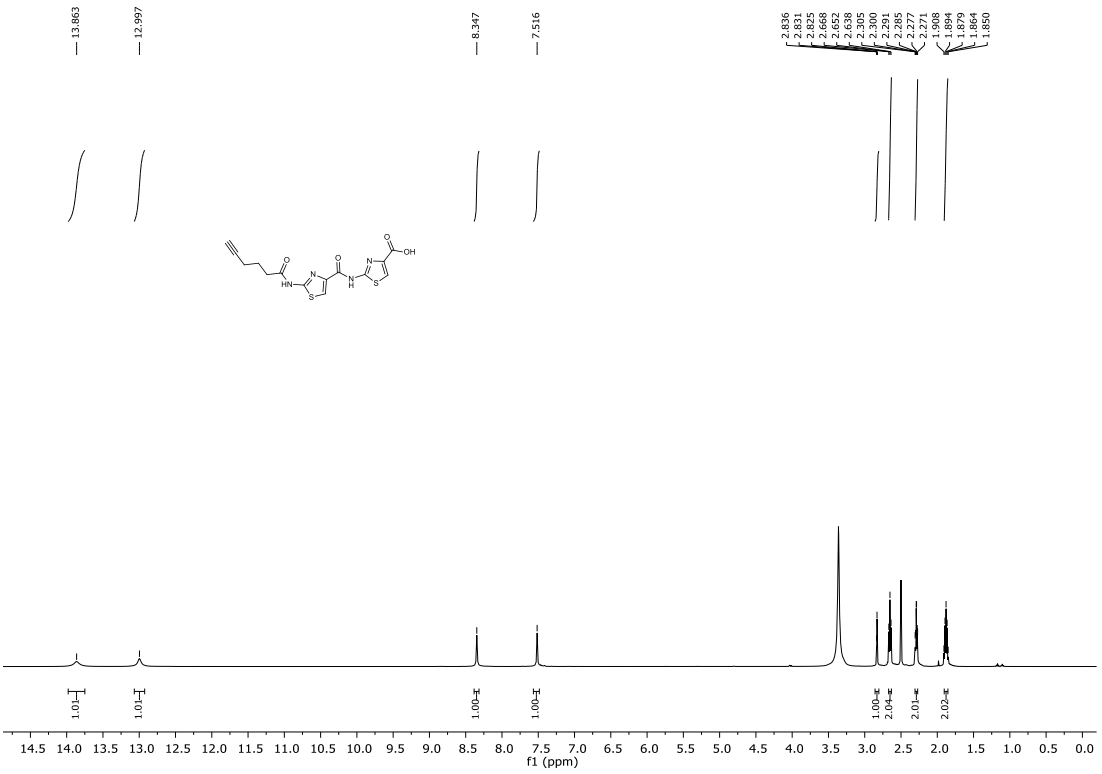


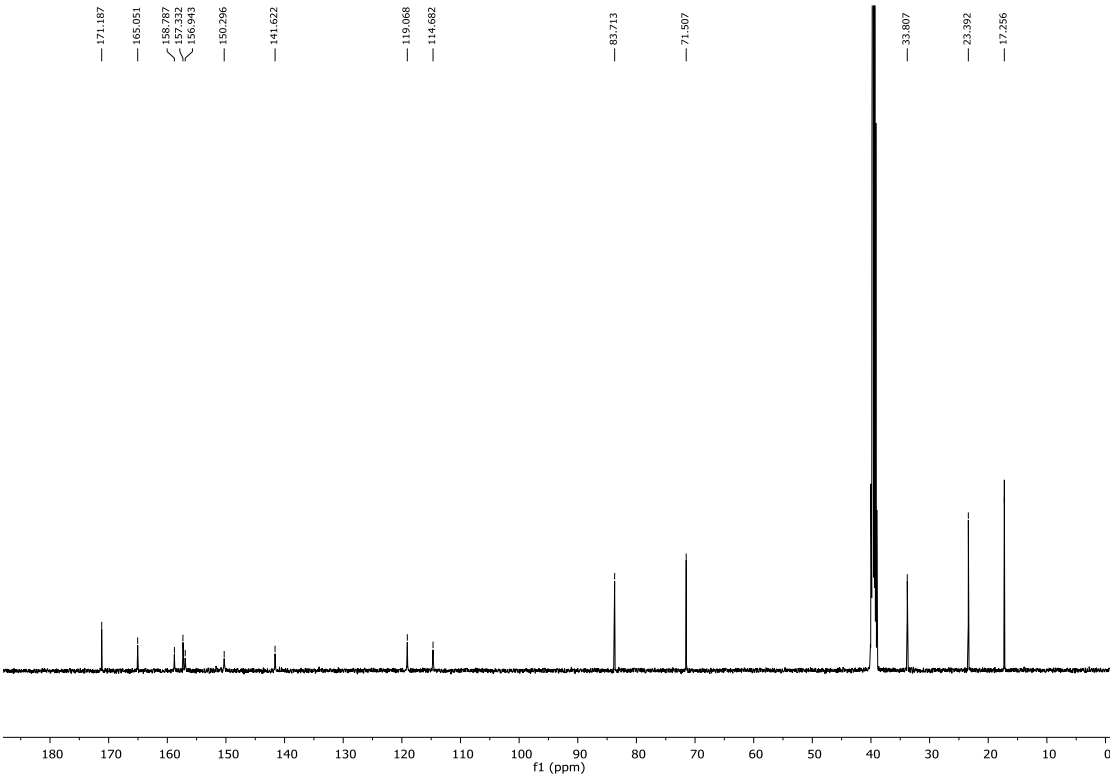
^{1}H and ^{13}C NMR of compound S5:



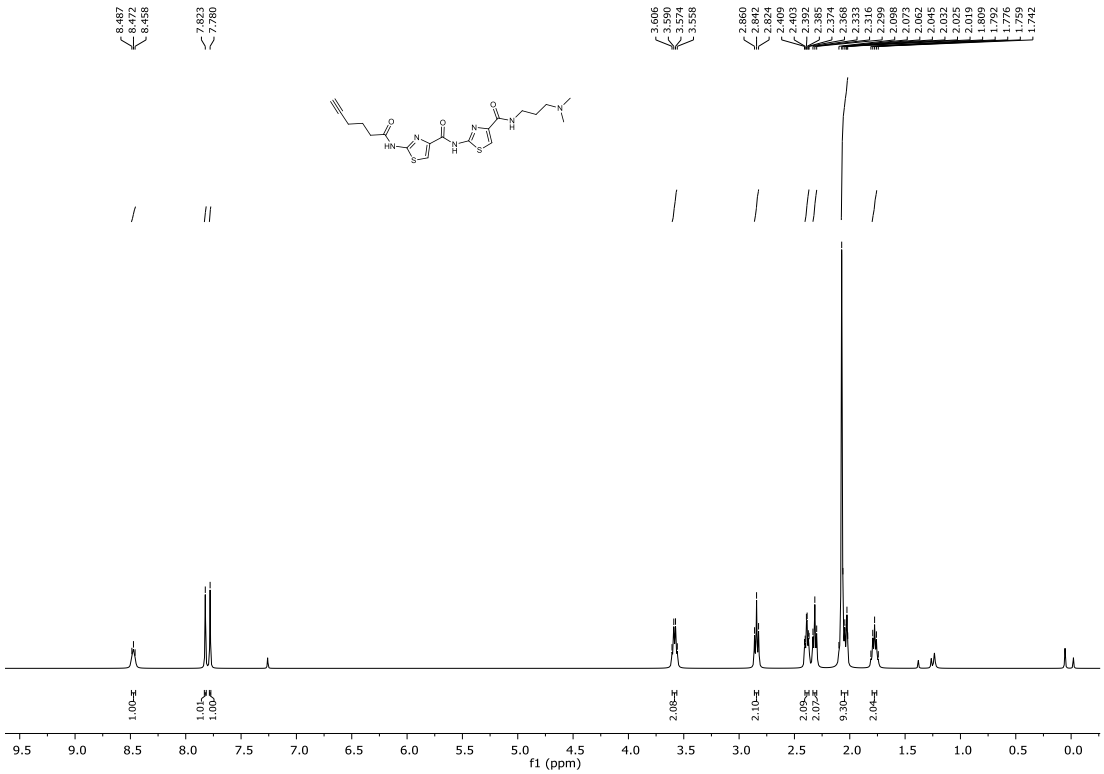


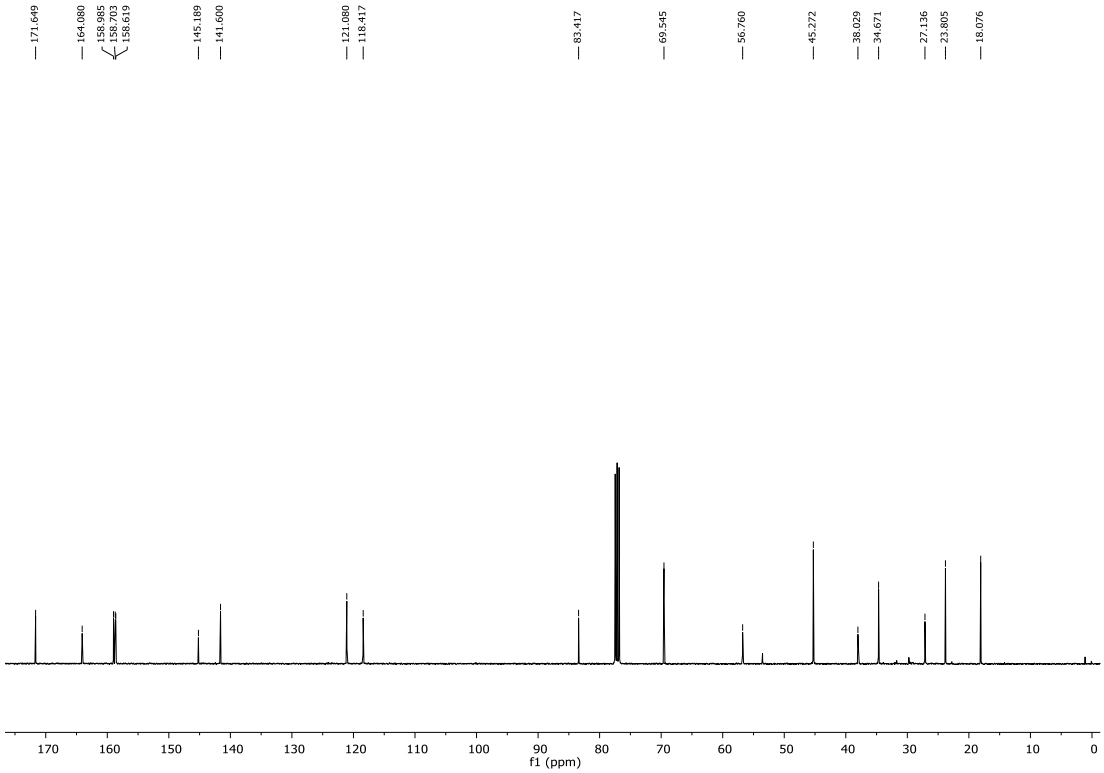
^{1}H and ^{13}C NMR of compound S6:



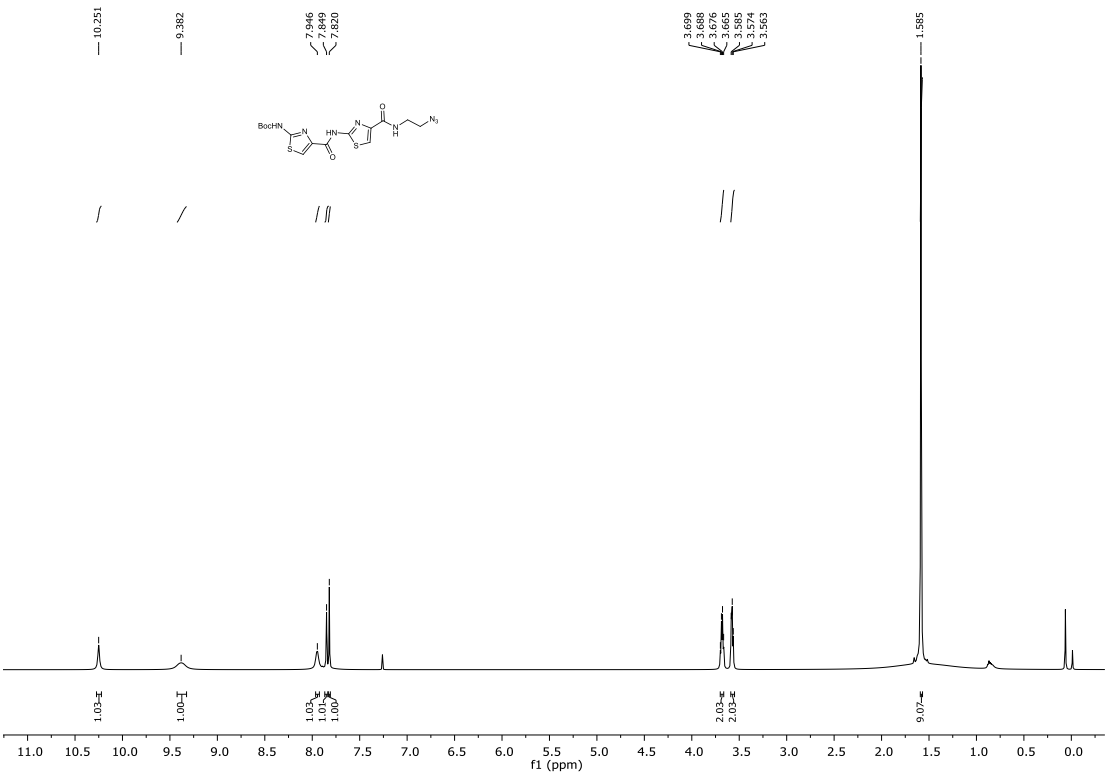


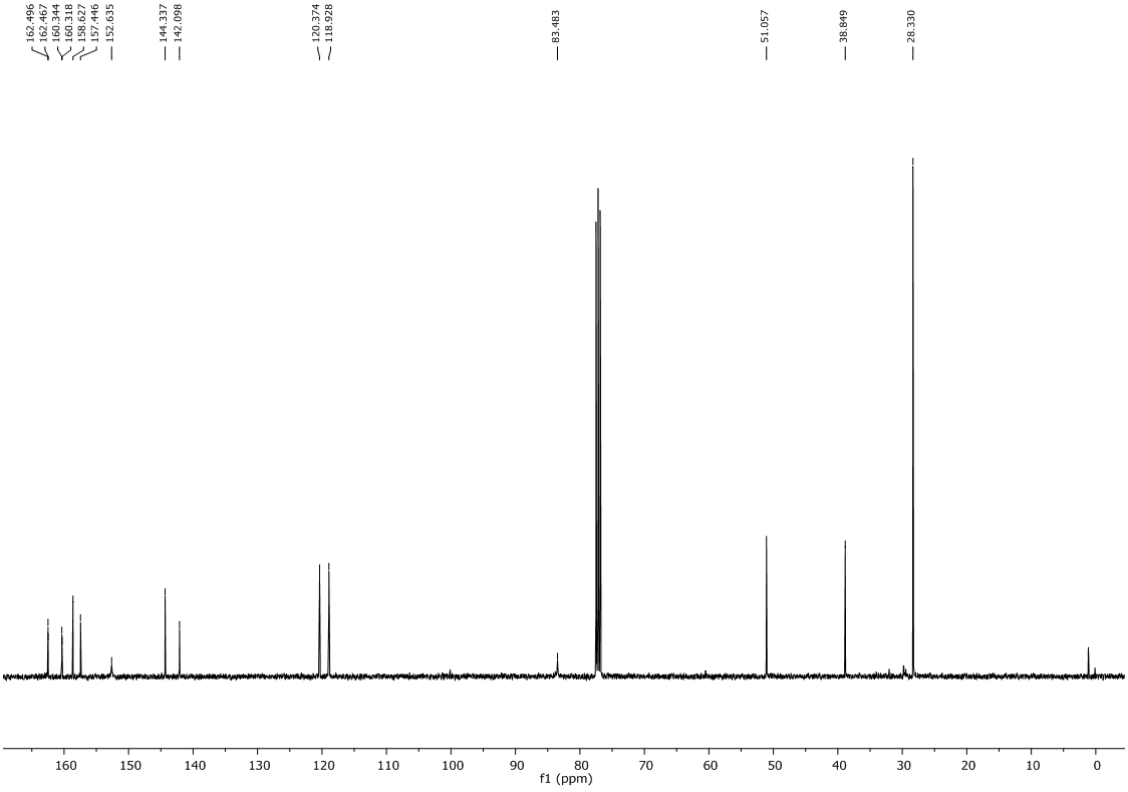
^{1}H and ^{13}C NMR of compound 2:



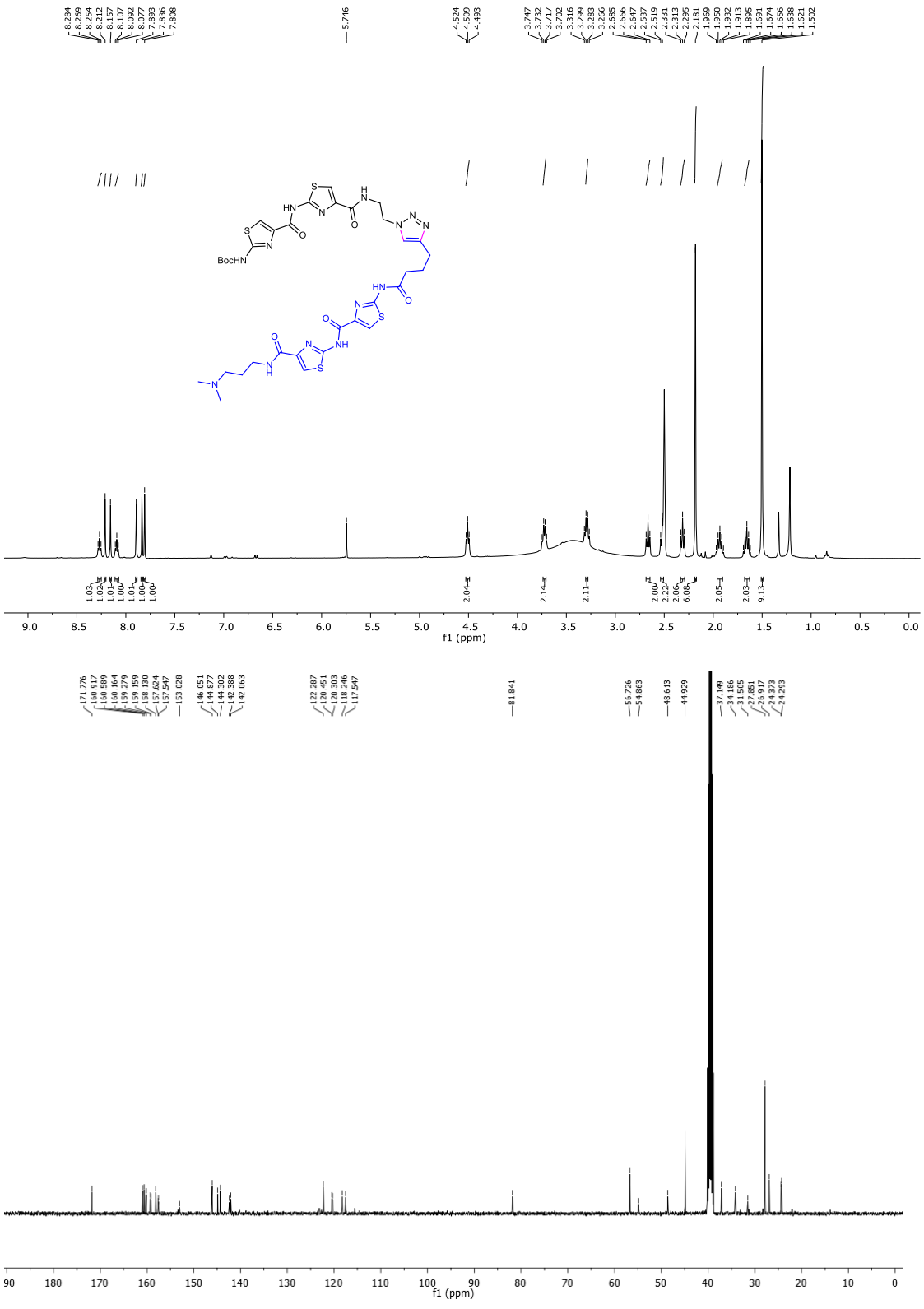


^{1}H and ^{13}C NMR of compound 1:

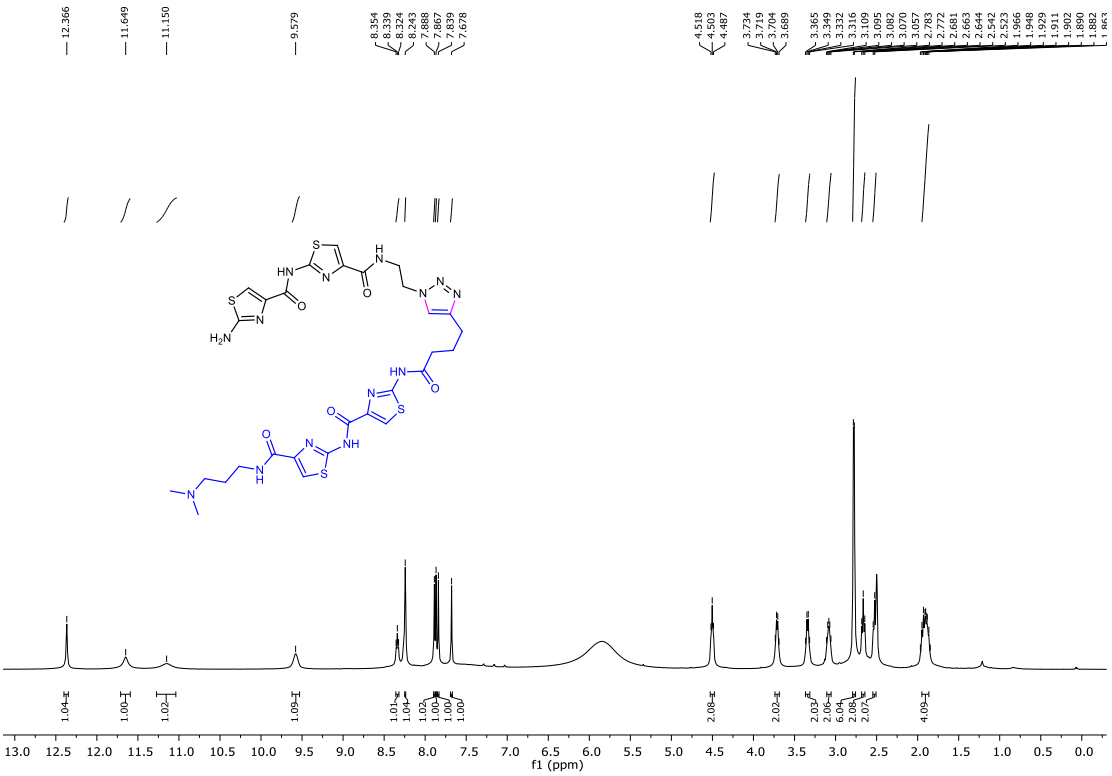


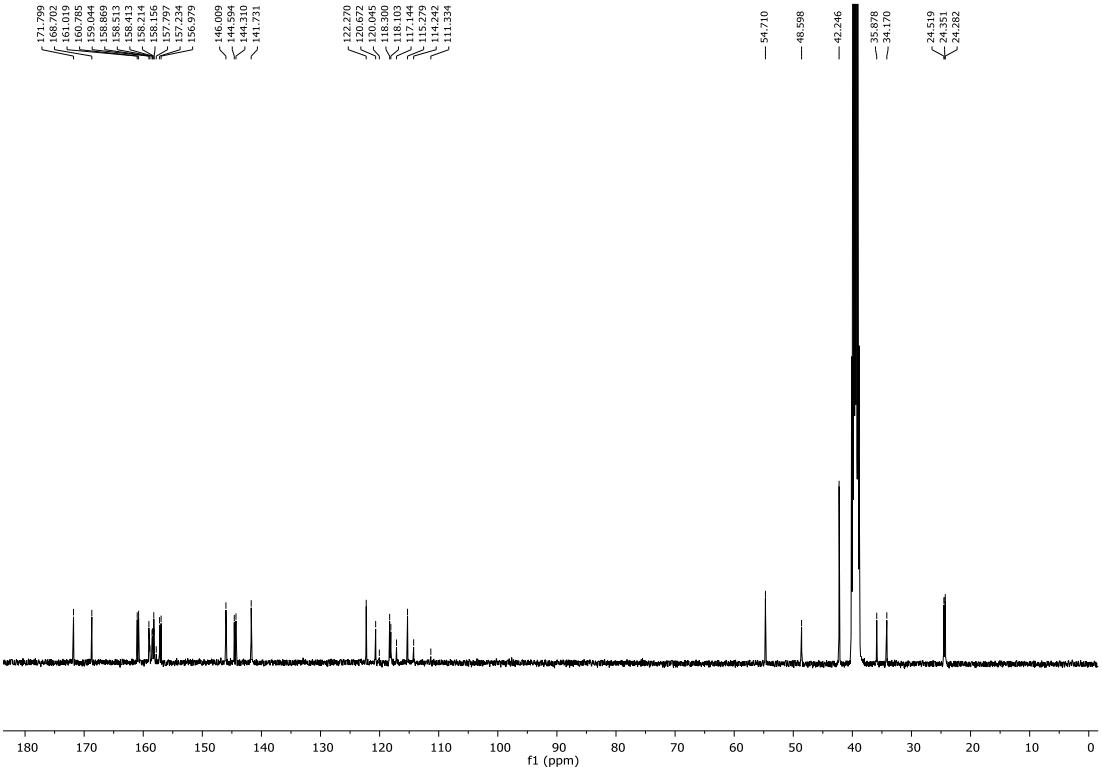


^{1}H and ^{13}C NMR of compound TBP1:



^{1}H and ^{13}C NMR of compound TBP2:


12.366
11.649
11.150
9.579
8.354
8.339
8.324
7.888
7.867
7.839
7.678
4.518
4.503
4.487
3.734
3.719
3.704
3.689
3.365
3.349
3.332
3.316
3.109
3.095
3.082
3.070
3.057
2.783
2.772
2.681
2.663
2.644
2.542
2.523
1.966
1.948
1.930
1.911
1.902
1.890
1.882
1.04
1.00
1.02
1.09
1.01
1.04
1.00
1.00
1.00
2.08
2.02
2.03
2.06
6.04
2.08
2.07
4.09
f1 (ppm)


171.799
168.702
161.019
160.785
159.944
158.869
158.513
158.413
158.214
158.156
157.797
157.234
156.979
146.009
144.564
144.310
141.731
122.270
120.672
120.045
119.700
118.103
117.144
115.279
114.242
111.334
54.710
48.598
42.246
35.878
34.170
24.519
24.351
24.282
f1 (ppm)

References

1 S. Litvinchuk, G. Bollot, J. Mareda, A. Som, D. Ronan, M. R. Shah, P. Perrottet, N. Sakai and S. Matile, *J. Am. Chem. Soc*., 2004, **126**, 10067-10075.
2 R. Paul, D. Dutta, T. K. Mukhopadhyay, D. Müller, B. Lala, A. Datta, H. Schwalbe and J. Dash, *Nat. Commun.*, 2024, **15**, 5275.