ELECTRONIC SUPPLEMENTARY INFORMATION

for the paper entitled

Novel hydrophilic 2,9-bis-triazolyl-1,10-phenanthroline ligands with improved solubility and performance in An/Ln separations

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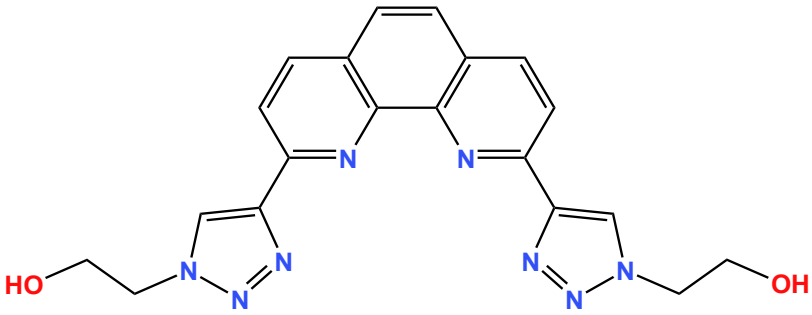
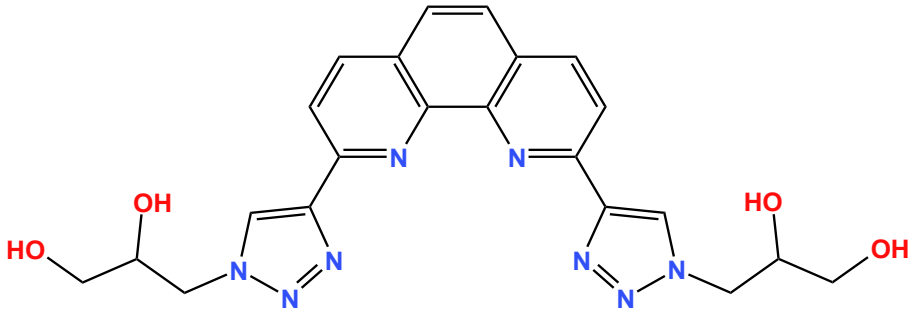
Contents

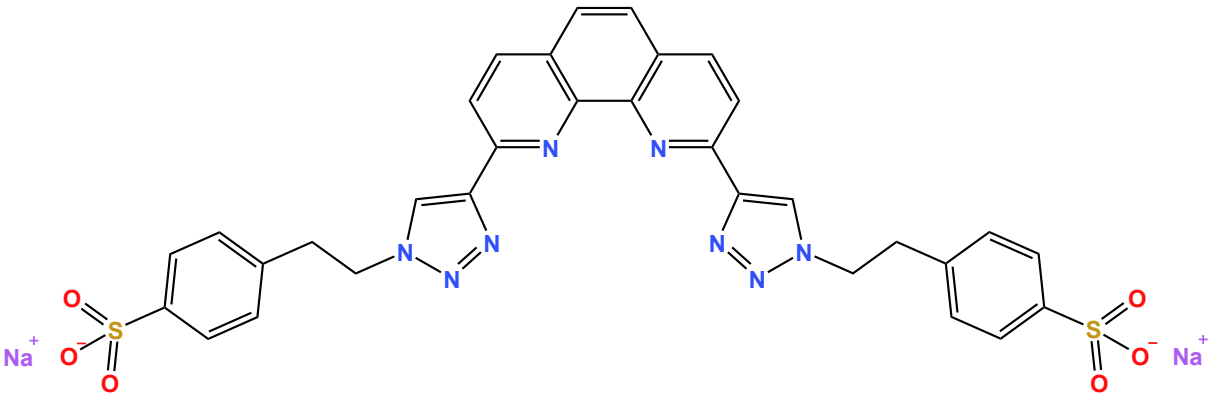
1. Molecular Structures



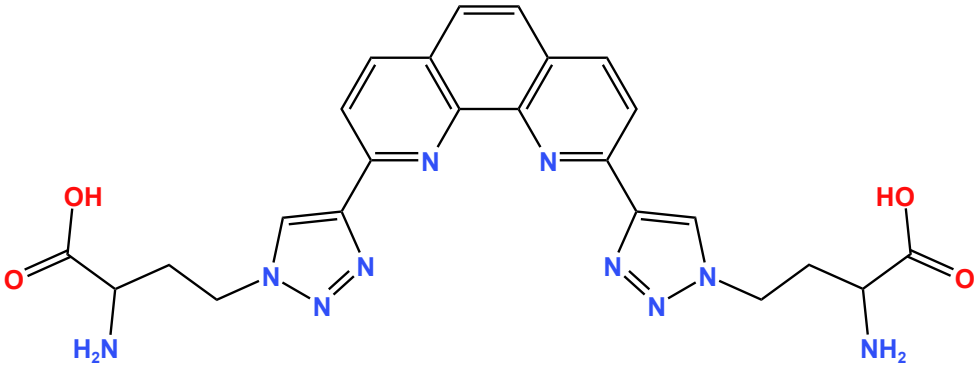
Structure 1: 2OH-BTrzPhen[1]



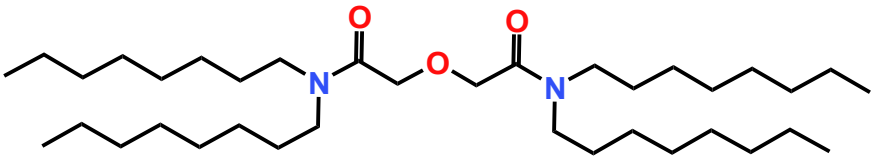
Structure 2: 4OH-BTrzPhen[1]



Structure 3: DS-BTrzPhen, Ligand 1



Structure 4: DAA-BTrzPhen, Ligand 2



Structure 5: TODGA

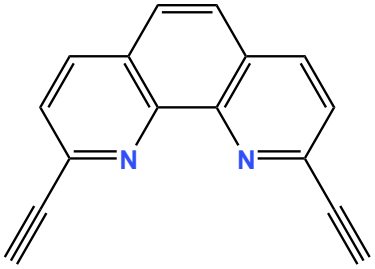
2. Synthetic Procedures and Characterization Data

2.1. General procedures, materials, and instruments

The reagents and solvents were purchased from the multiple vendors and suppliers such as Macklin, TCI, Innochem, Keshi, Xilong Sci and Rionlon and were of standard reagent purity and quality. When necessary, solvents were purified and dried using standard procedures involving solvent distillation over appropriate drying agent and/or using activated molecular sieves Å3 or Å4 . Normal phase thin layer chromatography was performed by using TLC silica gel 60 on aluminium plates with F_{254} indicator (Merck, product code 1.05554.0001), while the reverse phase TLC was performed by using 60 RP-18 silica aluminium TLC plates (5 × 7.5 cm) with $F_{254}S$ indicator (Merck, product code 1.05560.0001). As an inert gas, 99.999% dinitrogen was used. Preparative column chromatography was performed using technical grade silica gel (pore size: 60 Å, 60-200 μm) procured from Sigma-Aldrich or Bangkai (Qingdao, China). Reverse phase preparative column chromatography was performed by using glass semi-preparative columns (Suke Shiye Co. Shanghai) and EasySep-1050 pump stations (UniMicro Tech. Shanghai), collected manually, C-18 silica (40-60 μm) was supplied by Bangkai (Qingdao, China). ^{1}H and ^{13}C NMR spectra were recorded with JEOL JMN ECS 400M spectrometer in deuterated solvents ($CDCl_3$, DMSO-d_6 or D_2O, in certain cases in D_2O with added TFA-d) with ^{1}H-NMR at 400 MHz and ^{13}C-NMR at 100.5 MHz. NMR assignments were supported by 2D, ^{1}H-^{1}H COSY and ^{13}C-^{1}H HSQC and HMBC experiments. Chemical shifts (δ) are quoted in parts per million (ppm) to the nearest 0.01 ppm, calibrated to the relevant residual solvent peaks. Coupling constants are reported in Hz. Signal multiplicity is described with the use of the abbreviations: [s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad]. IR spectroscopy was done using KBr disc method by using Nicolete NEXUS 670 FTIR spectrometer, spectral bands are estimated as s (strong), m(medium) or weak(w). Mass spectroscopy characterisation (low resolution) was routinely performed by using Bruker micrOTOF II mass spectrometer (ESI-TOF) in either positive or negative mode. MS with APCI ionisation for the compound **3** was performed on Thermo Fisher Ultimate 3000 Analytical and MSQ Plus instrument, while the high-resolution mass spectroscopy was performed on LCMS-IT/TOF (Shimadzu, Japan) at Department of Chemistry, Tsinghua University. Elemental analysis (CHN) was performed by using Vario EL cube elemental analyser. UV-Vis characterisation was performed using UNICO UV-4802S spectrometer. Spectroscopic titrations were performed on Perkin Elmer Lambda 35 UV-Vis spectrometer and fluorescence emission was recorded on fluorescence spectroscopy system consisting of Kymera 32 Bi-A detectors/cameras and Opotek Radiant 355 LD laser light source.

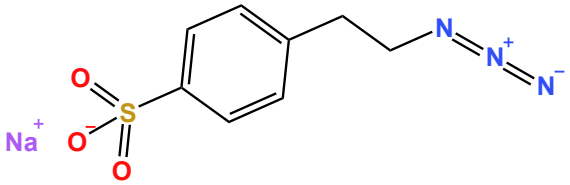
2.2. Synthetic Procedures

2.2.1 2,9-Diethynyl-1,10-Phenanthroline (PhenDE, compound **3**)[1]



Two-neck flask (500 ml) equipped with proper magnetic stir bar, suba-seal, and a supply of inert gas (N_2) was charged with 3.0 g (12.7 mmol) of 2,9-dicarbalehyde-1,10-phenanthroline[1] (**1**) and 5.27 g (38.1 mmol, 3 equiv.) K_2CO_3 and 150 ml of dry methanol was added. Then 5.04 ml of dimethyl (1-diazo-2-oxopropyl) phosphonate (**2**) (Ohira-Bestmann reagent, 26.67 mmol, 2.1 equiv.) was dissolved in dry methanol (100 ml) and added into the flask. The reaction was left to stir for 3 hours at room temperature. After 3 hours, the solution was diluted with chloroform (500 ml) and washed twice with 200 ml saturated aqueous $NaHCO_3$ and then twice with 100 ml of brine. The organic solution was then dried by $MgSO_4$ and evaporated by using a rotary evaporator. The raw material was purified by chromatography with a solution blend (chloroform: ethyl acetate: methanol: triethylamine = 80:14:6:0.1) as a mobile phase, 1.103 g of pale-yellow solid was obtained (38%). ^{1}H-NMR ($CDCl_3$) δ 8.20-8.18 (d, J = 8.2 Hz, 2H), 7.78-7.76 (d, J = 8.3 Hz, 4H), 3.29 (t, *2*H); ^{13}C-NMR ($CDCl_3$) δ 145.67, 142.90, 136.44-136.17, 128.27, 127.21, 126.91, 83.71-83.5, 78.71-78.13; MS (APCI$^+$) *m/z* calcd. for $[M+H]^+$:229.08 found: 229.2, calcd. for $[M+Na]^+$:251.06 found: 251.1

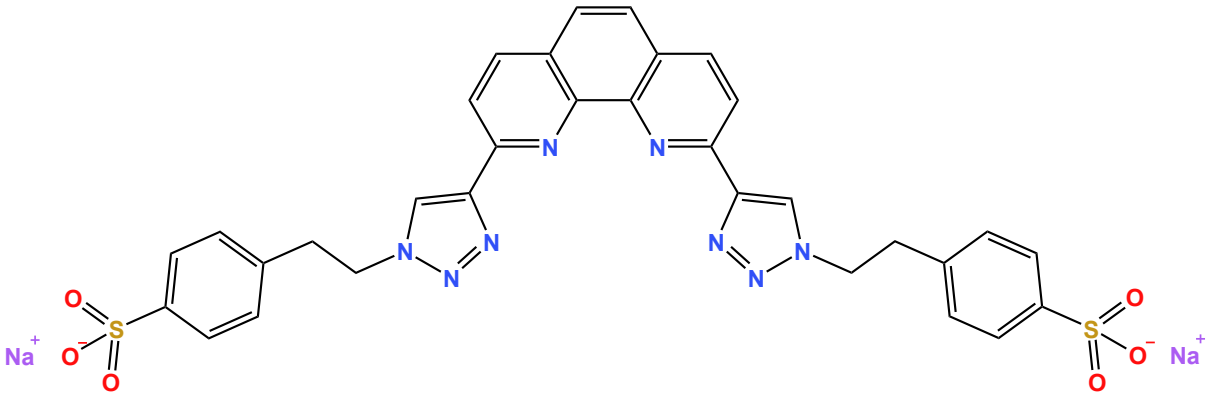
2.2.2 Sodium 4-(2-bromoethyl)benzenesulfonate (AzEBS, compound **4**)[2]



2.0 g (7 mmol) of 4-(2-bromoethyl) benzene sulfonate was dissolved in 10 ml of H_2O and 10 ml of ethanol in a round bottom flask (100 ml) and equipped with a magnetic stir bar. Then 1.0 g (15.33 mmol, 2.2 equiv.) of sodium azide was dissolved in 10 ml of water and 10 ml of ethanol and transferred into the reaction flask, The reaction mixture was stirred and heated to 98°C for 12 hours. After 12 hours, the reaction mixture was evaporated by using a rotary

evaporator and the product was dried in high vacuum. The raw material was purified by recrystallization with water and isopropanol system. Obtained was 961 mg (68%) of pure product. ^{1}H-NMR (D_2O) δ 7.81-7.79 (d, J = 8.4 Hz, 2H), 7.50-7.48 (d, J =8.3 Hz, 2H), 3.65 (t, J = 6.8, 2H), 3.03 (t, J = 6.8, 2H); ^{13}C-NMR (D_2O) δ 142.71, 140.72, 129.47, 125.74, 51.79, 34.30; ESI-MS: *m/z* calcd. for $C_8H_8N_3O_3S^-$ or [M-Na]$^-$: 226.08, found: 226.0779; FT-IR (KBr disc): ν_{max} 3413(m), 2137(s), 1236(s), 1184(s), 1134(s), 1051(s), 837(m), 700(s).

2.2.3. Disodium 2,9-bis[1-(2-(4-sulfonatophenyl)ethyl)-1H-1,2,3-triazol-4-yl]-1,10-phenanthroline (DS-BTrzPhen, Ligand **1**)[1]

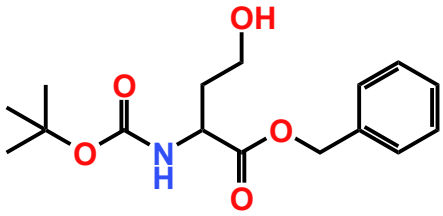


A Schlenk tube (250 ml) was charged with 350 mg (1.53 mmol) of 2,9-diethynyl-1,10-phenanthroline (Compound **2**), 864 mg (3.47 mmol, 2.26 equiv.) of Sodium 4-(2-bromoethyl)benzenesulfonate (AzEBS, compound **3**), 594 mg (3.37 mmol, 2.2 equiv.) of sodium ascorbate and a proper stirring bar. The Schlenk tube was capped with a rubber septum seal and hooked onto Schlenk line. It was evacuated and refilled with inert gas three times and kept under inert gas. Then 38 ml of degassed dichloromethane was added as well as with 33 ml of degassed water *via* septum by using syringe and needle. Next, 1.34 ml (7.67 mmol, 5 equiv.) of diisopropylethylamine (DIPEA) was added into the Schlenk tube and finally 3.53 ml (2.3 mol%) of Cu (II)-TBTA solution (prepared by mixing 65 mg of TBTA and 30 mg of $CuSO_4 \times 5H_2O$ in 11.8 ml of degassed water/DMSO 1:1 solvent blend) was added drop by drop by using gas-tight syringe and needle while vigorously stirring the reaction mixture. During the addition of the copper catalyst colour of the reaction mixture changed from light yellow orange into deep red brown. The reaction mixture was left to stir at room temperature under inert gas for 72 hours. During this time deep red-brown colour of the dichloromethane layer moved onto aqueous layer indicating transfer of phenanthroline moiety from

dichloromethane to water. After 72 hours the reaction mixture was centrifuged (5 minutes at 5000 rpm) to fully remove light yellow dichloromethane layer from deep red-brown aqueous layer. The dichloromethane layer was discarded while aqueous layer was transferred into 250 ml RB flask and carefully evaporated by using rotary evaporator to full dryness.

The resulting raw material was re-dissolved in a mixture of 15 ml of water and 15 ml of methanol (sonication was applied to help dissolving). Next, the mixture was heated by using heat gun and it was cooled down, left overnight to crystallize. After crystallization, the mixture was filtered and the solid was washed by acetone and diethyl ether. Then the solid was dried, raw yellow product was weighted to yield 0.879 g. The raw product was purified by reverse phase chromatography on C-18 silica starting with water as mobile phase and then gradually increasing concentration of methanol from 0% to 30%. The purified material was evaporated, triturated with acetone, filtered washed with diethyl ether, and dried under high vacuum. Total yield was 0.774 g (80%). Found: C, 47.40; H, 4.01; N, 13.82 %; $Na_2C_{32}H_{24}O_6N_8S_2 \times 4.5H_2O$ requires C, 47.58; H, 4.13; N, 13.87 %; ^{1}H NMR (DMSO-d_6) δ 9.21 (s, 2H), 8.63-8.61 (d, J = 8.4 Hz, 2H), 8.38-8.36 (d, J =8.2 Hz, 2H), 8.01 (s, 2H), 7.55-7.53 (d, J =8.1 Hz, 4H), 7.07 (s, 4H), 4.54 (s, 4H), 3.09 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 149.42, 146.73, 146.66, 144.56, 137.74, 137.30, 128.02, 127.52, 126.14, 125.51, 124.31, 120.16, 50.32, 34.90; MS(ESI$^-$) *m/z* calcd. for $C_{32}H_{25}O_6N_8S_2^-$ or $[M-2Na+H]^-$: 681.1338, found: 681.1406; HRMS (ESI) *m/z* calcd. for $C_{32}H_{25}O_6N_8S_2^-$ or $[M-2Na+H]^-$: 681.1338, found: 681.1334.

2.2.4. Benzyl *N*-(*tert*-butoxycarbonyl)homoserinate (NBOB-HS, Compound **5**)[3]

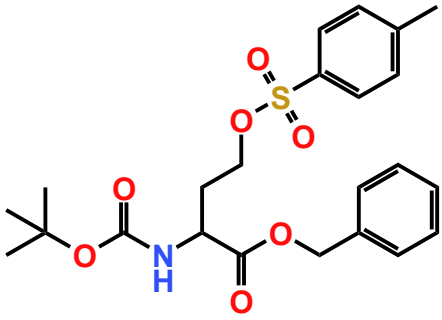


A cryo-reactor was set to the temperature of −10°C. A 1 L three-neck round bottom flask was equipped with a proper stirring bar and flame dried under high vacuum by using a heat gun. 5 g (15.15 mmol) of *N*-Boc-*O*-Bn-L-aspartic acid was placed into the flask and the flask was connected with inert gas (N_2). 60 mL of dry THF was added by a syringe and needle under a constant stream of N_2. The flask was immersed into the cooler and let to stir for 5 minutes at −10 °C. Then 1.83 mL (16.67 mmol, 1.1 equiv.) of *N*-methyl morpholine was added. Then, 2.11 mL (15.91 mmol, 1.05 equiv.) *iso*-butyl chloroformate was added over 15 minutes by using a syringe pump and the reaction mixture was stirred for additional 10 minutes at −10 °C.

Next, 3.61 g (92.44 mmol,6.1 equiv.) sodium borohydride was added quickly, then 150 mL of the dry methanol was added over a time period of 45 minutes by using a syringe pump. The reaction mixture was left stir for additional 50 minutes at −10 °C.

Reaction was quenched with 40 mL aqueous 1 M hydrochloric acid solution and reaction mixture was neutralised. Then the reaction mixture was warmed to room temperature and evaporated by using a rotary evaporator until only the aqueous solution remained. The solution was transferred into a 500 mL separating funnel, aqueous solution was extracted with three 100 mL portions of ethyl acetate. The organic layers were combined washed successively with 100 mL of saturated ammonium solution, two 100 mL portions of pure water, 100 mL of saturated sodium bicarbonate, and two 100 mL portions of brine. The organic layer was dried with $MgSO_4$, filtered, and evaporated to obtain 5.5 g of raw oily material. The raw material was purified by chromatography using 3% methanol in dichloromethane as mobile phase. Obtained was 2.05 g (47%) of white product. ^{1}H-NMR ($CDCl_3$) δ 7.35 (m, 5H), 5.40 (s, 1H), 5.18 (m, 2H), 4.53 (m, 1H), 3.69 (m, 2H), 2.77 (s, 1H), 2.16 (m, 1H), 1.63 (m, 1H), 1.44 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 172.84, 156.58, 135.33, 128.77, 128.65, 128.41, 80.64, 67.43, 58.38, 50.77, 36.29, 28.38; MS (ESI^+) *m/z* calcd. for $C_{16}H_{23}O_5N$+Na or $[M+Na]^+$: 332.21, found: 332.2071.

2.2.5. Benzyl *N*-(*tert*-butoxycarbonyl)-*O*-tosyl-homoserinate (NBOB-HS-Ts, Compound **6**)[3]

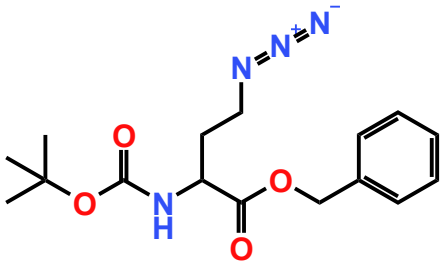


A 50 mL Schlenk tube was dried and equipped with a proper magnetic stirring bar. Then 1.7 g (5.50 mmol) of benzyl (tert-butoxycarbonyl)homoserinate (NBOB-HS, Compound **5**) and 136 mg (1.1 mmol, 0.2 equiv.) of DMAP was added into the tube. The Schlenk tube was capped with a rubber septum seal, hooked onto Schlenk line, and evacuated/refilled with inert gas three times and kept under inert gas. 68 ml of dry dichloromethane and 1.82 mL (13.08 mmol, 2.38 equiv.) of triethylamine were added by syringe and the Schlenk tube was placed into an ice bath. Then 1.306 g (6.81 mmol,1.24 equiv.) *p*-toluene sulfonyl chloride (TosCl) was added by using 5 mL of dry dichloromethane and a gas tight syringe, into the Schlenk tube. The reaction

mixture turned cloudy and yellow and the Schlenk tube was taken out of the ice bath and was left to stir for 3 hours at room temperature.

After 3 hours, reaction mixture was quenched by adding 75 mL of saturated ammonium chloride solution, and the reaction mixture was transferred into to a 500 mL separating funnel. The organic layer was collected and washed with two twice with 75 mL of saturated sodium chloride solution. The aqueous layer was back extracted with two 100 mL portions of dichloromethane. All of the organic layer was combined into a conical flask, dried with $MgSO_4$, filtered and evaporated by using a rotary evaporator. The raw material was purified by chromatography with a mixture of 5% ethyl acetate in dichloromethane as mobile phase. Finally, 1.825 g of white product was obtained (72 %). ^{1}H-NMR ($CDCl_3$) δ 7.78-7.75 (d, J = 8.3 Hz, 2H), 7.35-7.31 (m, 7H), 5.13 (s, 2H), 5.10 (m, 1H), 4.35 (s, 1H), 4.10 (m, 2H), 2.44 (s, 3H), 2.23 (m, 1H), 212 (m, 1H), 1.40 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 171.56, 155.27, 145.05, 135.21, 132.81, 130.00, 128.77, 128.66, 128.55, 128.15, 80.31, 67.68, 66.35, 50.73, 31.62, 28.36, 21.78; MS (ESI$^+$) *m/z* calcd. for $C_{23}H_{29}O_7NS+Na^+$ or $[M+Na]^+$: 486.26; found: 486.2599

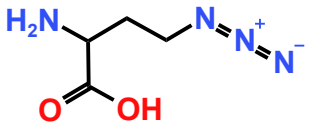
2.2.6. Benzyl 4-azido-2-*N*-((*tert*-butoxycarbonyl)amino)butanoate (NBOB-AHA, Compound **7**)[3]



A 250 mL Schlenk tube was dried and equipped with a magnetic stirring bar. 4 g (12.20 mmol) of Benzyl *N*-(*tert*-butoxycarbonyl)-*O*-tosyl-homoserinate (NBOB-HS-Ts, Compound **6**) and 2.380 g (36.61 mmol, 3 equiv.) of sodium azide was added into the Schlenk tube. The Schlenk tube was capped with a rubber septum seal and hooked onto Schlenk line. It was evacuated and refilled with inert gas three times and kept under inert gas. 80 mL of dry *N,N*-dimethyl formamide was added by syringe and the Schlenk tube was placed in an oil bath (80 °C). The reaction mixture was left to stir for overnight. After 24 hours, solvent was evaporated by using a rotary evaporator. Then the compound was dissolved and transferred into a 1 L separating funnel by using 400 mL of dichloromethane. The dichloromethane solution of the product was washed by two 150 mL portions of brine. Organic layers were collected into a 500 mL conical flask, dried with $MgSO_4$, filtered, and evaporated by using a rotary evaporator. The raw material was purified by chromatography with 20% of ethyl acetate in petroleum ether as

mobile phase, 2.642 g of pure product was obtained (65%). ^{1}H-NMR ($CDCl_3$) δ 7.36-7.26 (m, 5H), 5.20-5.18 (m, 3H), 4.44 (s, 1H), 3.37 (t, J = 6.7 Hz, 2H), 2.21 (m, 1H), 1.93 (m, 1H), 1.44 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 171.96, 155.40, 135.26, 128.78, 128.70, 128.55, 80.33, 67.54, 51.54, 47.81, 31.92, 28.39; MS(ESI$^+$) *m/z* calcd. for $C_{16}H_{22}O_4N_4$+Na^+ or $[M+Na]^+$: 357.26 found: 357.2605, *m/z* calcd. for $C_{16}H_{22}O_4N_4$+K^+ or $[M+K]^+$: 373.23, found: 373.2349.

2.2.7. L-Azidohomoalanine hydrochloride (L-AHA, Compound **8**)[3]



First step: the removal of the benzyl protecting group (NB-L-AHA).

A round bottom flask (250 ml) was charged with 3.628 g (11.07 mmol) of Benzyl 4-azido-2-*N*-((*tert*-butoxycarbonyl)amino)butanoate (NBOB-AHA, Compound **7**) and a proper stirring bar. Then 31mL of methanol and 31 mL of THF were added into the flask. Then the flask was closed with a stopper and it was placed in an ice bath for 5 minutes. Next, 31 mL of LiOH aqueous solution (2 M) was added dropwise. The flask was removed from ice bath and stir for 1 hour. After 1 hour the solvents were evaporated by a rotary evaporator. 50 mL of pure water was added, and the pH of the solution was adjusted to 7 with aqueous 1 M $KHSO_4$. Then the solution was transferred into a 250 mL separating funnel and was extracted five times with 100 mL of dichloromethane. All dichloromethane layers were combined into a 1 L conical flask dried with $MgSO_4$, filtered, and evaporated by using a rotary evaporator. Obtained was 3.346 g of raw material suitable for the second step.

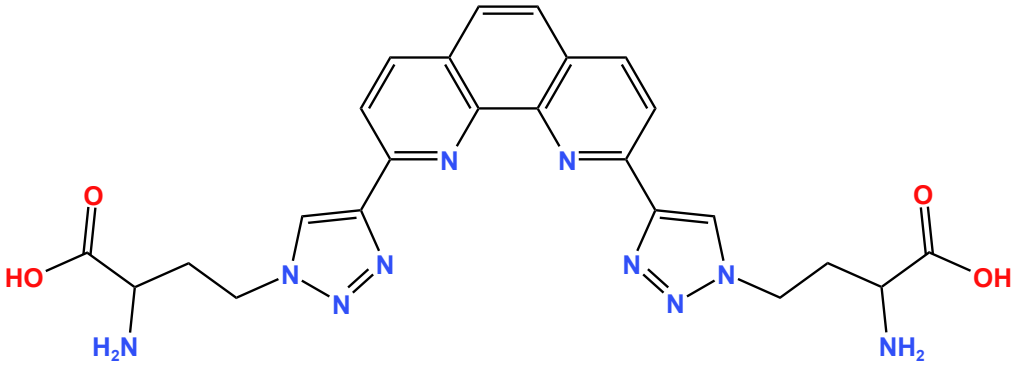
Second step: the removal of the Boc group

A round bottom flask (100 ml) was charged with 3.346 g of raw material from the previous step (NB-L-AHA) and a proper stirring bar was added. Then 41 mL of HCl in 1,4-dioxane (4 M) was added into the flask by a syringe. The mixture was stirred for 1 hour. After 1 hour formed suspension was filtered by using a fritted funnel. The collected solid was washed twice with 20 mL portions of 1,4-dioxane, dry, and weighted to obtain 1.228 g of L-AHA product. Then filtrate was evaporated and washed with dichloromethane and petroleum ether, after which additional 0.296 g of product was obtained. The total yield was 1.524 g of L-AHA (78%).

^{1}H NMR (D_2O) δ 4.18 (t, J = 6.4 Hz, 1H), 3.64 (m, 2H), 2.23 (m, 2H); ^{13}C NMR (D_2O) δ 171.73, 51.08, 47.09, 29.06; MS (ESI$^+$) *m/z* calcd. for $[M+H]^+$: 145.07; found: 145.0968; FT-

IR (KBr disc): ν_{max} 3457 (s), 3124 (m), 2151(m), 2109 (s), 1741 (s), 1502 (m), 1401 (s), 1369(m), 1295(m), 1215(s).

2.2.7. 2,9-bis[1-(3-amino-3-carboxyl-propyl)-1H-1,2,3-triazol-4-yl]-1,10-phenanthroline, (DAA-BTrzPhen, Ligand **2**)[1]



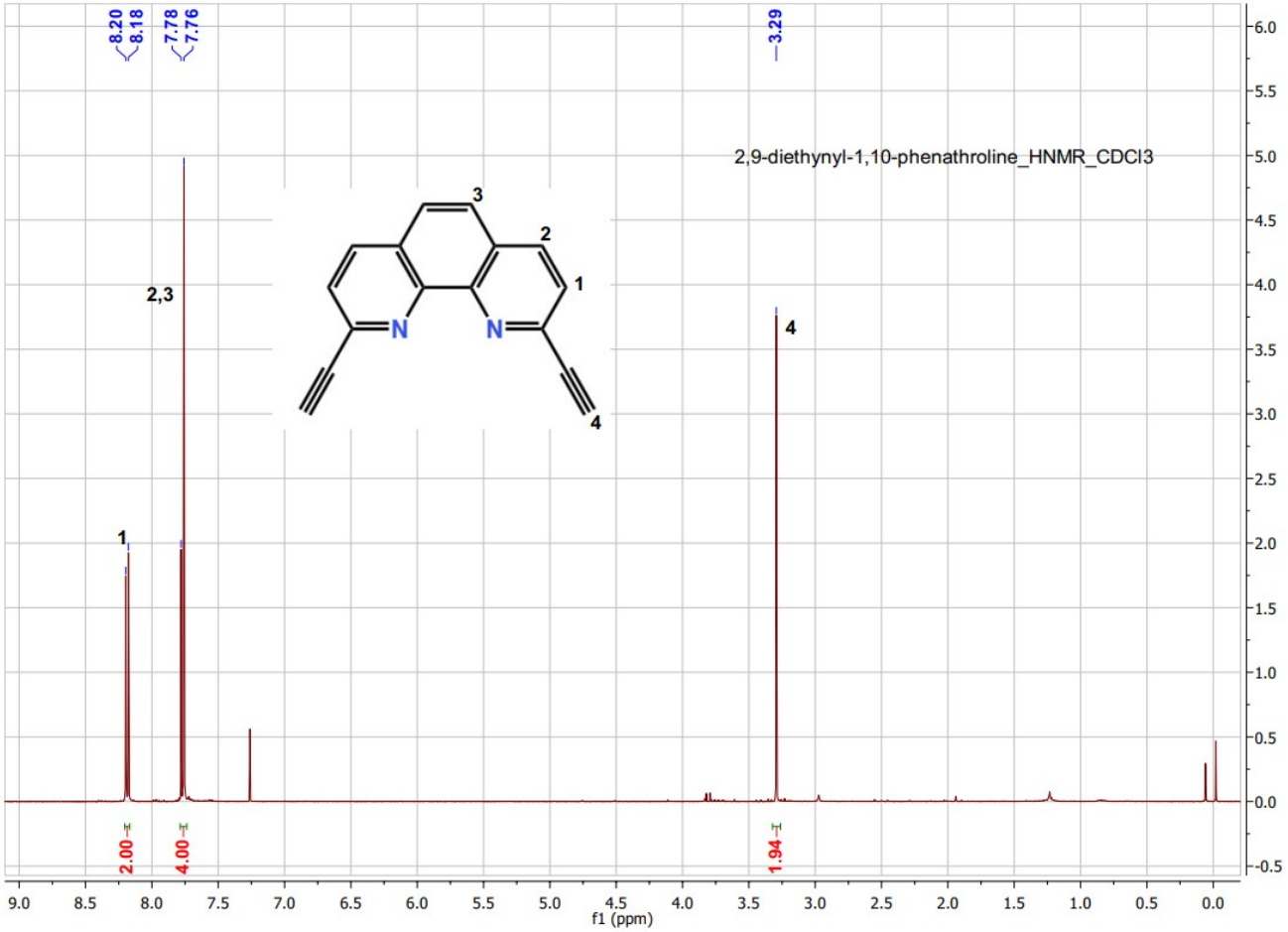
A Schlenk tube (250 ml) was charged with 500 mg (2.19 mmol) of 2,9-diethynyl-1,10-phenanthroline (Compound **2**), 895 mg (4.95 mmol, 2.26 equiv.) of L-azidohomoalanine hydrochloride (Compound **6**), 850 mg (4.82 mmol, 2.2 equiv.) of sodium ascorbate and a proper stirring bar. The Schlenk tube was capped with a rubber septum seal and hooked onto Schlenk line, evacuated and refilled with inert gas three times and kept under inert gas. Then, 54 ml of degassed dichloromethane was added as well as with 49 ml of degassed water *via* septum by using syringe and needle. Next, 2.8 ml (16.1 mmol, 7.35 equiv.) of diisopropylethylamine (DIPEA) was added into the Schlenk tube, and finally 5.04 ml (2.3 mol%) of Cu(II)-TBTA solution (prepared by mixing 65 mg of TBTA and 30 mg of $CuSO_4 \times 5H_2O$ in 11.8 ml of degassed water/DMSO 1:1 solvent mixture) was added drop by drop while vigorously stirring the reaction mixture. During the addition of the copper catalyst colour of the reaction mixture changed from light yellow orange into deep red brown. The reaction mixture was left to stir at room temperature under inert gas for 72 hours. During this time deep red-brown colour of the dichloromethane layer moved into the aqueous layer indicating transfer of phenanthroline moiety from dichloromethane to water. After 72 hours the reaction mixture was centrifuged to fully remove light yellow dichloromethane layer from deep red-brown aqueous layer. The dichloromethane layer was discarded while aqueous layer was transferred into 250 ml round bottom flask and carefully evaporated by using rotary evaporator to full dryness. The resulting raw material was re-dissolved in 30 ml of water (sonication was applied to help solubilise solid) and pH was adjusted to neutral with acetic acid. Next, 30 ml of methanol was added inducing precipitation. The suspension was sonicated to fully remove the precipitate from the flask wall and then filtered on a fritted funnel. The raw yellow product was weighted to yield 1.477 g. The raw product was purified by reverse phase chromatography on

C-18 silica starting with 1% of ammonia in water as mobile phase and then gradually increasing concentration of methanol from 0% to 10%. The purified material was evaporated and triturated with methanol, filtered, washed with methanol and acetone, and dried under high vacuum. Total yield was 1.43 g (88%). Found: C, 44.81; H, 5.94; N, 21.83 %; $C_{24}H_{24}O_4N_{10}\times 7H_2O$ requires C, 44.85; H, 5.97; N, 21.79 %; ^{1}H-NMR (D_2O/TFA-*d*) δ 8.52 (s, 2H), 7.80-7.78 (d, *J* = 8.2 Hz, 2H), 7.42-7.39 (d, *J* =8.2 Hz, 2H), 7.08 (s, 2H), 4.66 (s, 4H), 4.54 (s, 4H), 4.15 (t, *J* = 6.5 Hz, 2H), 2.61 (m, 4H); ^{13}C NMR (D_2O/TFA-*d*) δ 171.54, 145.70, 142.79, 140.52, 136.98, 127.70, 126.38, 121.16, 117.81, 50.72, 46.96, 30.32; MS (ESI$^+$) *m/z* calcd. for $[M+H]^+$: 517.27, found: 517.2664 , *m/z* calcd. for $[M+Na]^+$: 539.25, found: 539.2479; HRMS (ESI$^+$) *m/z* calcd. for $[M+H]^+$: 517.2055, found: 517.2055, *m/z* calcd. for $[M+Na]^+$: 539.1874, found: 539.1872. ΔH = -[slope] x R x 2.303

2.3. Characterization data

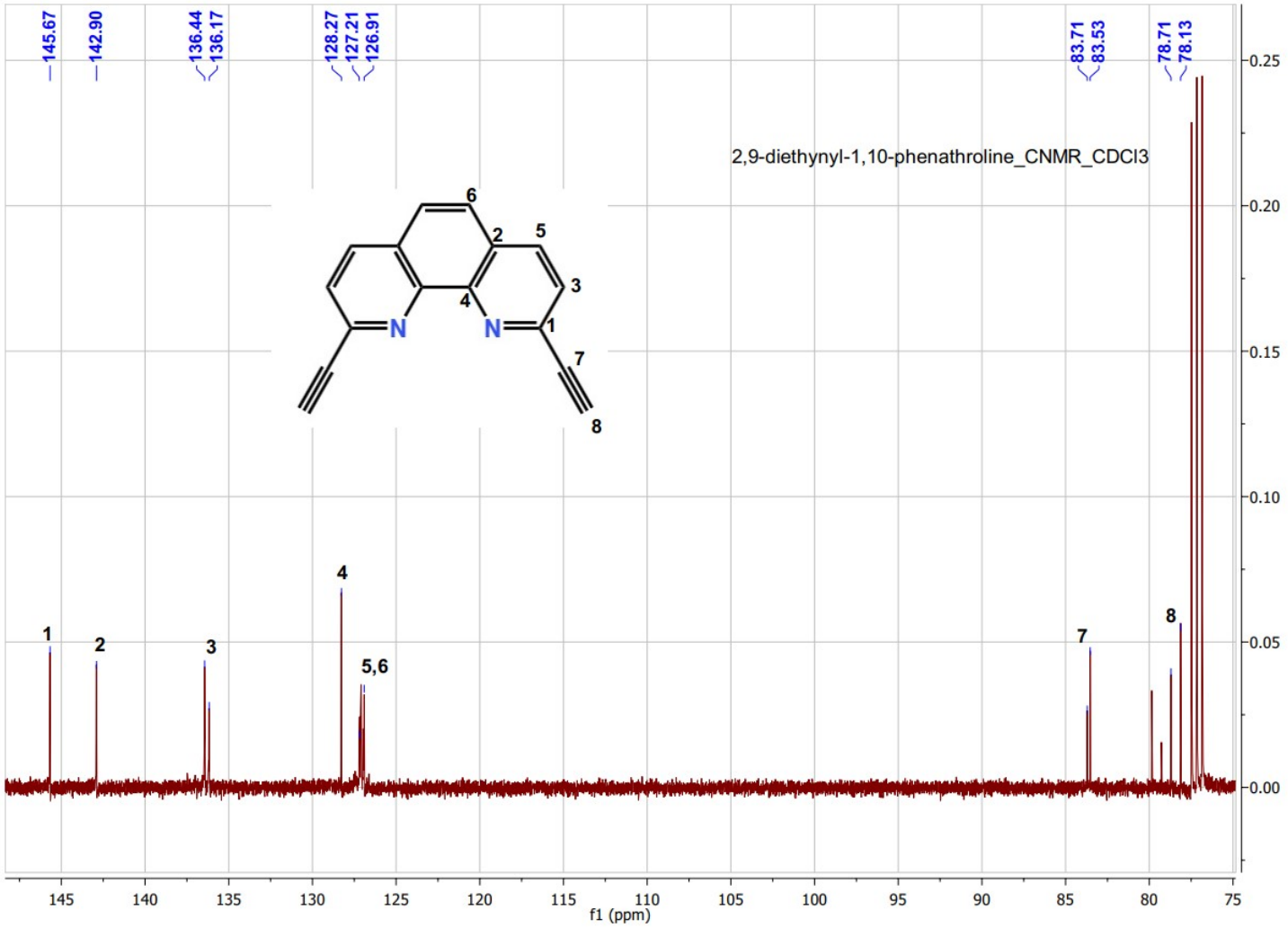
2.3.1. NMR

2.3.1.1. 2,9-Diethynyl-1,10-Phenanthroline (PhenDE, Compound **3,** ^{1}H-NMR, $CDCl_3$)



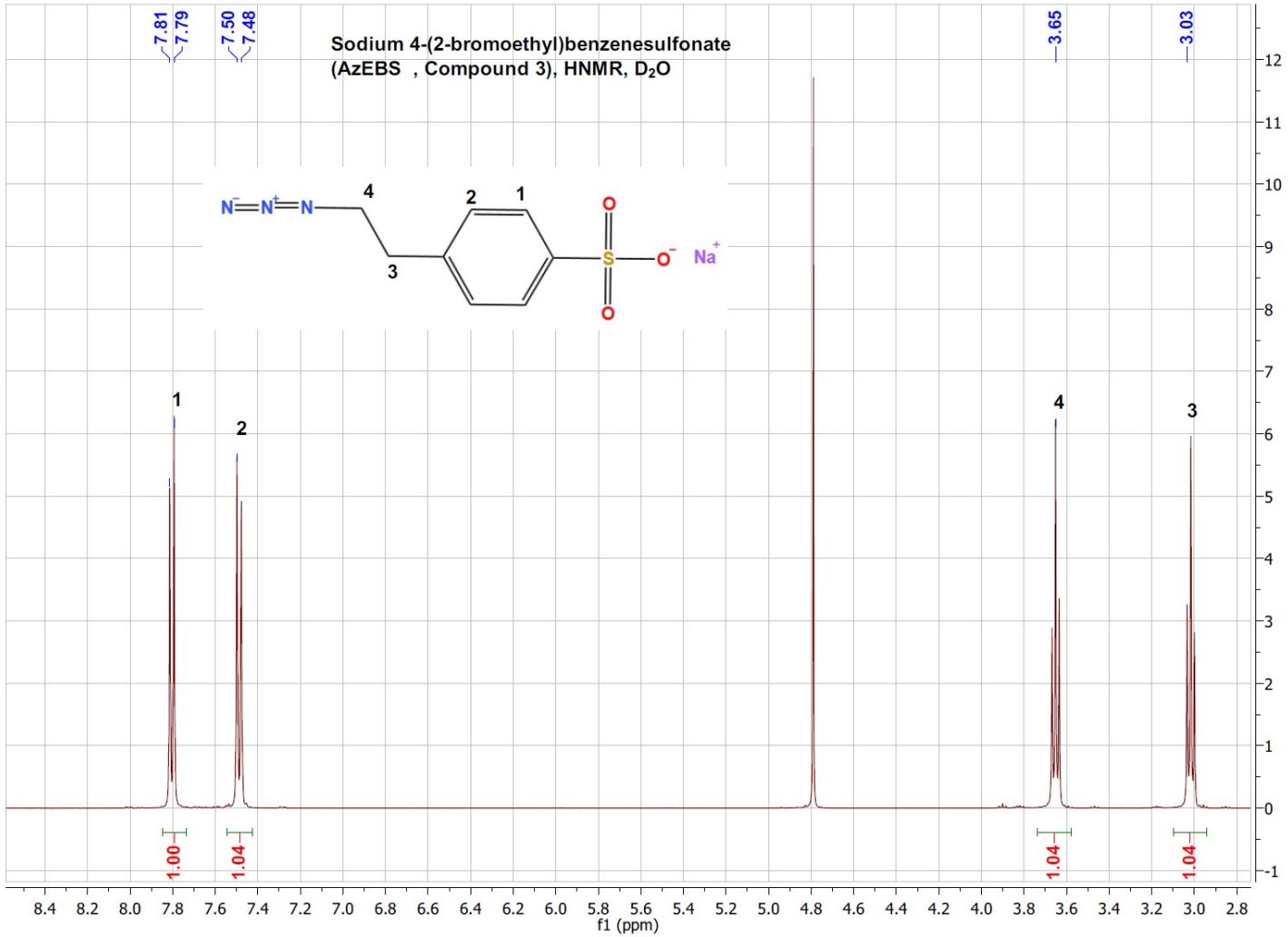
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20-8.18 (d, *J* = 8.2 Hz, 2H), 7.78-7.76 (d, *J* =8.3 Hz, 4H), 3.29 (3, *2*H)

2,9-Diethynyl-1,10-Phenanthroline (PhenDE, Compound **3**, ^{13}C-NMR, $CDCl_3$)



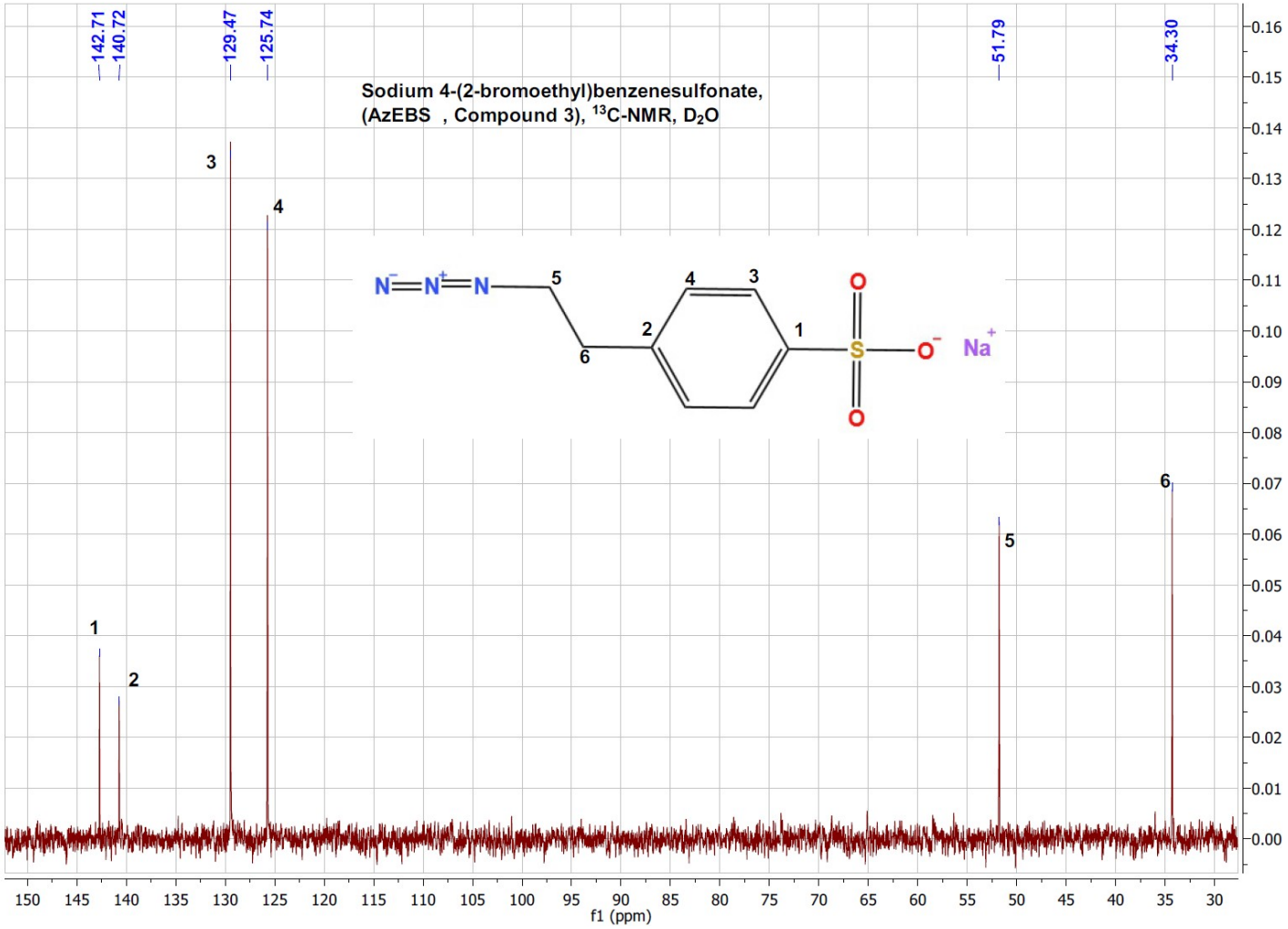
^{13}C NMR (400 MHz, D2O) δ (ppm): 145.67 (2C), 142.90 (2C), 136.44-136.17 (2C), 128.27 (2C), 127.21 (2C), 126.91 (2C), 83.71-83.53 (2C), 78.71-78.13 (2C)

2.3.1.2 Sodium 4-(2-azidoethyl)benzenesulfonate (AzEBS, Compound **4**, ^{1}HMR, D_2O)



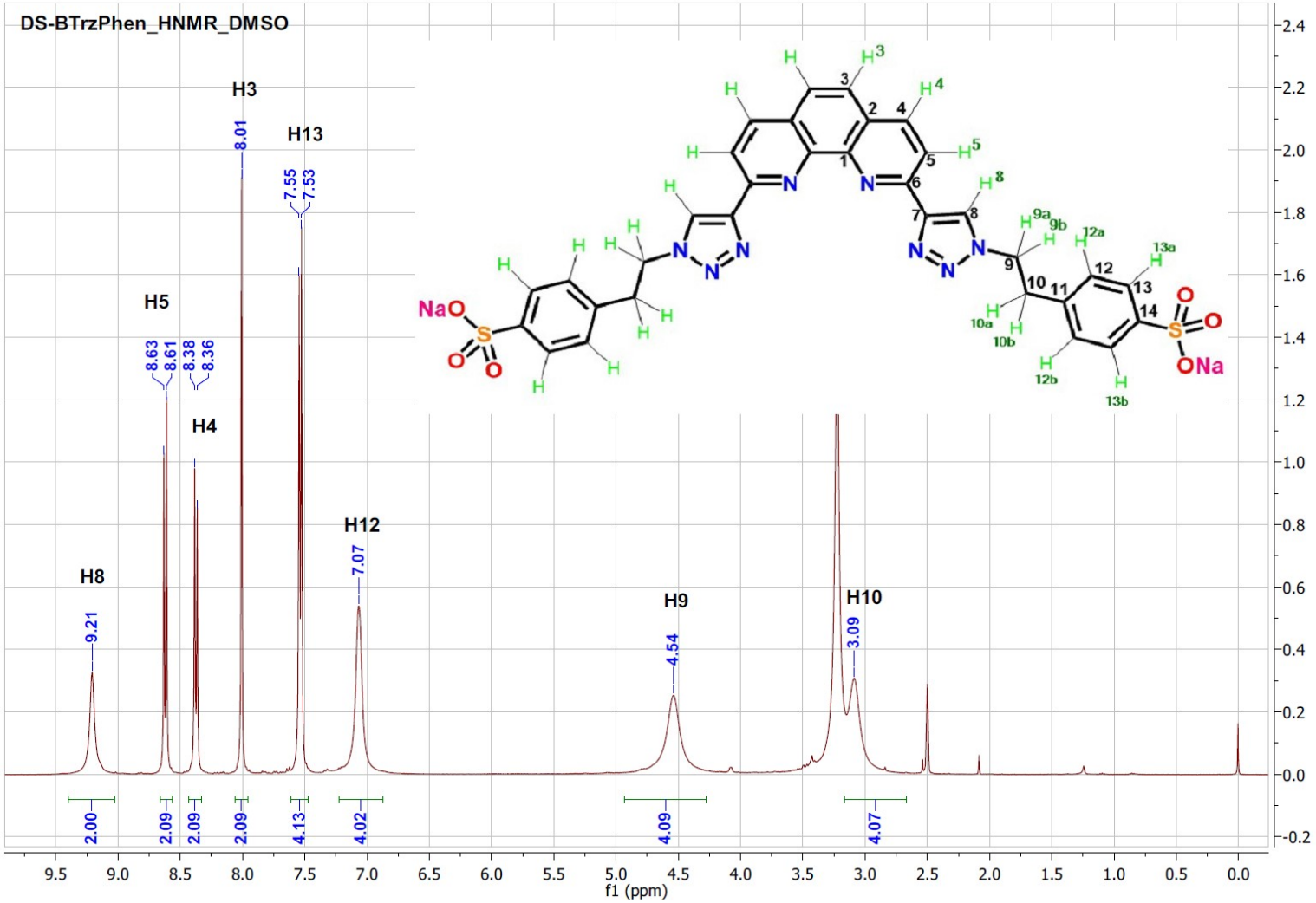
^{1}H NMR (400 MHz, D_2O) δ (ppm): 7.81-7.79 (d, J = 8.4 Hz, 2H), 7.50-7.48 (d, J =8.3 Hz, 2H), 3.65 (t, J = 6.8, 2H), 3.03 (t, J = 6.8, 2H)

Sodium 4-(2-azidoethyl)benzenesulfonate (AzEBS, Compound **4**, ^{13}C-NMR, D_2O)

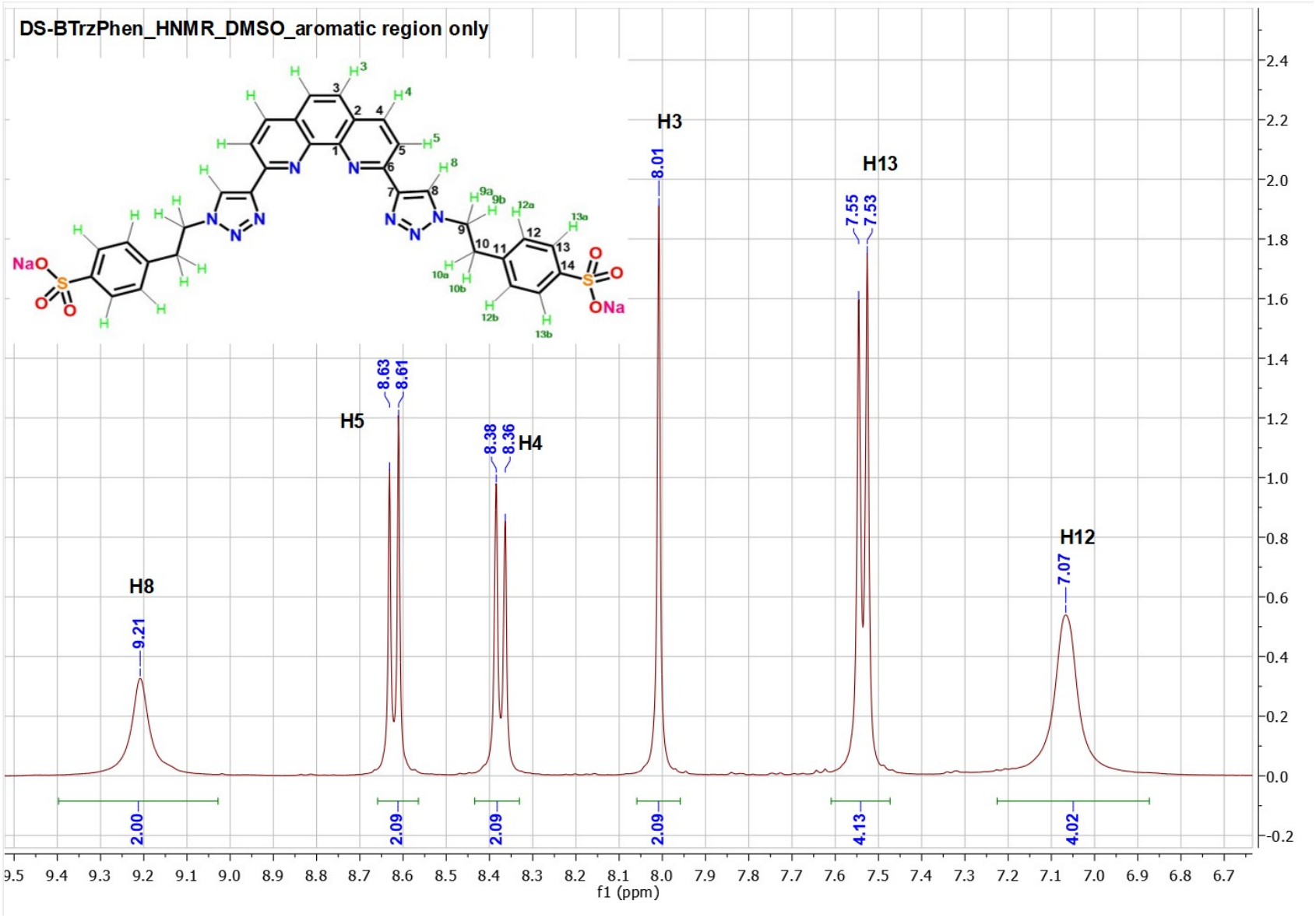


^{13}C NMR (400 MHz, D2O) δ (ppm): 142.71 (1C), 140.72 (1C), 129.47 (2C), 125.74 (2C), 51.79 (1C), 34.30 (1C)

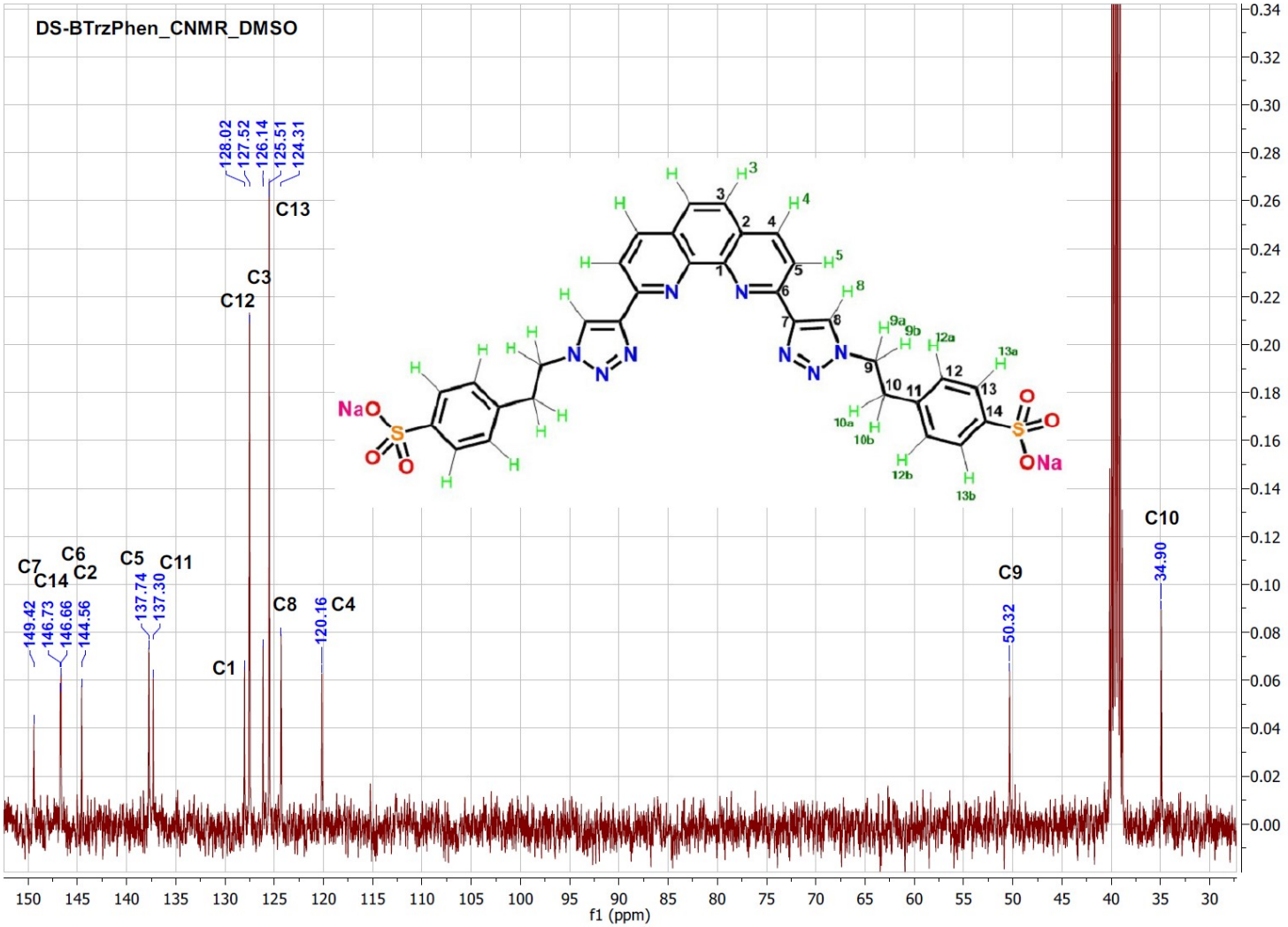
2.3.1.3. DS-BTrzPhen, Ligand **1**, ^{1}H-NMR, DMSO-d_6 @ 80°C



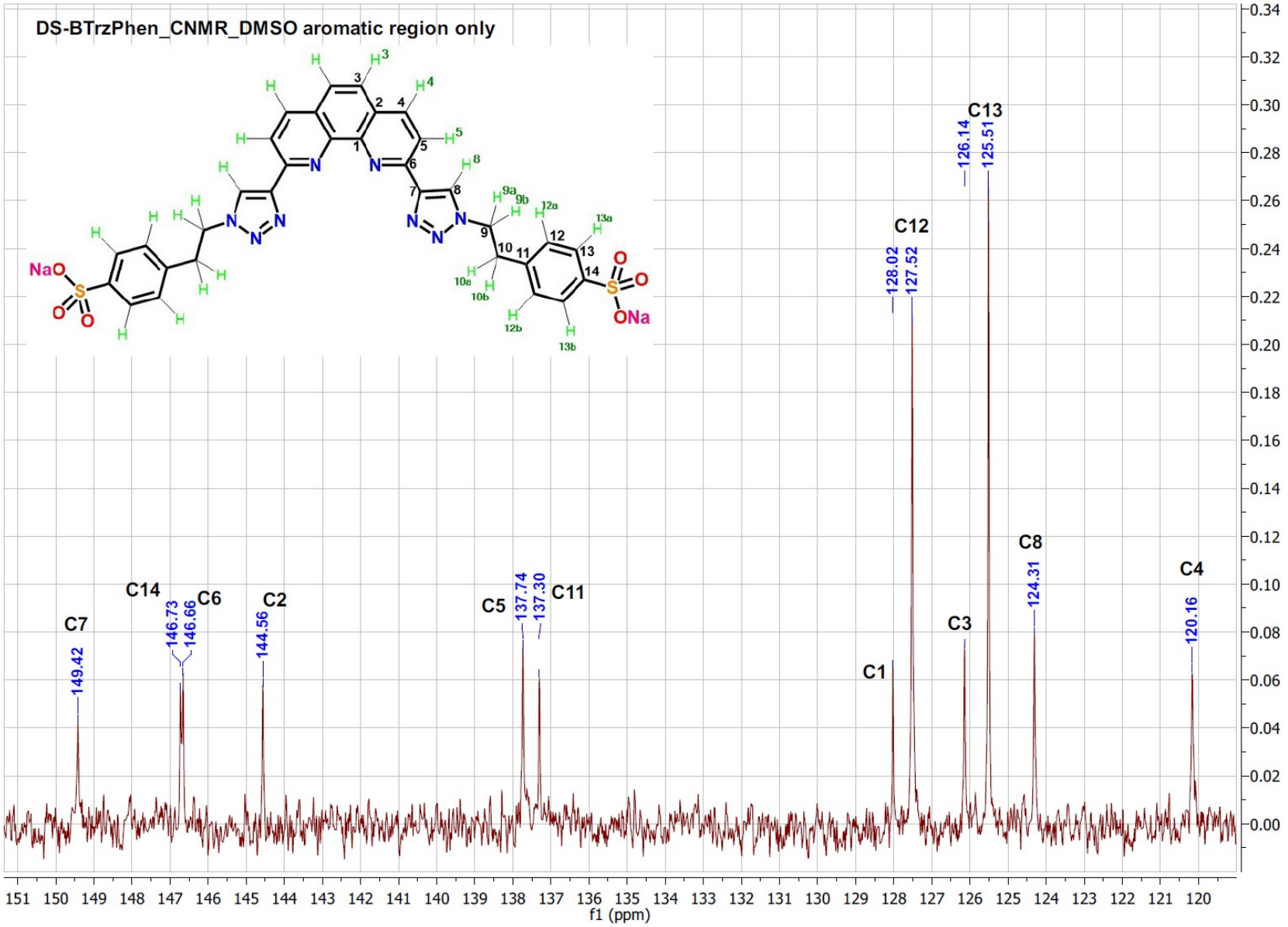
^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.21 (s, 2H), 8.63-8.61 (d, J = 8.4 Hz, 2H), 8.38-8.36 (d, J =8.2 Hz, 2H), 8.01 (s, 2H), 7.55-7.53 (d, J =8.1 Hz, 4H), 7.07 (s, 4H), 4.54 (s, 4H), 3.09 (s, 4H)


DS-BTrzPhen_HNMR_DMSO_aromatic region only
NaO
ONa
H3
8.01
H13
7.55
7.53
H5
8.63
8.61
H4
8.38
8.36
H8
9.21
H12
7.07
2.00
2.09
2.09
2.09
4.13
4.02
f1 (ppm)

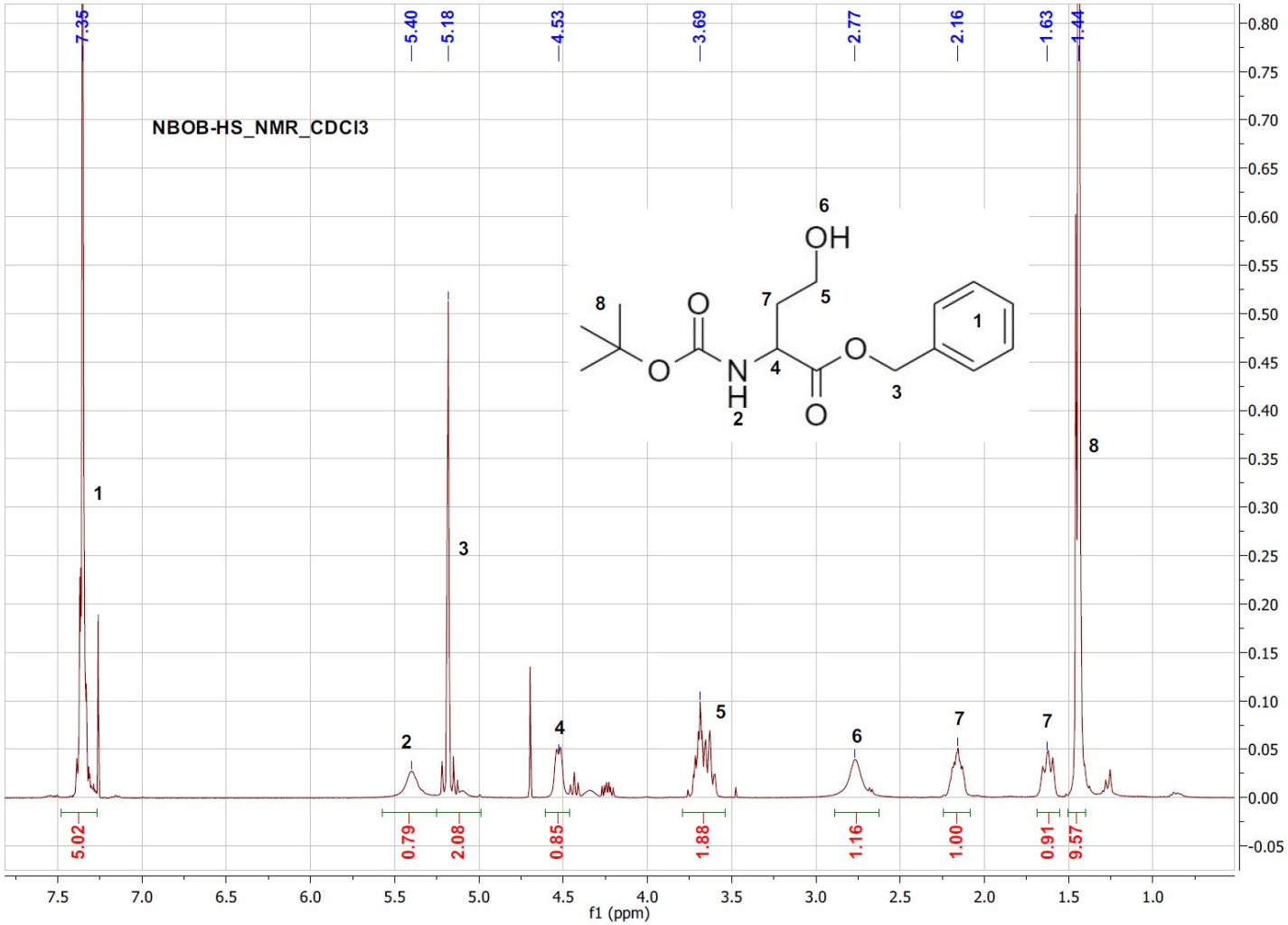
DS-BTrzPhen, Ligand **1**, ^{13}C-NMR, DMSO-d_6 @ 80°C



^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm): 149.42 (2C), 146.73 (2C), 146.66 (2C), 144.56 (2C), 137.74 (2C), 137.30 (2C), 128.02 (2C), 127.52 (2C), 126.14 (2C), 125.51 (2C), 124.31 (2C), 120.16 (2C), 50.32 (2C), 34.90 (2C)

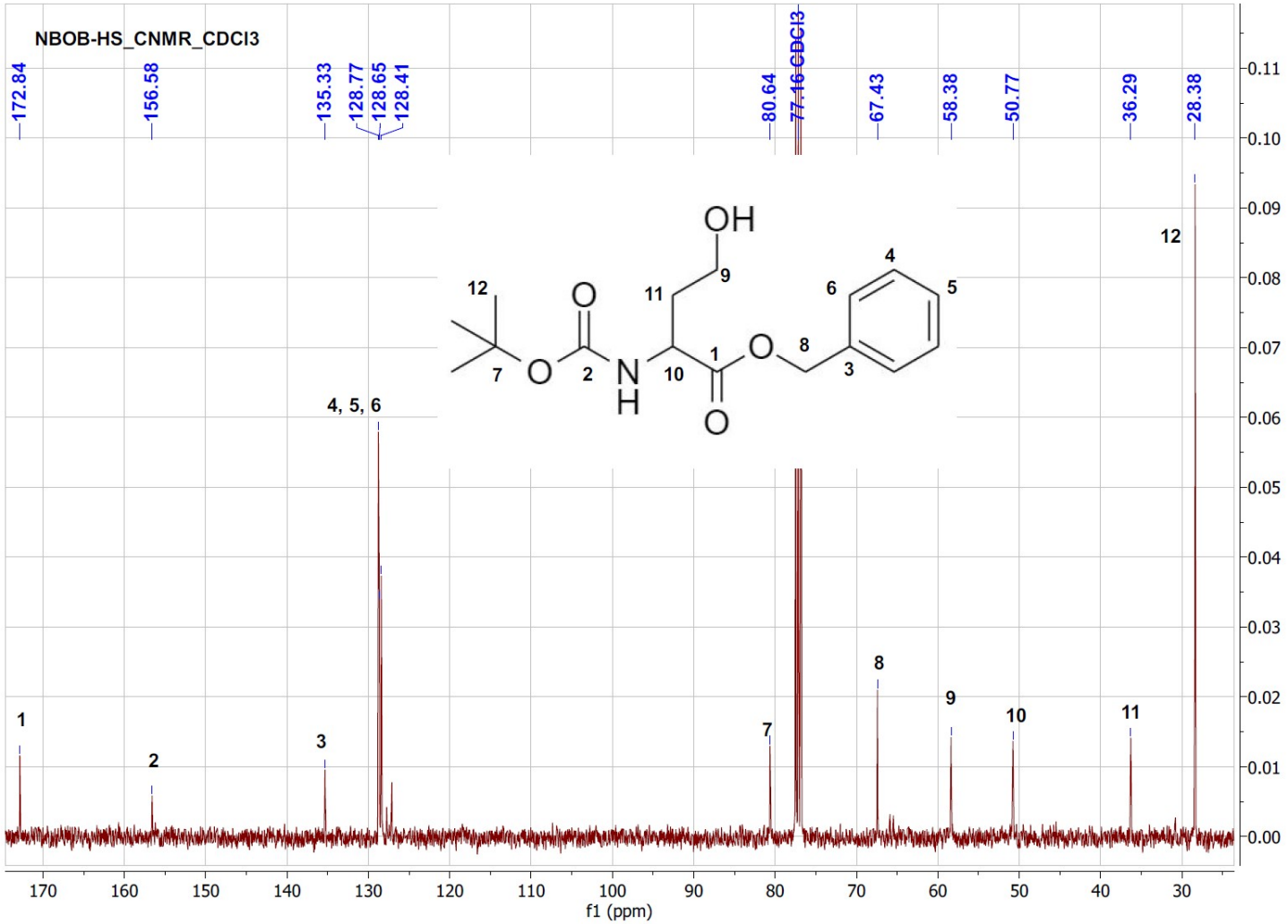

DS-BTrzPhen_CNMR_DMSO aromatic region only
NaO
S
O
O
ONa
C7
149.42
C14
146.73
146.66
C6
C2
144.56
C5
137.74
137.30
C11
C1
C12
128.02
127.52
C3
C13
126.14
125.51
C8
124.31
C4
120.16
f1 (ppm)

2.3.1.4. Benzyl (tert-butoxycarbonyl) homoserinate (NBOB-HS, Compound **5**, ^{1}H-NMR, $CDCl_3$)



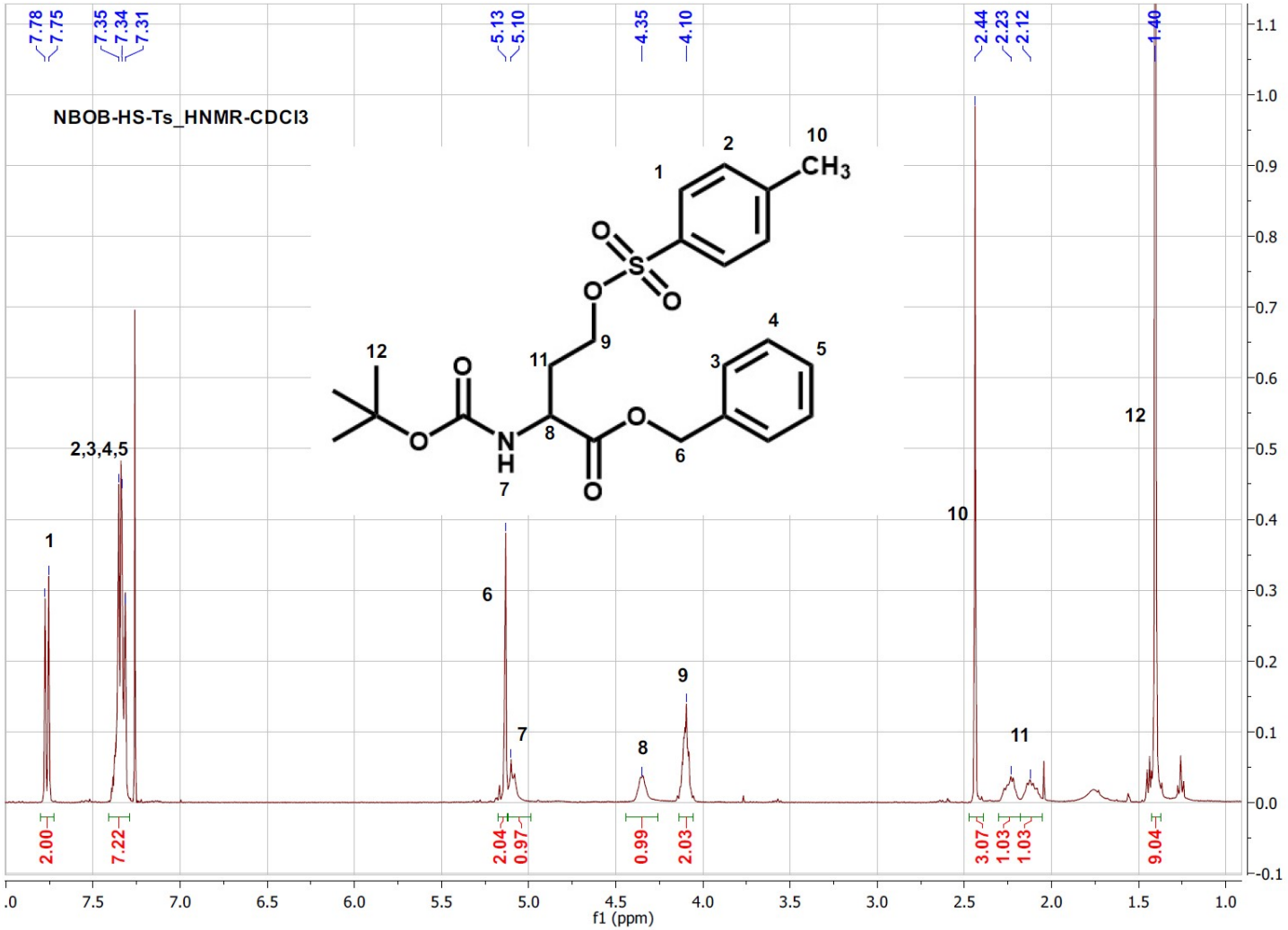
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35 (m, 5H), 5.40 (s, 1H), 5.18 (m, 2H), 4.53 (m, 1H), 3.69 (m, 2H), 2.77 (s, 1H), 2.16 (m, 1H), 1.63 (m, 1H), 1.44 (s, 9H)

Benzyl (tert-butoxycarbonyl) homoserinate (NBOB-HS, Compound **5**, ^{13}C-NMR, $CDCl_3$)



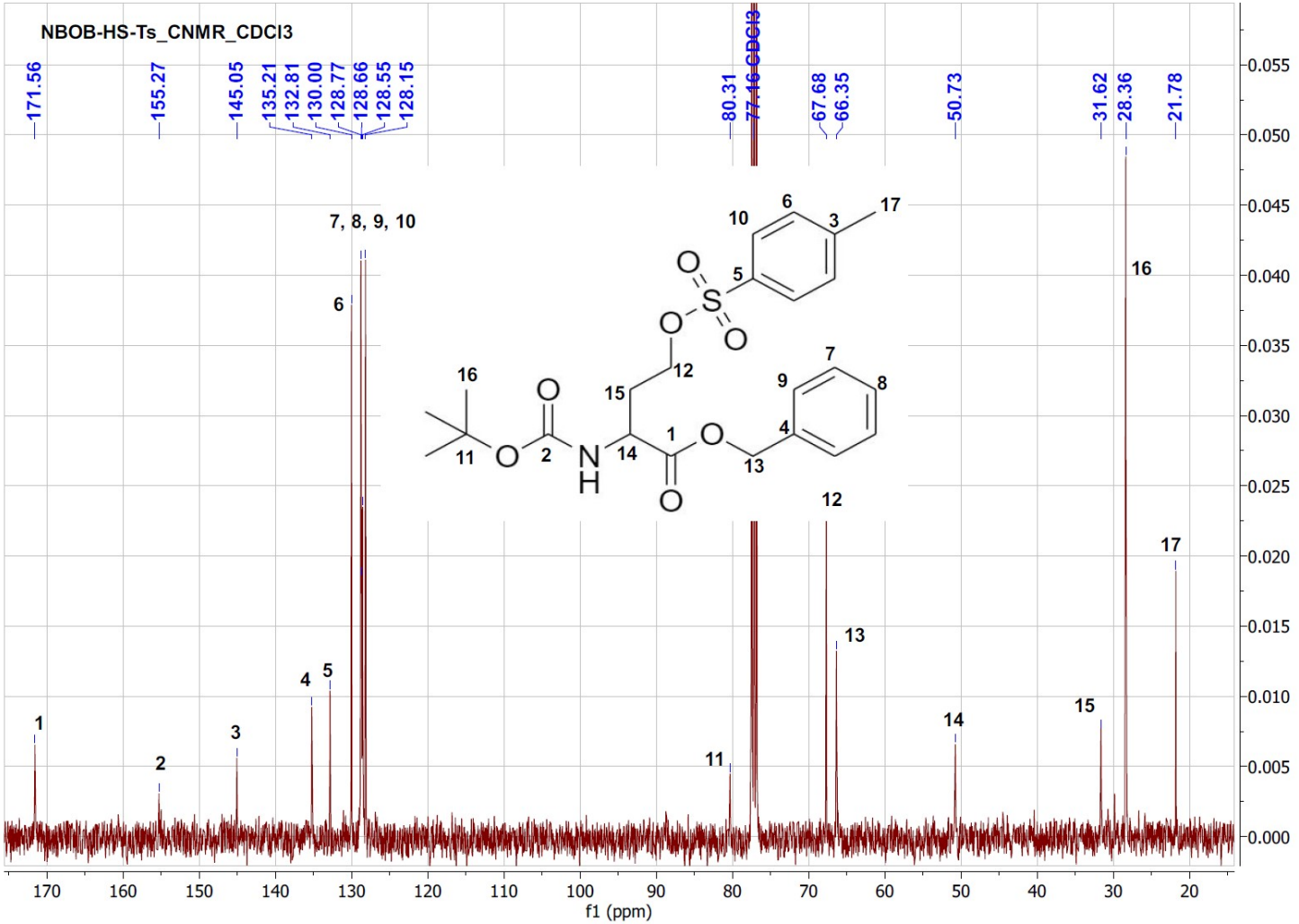
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 172.84 (1C), 156.58 (1C), 135.33 (1C), 128.77 (2C), 128.65 (1C), 128.41 (2C), 80.64 (1C), 67.43 (1C), 58.38 (1C), 50.77 (1C), 36.29 (1C), 28.38 (3C)

2.3.1.5. Benzyl N-(tert-butoxycarbonyl)-O-tosylhomoserinate (NBOB-HS-Ts, Compound **6**, ^{1}H-NMR, $CDCl_3$)



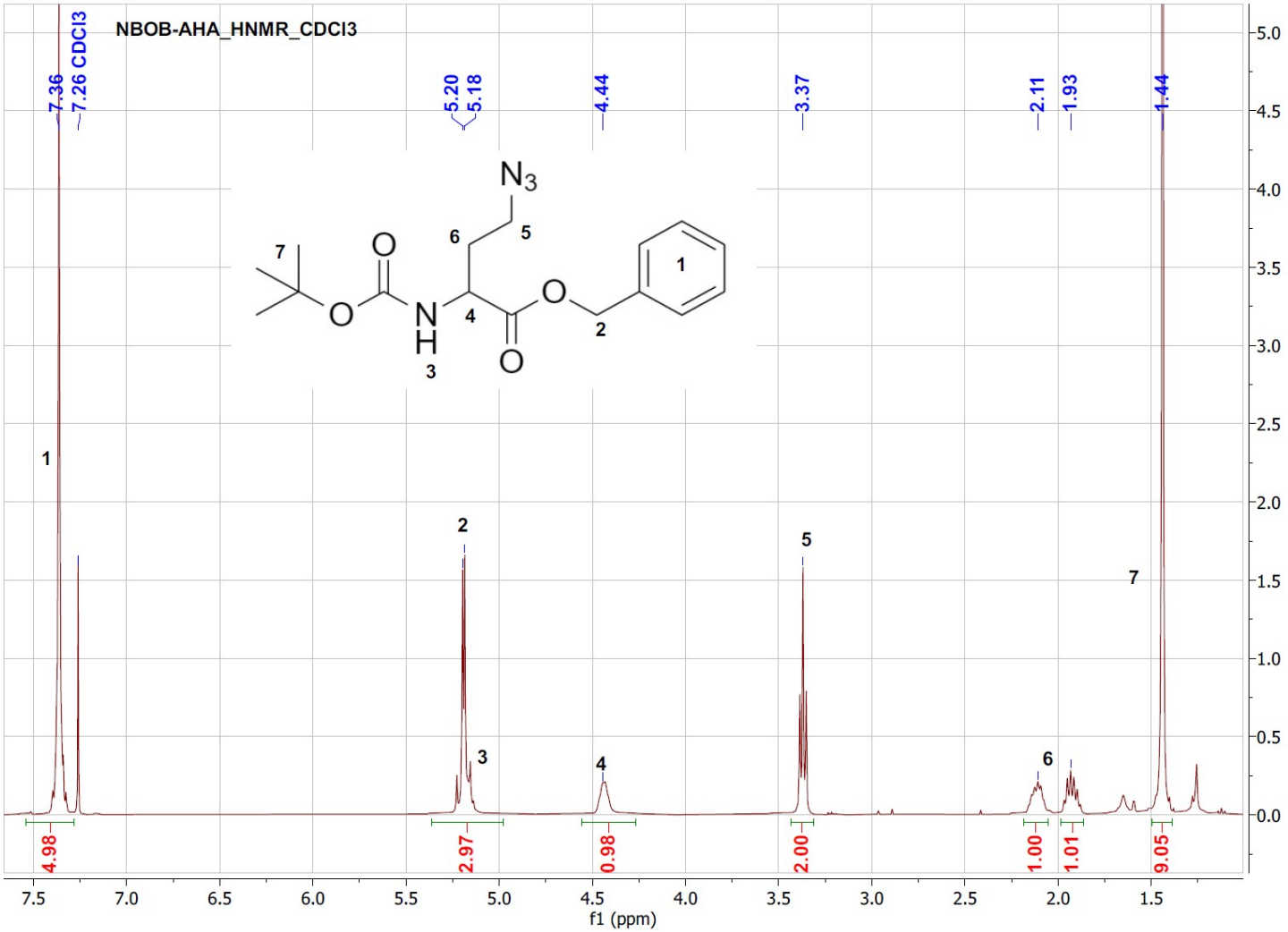
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78-7.75 (d, J = 8.3 Hz, 2H), 7.35-7.31 (m, 7H), 5.13 (s, 2H), 5.10 (m, 1H), 4.35 (s, 1H), 4.10 (m, 2H), 2.44 (s, 3H), 2.23 (m, 1H), 212 (m, 1H), 1.40 (s, 9H)

Benzyl N-(tert-butoxycarbonyl)-O-tosylhomoserinate (NBOB-HS-Ts, Compound **6**, ^{13}C-NMR, $CDCl_3$)



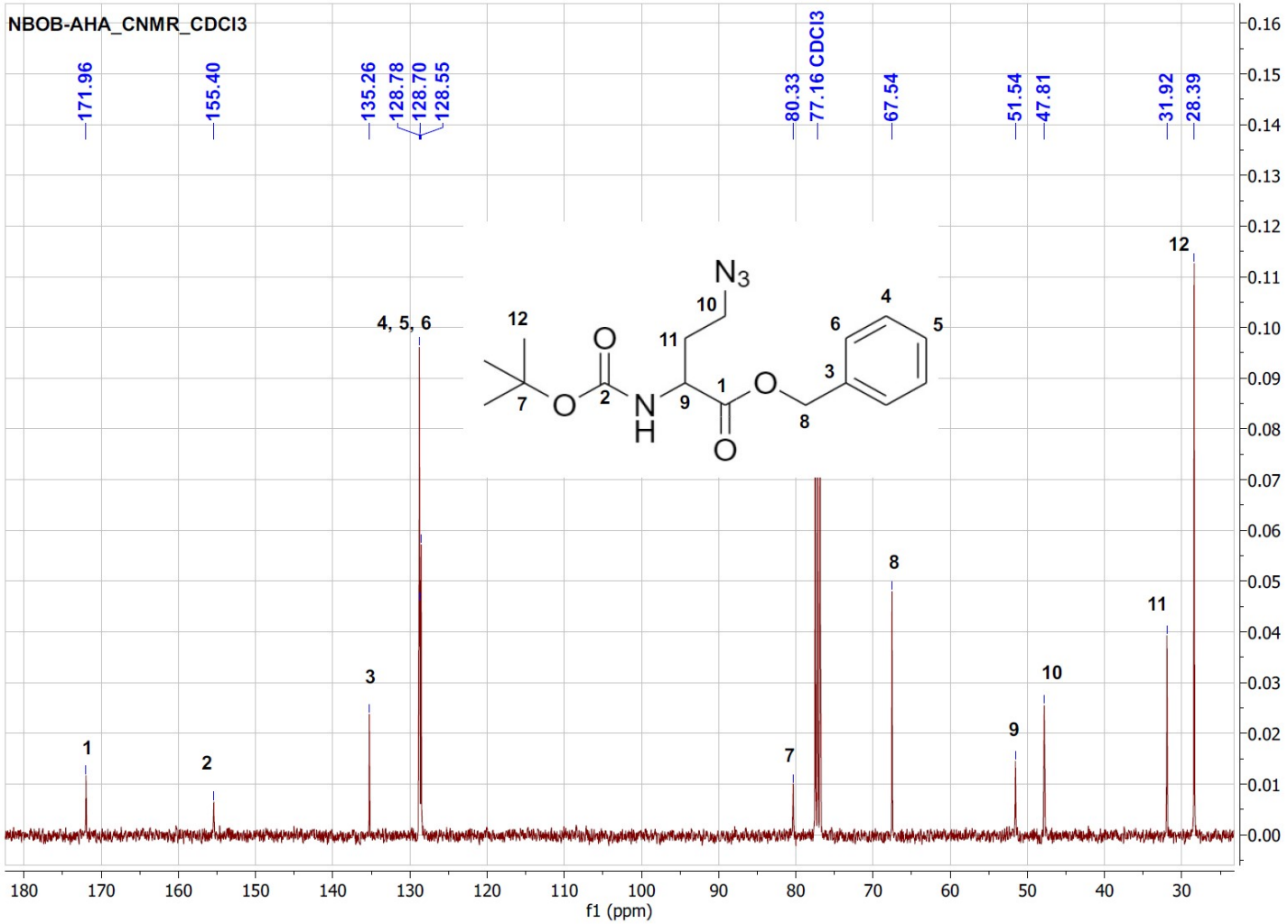
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 171.56 (1C), 155.27 (1C), 145.05 (1C), 135.21 (1C), 132.81 (1C), 130.00 (2C), 128.77 (2C), 128.66 (1C), 128.55 (2C), 128.15 (2C), 80.31 (1C), 67.68 (1C) 66.35 (1C), 50.73 (1C), 31.62 (1C), 28.36 (3C), 21.78 (1C)

2.3.1.6. Benzyl 4-azido-2-*N*-((tert-butoxycarbonyl)amino)butanoate (NBOB-AHA, Compound **7**, ^{1}H-NMR, $CDCl_3$)



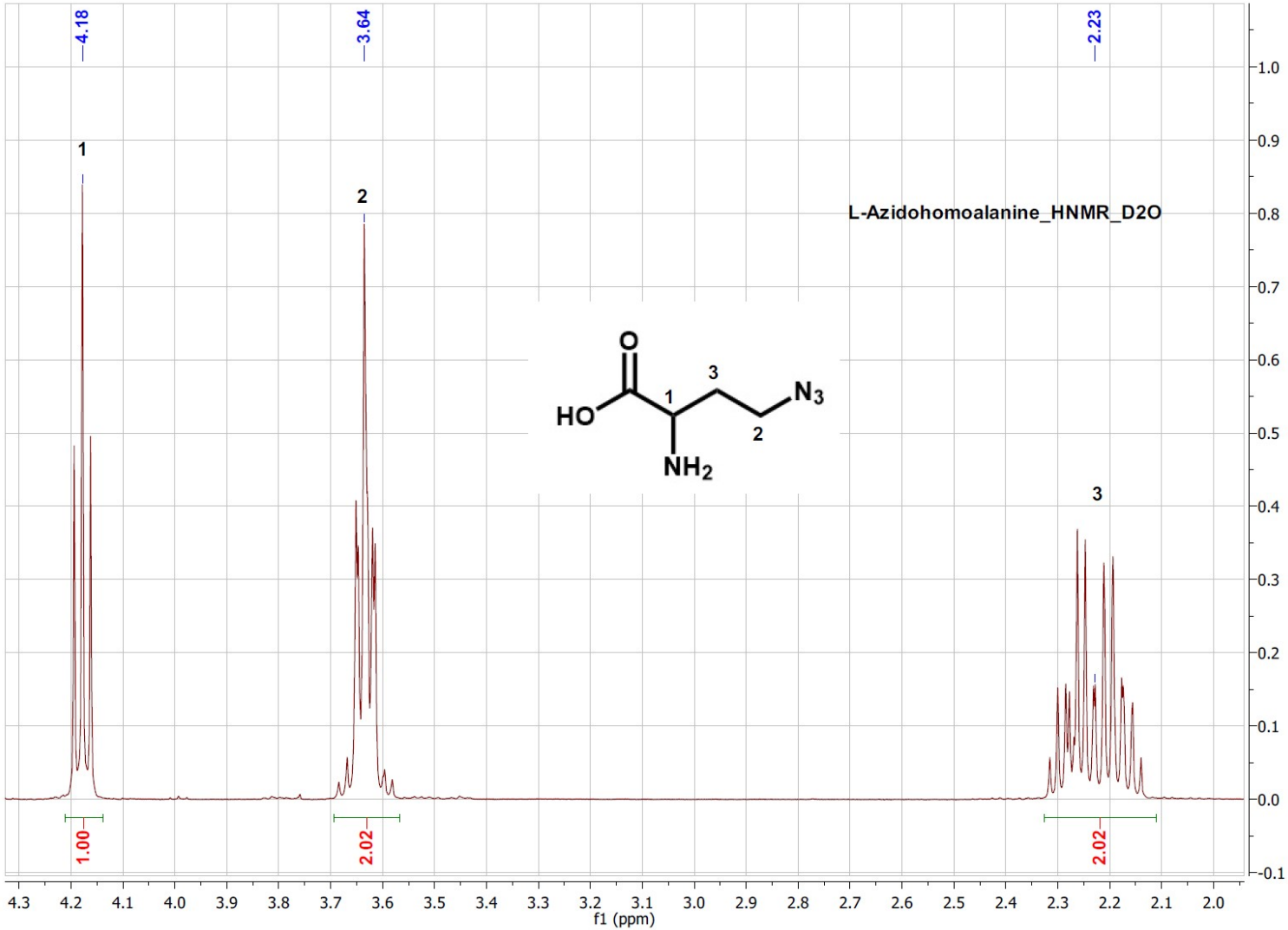
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.26 (m, 5H), 5.20-5.18 (m, 3H), 4.44 (s, 1H), 3.37 (t, J = 6.7 Hz, 2H), 2.21 (m, 1H), 1.93 (m, 1H), 1.44 (s, 9H)

Benzyl 4-azido-2-((tert-butoxycarbonyl)amino)butanoate (NBOB-AHA, Compound **7**, ^{13}C-NMR, $CDCl_3$)



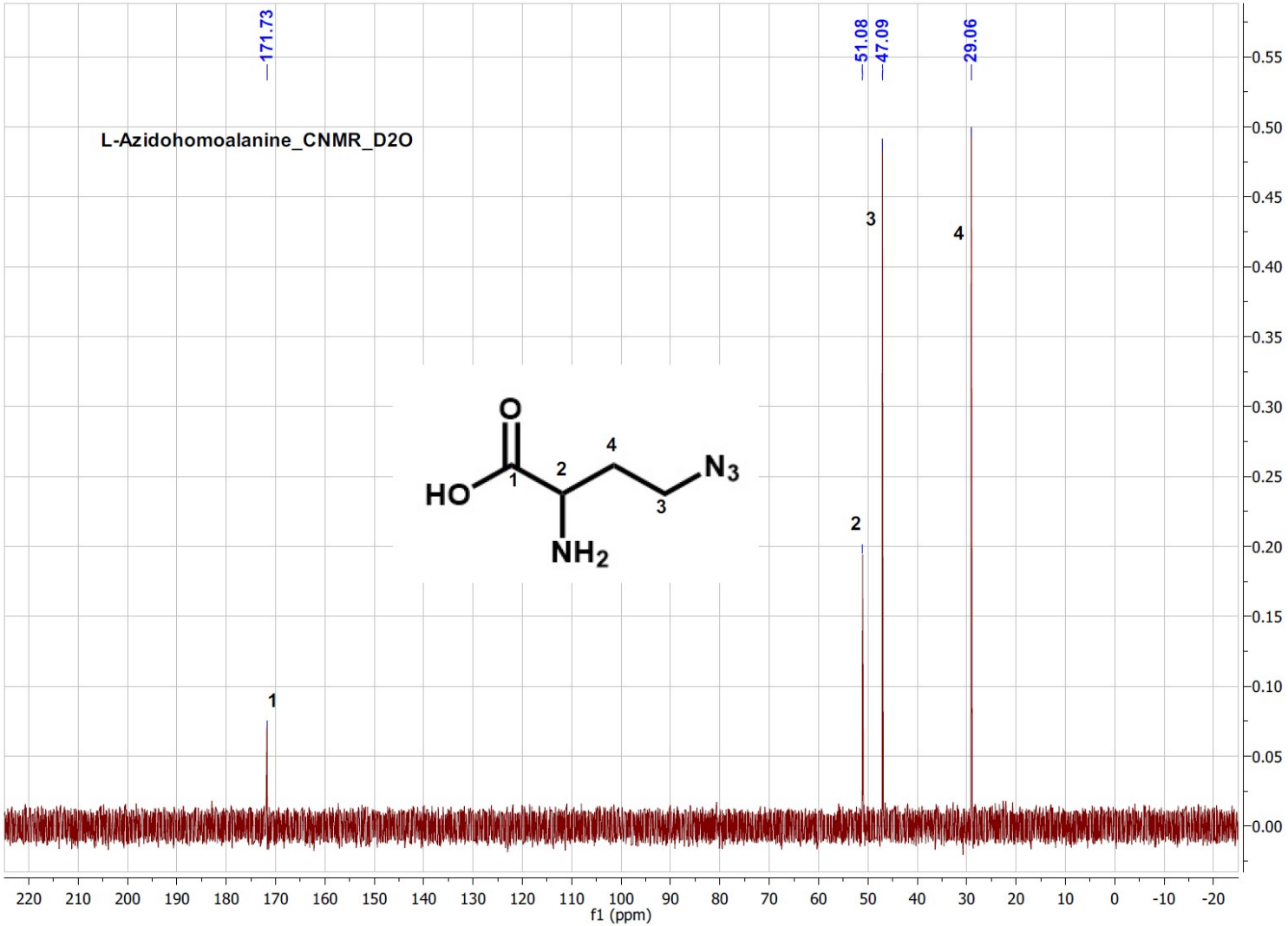
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 171.96 (1C), 155.40 (1C), 135.26 (1C), 128.78 (2C), 128.70 (1C), 128.55 (2C), 80.33 (1C), 67.54 (1C) 51.54 (1C), 47.81 (1C), 31.92 (1C), 28.39 (3C)

2.3.1.7. L-Azidohomoalanine hydrochloride (L-AHA, Compound **8**, ^{1}H-NMR, D_2O)



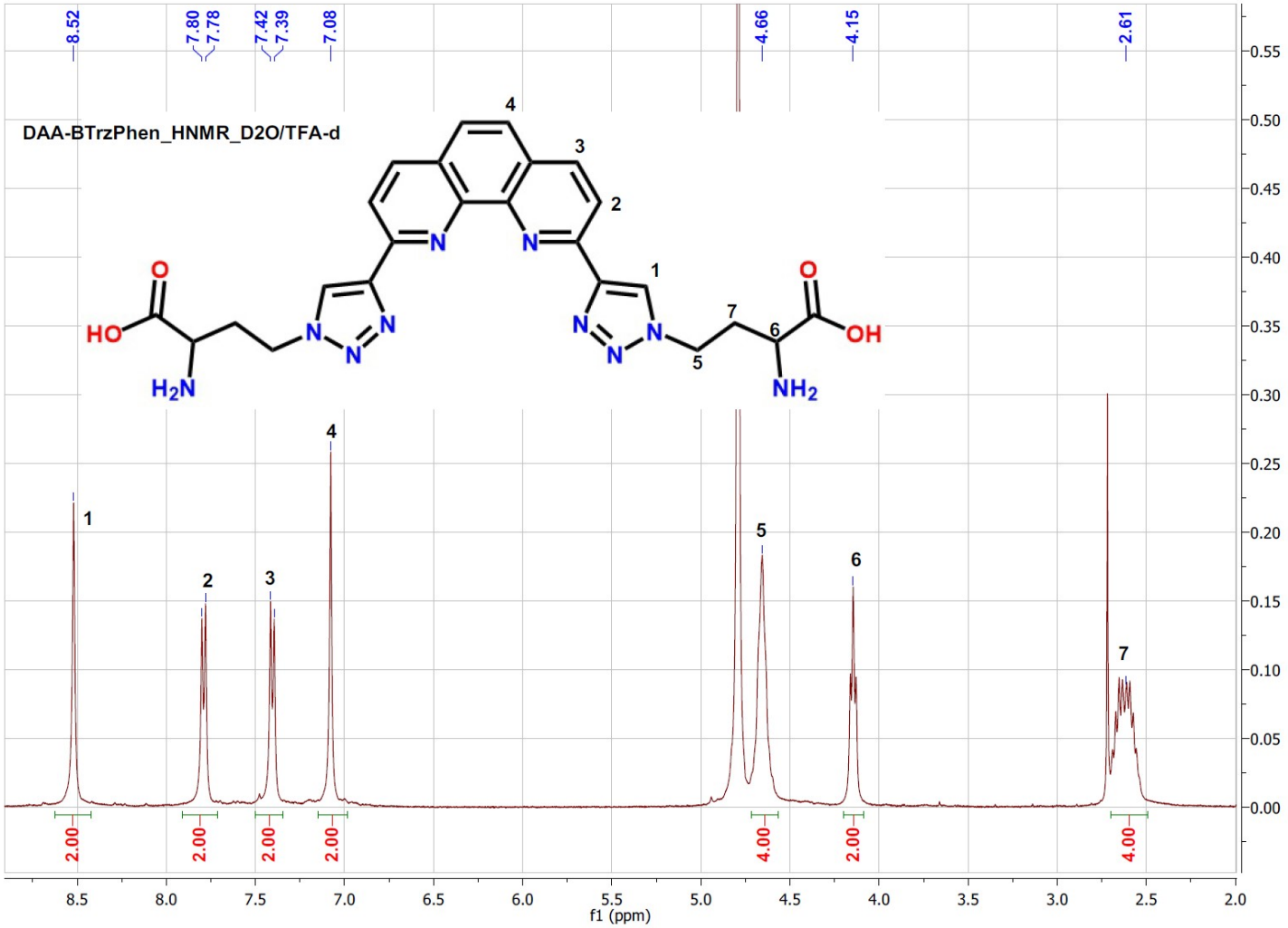
^{1}H NMR (400 MHz, D_2O) δ (ppm): 4.18 (t, J = 6.4 Hz, 1H), 3.64 (m, 2H), 2.23 (m, 2H)

L-Azidohomoalanine hydrochloride (L-AHA, Compound **8**, ^{13}C-NMR, D_2O)



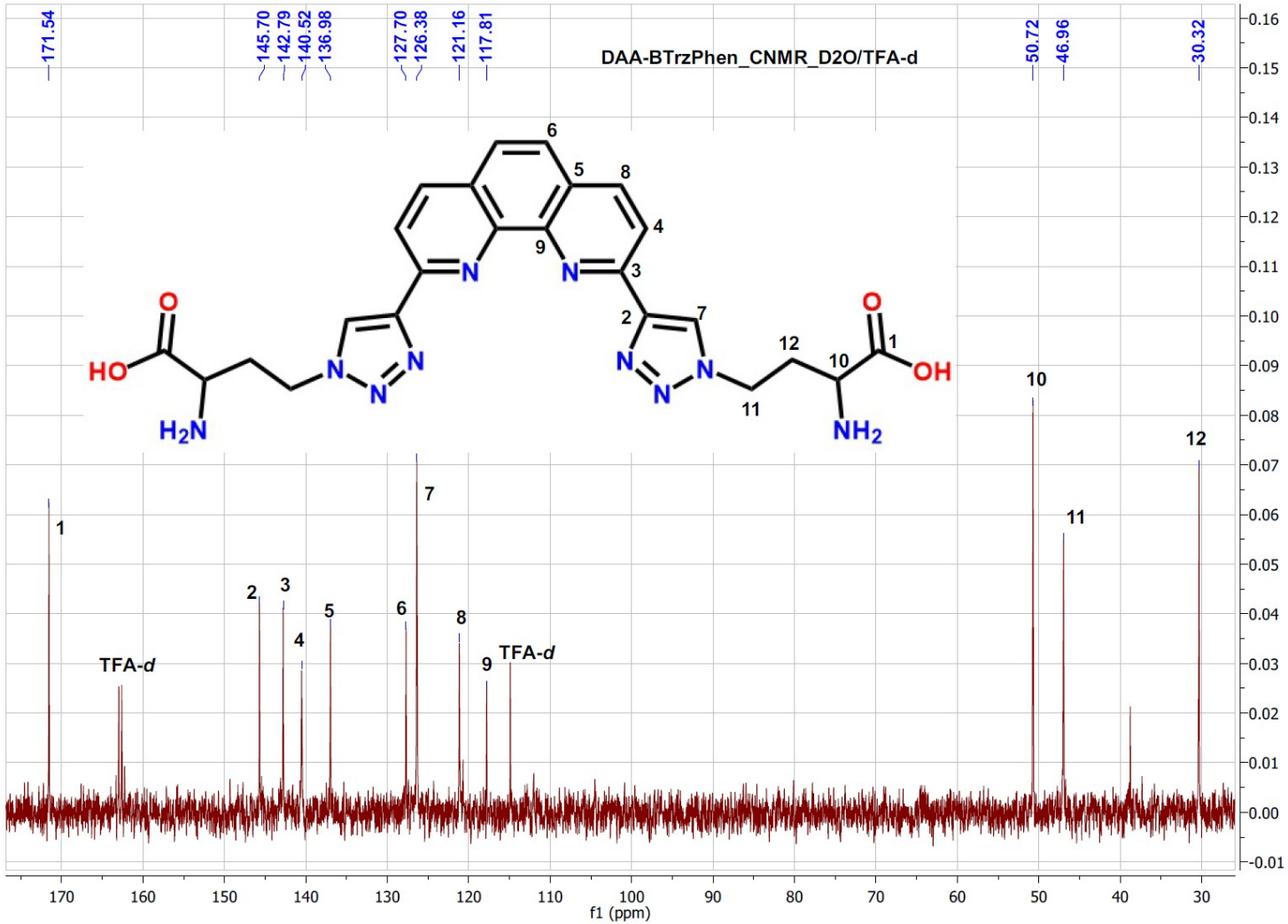
^{13}C NMR (400 MHz, D_2O) δ (ppm): 171.73 (1C), 51.08 (1C), 47.09 (1C), 29.06 (1C)

2.3.1.8. DAA-BTrzPhen, Ligand **2**, ^{1}H-NMR, D_2O/TFA-*d* @ 50°C



^{1}H NMR (400 MHz, D_2O/TFA-*d*) δ (ppm): 8.52 (s, 2H), 7.80-7.78 (d, *J* = 8.2 Hz, 2H), 7.42-7.39 (d, *J* =8.2 Hz, 2H), 7.08 (s, 2H), 4.66 (s, 4H), 4.54 (s, 4H), 4.15 (t, *J* = 6.5 Hz, 2H), 2.61 (m, 4H)

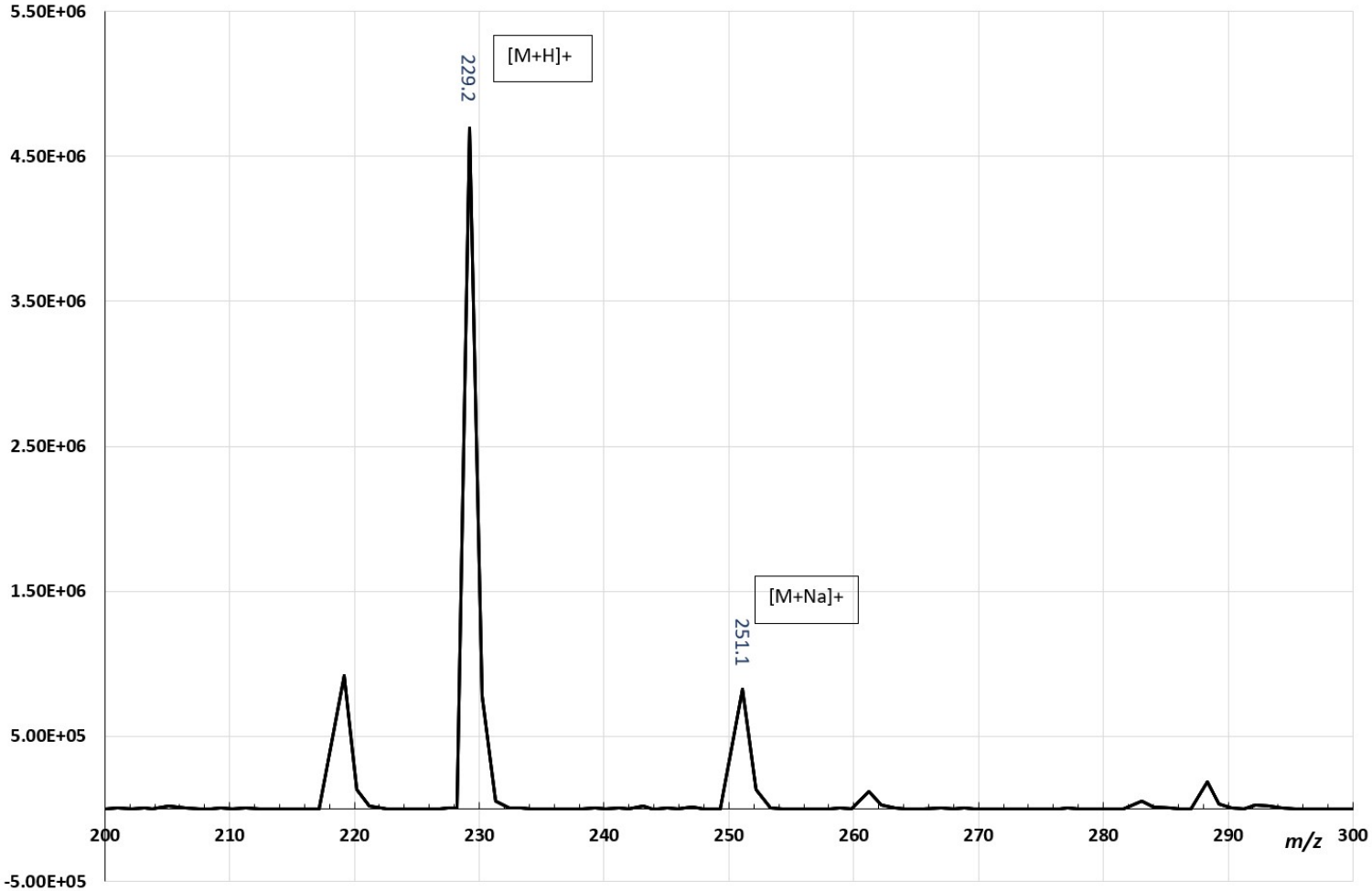
DAA-BTrzPhen, Ligand **2**, ^{13}C-NMR, D_2O/TFA-*d* @ 50°C



^{13}C NMR (400 MHz, D_2O/TFA-*d*) δ (ppm): 171.54 (2C), 145.70 (2C), 142.79 (2C), 140.52 (2C), 136.98 (2C), 127.70 (2C), 126.38 (2C), 121.16 (2C), 117.81 (2C), 50.72 (2C), 46.96 (2C), 30.32 (2C)

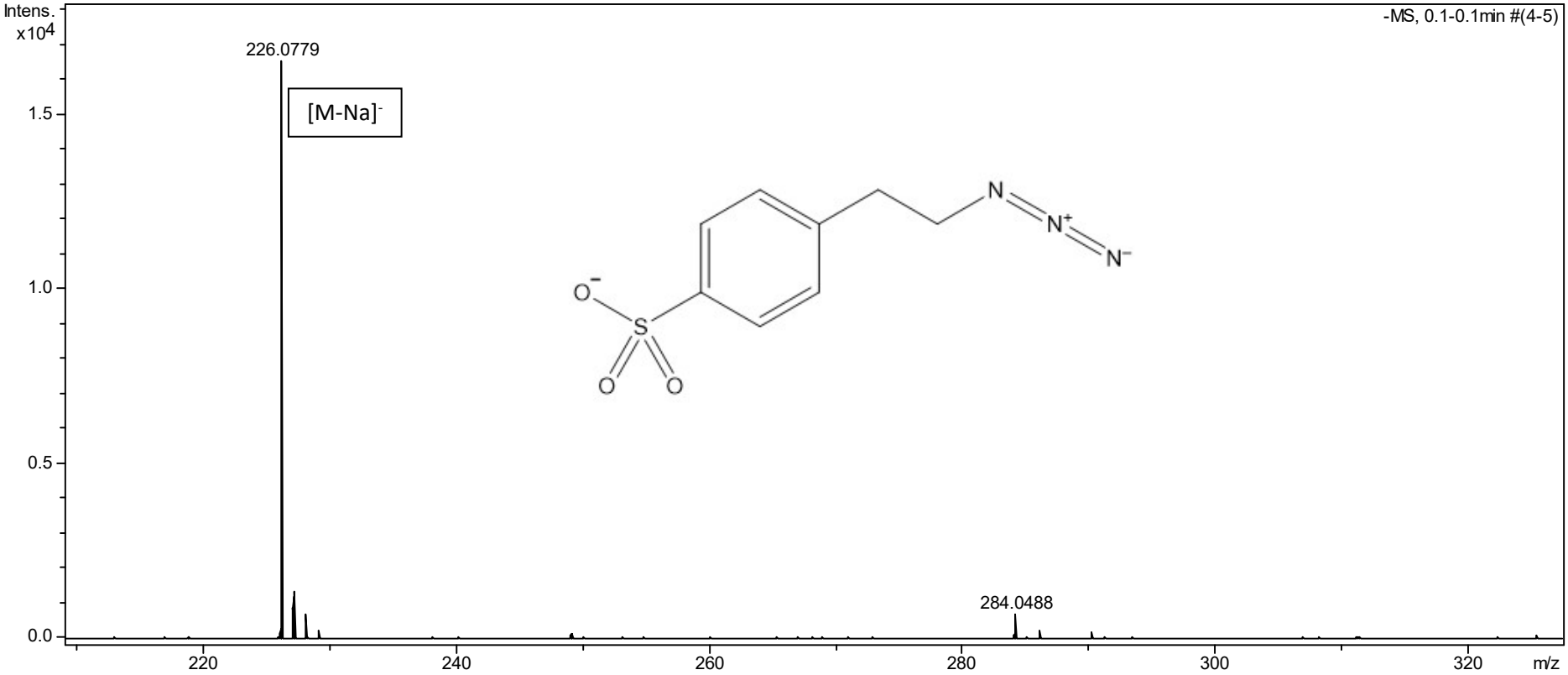
Mass spectra

2.3.2.1 2,9-Diethynyl-1,10-Phenanthroline (PhenDE, Compound **3**, APCI+)



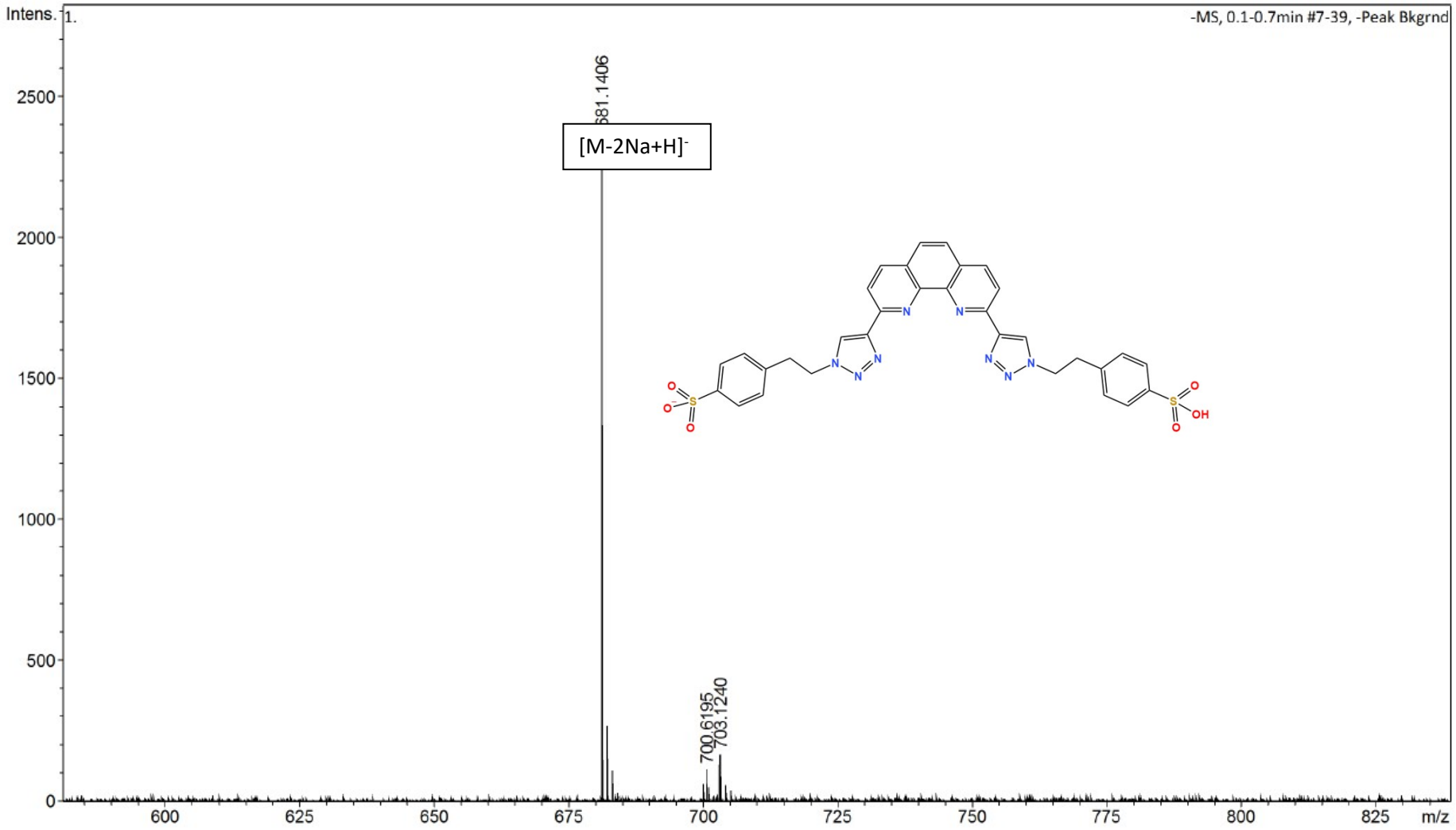
Method: APCI positive mode, Chemical Formula: $C_{16}H_9N_2$ as $[M+H]^+$, Exact Mass: 229.08, MS ($APCI^+$) *m/z* calcd. for $[M+H]^+$:229.08 found: 229.2, calcd. for $[M+Na]^+$:251.06 found: 251.1

2.3.2.2 Sodium 4-(2-azidoethyl)benzenesulfonate (AzEBS, Compound **4**, ESI$^-$)



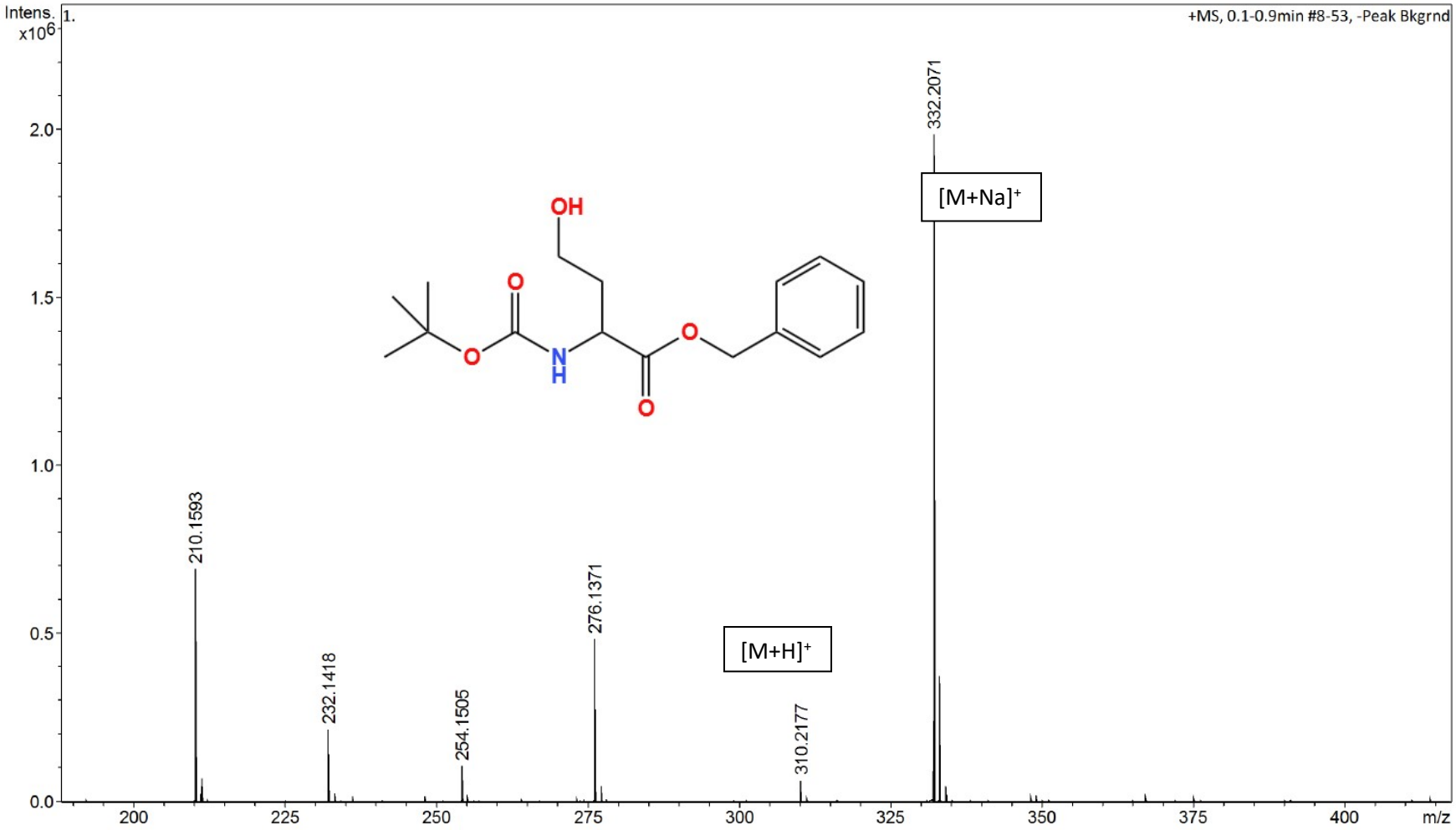
Method: ESI negative mode, Chemical Formula: $C_8H_8N_3O_3S^-$, $[M-Na]^-$, Exact Mass: 226.08, MS (ESI$^-$) *m/z* calcd. for $[M-Na]^-$:226.08 found: 226.0779

2.3.2.3 DS-BTrzPhen, Ligand **1** (ESI^-)



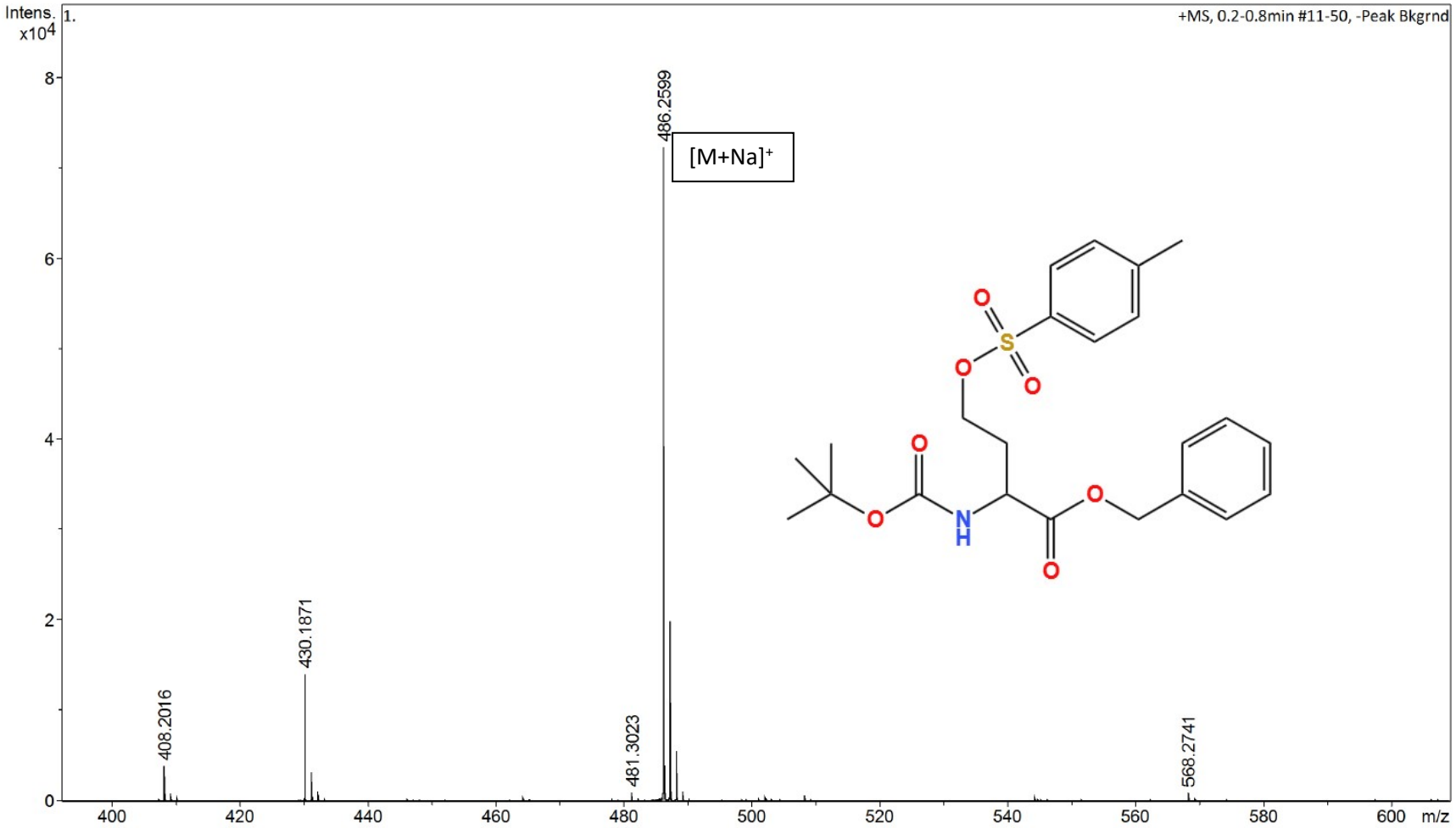
Method: ESI negative mode, Chemical Formula: $C_{32}H_{25}O_6N_8S_2^-$, $[M-Na+H]^-$, Exact Mass: 681.13, MS (ESI^-) *m/z* calcd. for $[M-Na+H]^-$: 681.14; found: 681.1406

2.3.2.4 Benzyl N-(*tert*-butoxycarbonyl) homoserinate (NBOB-HS, Compound **5**, ESI^+)



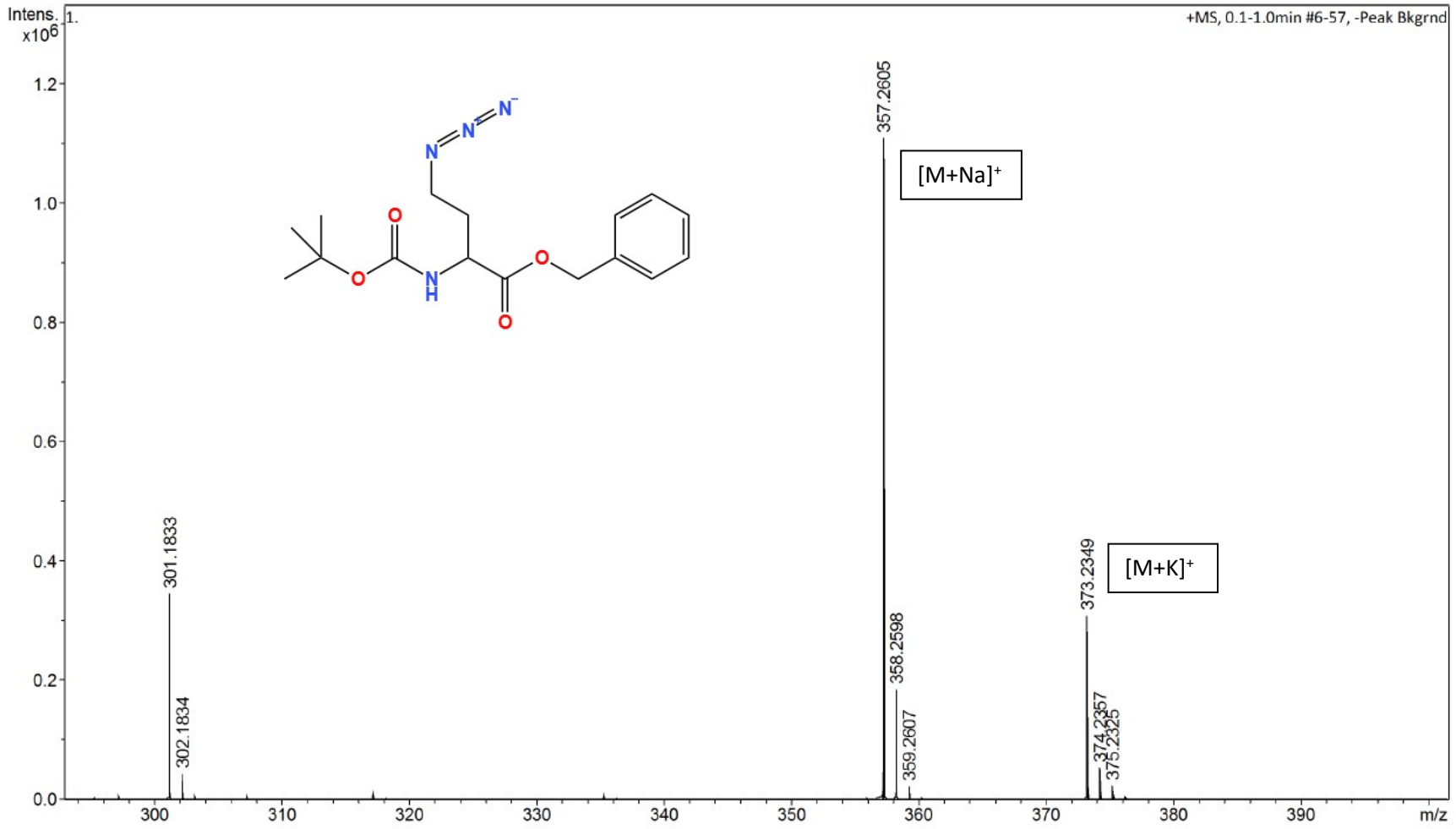
Method: ESI positive mode, Chemical Formula: $C_{16}H_{23}O_5N$+Na or $[M+Na]^+$, Exact Mass: 332.15, MS (ESI^+) *m/z* calcd. for $C_{16}H_{23}O_5N$+Na^+: or $[M+Na]^+$: 332.21; found: 332.2071.

2.3.2.5 Benzyl N-(tert-butoxycarbonyl)-O-tosylhomoserinate (NBOB-HS-Ts, Compound **6**, ESI$^+$)



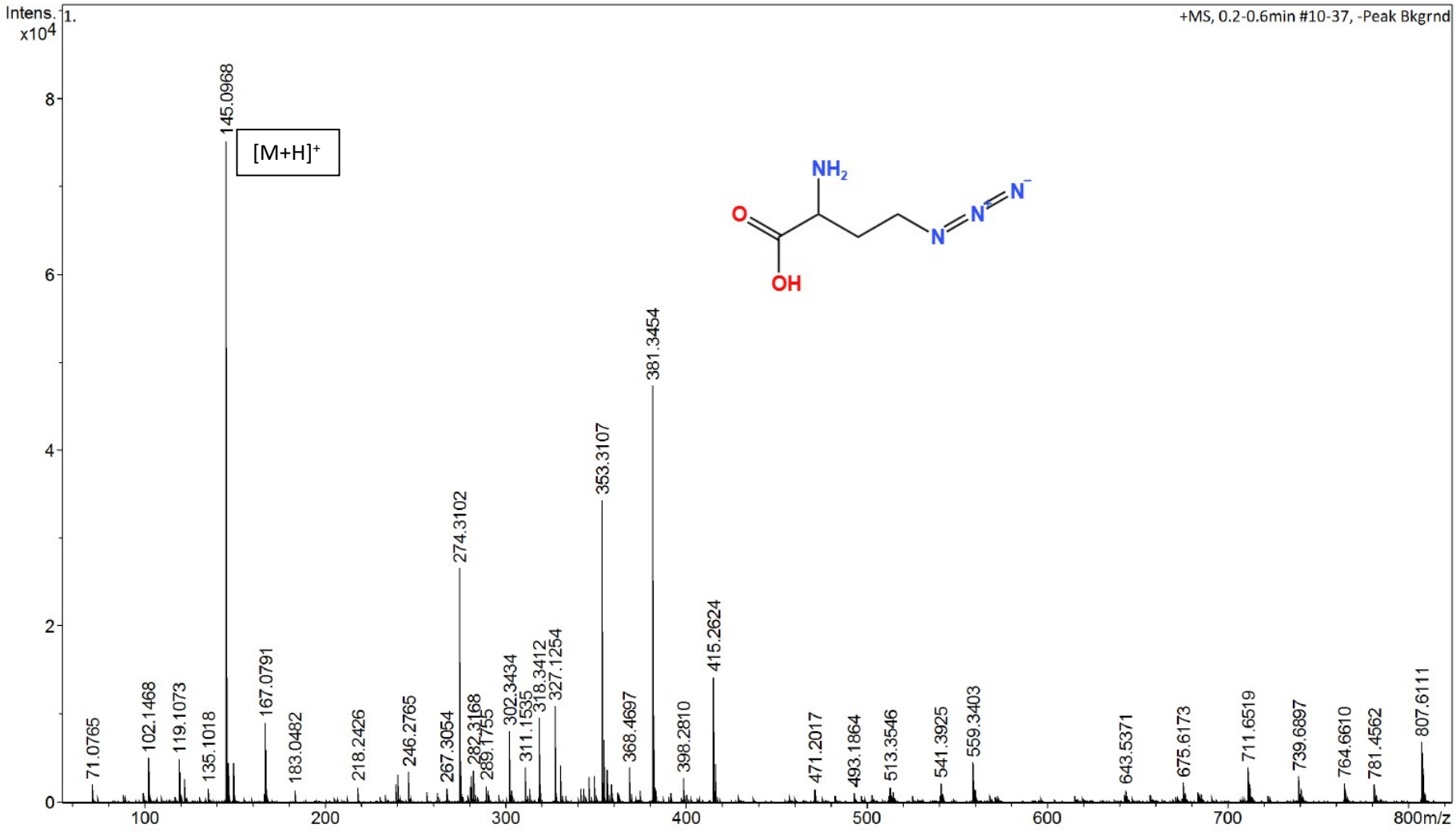
Method: ESI positive mode, Chemical Formula: $C_{23}H_{29}O_7NS$+Na or $[M+Na]^+$, Exact Mass: 486.16, MS (ESI$^+$) *m/z* calcd. for $[M+Na]^+$: 486.26; found: 486.2599.

2.3.2.6 Benzyl 4-azido-2-*N*-((*tert*-butoxycarbonyl)amino)butanoate (NBOB-AHA, Compound **7**, ESI$^+$)



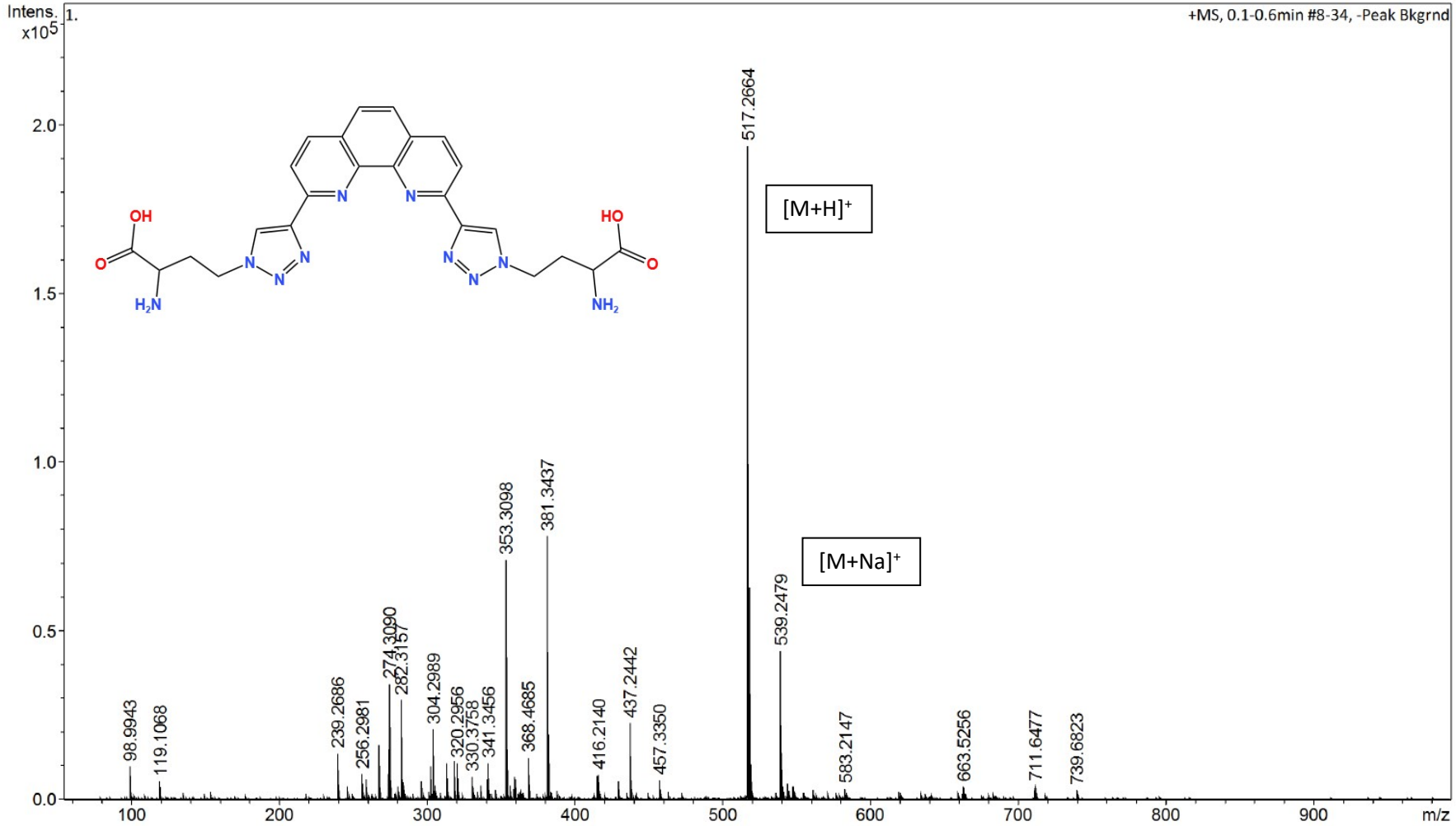
Method: ESI positive mode, Chemical Formula: $C_{16}H_{22}O_4N_4$+Na^+ or $[M+Na]^+$, Exact Mass: 357.26; $C_{16}H_{22}O_4N_4$+K^+ or $[M+K]^+$, Exact Mass: 373.235; MS(ESI$^+$) *m/z* calcd. for $[M+Na]^+$: 357.26 found: 357.2605, for $[M+K]^+$: 373.23 found: 373.2349

2.3.2.7 L-Azidohomoalanine hydrochloride (L-AHA, Compound **8**, ESI$^+$)



Method: ESI positive mode, Chemical Formula: $C_4H_8O_2N_4$+H^+ or $[M+H]^+$, Exact Mass: 145.07, MS (ESI$^+$) *m/z* calcd. for $[M+H]^+$: 145.07 ; found: 145.0968.

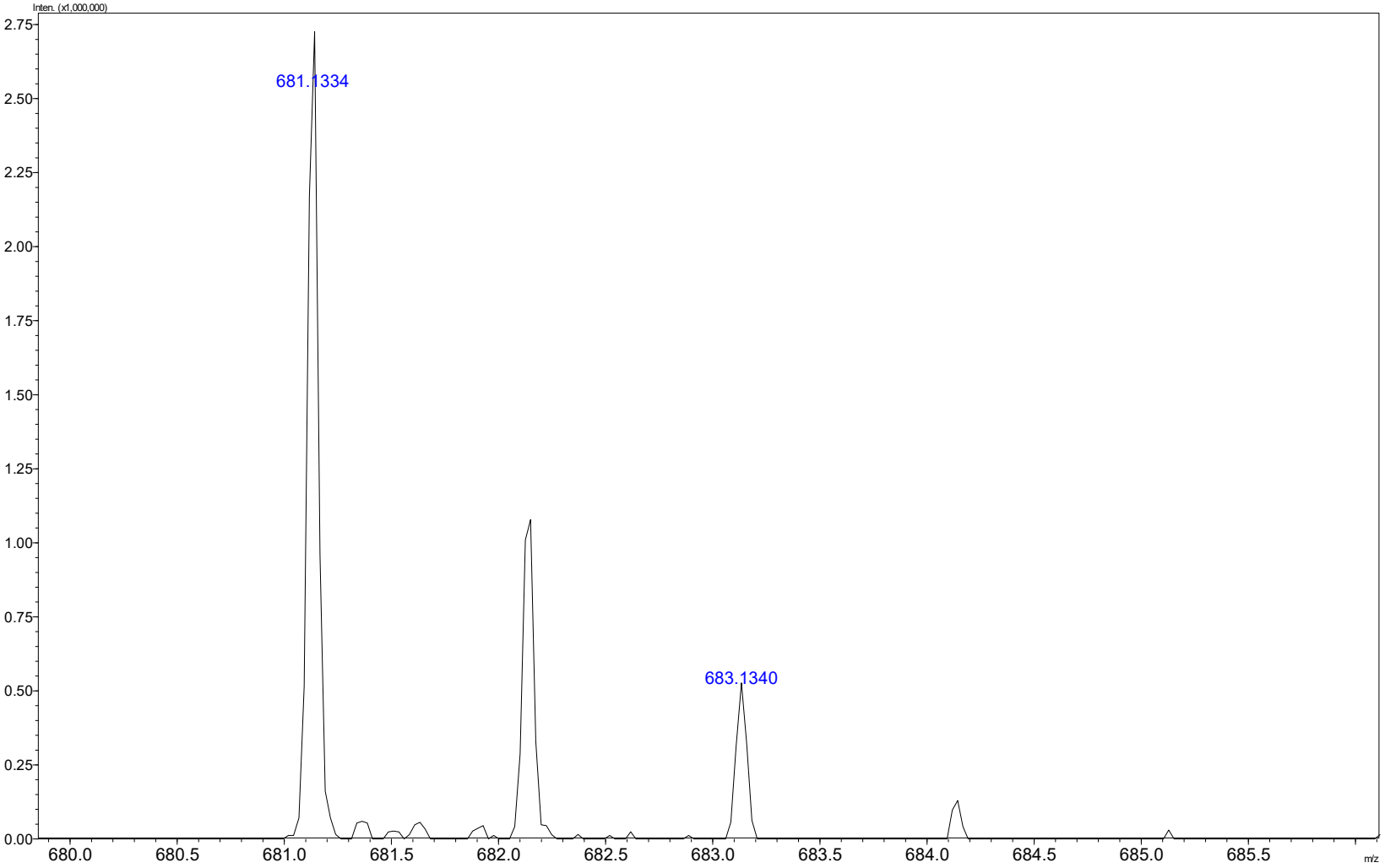
2.3.2.8 DAA-BTrzPhen, Ligands **2**, ESI^+



Method: ESI positive mode, Chemical Formula: $C_{24}H_{24}O_4N_{10}+H^+$ or $[M+H]^+$, Exact Mass: 517.27 ; $C_{24}H_{24}O_4N_{10}+Na^+$ or $[M+Na]^+$, Exact Mass: 539.25; MS(ESI^+) *m/z* calcd. for $[M+H]^+$: 517.27 found: 517.2664 , *m/z* calcd. for $[M+Na]^+$: 539.25 found: 539.2479

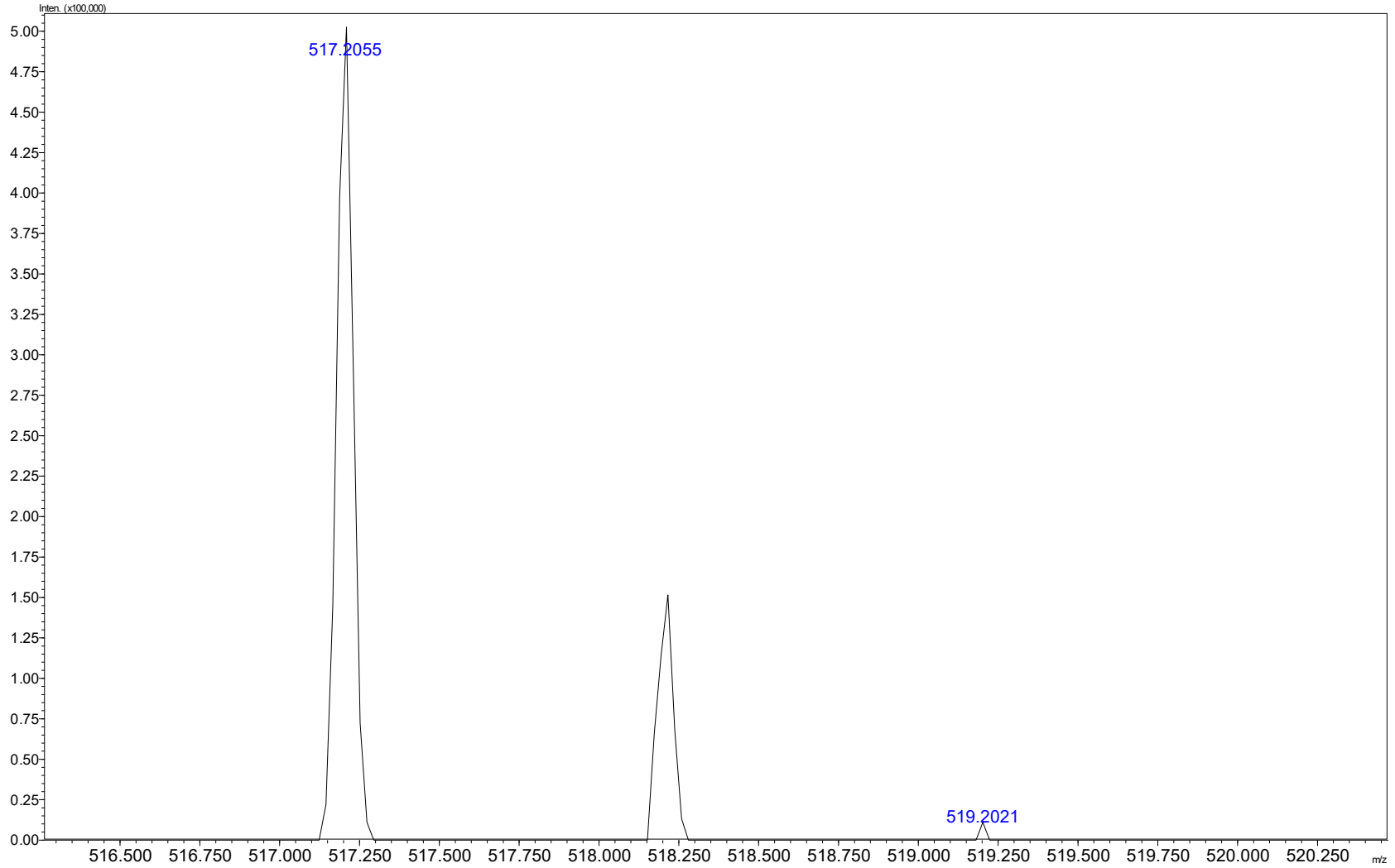
2.2.8. High Resolution Mass Spectra

2.2.8.1. DS-BTrzPhen, Ligand **1**, ESI^+:

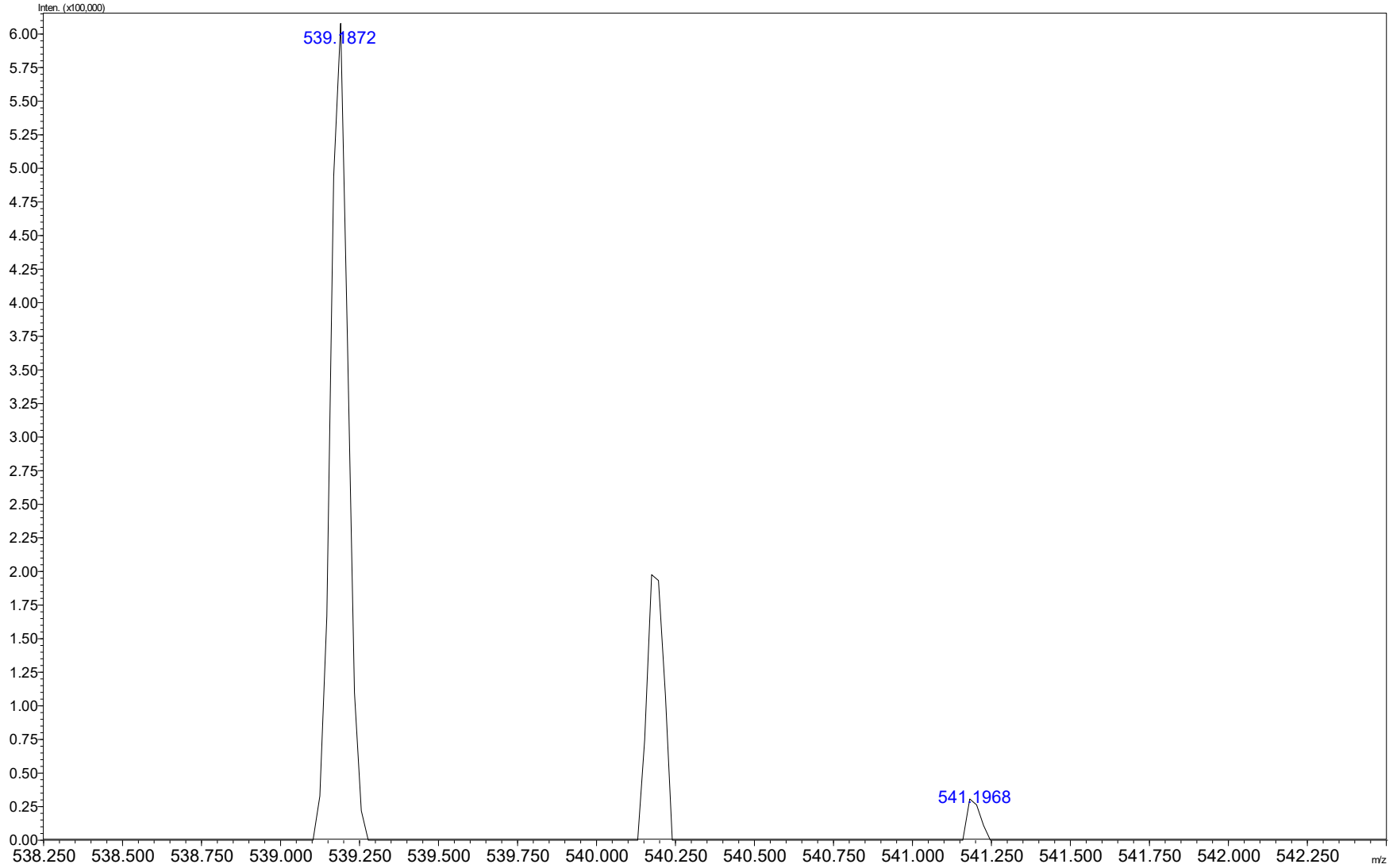


Method: ESI negative mode, Chemical Formula: $C_{32}H_{25}O_6N_8S_2^-$, $[M-Na+H]^-$, Exact Mass: 681.1333, HRMS (ESI^-) *m/z* calcd. for $[M-Na+H]^-$: 681.1333; found: 681.1334.

2.2.8.2. DAA-BTrzPhen, Ligand **2**, ESI^+:



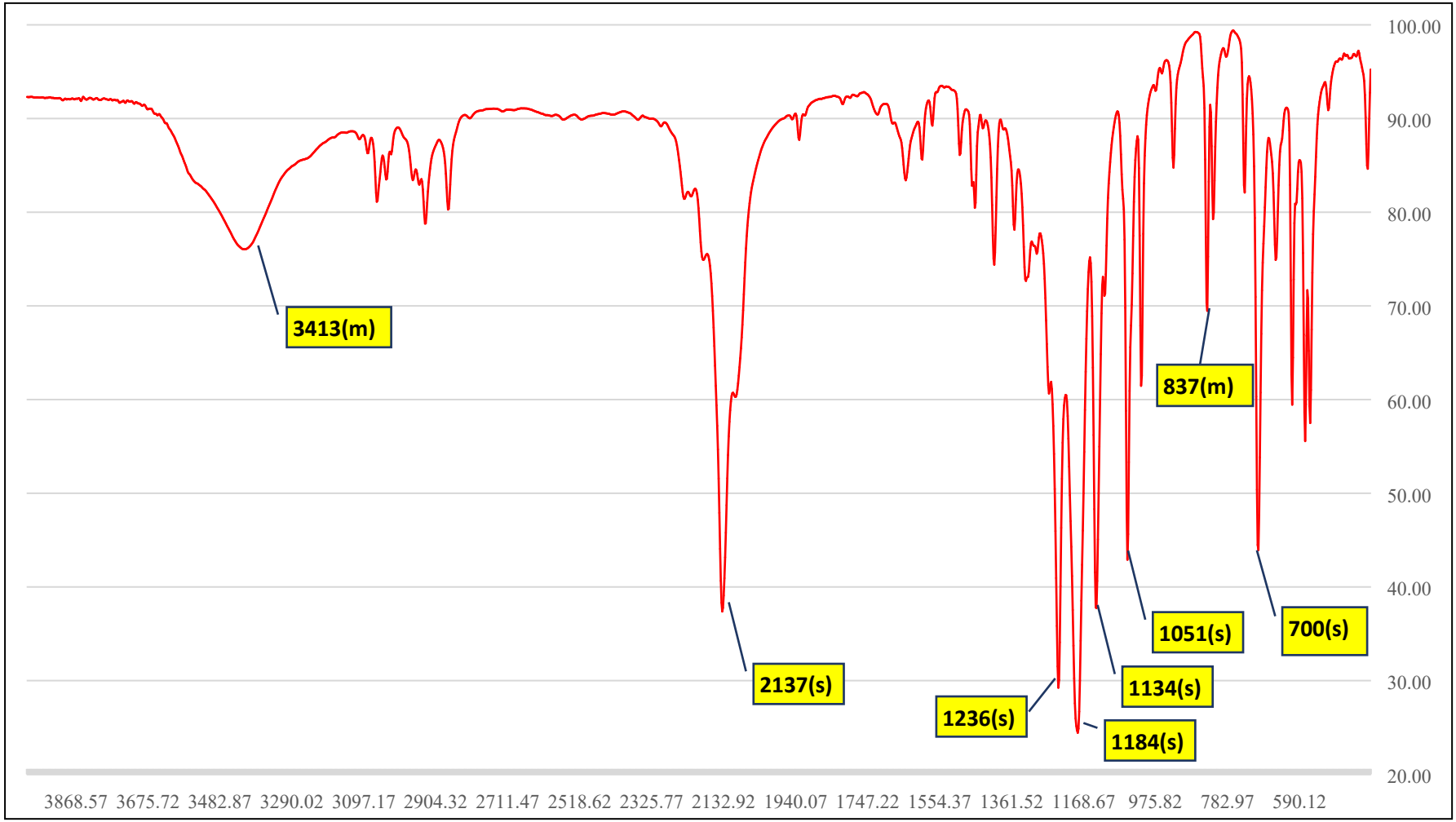
Method: ESI positive mode, Chemical Formula: $C_{24}H_{24}O_4N_{10}+H^+$ or $[M+H]^+$, Exact Mass: 517.27; HRMS(ESI^+) *m/z* calcd. for $[M+H]^+$: 517.2055, found: 517.2055.



Method: ESI positive mode, Chemical Formula: $C_{24}H_{24}O_4N_{10}$+Na^+ or $[M+Na]^+$, Exact Mass: 517.27; HRMS (ESI^+) *m/z* calcd. for $[M+Na]^+$: 539.1874, found: 539.1872.

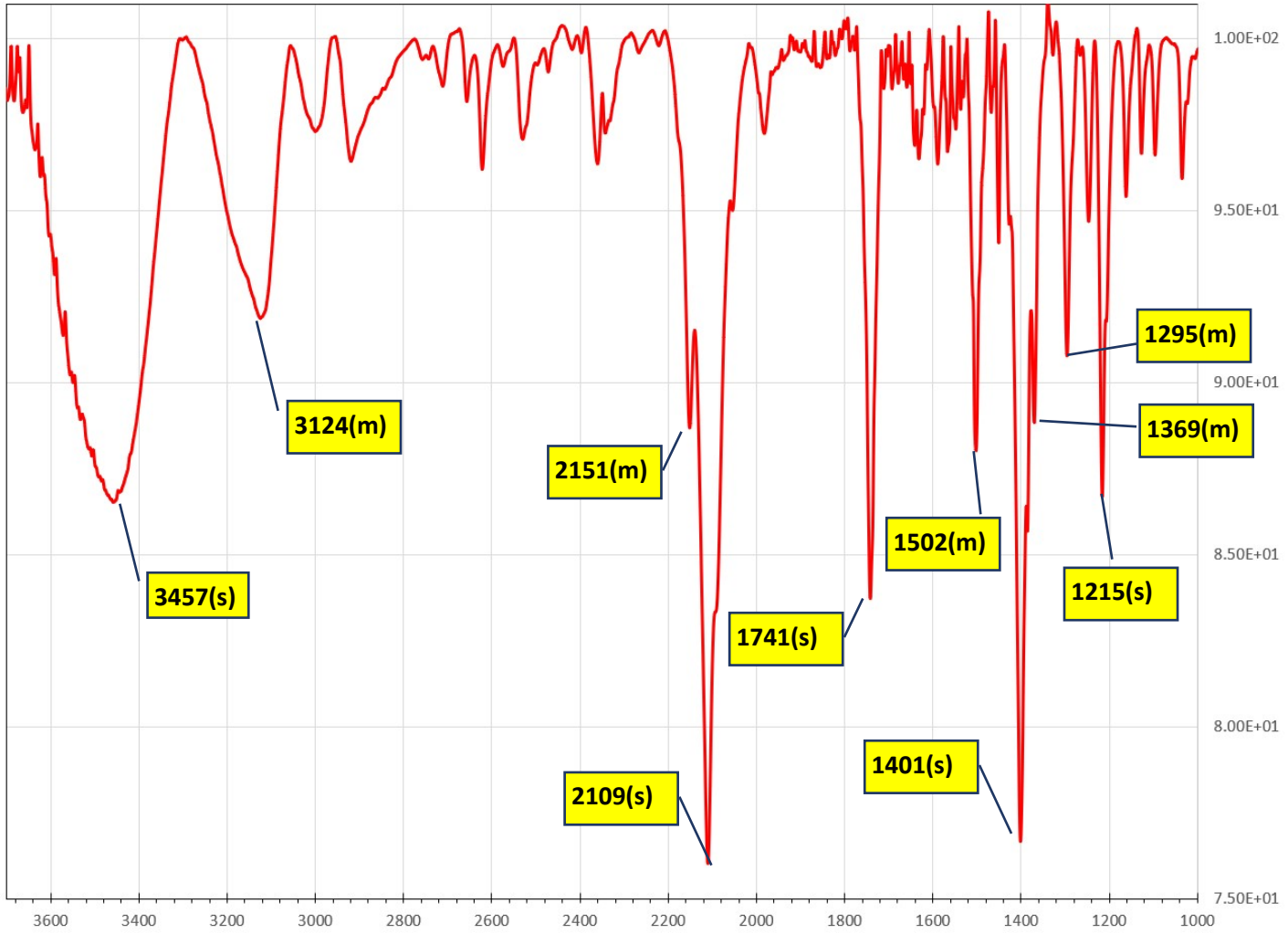
2.2.4. FTIR spectra

2.3.4.1 FTIR spectrum of Sodium 4-(2-bromoethyl)benzenesulfonate (AzEBS, compound **4**)



FT-IR (KBr disc): ν_{max} 3413(m), 2137(s), 1236(s), 1184(s), 1134(s), 1051(s), 837(m), 700(s).

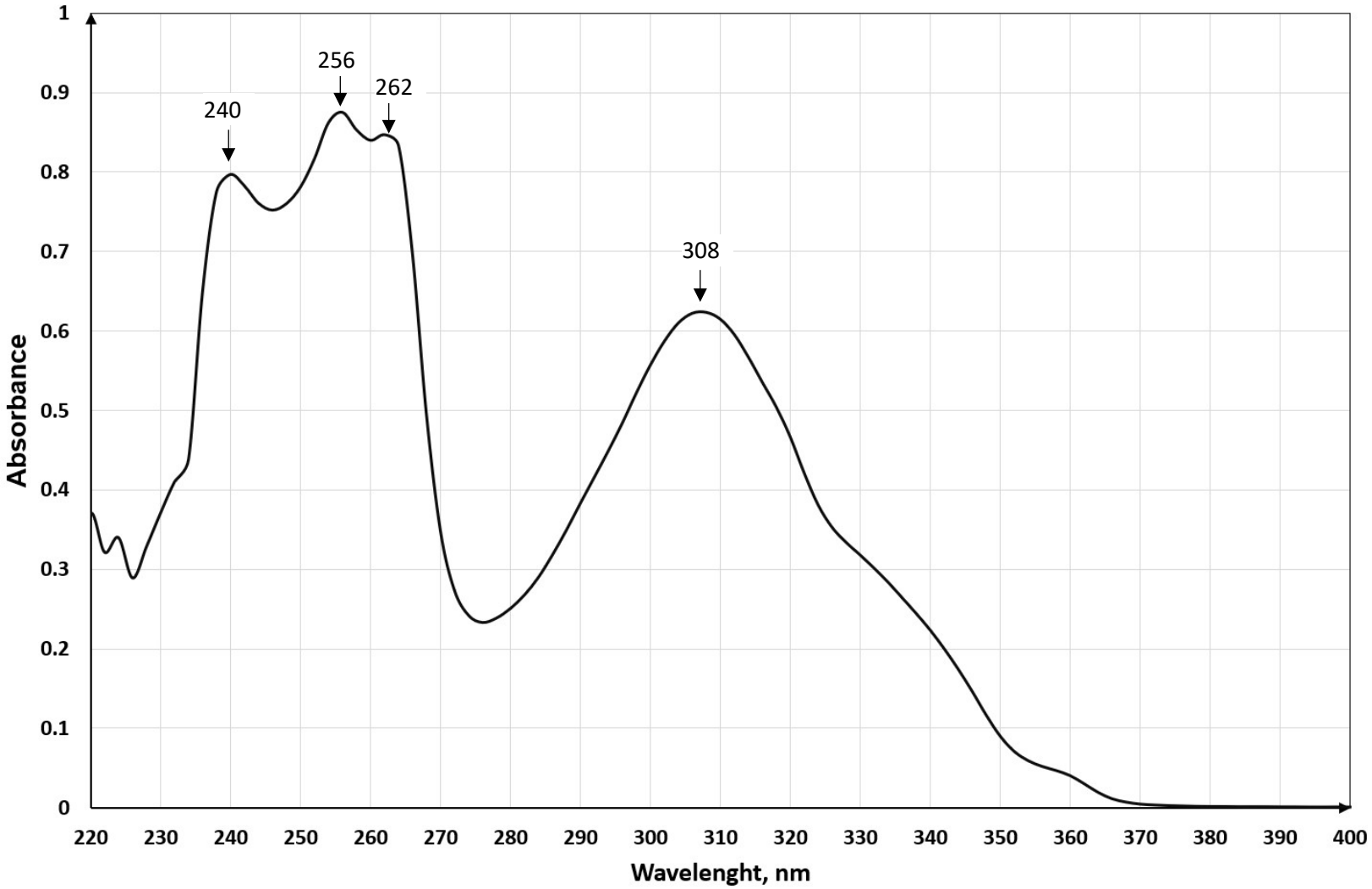
2.3.4.2 IR spectrum of L-Azidohomoalanine hydrochloride (**8**)



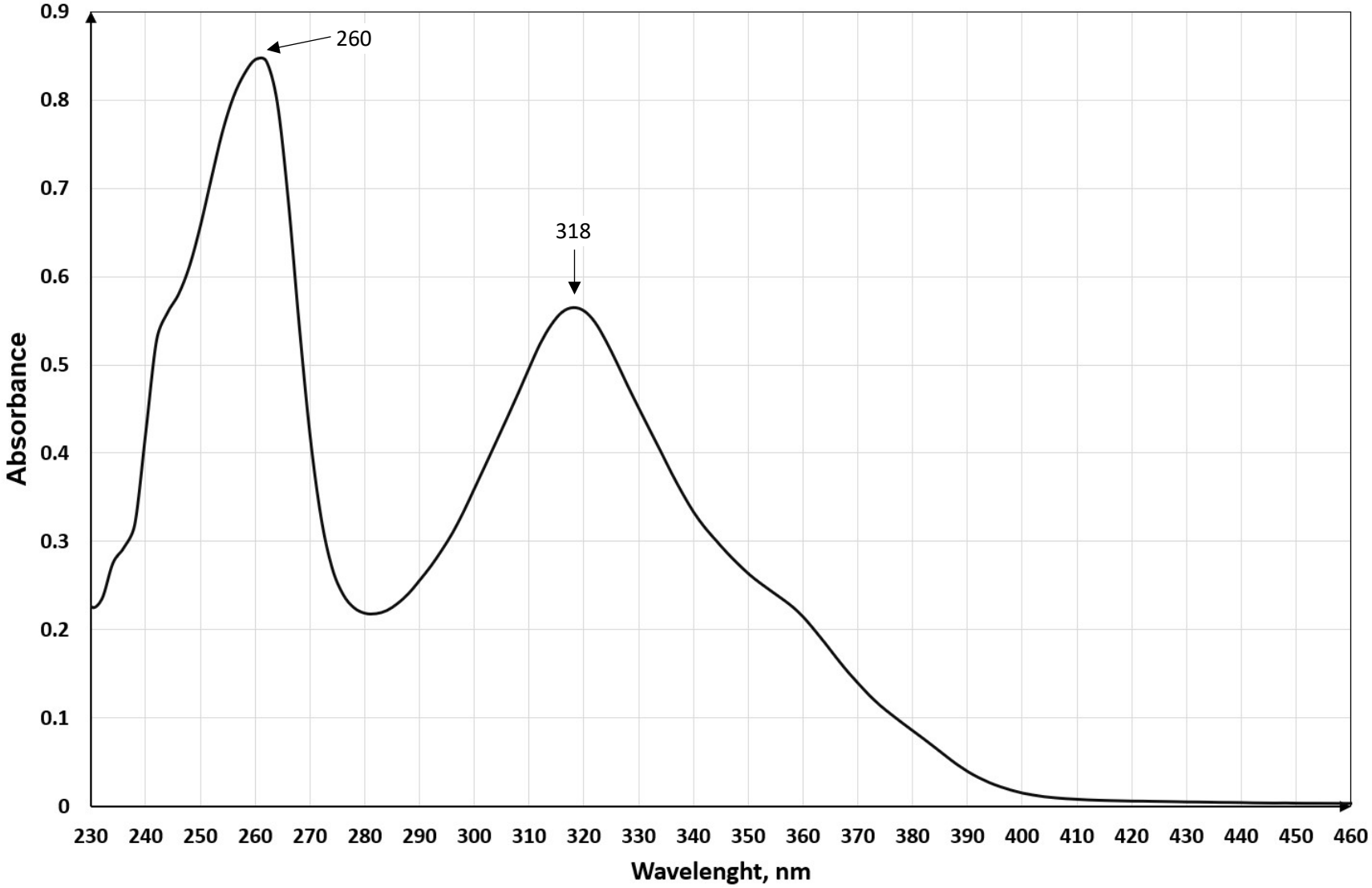
FT-IR (KBr disc): ν_{max} 3457 (s), 3124 (m), 2151 (m), 2109 (s), 1741 (s), 1502 (m), 1401 (s), 1369 (m), 1295 (m), 1215 (s).

2.3.5. UV-Vis spectra

2.3.5.1. UV-Vis spectrum of Ligand **1** (DS-BTrzPhen), aqueous solution (I = 0.01 M Me_4NNO_3), c = 2.0×10^{-5} M



2.3.5.1. UV-Vis spectrum of Ligand **2** (DAA-BTrzPhen), aqueous nitric acid solution ([HNO_3] = 0.0286 M) [ligand] = 2.0×10^{-5} M, (I = 0.01 M Me_4NNO_3)



3. Solvent Extraction Studies

3.1. General information and procedures for the solvent extraction studies

All inorganic chemicals used for solvent extraction studies (NaOH, HNO_3 and $NaNO_3$) were of spectroscopic grade. Deionised water used was of low conductivity (18.2 MΩ). Organic chemicals were purchased from Macklin, TCI, and TODGA from Qingdao Beitwall Technology Co., Ltd. ^{241}Am-241 tracer used was obtained from Institute of Nuclear and New Energy Technology (INET) and had radio-concentration of 10^7 cpm/ml. Radioactive europium tracer contained ^{152}Eu and ^{154}Eu was obtained from China Institute of Atomic Energy (CIAE) and had total radio-concentration of 1.6×10^7 cpm/ml.

Bulk ligands **1** and **2** were tested by elemental analysis and % of the ligand in the bulk material was estimated taking into account content of water. Bulk ligand **1** powder was found to be 89.7 % pure, while the rest was water. Bulk ligand **2** powder was found to be 80.2 % pure, the rest was water.

All aqueous phases contained either ligand **1** or **2**, 0.5 M of $NaNO_3$, ^{241}Am and ^{152}Eu/^{154}Eu tracers and variable concentrations of HNO_3.

All the extraction experiments were carried out in a 4 mL polypropylene screw cap vials with rubber "O" ring to prevent leakage/contamination. Stock solutions were mix and handled with precise syringes or high quality calibrated automatic pipettes.

Shaker instrument used was VX-IV vortex oscillator. Centrifugation instrument used was BY-400C centrifuge.

Activities of ^{241}Am and $^{152/154}$Eu were counted using Quantulus 1220 (PerkinElmer) liquid scintillation counter and the LSC cocktail used was Hisafe 3.

3.1.1. Stock solutions:

- The organic phase for all the solvent extraction experiment was 0.2 M tetraoctyl diglycolamide (TODGA) in 30 ml of kerosene/1-octanol (95:5) solution.
- Stock solution of the ligand **1** was prepared by dissolving 162 mg of the ligand powder in exactly 5 ml of purified water. Obtained stock solution was 40 mM.
- Stock solution of the ligand **2** was prepared by dissolving by dissolving 129 mg of the ligand powder in 6.04 ml of 0.68 M aqueous solution of HNO_3. Obtained stock solution was 33.085 mM. The stock solution of DAA-BTrzPhen used for thermodynamics test was 40 mM (Table 9).
- Stock solution of $^{241}Am(NO_3)_3$ contained 0.01 M of nitric acid.
- Stock solution of $^{152/154}Eu(NO_3)_3$ contained 0.01 M of nitric acid.
- Stock solution of HNO_3 was 1 M
- Stock solution of NaOH were 0.01 M, 1 M or 2 M
- Stock solution of $NaNO_3$ was 4 M.

3.2. Protocols and tables

Try types of studies were performed:

1. Solvent extraction studies of acidity to determine influence of nitric acid concentration on

distribution ratios and $SF_{Eu/Am.}$ For the ligand **1** (DS-BTrzPhen) acidity studies were performed at the acidities of 0, 0.001, 0.005, 0.01, 0.05 and 0.1 M of nitric acid, while for the ligand **2** (DAA-BTrzPhen) studies were performed at 0.005, 0.01, 0.05, 0.1, 0.25 and 0.5 M. In both cases standard concentration of the ligand was 10 mM.

2. Kinetics solvent extraction studies to determine kinetics of extraction process. For the kinetics study in the cases of both ligands aqueous phase contained constant acidity of 0.05 M nitric acid and constant concentration of ligands (10 mM) while samples were taken at intervals of 1, 2, 5, 10, 15 and 30 minutes.

3. Ligand concentration solvent extraction studies to determine influence of ligand concentration on distribution ratios and $SF_{Eu/Am}$. For the ligand concentration study, DS-BTrzPhen was tested at concentrations of 1, 2.5, 5, 10, 15, 20 and 25 mM, while DAA-BTrzPhen at 5, 10, 15, 20, 25 mM. Standard acidity was 0.05 M of nitric acid, while ligand **1** was additionally tested at concentrations of 1, 2.5 and 5 at 0.01 M nitric acid.

4. Thermodynamic solvent extraction studies to determine influence of temperature as well as thermodynamic parameters, namely ΔH. Both ligands are tested at different temperatures: 15, 20, 25, 30, 35 and 40°C. Standard acidity was 0.05 M of nitric acid, while the standard concentrations of the ligands were 10 mM.

Aqueous and organic phases, each one 1 mL, were mixed in a PP vial, shaken by using a vortex oscillator (standard of 15 minutes), then centrifuged (4000 rpm for 2 minutes) to completely separate the two phases. Samples of aqueous and organic phase were then taken, and activities counted (in cmp) using LSC in different channels, which can differentiate[4] alpha emission from ^{241}Am and beta emission from $^{152}Eu/^{154}Eu$. Each of the sample was measured in triplicate for at least 10 min to ensure the accuracy of the data. Ratio of counts in two phases are then interpreted as extraction parameters D_{Am} and D_{Eu} respectively, while $SF_{Eu/Am}$ was calculated as D_{Eu}/D_{Am} ratio.

3.2.1. Protocol tables for ligand 1 (DS-BTrzPhen)

The protocols for the preparation of aqueous phases for the ligand **1** are shown in the tables below:

	$[HNO_3]$ / M	Components of the aqueous phases for each experiment							
		H_2O / µL	NaOH (0.01M) / µL	$NaNO_3$ (4 M) / µL	**Ligand 1** (40 mM) / µL	HNO_3 (1 M) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L1	0.000	617	4	125	250	0	2	2	1000
L2	0.001	620	0	125	250	1	2	2	1000
L3	0.005	616	0	125	250	5	2	2	1000
L4	0.010	611	0	125	250	10	2	2	1000
L5	0.050	571	0	125	250	50	2	2	1000
L6	0.100	521	0	125	250	100	2	2	1000

Table 1. Protocol for the preparation of the aqueous phases for solvent extraction studies of acidity for the Ligand **1**.

	Time / min	Components of the aqueous phases for each experiment							
		$[HNO_3]$ / M	H_2O / µL	HNO_3 (1 M) / µL	$NaNO_3$ (4 M) / µL	**Ligand 1** (40 mM) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L7	1	0.050	571	50	125	250	2	2	1000
L8	2	0.050	571	50	125	250	2	2	1000
L9	5	0.050	571	50	125	250	2	2	1000
L10	10	0.050	571	50	125	250	2	2	1000
L11	15	0.050	571	50	125	250	2	2	1000
L12	30	0.050	571	50	125	250	2	2	1000

Table 2. Protocol for the preparation of the aqueous phases for the solvent extraction studies of kinetics for the Ligand **1**.

	Components of the aqueous phases for each experiment								
	[Ligand] /mM	$[HNO_3]$ / M	H_2O / µL	HNO_3 (1 M) / µL	$NaNO_3$ (4 M) / µL	**Ligand 1** (40 mM) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L13	5	0.050	696	50	125	125	2	2	1000
L14	10	0.050	571	50	125	250	2	2	1000
L15	15	0.050	446	50	125	375	2	2	1000
L16	20	0.050	321	50	125	500	2	2	1000
L17	25	0.050	196	50	125	625	2	2	1000

Table 3. Protocol for the preparation of the aqueous phases for the solvent extraction studies of ligand concentration for the Ligand **1**.

	Components of the aqueous phases for each experiment								
	[Ligand] /mM	$[HNO_3]$ / M	H_2O / µL	HNO_3 (1 M) / µL	$NaNO_3$ (4 M) / µL	**Ligand 1** (40 mM) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L18	5	0.010	736	10	125	125	2	2	1000
L19	5	0.050	696	50	125	125	2	2	1000
L20	2.5	0.010	799	10	125	62	2	2	1000
L21	2.5	0.050	759	50	125	62	2	2	1000
L22	1	0.010	834	10	125	25	3	3	1000
L23	1	0.050	796	50	125	25	2	2	1000

Table 4. Additional protocol for the preparation of the aqueous phases for additional solvent extraction studies of acidity and ligand concentration for the Ligand **1**.

	Tempe-rature /°C	Components of the aqueous phases for each experiment						
		H_2O / µL	HNO_3 (1 M) / µL	$NaNO_3$ (4 M) / µL	Ligand stock sol. / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L24	15	571	50	125	250	2	2	1000
L25	20	571	50	125	250	2	2	1000
L26	25	571	50	125	250	2	2	1000
L27	30	571	50	125	250	2	2	1000
L28	35	571	50	125	250	2	2	1000
L29	40	571	50	125	250	2	2	1000

Table 5. Protocol for the preparation of the aqueous phases for the solvent extraction studies of variable temperature (thermodynamic study) for the Ligand **1**.

*3.2.2. Protocol tables for ligand **2** (DAA-BTrzPhen)*

The protocols for the preparation of aqueous phases for the ligand **2** are shown in the tables below:

	$[HNO_3]$ / M	Components of the aqueous phases for each experiment							
		H_2O / µL	NaOH (1M) / µL	$NaNO_3$ (4 M) / µL	**Ligand 2** (33.085 mM) / µL	HNO_3 (1 M) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L1	0.005	417	203	74	302	0	2	2	1000
L2	0.010	421	198	75	302	0	2	2	1000
L3	0.050	451	158	85	302	0	2	2	1000
L4	0.100	488	108	98	302	0	2	2	1000
L5	0.250	527		125	302	42	2	2	1000
L6	0.500	277		125	302	292	2	2	1000

Table 6. Protocol for the preparation of the aqueous phases for solvent extraction studies of acidity for the Ligand **2**.

	Time / min	Components of the aqueous phases for each experiment							
		$[HNO_3]$ / M	H_2O / µL	NaOH (1 M) / µL	$NaNO_3$ (4 M) / µL	**Ligand 2** (33.085 mM) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L7	1	0.050	451	158	85	302	2	2	1000
L8	2	0.050	451	158	85	302	2	2	1000
L9	5	0.050	451	158	85	302	2	2	1000
L10	10	0.050	451	158	85	302	2	2	1000
L11	15	0.050	451	158	85	302	2	2	1000
L12	30	0.050	451	158	85	302	2	2	1000

Table 7. Protocol for the preparation of the aqueous phases for the solvent extraction studies of kinetics for the Ligand **2**.

	Components of the aqueous phases for each experiment								
	[Ligand] /mM	[HNO_3] / M	H_2O / µL	NaOH (2 M) / µL	$NaNO_3$ (4 M) / µL	**Ligand 2** (33.085 mM) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L13	5.0	0.05	706	27	112	151	2	2	1000
L14	10.0	0.05	529	79	86	302	2	2	1000
L15	15.0	0.05	352	131	60	453	2	2	1000
L16	20.0	0.05	176	183	34	603	2	2	1000
L17	25.0	0.05	0	236	5	755	2	2	1000

Table 8. Protocol for the preparation of the aqueous phases for the solvent extraction studies of ligand concentration for the Ligand **2**.

	Tempe-rature / °C	Components of the aqueous phases for each experiment						
		H_2O / µL	NaOH (1 M) / µL	$NaNO_3$ (4 M) / µL	Ligand stock sol. (**40 mM**) / µL	Am^{3+} (in 0.01 M HNO_3) / µL	Eu^{3+} (in 0.01 M HNO_3) / µL	Total / µL
L18	15	546	100	100	250	2	2	1000
L19	20	546	100	100	250	2	2	1000
L20	25	546	100	100	250	2	2	1000
L21	30	546	100	100	250	2	2	1000
L22	35	546	100	100	250	2	2	1000
L23	40	546	100	100	250	2	2	1000

Table 9. Protocol for the preparation of the aqueous phases for the solvent extraction studies of variable temperature (thermodynamic study) for the Ligand **2**.

3.3. Results

3.3.1. Tables:

3.3.1.1. Results for ligand **1** (DS-BTrzPhen)

Effect of HNO_3 concentration							
	[HNO_3]/M	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	D_{Eu}	**$SF_{Eu/Am}$**
L1	**0.000**	A*	4119.592	2827.143	0.0163	0.2890	**17.75**
		O*	67.089	817.064			
L2	**0.001**	A	3980.393	3373.474	0.0004	0.0375	**91.89**
		O	1.626	126.630			
L3	**0.005**	A	4061.739	3643.068	0.0002	0.0135	**89.94**
		O	0.610	49.180			
L4	**0.010**	A	3526.623	3189.853	0.0005	0.0658	**142.62**
		O	1.626	209.763			
L5	**0.050**	A	3232.224	177.727	0.0636	19.0007	**298.63**
		O	205.655	3376.932			
L6	**0.100**	A	2572.303	63.242	0.4321	53.5668	**123.98**
		O	1111.382	3387.651			

Table 10: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 0, 1, 5, 10, 50 and 100 mM of nitric acids and 10 mM of ligand **1**. * A = aqueous phase, O = organic phase.

Effect of contact time							
	Time/min	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	D_{Eu}	**$SF_{Eu/Am}$**
L7	**1**	A*	3326.735	962.408	0.0257	2.2043	**85.86**
		O*	85.412	2121.475			
L8	**2**	A	3184.570	618.081	0.0363	4.4964	**123.95**
		O	115.525	2779.119			
L9	**5**	A	3259.473	295.669	0.0414	10.7333	**259.05**
		O	135.051	3173.492			
L10	**10**	A	3280.640	188.110	0.0575	17.1419	**297.93**
		O	188.759	3224.558			
L11	**15**	A	3085.545	152.126	0.0650	21.5718	**331.87**
		O	200.563	3281.622			
L12	**30**	A	3152.308	160.442	0.0860	23.3487	**271.62**
		O	270.980	3746.109			

Table 11: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 1, 2, 5, 10, 15 and 30 minutes of contact time, 50 mM of nitric acids and 10 mM of ligand **1**. * A = aqueous phase, O = organic phase.

Effect of ligand concentration							
	[Ligand 1] / mM	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	D_{Eu}	**$SF_{Eu/Am}$**
L13	**5**	A*	3423.575	131.160	0.099	26.685	**269.3**
		O*	339.300	3500.000			
L14	**10**	A	3096.892	136.849	0.078	26.048	**335.2**
		O	240.667	3564.642			
L15	**15**	A	3098.112	175.280	0.053	18.968	**361.1**
		O	162.734	3324.654			
L16	**20**	A	2945.299	254.796	0.037	13.518	**361.2**
		O	110.245	3444.437			
L17	**25**	A	2956.690	375.153	0.023	7.893	**345.6**
		O	67.528	2961.253			

Table 12: Effect of ligand **1** concentration at the constant 0.05 M acidity, ligand **1** concentration ranging from 5 mM to 25 mM. * A = aqueous phase, O = organic phase.

Effect of ligand and HNO3 concentration								
	[Ligand 1] / mM	**[HNO_3]/M**	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	D_{Eu}	**$SF_{Eu/Am}$**
L18	**5**	**0.010**	A*	3621.658	2290.278	0.0023	0.5211	**225.76**
			O*	8.359	1193.415			
L19	**5**	**0.050**	A	3322.093	156.840	0.0600	21.8570	**364.16**
			O	199.395	3428.061			
L20	**2.5**	**0.010**	A	3691.586	1744.904	0.0030	1.0196	**341.85**
			O	11.010	1779.020			
L21	**2.5**	**0.050**	A	3930.173	166.749	0.0667	19.9138	**298.47**
			O	262.218	3320.607			
L22	**1**	**0.010**	A	4336.360	1417.976	0.0042	1.5431	**368.71**
			O	18.148	2188.112			
L23	**1**	**0.050**	A	3637.998	140.735	0.0835	25.0259	**299.64**
			O	303.845	3522.014			

Table 13: Additional experiments on effect of ligand **1** concentration at 10 or 50 mM of acidity, ligand **1** concentration ranging from 1 mM to 5 mM. * A = aqueous phase, O = organic phase.

Effect of temperature											
	T/°C	T/K	1000/T [mK^{-1}]	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	log(D_{Am})	D_{Eu}	log(D_{Eu})	$SF_{Eu/Am}$
L24	**15**	**288.15**	**3.47**	A	2518.152	112.763	0.3750	-0.4260	28.6797	1.4576	**76.48**
				O	944.244	3234.004					
L25	**20**	**293.15**	**3.41**	A	2936.855	158.661	0.0697	-1.1567	21.2458	1.3273	**304.74**
				O	204.752	3370.876					
L26	**25**	**298.15**	**3.35**	A	3158.405	261.728	0.0454	-1.3434	12.7409	1.1052	**280.91**
				O	143.255	3334.648					
L27	**30**	**303.15**	**3.30**	A	3321.170	421.068	0.0211	-1.6754	7.2024	0.8575	**341.06**
				O	70.136	3032.686					
L28	**35**	**308.15**	**3.25**	A	3423.383	757.784	0.0089	-2.0520	3.2523	0.5122	**366.62**
				O	30.368	2464.502					
L29	**40**	**313.15**	**3.19**	A	3676.581	1441.956	0.0034	-2.4696	1.2653	0.1022	**373.04**
				O	12.471	1824.543					

Table 15: Effect of temperature for the ligand **1** (10 mM) at 50 mM of acidity, * A = aqueous phase, O = organic phase.

3.3.1.2. Results for ligand **2** (DS-BTrzPhen)

Effect of HNO_3 concentration							
	[HNO_3]/M	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
L1	**0.005**	A*	2282.762	206.653	0.2222	13.5072	**60.78**
		O*	507.278	2791.300			
L2	**0.010**	A	1289.743	174.812	0.2404	15.1238	**62.91**
		O	310.058	2643.811			
L3	**`0.050**	A	3176.204	193.093	0.2178	18.3895	**84.43**
		O	691.823	3550.887			
L4	**0.100**	A	2815.226	123.519	0.4667	29.4589	**63.13**
		O	1313.777	3638.732			
L5	**0.250**	A	1167.241	92.230	2.2912	37.9280	**16.55**
		O	2674.401	3498.108			
L6	**0.500**	A	315.949	65.004	13.0089	53.5591	**4.12**
		O	4110.149	3481.544			

Table 16: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 5, 10, 50, 100, 250 and 500 mM of nitric acids and 10 mM of ligand **2**. * A = aqueous phase, O = organic phase.

Effect of contact time							
	Time / min	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
L7	**1.00**	A*	2558.17	154.34	0.21	19.74	**92.18**
		O*	547.81	3046.50			
L8	**2.00**	A	2793.71	166.95	0.24	19.21	**81.39**
		O	659.43	3207.37			
L9	**5.00**	A	2799.26	145.26	0.23	21.80	**93.99**
		O	649.34	3167.00			
L10	**10.00**	A	2821.69	150.82	0.23	21.47	**94.76**
		O	639.25	3237.64			
L11	**15.00**	A	2831.24	152.57	0.23	20.96	**89.34**
		O	664.24	3198.11			
L12	**30.00**	A	2889.04	163.17	0.21	19.57	**92.48**
		O	611.42	3193.48			

Table 17: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 1, 2, 5, 10, 15 and 30 minutes of contact time, constant 50 mM of nitric acids and 10 mM of ligand **2**. * A = aqueous phase, O = organic phase.

Effect of ligand concentration							
	[Ligand 2] / mM	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	D_{Eu}	**$SF_{Eu/Am}$**
L13	**5**	A	2450.677	100.361	0.3924	31.5610	**80.44**
		O	961.554	3167.508			
L14	**10**	A	2739.005	160.040	0.2202	19.9433	**90.55**
		O	603.229	3191.726			
L15	**15**	A	2831.997	164.535	0.1965	18.8480	**95.92**
		O	556.497	3101.152			
L16	**20**	A	2931.346	173.393	0.1614	17.8989	**110.89**
		O	473.135	3103.533			
L17	**25**	A	3028.293	196.984	0.1187	15.7355	**132.51**
		O	359.598	3099.638			

Table 18: Effect of ligand **2** concentration at the constant 0.05 M acidity, ligand **2** concentration ranging from 5 mM to 25 mM. * A = aqueous phase, O = organic phase.

Effect of temperature											
	T/°C	**T/K**	**1000/T [mK^{-1}]**	phase	Am counting rate/cpm	Eu counting rate/cpm	D_{Am}	$\log(D_{Am})$	D_{Eu}	$\log(D_{Eu})$	$SF_{Eu/Am}$
L18	**15**	**288.15**	**3.47**	A	2171.598	97.545	0.5489	-0.2605	32.1337	1.5070	**58.55**
				O	1191.915	3134.492					
L19	**20**	**293.15**	**3.41**	A	2823.226	143.319	0.2128	-0.6720	20.8400	1.3189	**97.92**
				O	600.861	2986.776					
L20	**25**	**298.15**	**3.35**	A	2869.453	210.793	0.1417	-0.8487	14.9289	1.1740	**105.37**
				O	406.528	3146.891					
L21	**30**	**303.15**	**3.30**	A	3230.592	455.396	0.0381	-1.4188	5.9729	0.7762	**156.66**
				O	123.173	2720.047					
L22	**35**	**308.15**	**3.25**	A	3385.753	749.337	0.0260	-1.5846	3.4979	0.5438	**134.40**
				O	88.116	2621.125					
L23	**40**	**313.15**	**3.19**	A	3053.097	1303.530	0.0137	-1.8626	1.4915	0.1736	**108.69**
				O	41.897	1944.241					

Table 19: Effect of temperature for the ligand **2** (10 mM) at 50 mM of acidity, * A = aqueous phase, O = organic phase.

3.3.2. Diagrams

3.3.2.1. Diagrams for ligand **1** (DS-BTrzPhen)

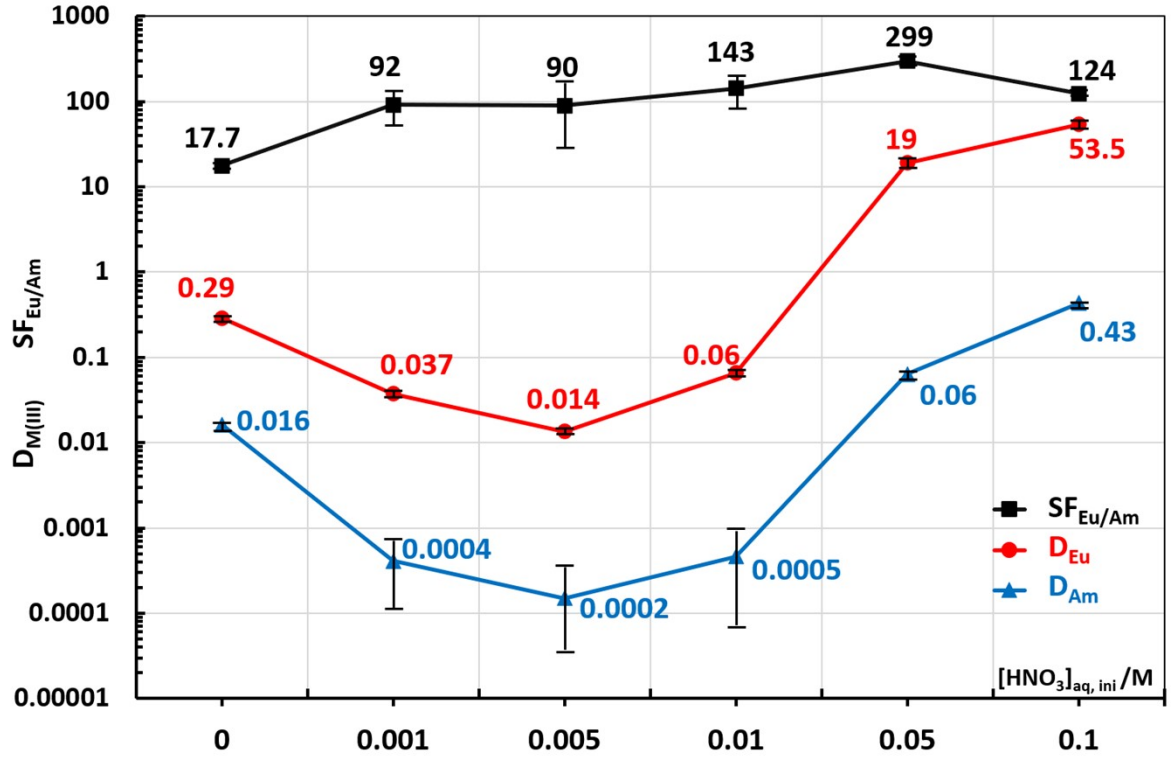


Diagram 1: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 0, 1, 5, 10, 50 and 100 mM of nitric acid and 10 mM of ligand **1**.

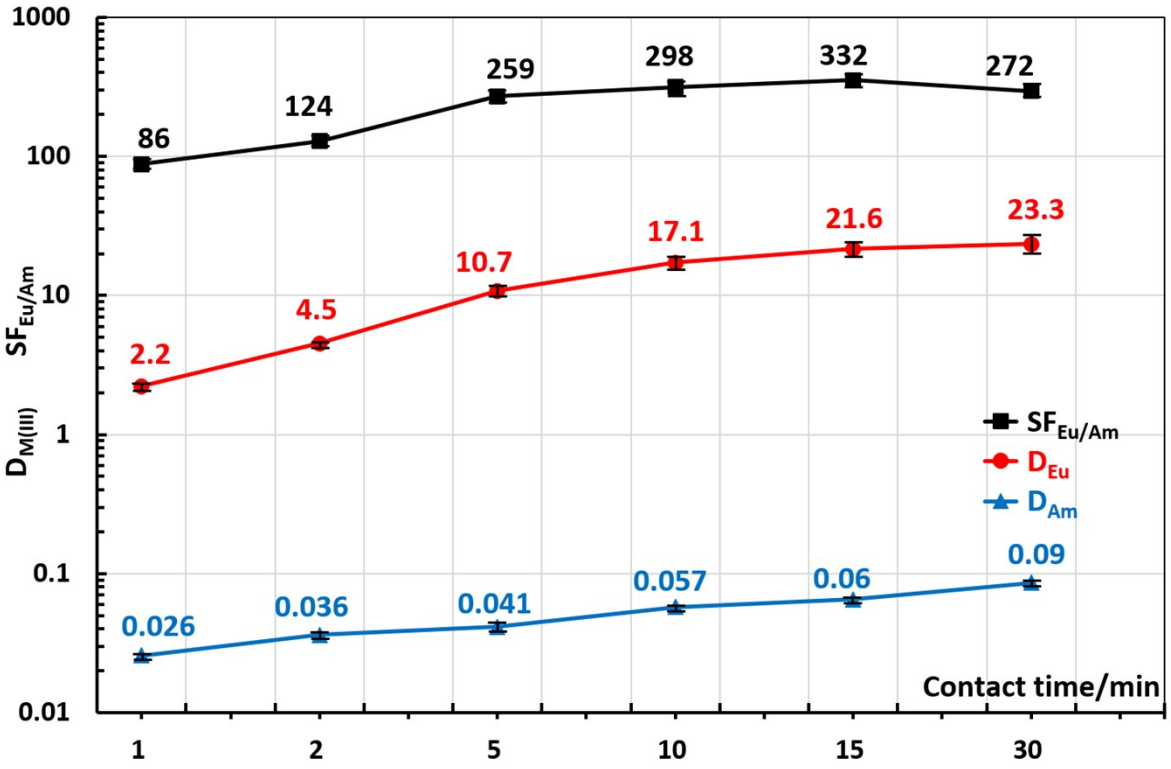


Diagram 2: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 1, 2, 5, 10, 15 and 30 minutes of contact time, 50 mM of nitric acids and 10 mM of ligand **1**.

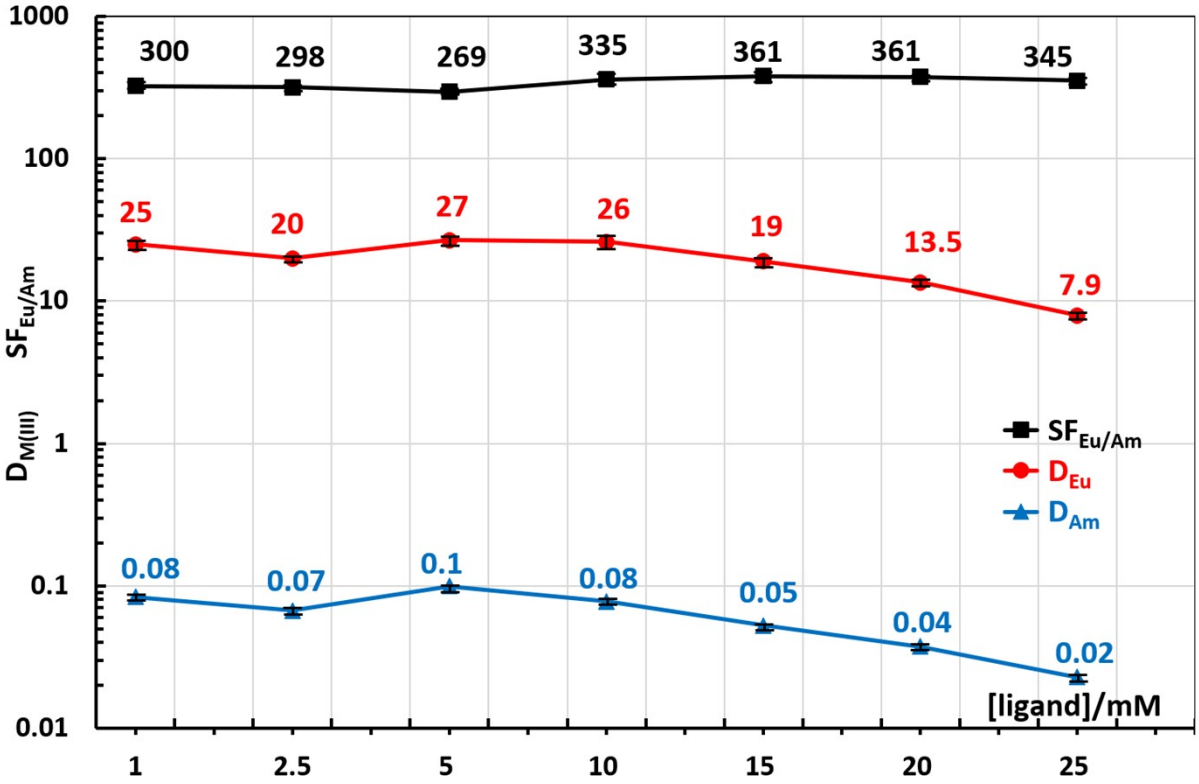


Diagram 3: Effect of ligand **1** concentration at the constant 0.05 M acidity, ligand **1** concentration ranging from 1 mM to 25 mM.

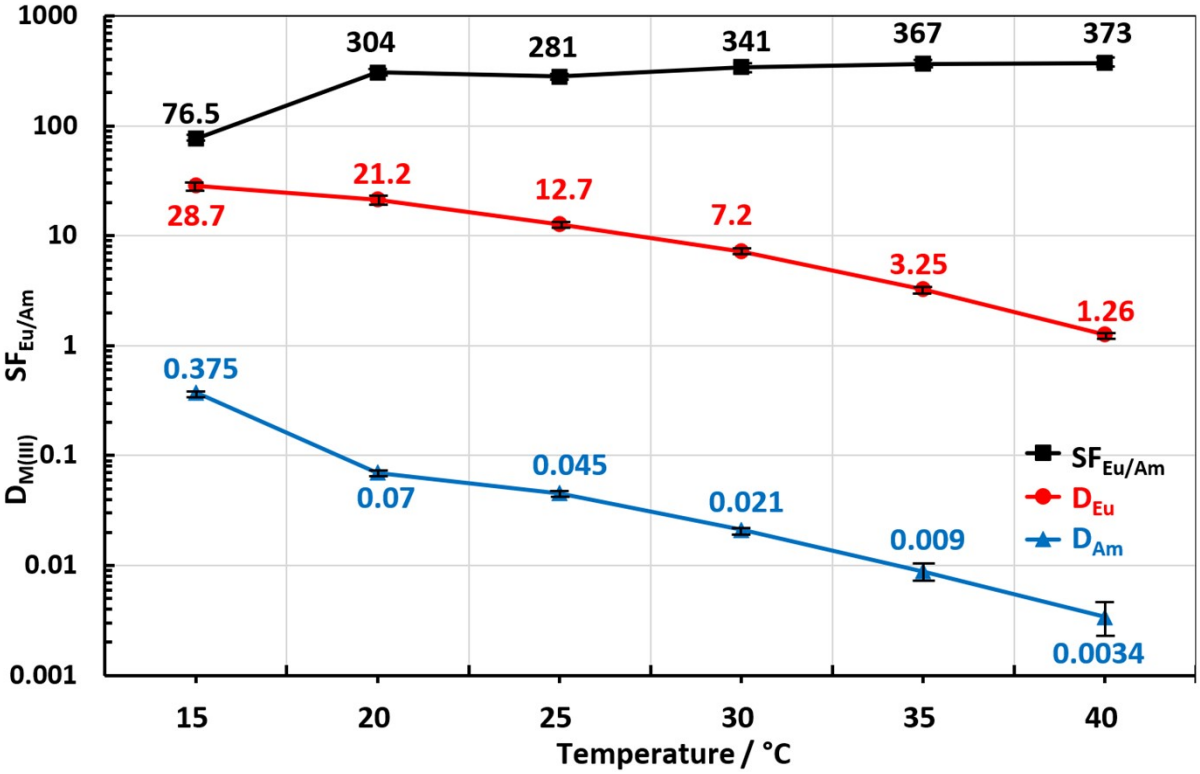


Diagram 4: Effect of temperature at 15, 20, 25, 30, 35, and 40°C on D_{Am}, D_{Eu} and $SF_{Eu/Am}$ of ligand **1** at the constant 0.05 M acidity, ligand **1** concentration at 10 mM.

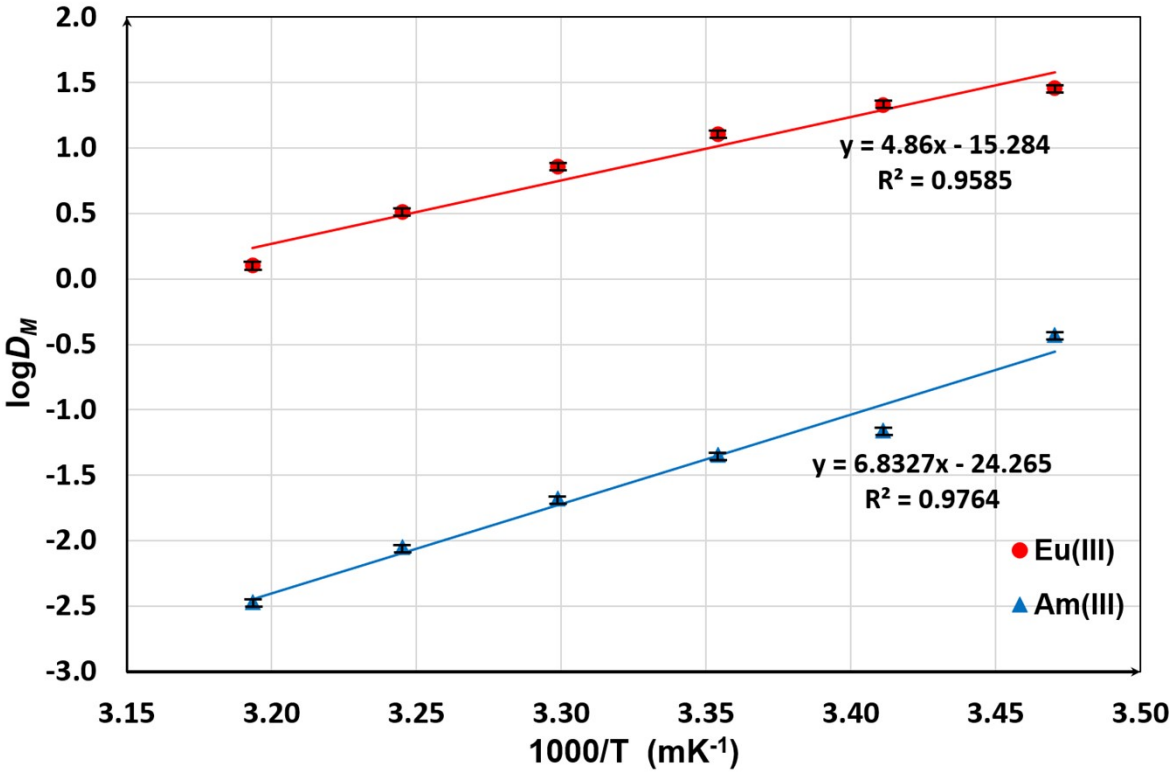


Diagram 5: Effect of temperature on the extraction of Am(III) vs Eu(II) in 0.05 M HNO_3 with 10 mM of DS-BTrzPhen (**1**): plots of logD vs. (1/T).

3.3.2.2. Diagrams for ligand **2** (DAA-BTrzPhen)

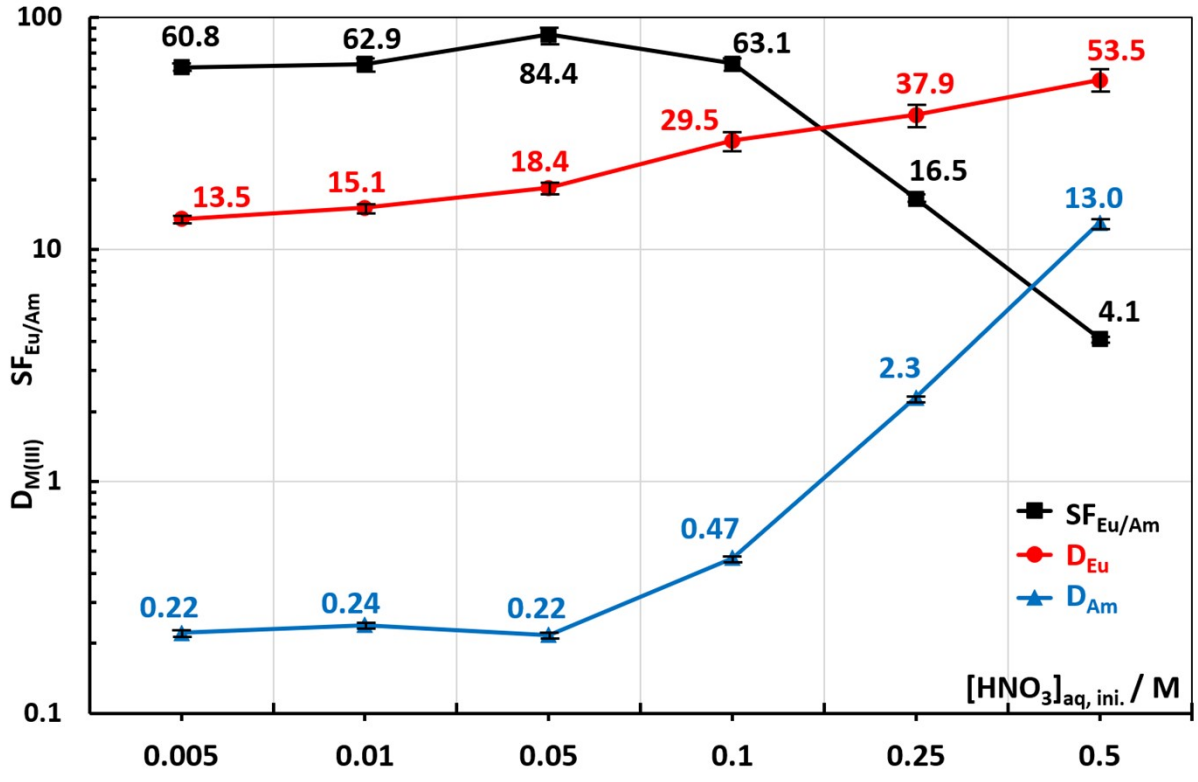


Diagram 6: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 5, 10, 50, 100, 250 and 500 mM of nitric acids and 10 mM of ligand **2**.

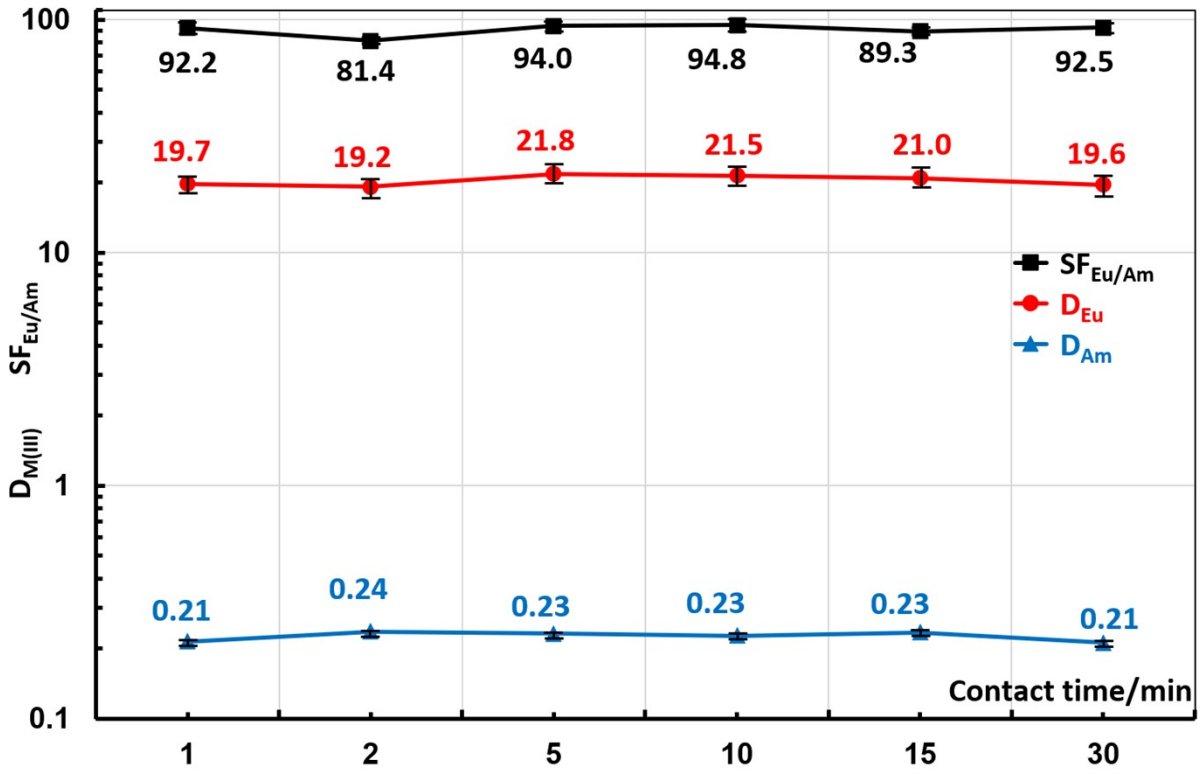


Diagram 7: D_{Am}, D_{Eu} and $SF_{Eu/Am}$ at 1, 2, 5, 10, 15 and 30 minutes of contact time, 50 mM of nitric acids and 10 mM of ligand **2**.

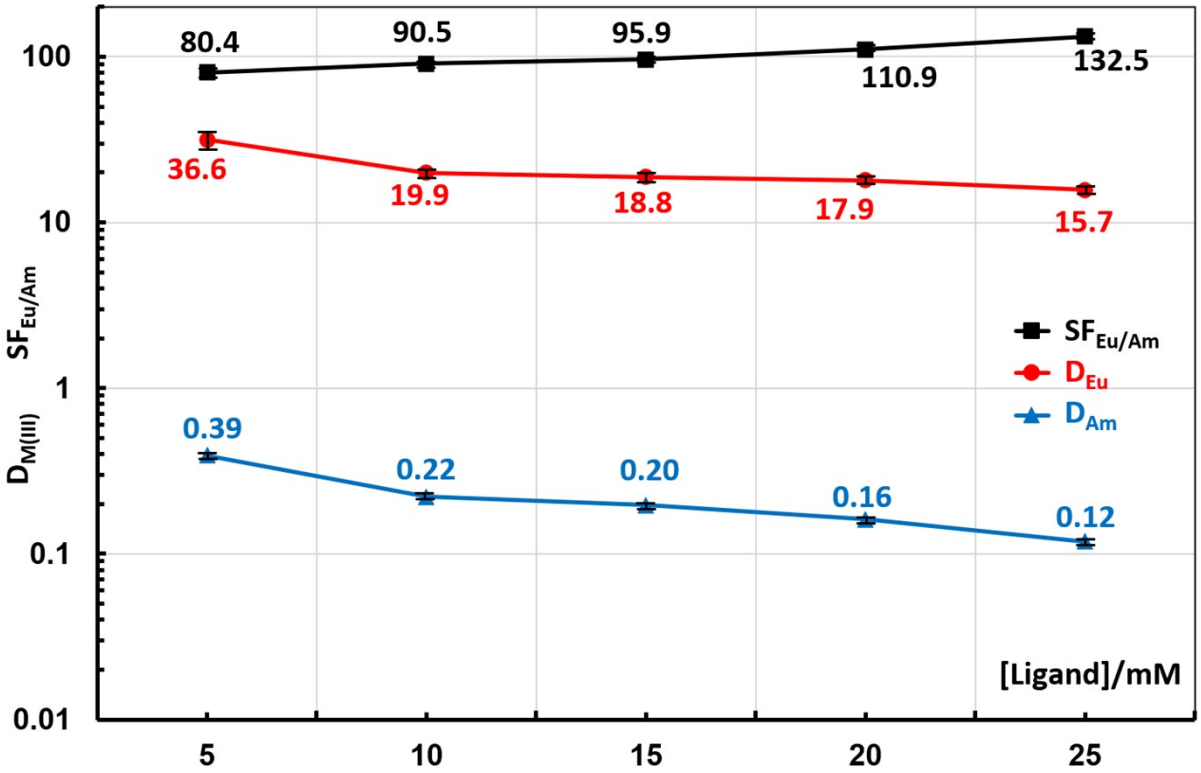


Diagram 8: Effect of ligand **2** concentration at the constant 0.05 M acidity, ligand **2** concentration ranging from 5 mM to 25 mM.

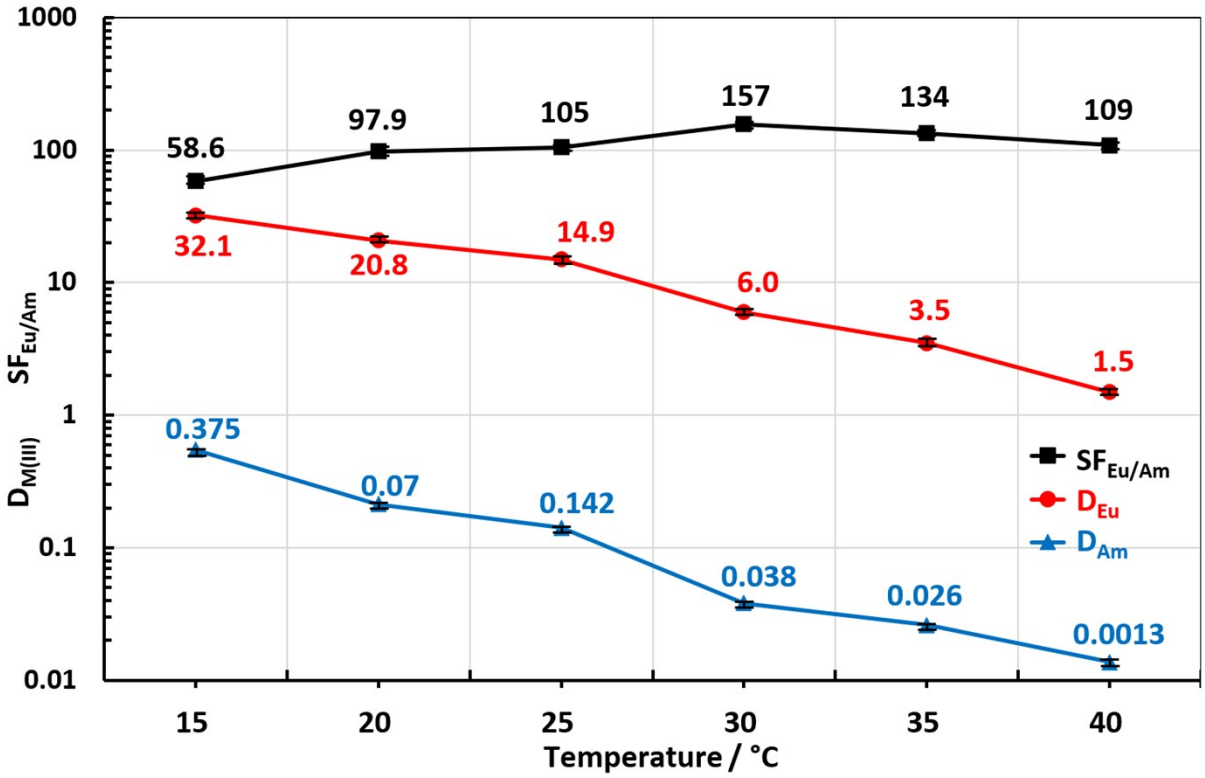


Diagram 9: Effect of temperature at 15, 20, 25, 30, 35, and 40°C on D_{Am}, D_{Eu} and $SF_{Eu/Am}$ of ligand **2** at the constant 0.05 M acidity, ligand **1** concentration at 10 mM.

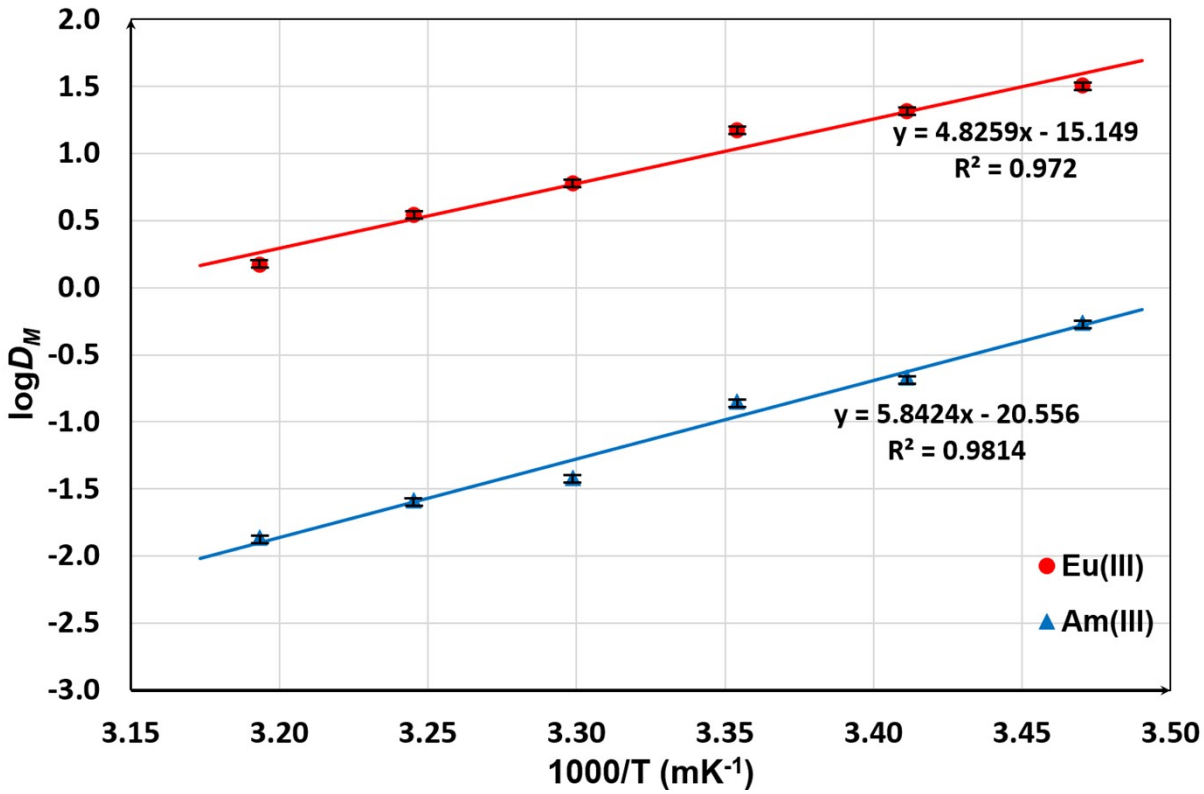


Diagram 10: Effect of temperature on the extraction of Am(III) vs Eu(II) in 0.05 M HNO_3 with 10 mM of DAA-BTrzPhen (**2**): plots of logD vs. (1/T).

4. Spectroscopic titrations

4.1. Spectroscopic titrations of DS-BTrzPhen:

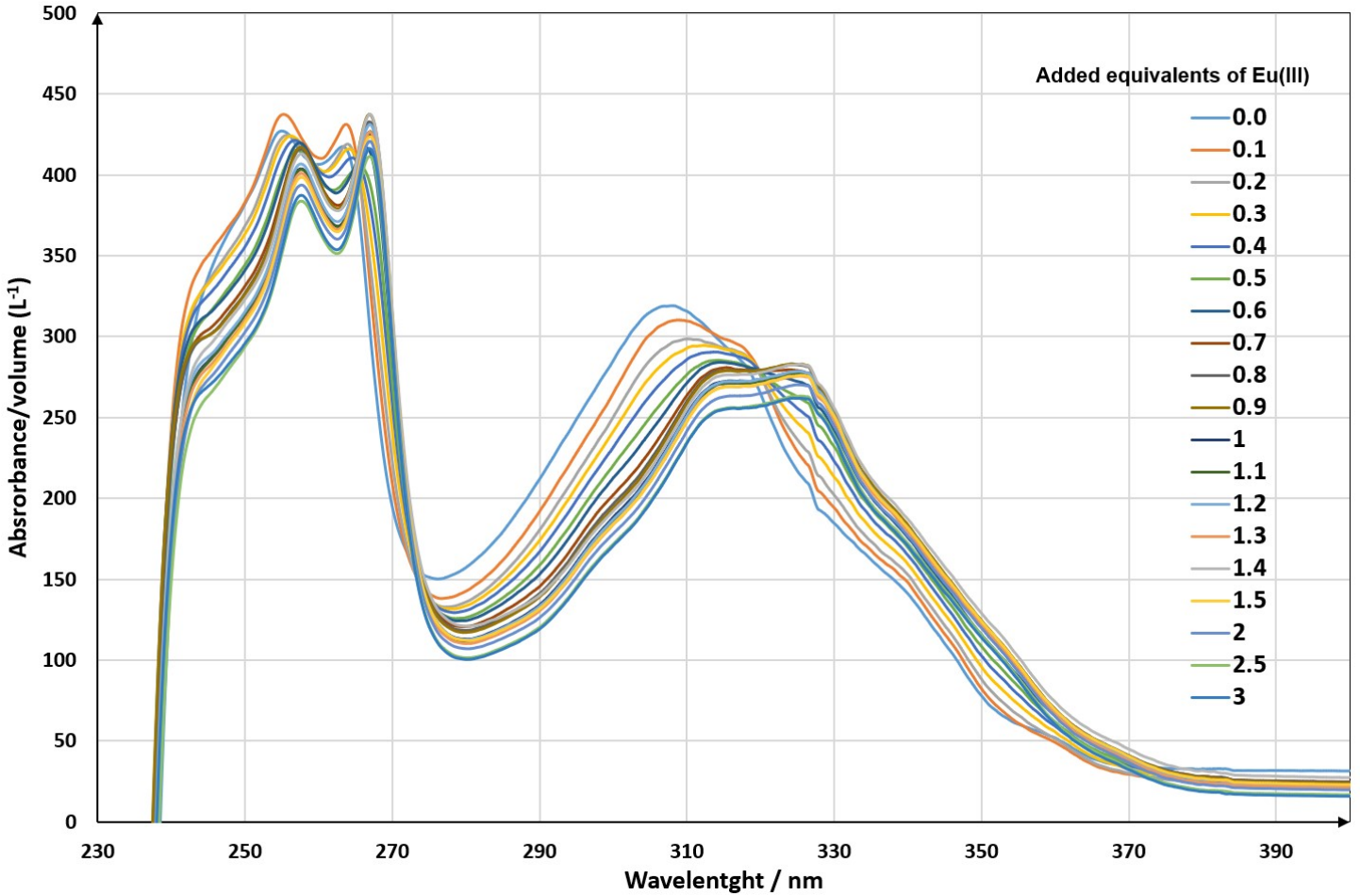


Diagram 11: Titration of DS-BTrzPhen (**1**) with $Eu(NO_3)_3$ in neutral water (I = 0.01 M Me_4NNO_3), initial conditions: [DS-BTrzPhen (**1**)] = 1×10^{-5} M, Volume = 2.0 mL; Titrant: [$Eu(NO_3)_3$] = 1 mM)

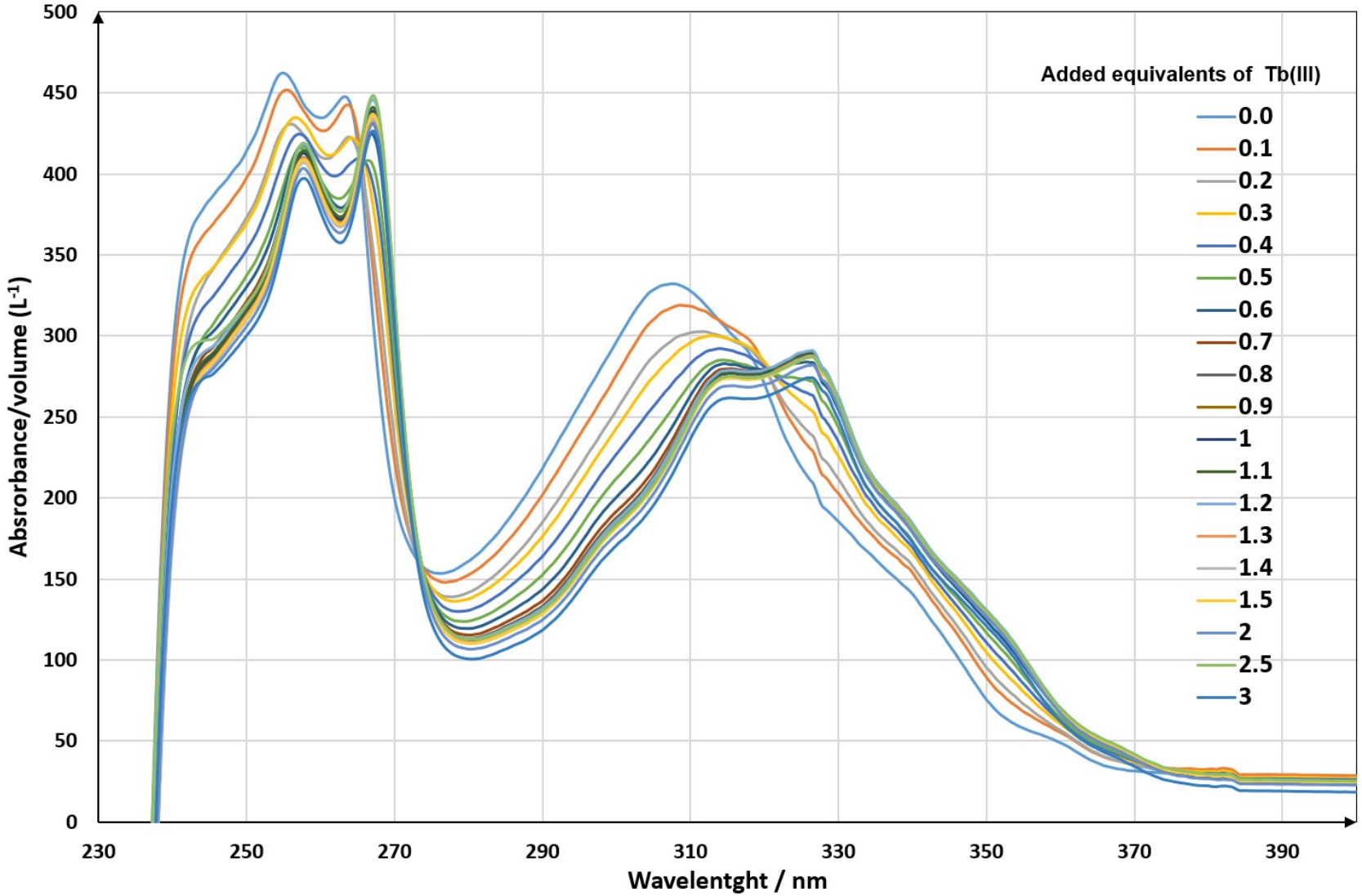


Diagram 12: Titration of DS-BTrzPhen (**1**) with $Tb(NO_3)_3$ in neutral water (I = 0.01 M Me_4NNO_3), initial conditions: [DS-BTrzPhen (**1**)] = 8×10^{-6} M, Volume = 2.0 mL; Titrant: [$Tb(NO_3)_3$] = 1 mM)

4.2. Spectroscopic titrations of DAA-BTrzPhen:

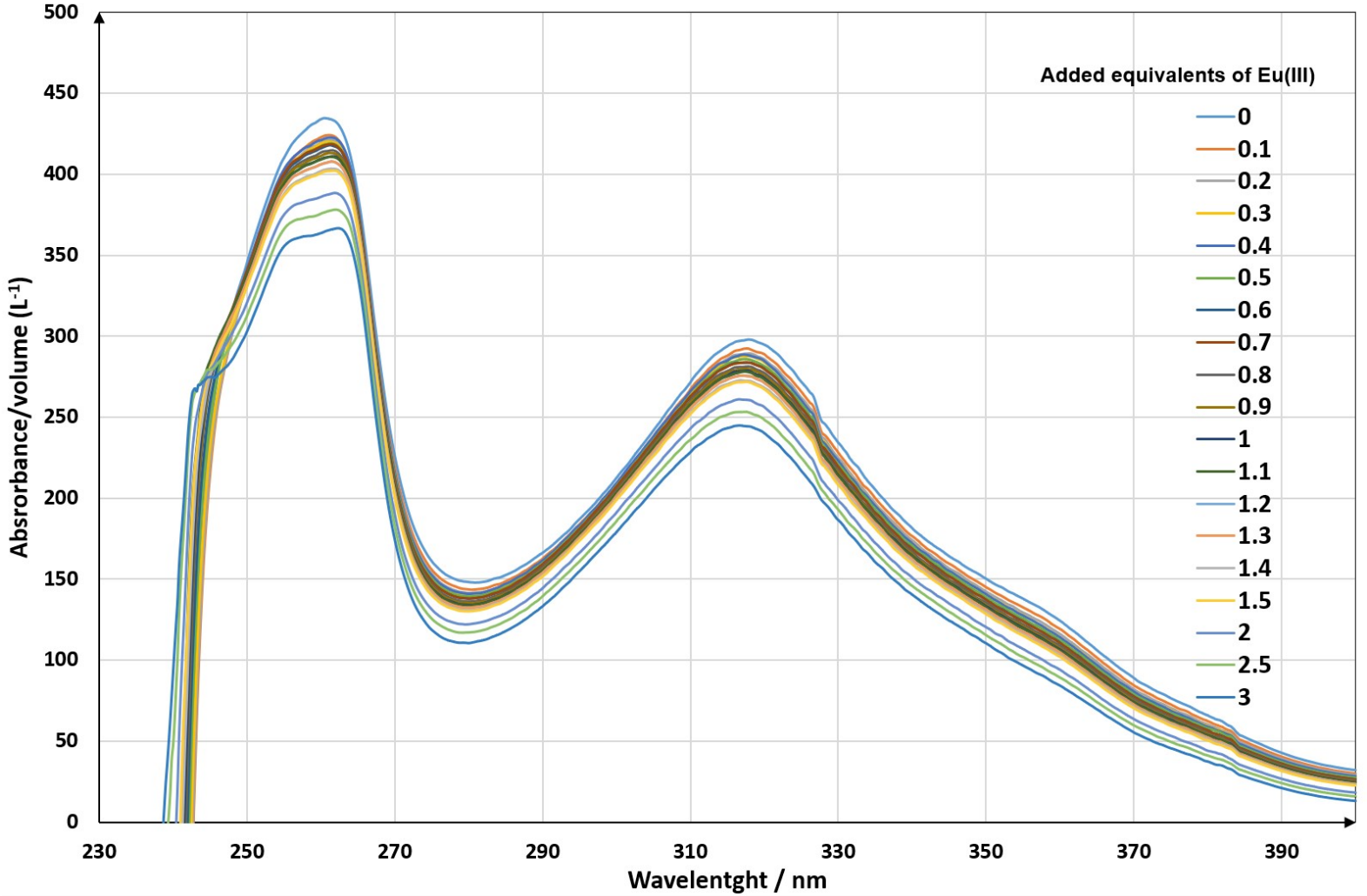


Diagram 13: Titration of DAA-BTrzPhen (**1**) with $Eu(NO_3)_3$ in acidic solution of nitric acid ([HNO3] = 0.028, I = 0.01 M Me_4NNO_3), initial conditions: [DAA-BTrzPhen (**1**)] = 2×10^{-5} M, Volume = 2.0 mL; Titrant: [$Eu(NO_3)_3$] = 1 mM)

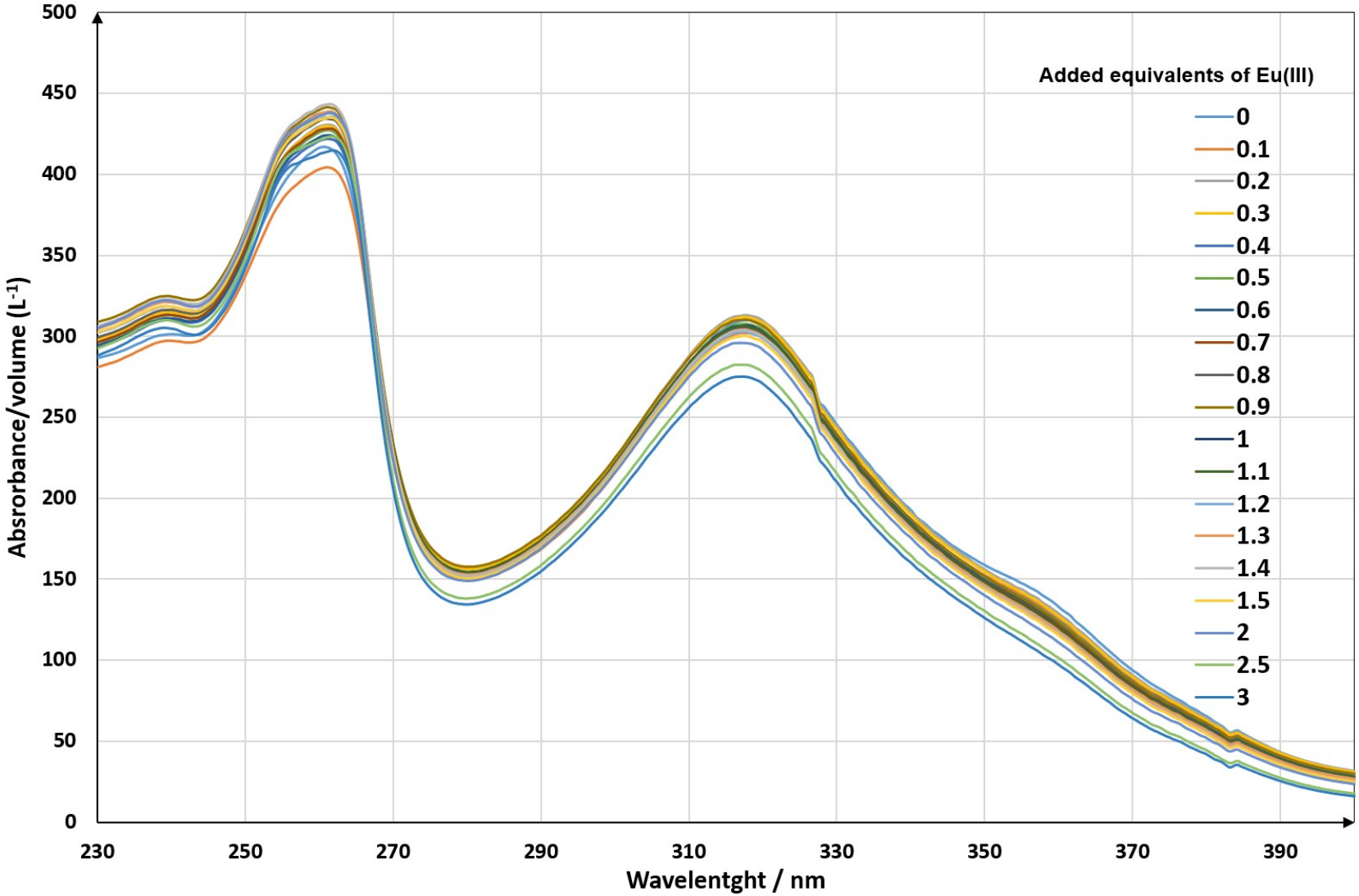


Diagram 14: Titration of DAA-BTrzPhen (**2**) with $Eu(OTf)_3$ in solution of $HClO_4$ (0.03 M), initial conditions: [DAA-BTrzPhen (**2**)] = 2×10^{-5} M, Volume = 2.0 mL; Titrant: [$Eu(OTf)_3$] = 1 mM)

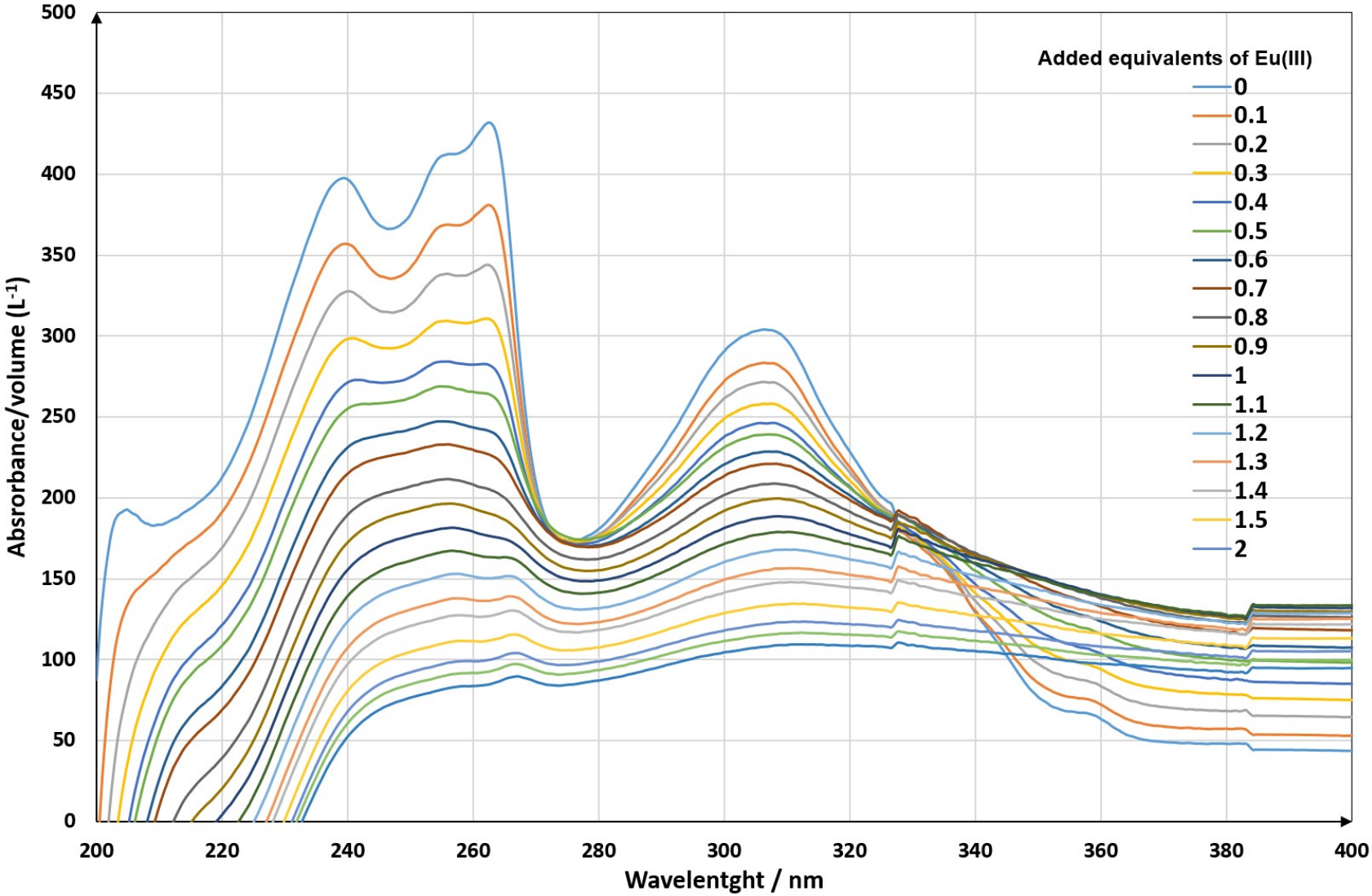


Diagram 15: Titration of DAA-BTrzPhen (**2**) with $Eu(OTf)_3$ in blend of solvents (Acetonitrile/Methanol/Water = 2:2:1), initial conditions: [DAA-BTrzPhen (**2**)] = 2×10^{-5} M, Volume = 2.0 mL; Titrant: [$Eu(OTf)_3$] = 1 mM)

ligand	Ln salt	Solvent	overall stability constants (log β_{ML})				
			$\log\beta_{11}$	standard deviation[b]	$\log\beta_{12}$	standard deviation[b]	σ
1	**$Eu(NO_3)_3$**	water[a]	7.052	0.0343	12.3672	0.1427	0.022057
	$Tb(NO_3)_3$	water[a]	6.5798	0.0262	12.0096	0.0792	0.014531

*Table 20: Stability constants for the 1:1 and 1:2 Metal to Ligand Complexes **8** and **9** Determined from Fits to Spectroscopic Data Using HyperQuad[5] (T = 25 °C). [a]I = 0.01 Me_4NNO_3, [b]Standard deviations determined by the fitting process, [c]Sigma*

4.3. Speciation diagrams for DS-BTrzPhen:

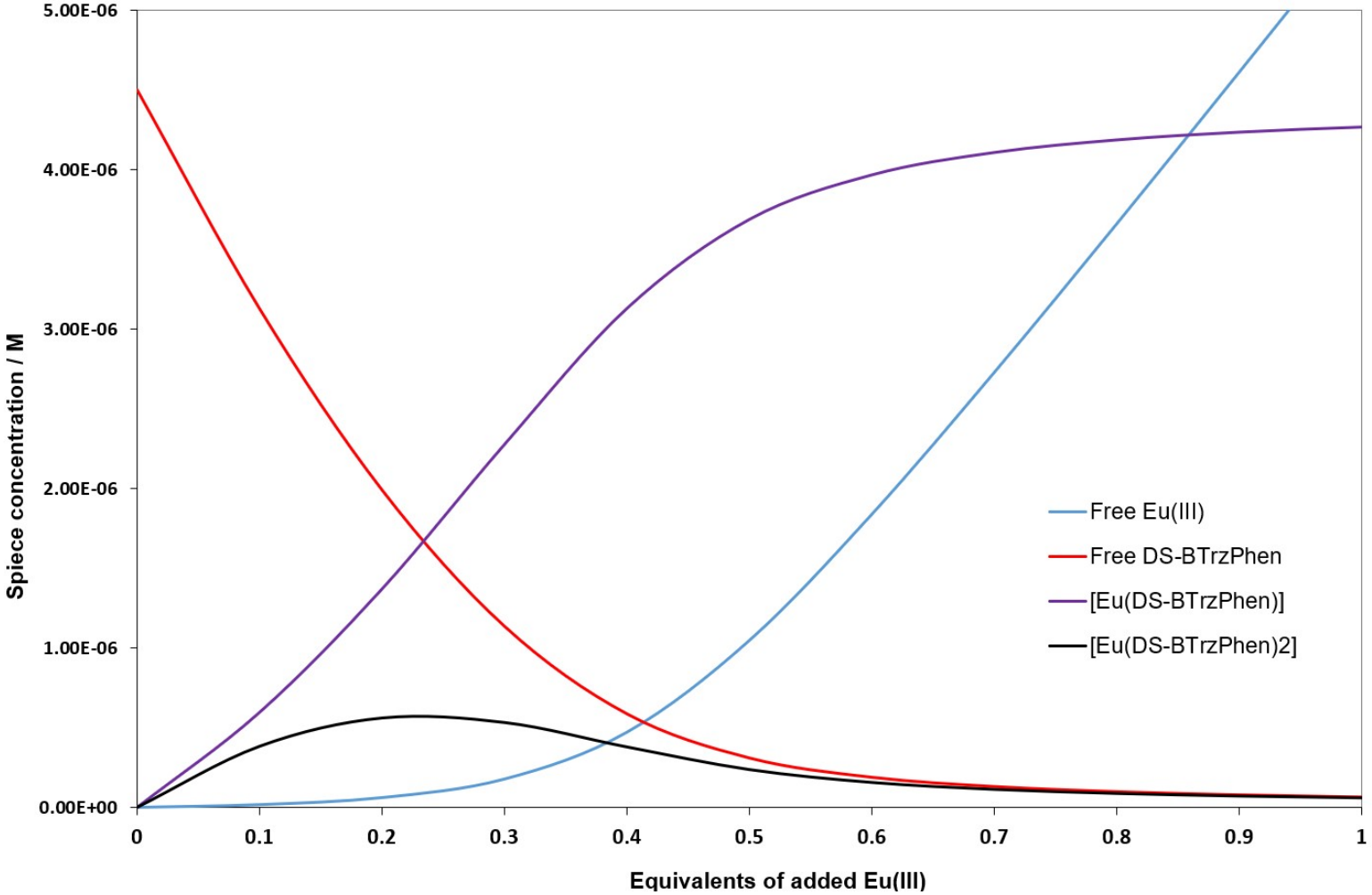


Diagram **16**: Speciation diagram for DS-BTrzPhen (**1**) complexed with $Eu(NO_3)_3$ in 0.028 HNO_3 using stability constants provides in the Table **20**.

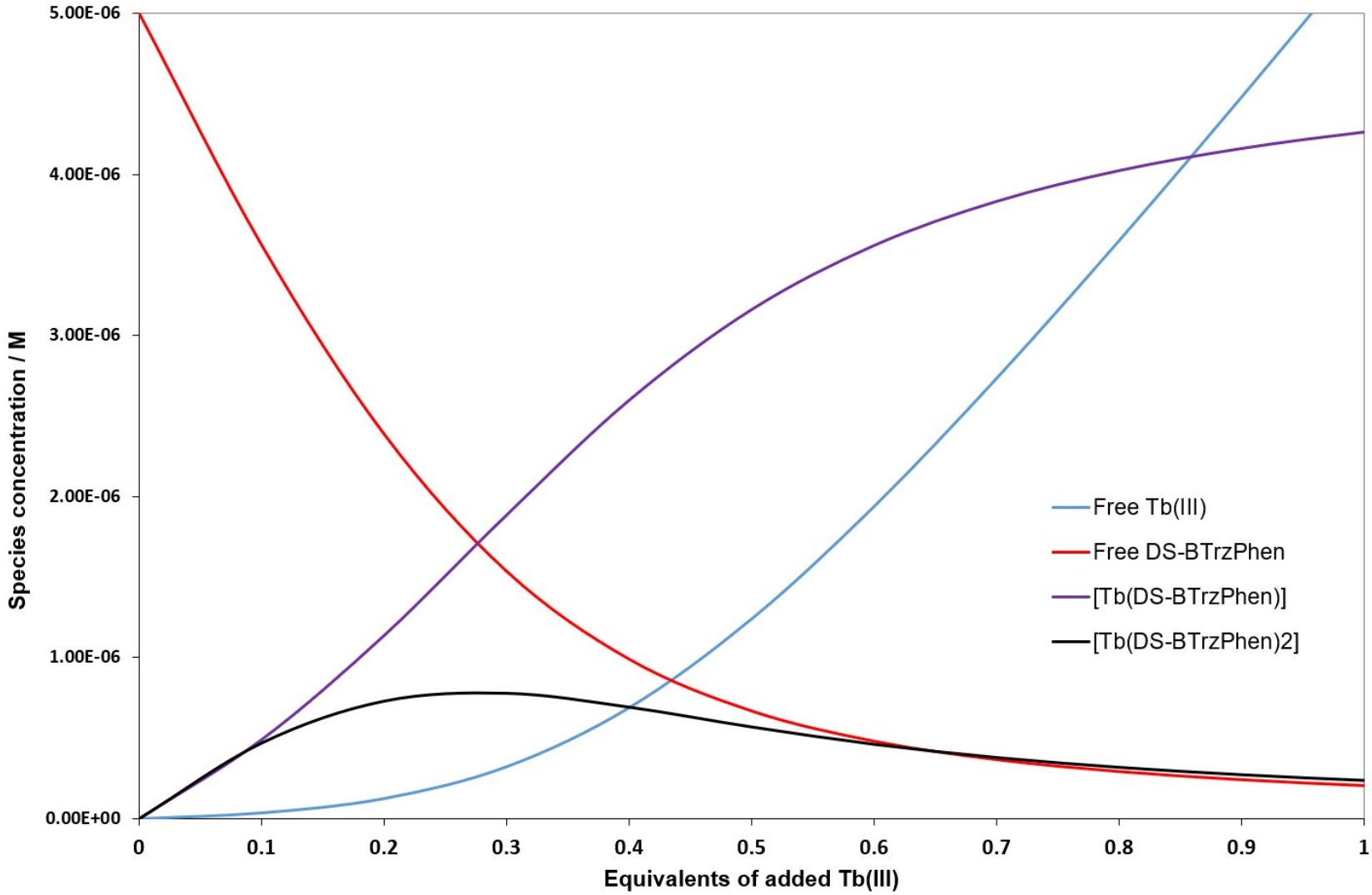


Diagram **17**: Speciation diagram for DS-BTrzPhen (**1**) complexed with $Tb(NO_3)_3$ in 0.028 HNO_3 using stability constants provides in the Table **20**.

5. Fluorescence spectroscopy

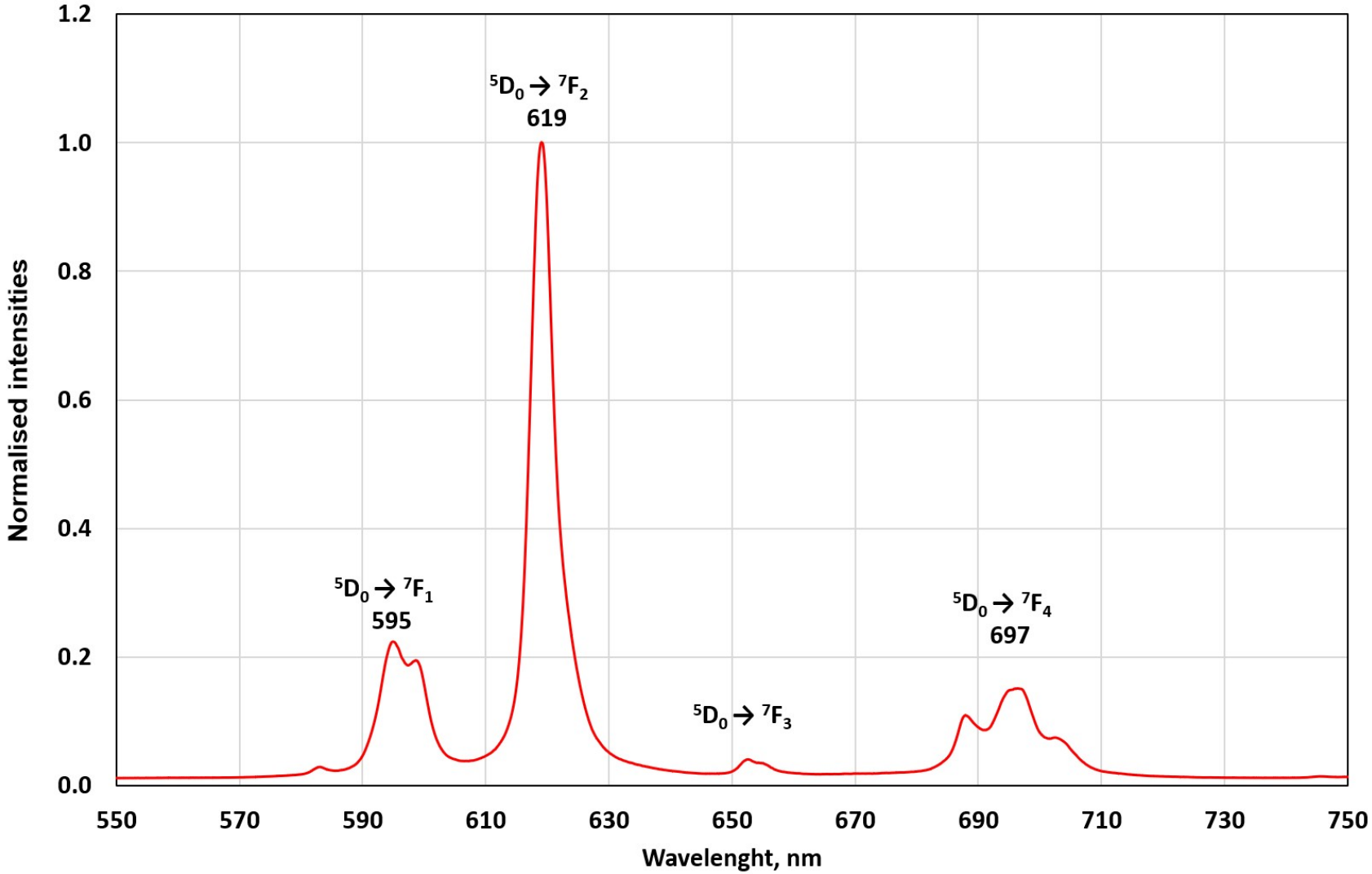


Diagram **18**: Fluorescence emission spectrum of DS-BTrzPhen-Eu complex (0.2 mM, molar ration 2:1) in water at excitation wavelength of 326 nm

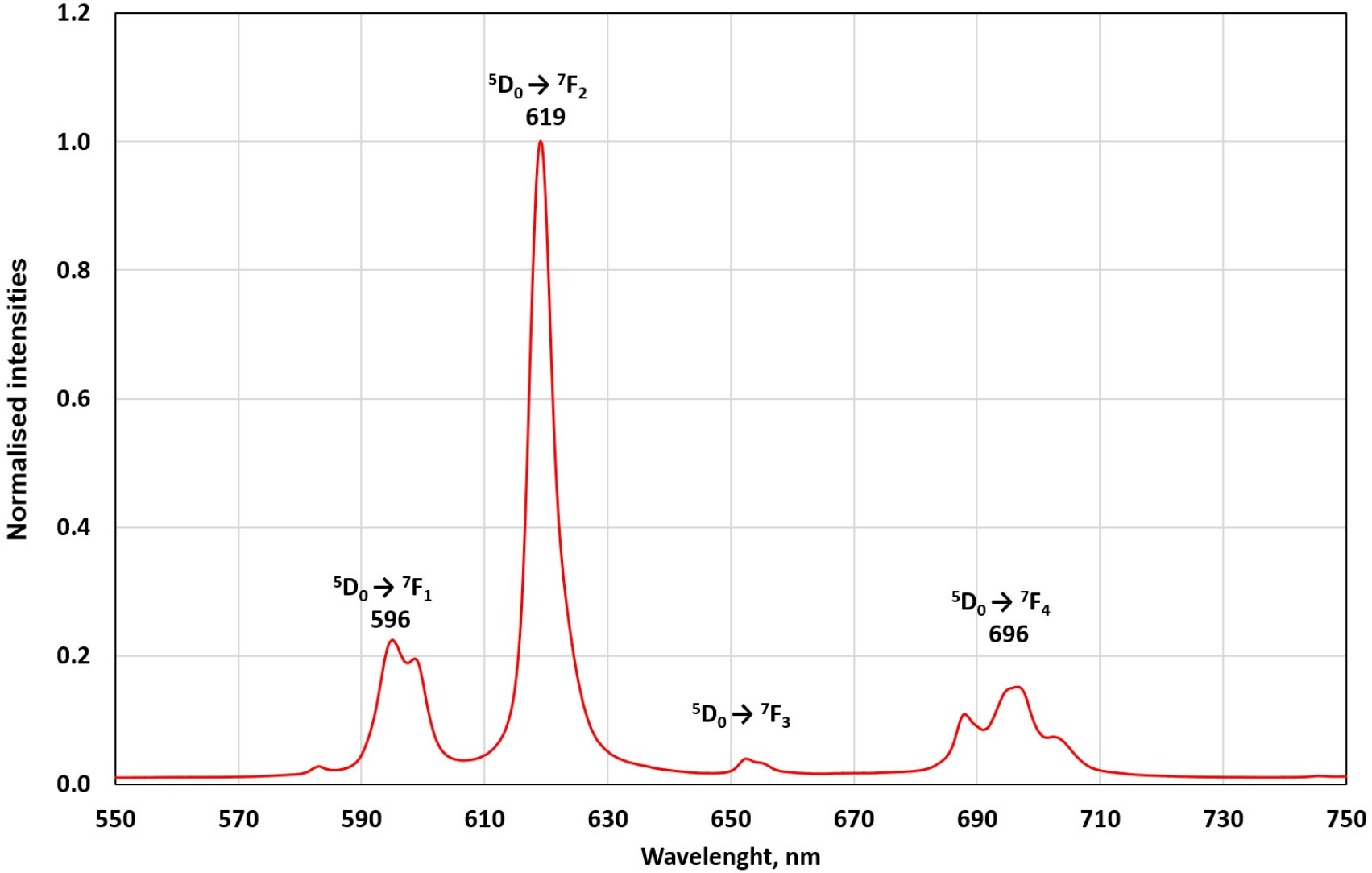


Diagram **19**: Fluorescence emission spectrum of DS-BTrzPhen-Eu complex (0.2 mM, molar ration 2:1) in water at excitation wavelength of 267 nm.

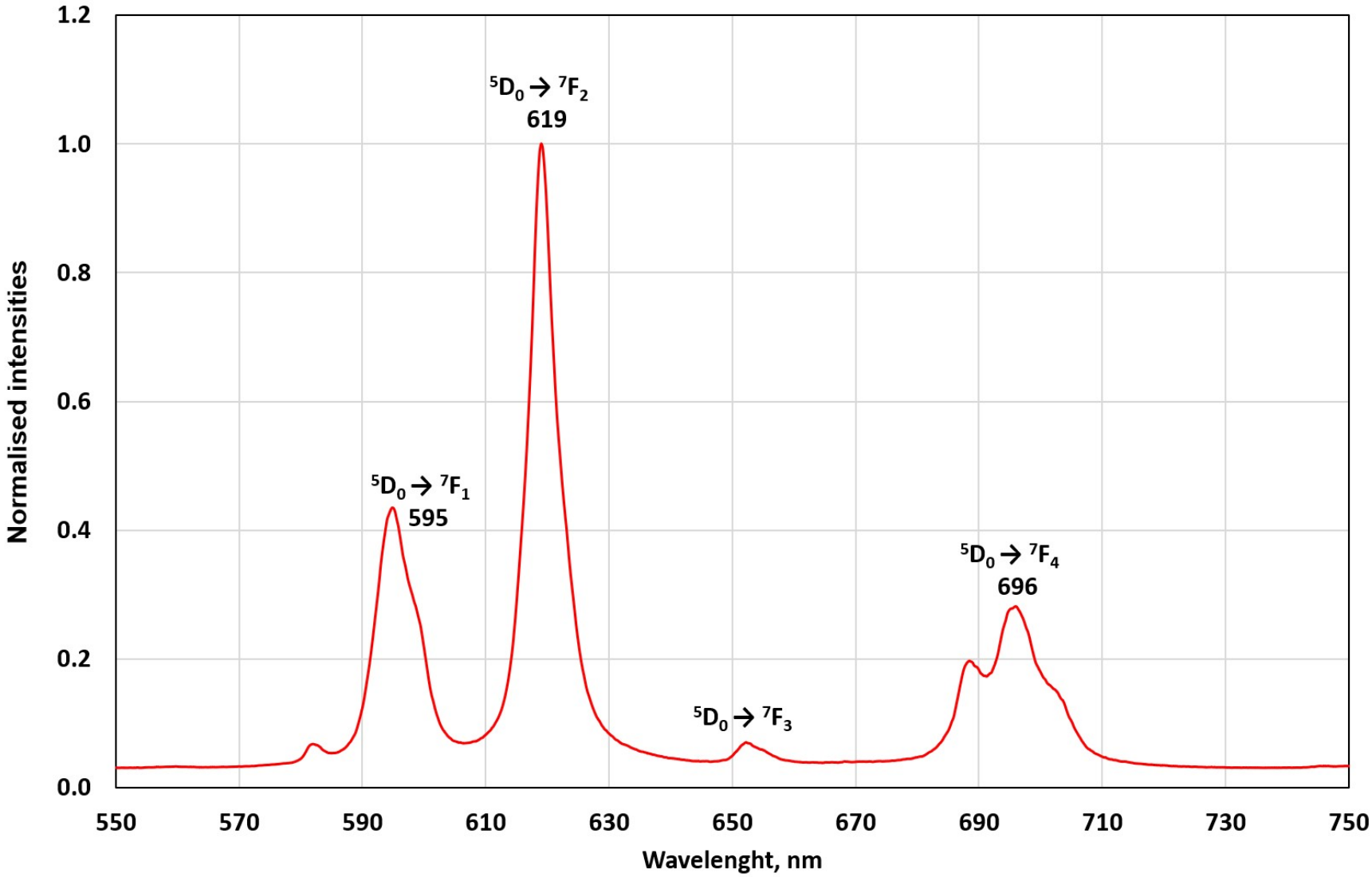


Diagram **20**: Fluorescence emission spectrum of DAA-BTrzPhen-Eu complex (0.2 mM, molar ration 2:1) in aqueous solution of $HClO_4$ (0.03 M) at excitation wavelength of 326 nm.

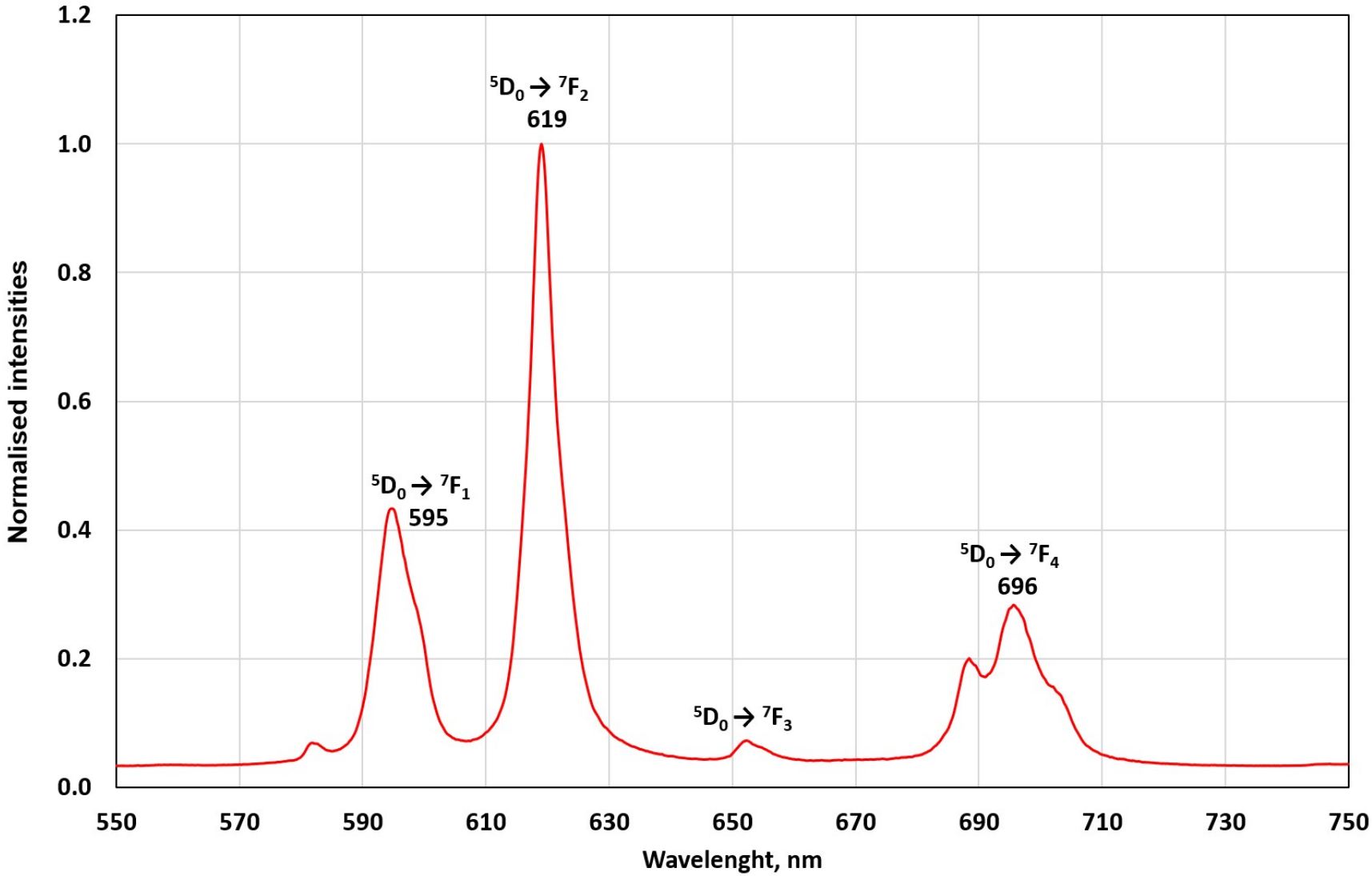


Diagram **21**: Fluorescence emission spectrum of DAA-BTrzPhen-Eu complex (0.2 mM, molar ration 2:1) in aqueous solution of $HClO_4$ (0.03 M) at excitation wavelength of 267 nm.

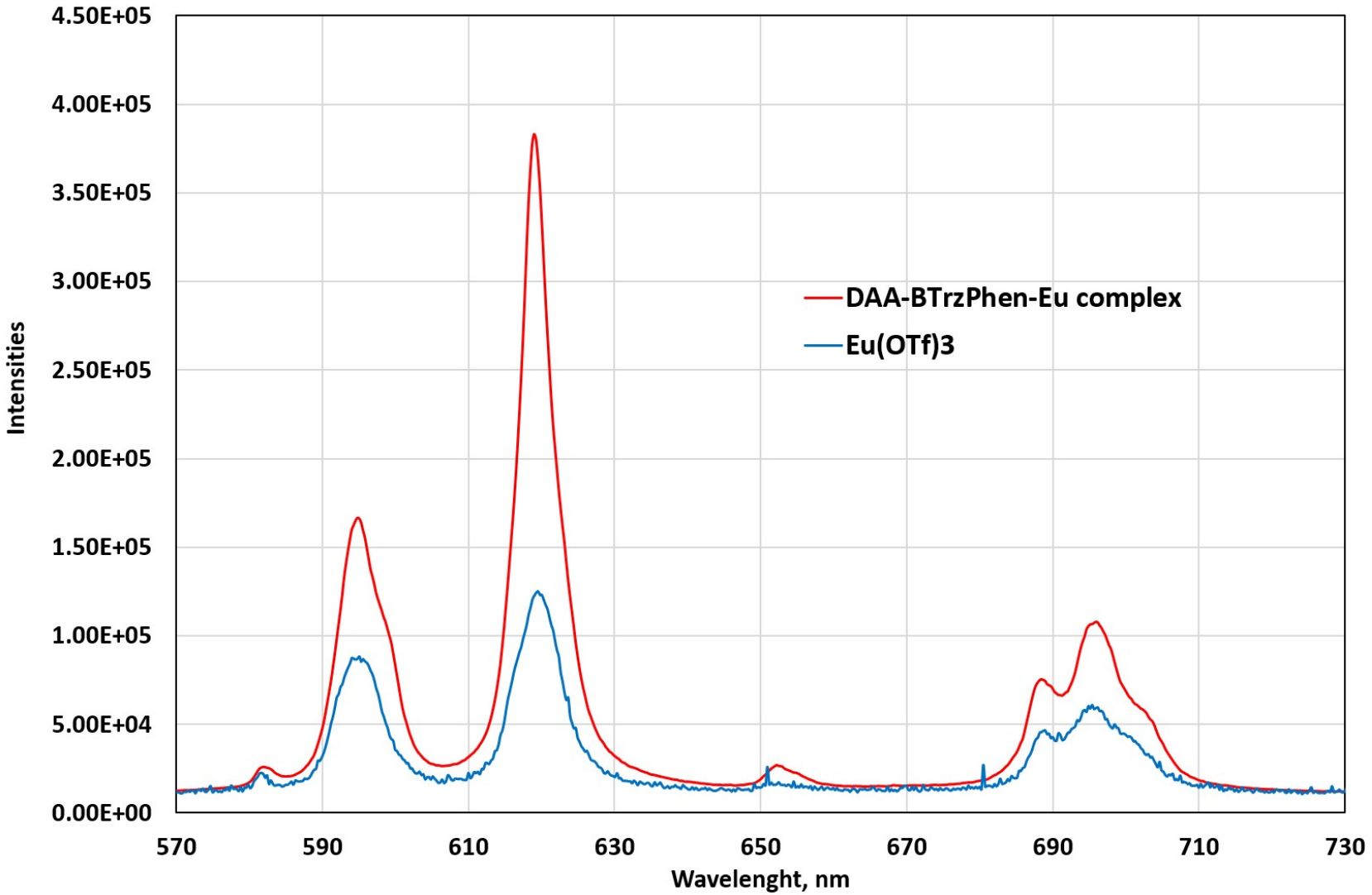


Diagram **22**: Superimposition of the fluorescence emission spectrum of DAA-BTrzPhen-Eu complex (0.2 mM, molar ration 2:1) and fluorescence emission spectrum of DAA-BTrzPhen-$Eu(OTf)_3$ (2.8 mM), both in aqueous solution of $HClO_4$ (0.03 M) at excitation wavelength of 326 nm.

6. References

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