Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

A versatile and highly efficient post-functionalization method for grafting organic molecules onto Anderson-type polyoxometalates.

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General remarks

Reagents and solvents were purchased from commercial sources and used without further purification and were used as such. The precursor TBA_4-Mo_8O_{26} POM was synthesized and characterized following a published procedure. All reactions were performed under an argon atmosphere with magnetic stirring. In the case of the CuAAC reactions the solvents were purged with argon for a short time.

Techniques

NMR spectroscopy

^1H and ^1H-decoupled ^{13}C NMR spectra were recorded on a bruker Avance 300 (300/75 Mhz), 400 (400/100 Mhz) and 600 (600/150 Mhz) spectrometer. 2D ^1H-^{13}C HSQC measurements were performed on a bruker Avance 400 (400-100) spectrometer. All measurements were performed at room temperature and in CD_3CN or DMSO-d_6, as mentioned in the description of every compound. TMS (δ = 0.00 ppm) [^1H] or the deuterated solvent peaks of CD_3CN (δ = 1.32 or 118.26 ppm) or DMSO-d6 (δ = 39.52 ppm) [^{13}C] were used as an internal reference. The ^1H NMR settings for compound 2,3 and 4a-4e were customized to visualize the protons in the proximity of the paramagnetic Mn(III) center: O1P = 35.00 ppm, SW = 90.05 ppm, TD= 64k. NMR spectra for all compounds can be found in figures S3-27.

IR spectroscopy

FT-IR spectra were recorded in solid state on a Bruker Vertex 70 spectrometer. Spectra were atmosphere corrected when measured.

Elemental analysis

Carbon, hydrogen and nitrogen contents were determined using a CE Instruments EA-1110 elemental analyser.

Crystallography

Single crystals of **3**, suitable for X-ray diffraction were obtained by diffusing diethyl ether in a solution of the compound in acetonitrile at room temperature. X-ray intensity data were collected at 100K on an Agilent Supernova diffractometer, equipped with an Atlas CCD detector, using Mo Kα radiation (λ = 0.71073 Å). The images were interpreted and integrated with the CrysAlisPro software from Agilent Technologies.[1] Using Olex2[2], the structure was solved with the ShelxS[3] structure solution program using Direct Methods and refined with the ShelxL[3] refinement package using full-matrix least squares minimization on F2. The asymmetric unit contains four polyoxometalate clusters, twelve TBA, ten acetonitriles and a half ethanol molecule. Several acetonitriles and butyl or azide chains were refined with double conformations. Distance restraints (DFIX) were used for some TBA and acetonitrile moieties. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times Ueq of the parent atoms (1.5 for methyl groups). Some acetonitriles, butyl or azide chains were restrained to isotropic behavior (ISOR) or to have the same Uij component (SIMU). Enhanced rigid bond restraints (RIGU) were used for all atoms. The four Mn atoms, some TBA side chains and solvent molecules were refined isotropically. The PLATON SQUEEZE[4] method was used to address solvent disorder (62.7 electrons in solvent accessible volume of 324.7 Å3). CCDC 1401599 contains the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Crystallographic data

$C_{259.62}H_{531.23}Mn_4Mo_{24}N_{54}O_{104.50}$, M =8604.29 g mol^{-1}, triclinic, P-1 (no. 2), a = 22.0899(3) Å, b = 29.6893(4) Å, c = 31.1610(5) Å, α = 112.9562(15)°, β = 91.6469(13)°, γ = 102.4493(12)°, V = 18230.3(5) Å^3, T = 100.01(10) K, Z = 2, ρ_{calcd} = 1.567 g cm^{-3}, μ(Mo Kα) = 1.008 mm^{-1}, F(000) = 8822, crystal size 0.4 x 0.2 x 0.2 mm^3, 133565 reflections measured, 66545 unique (R_{int} = 0.0401) which were used in all calculations, 4208 parameters, 4105 restraints. The final wR_2 was 0.1918 (all data) and R_1 was 0.0895 (I ≥2sigma(I)).

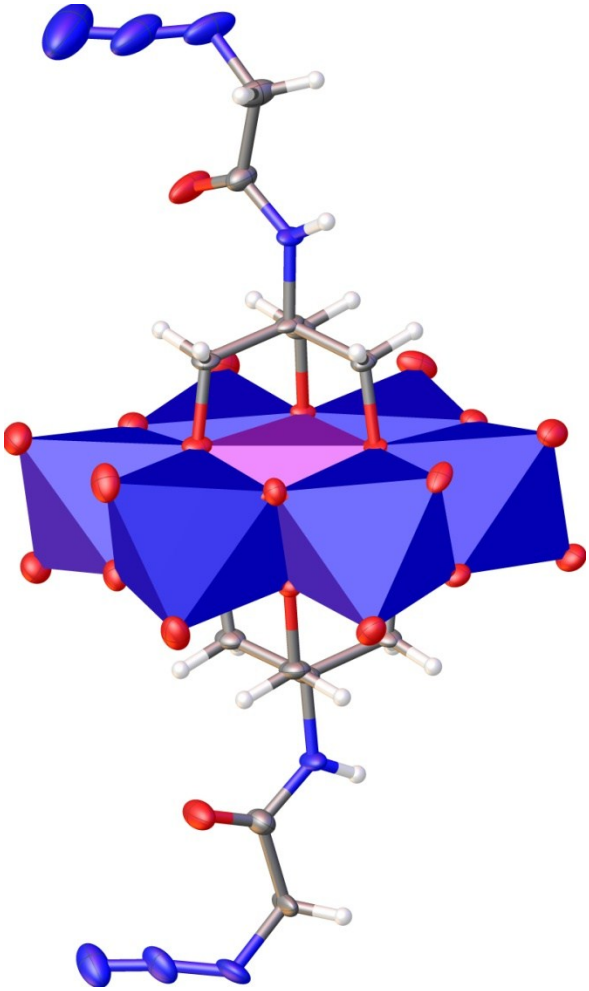


Figure S1: Molecular structure of compound 3. Only one of four equivalent POMs is shown. Tetrabutylammonium counterions were omitted for clarity. (Blue octahedra: Mo, Pink octahedron: Mn, Grey: C, Red: O, Blue: N, White: H)

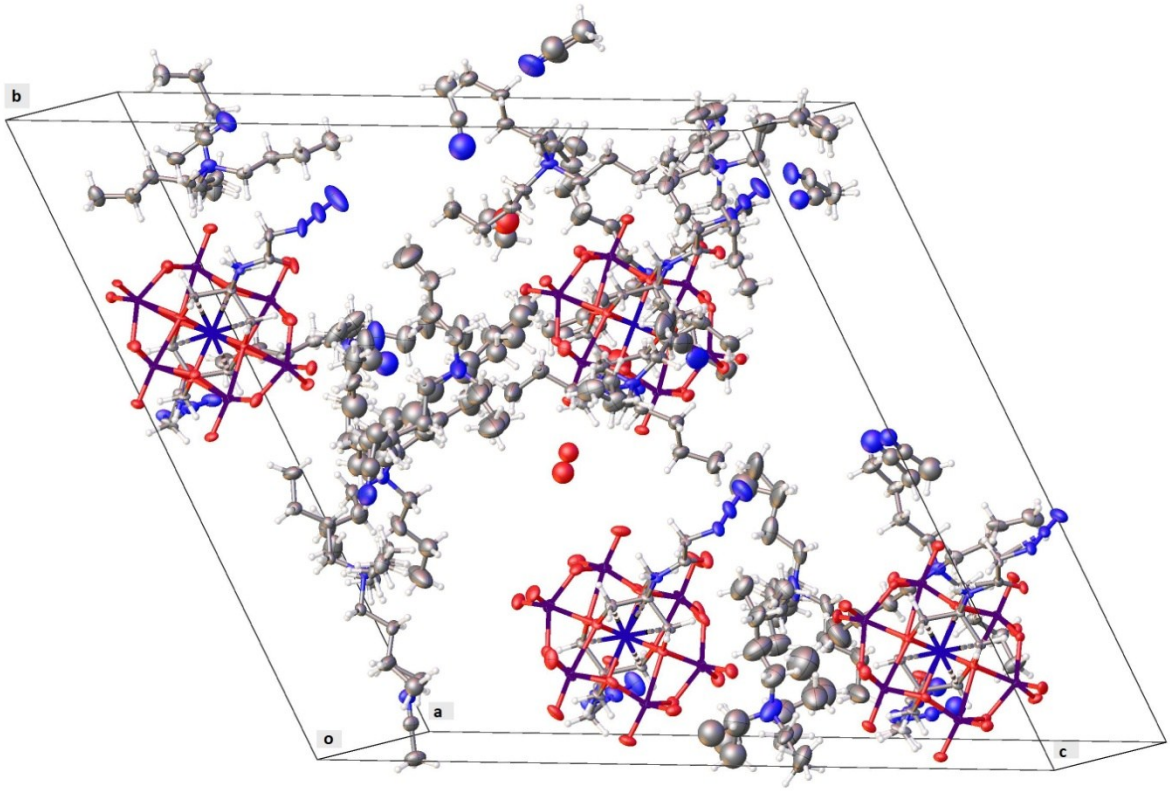


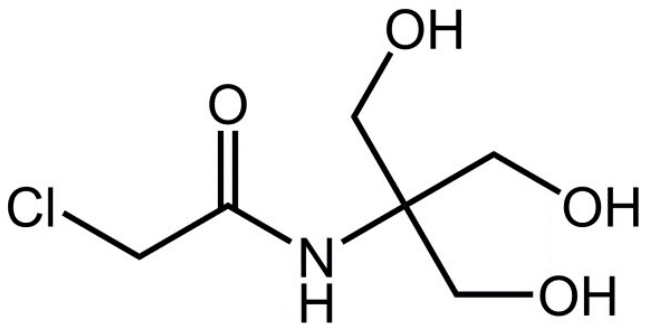
Figure S2: Assymmetric unit of compound 3. Thermal ellipsoids are drawn at 50% probability level.

Synthetic procedures and characterization

Synthesis of the azide-functionalized Anderson POM

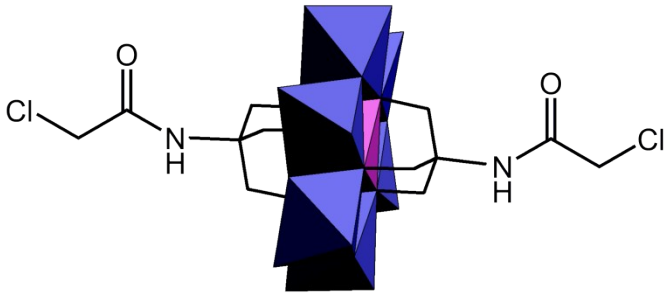
The synthesis of the double azide functionalized Anderson hybrid POM (compound 3) is straightforward, starting with cheap and easily obtained starting materials, and could easily be scaled up without loss of yield or purity. In a first step, the functional organic group is formed through an acylation reaction of tris and ethyl chloroacetate in methanol. In a next step this tri-alkoxy containing chloride functionalized organic moiety is reacted with a preformed TBA_4-Mo_8O_{26} species and Mn(III) acetate in acetonitrile. The resulting chloride functionalized Anderson POM (compound 2) is consequently reacted with sodium azide in DMF affording the final azide functionalized POM structure (compound 3). The compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and FT infrared spectroscopy. After recrystallization from acetontrile small orange needle-like crystals were obtained suitable for single crystal XRD measurements.

Compound 1: Chloride-functionalized tris ligand, $C_6H_{12}NO_4Cl$



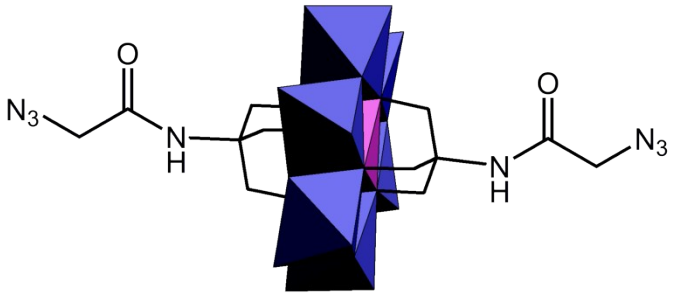
To an ice-cooled solution of 12.84 ml of ethyl chloroacetate (0.120 mmol, 1.2 eq.) in 7.5 ml of methanol was added 12.10 g of tris(hydroxymethyl)aminomethane (0.100 mmol, 1 eq.) in small portions together with an additional 25 ml of methanol. The ice bath was removed and the suspension was stirred for 2 days, during which the solid tris(hydroxymethyl)aminomethane slowly disappeared. The solution was partially evaporated and the remaining solution was placed in the fridge for 30 min, after which the obtained crystals were collected on a glass-filter. The product was recrystallized by redissolving in hot methanol and placing the solution in the fridge overnight. Large off-white crystals formed overnight which were collected on a glass-filter. Yield: 7.85 g (40 %). ^{1}H NMR (400 MHz, D_2O): δ = 4.20 ppm (s, 2H, CO-C**H$_2$**-Cl), 3.84 ppm (s, 6H, O-C**H$_2$**-C). ^{13}C NMR (100 MHz, D_2O): δ = 170.99 ppm (NH-**C**O), 63.65 ppm (CH_2-**C**-NH), 61.60 ppm (O-**C**H_2-C), 44.27 ppm (CO-**C**H_2-Cl). ESI-MS $C_4H_{11}NO_3Cl$: 220 [M+Na^+]. Elemental analysis (%) for $C_6H_{12}NO_4Cl$ (197.6 g mol^{-1}): calcd. C 36.47, H 6.12, N 7.09; found: C 36.26, H 4.92, N 6.93.

Compound 2: Chloride-functionalized POM, $(C_{16}H_{36}N)_3$-$[MnMo_6O_{18}((OCH_2)_3C_3H_3NOCl)_2]$



To a mixture of 1 equivalent of TBA_4-[α-Mo_8O_{26}][5] (3.00 g, 1.39 mmol), 1.5 equivalents of $Mn(OAc)_3 \cdot 2H_2O$ (0.56 g, 2.09 mmol) and 3.5 equivalents of compound 1 (0.96 g, 4.87 mmol) was added 90 ml of dry acetonitrile. The clear red solution was stirred and refluxed for two days under an argon atmosphere, after which a bright orange solution was obtained. The solution was centrifuged after which a small quantity of a black solid was discarded. The supernatant liquid was set for crystallization by slow diethylether diffusion. Needle-like orange crystals were obtained overnight, together with a small amount of cloudy white material. The latter was removed by repeated addition of fresh diethylether to the mixture, as the light cloudy material was suspended in the latter and could be easily removed by decantation. The pure crystalline material was dried at the air for several days. Yield: 2.72 g (72%). ^{1}H NMR (300 MHz, CD_3CN): δ = 65.28 ppm (br, 12H, O-C**H**$_2$-C), 6.95 ppm (s, 2H, -N**H**), 4.18 ppm (s, 4H, CO-C**H**$_2$-Cl), 3.11 ppm (m, 24H, **H**$_{TBA}$), 1.62 ppm (m, 24H, **H**$_{TBA}$), 1.36 ppm (m, 24H, **H**$_{TBA}$), 0.97 ppm (t, 36H, **H**$_{TBA}$). ^{13}C NMR (150 MHz, CD_3CN): δ = 167.4 ppm (NH-**C**O), 59.4 ppm (**C**$_{TBA}$), 42.4 ppm (CO-**C**H_2-Cl), 24.4 ppm (**C**$_{TBA}$), 20.7 ppm (**C**$_{TBA}$), 14.1 ppm (**C**$_{TBA}$). IR:. $\tilde{\nu}$ = 3296 (w), 3235 (w), 3067 (w), 2960 (m), 2872 (w), 1695 (m), 1551 (m), 1468 (m), 1380 (w), 1334 (w), 1223 (w), 1152 (w), 1110 (w), 1037 (m), 938 (s), 917 (s), 899 (s), 657 (vs), 563 (s), 459 (m), 411 (m) cm^{-1}. Elemental analysis (%) for $C_{60}H_{126}MnMo_6N_5O_{26}Cl_2$ (2035.26 g mol^{-1}): calcd. C 35.41, H 6.24, N 3.44; found: C 35.07, H 6.43, N 3.44.

Compound 3: Azide-functionalized POM, $(C_{16}H_{36}N)_3$-$[MnMo_6O_{18}((OCH_2)_3C_3H_3N_4O)_2]$



To a solution containing 2.04 grams (1 mmol) of compound 2 in 100 ml dry DMF was added 6 eq. of NaN_3 (0.39 g, 6 mmol). The mixture was stirred and heated to 55 °C under an argon atmosphere for 2 days, after which the solution was evaporated to complete dryness. A minimal amount of acetonitrile was added to the remaining solid to dissolve all POM material and subsequently the suspension was centrifuged. The precipitate containing the excess NaN_3 and formed NaCl was discarded. The orange supernatant was added drop wise to a ten-fold excess of diethylether. The precipitate was collected through centrifugation and washed with water, ethanol and diethylether (2x). The final product was dried at air for several days. Small orange needle-like crystals suitable for single-crystal XRD were obtained by slow ether diffusion into an acetonitrile solution containing a small amount of POM material. Yield: 1.72 g (84%). ^{1}H NMR (300 MHz, CD_3CN): δ = 65.31 ppm (br, 12H, O-C**H**$_2$-C), 6.80 ppm (s, 2H, -N**H**), 4.04 ppm (s, 4H, CO-C**H**$_2$-N_3), 3.10 ppm (m, 24H, **H**$_{TBA}$), 1.61 ppm (m, 24H, **H**$_{TBA}$), 1.36 ppm (m, 24H, **H**$_{TBA}$), 0.97 ppm (t, 36H, **H**$_{TBA}$). ^{13}C NMR (150 MHz, CD_3CN): δ = 169.2 ppm (NH-**C**O), 59.4 ppm (**C**$_{TBA}$), 50.1 ppm (CO-**C**H_2-N_3), 24.4 ppm (**C**$_{TBA}$), 20.6 ppm (**C**$_{TBA}$), 14.0 ppm (**C**$_{TBA}$). IR:. $\tilde{\nu}$ = 3293 (w), 3243 (w), 3087 (w), 2962 (m), 2872 (w), 2105 (s), 1689 (m), 1567 (m), 1466 (m), 1285 (w), 1251 (m), 1112 (w), 1031 (m), 940 (s), 912 (s), 897 (s), 657 (vs), 564 (s), 464 (m), 414 (m). Elemental analysis (%) for $C_{60}H_{126}MnMo_6N_{11}O_{26}$ (2048.40 g mol^{-1}): calcd. C 35.18, H 6.20, N 7.52; found: C 35.10, H 6.03, N 7.39.

Copper catalyzed azide-alkyne cycloaddition (CuAAC) coupling methods

CuAAC coupling with $Cu(I)(CH_3CN)_4PF_6$ / DIPEA catalyst (Method A)

To a solution of compound **3** and 4 eq. of alkyne-substrate in dry acetonitrile, x equivalents of $Cu(I)(CH_3CN)_4PF_6$ were added . While stirring, x equivalents of DIPEA were added to the homogeneous solution. The reaction mixture was kept under argon during the course of the reaction. The progress of the reaction was monitored by taking a sample from the reaction mixture and recovering the POM by precipitation in diethylether, after which an IR absorbance spectrum was taken. The disappearance of the absorption peak at 2105 cm^{-1} assigned to the azide functionality was a clear indication for the course of the cycloaddition reaction. When the reaction was complete, a TBA^+-loaded cation-exchange resin was added and the reaction was stirred overnight or until all precipitate disappeared. The resin was filtered off and the clear solution was evaporated to dryness. A minimal amount of fresh acetonitrile was added to redissolve the POM and the solution was added dropwise to an excess of diethylether. The precipitate was collected by centrifugation and subsequently the remaining solid was washed with water and diethylether and dried at air for several days.

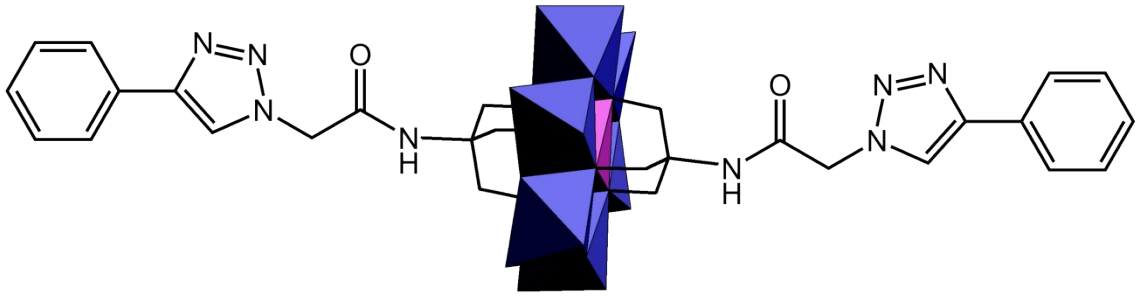
CuAAC coupling with $Cu(II)SO_4$ / NaAsc catalyst (Method B)

To a solution of compound **3** and 4 equivalents of alkyne-substrtate in dry DMF, x equivalents of $CuSO_4 \cdot 5H_2O$ were added from a stock solution in DMF. While stirring, 2 equivalents of crystalline sodium ascorbate were added to the solution. The reaction mixture was kept under argon during the course of the reaction. The progress of the reaction was monitored by taking a sample from the reaction mixture and recovering the POM by precipitation in diethylether, after which an IR absorbance spectrum was taken. The disappearance of the absorption peak at 2105 cm^{-1} assigned to the azide function was a clear indication for the course of the cycloaddition reaction. When the reaction was complete, a TBA^+-loaded cation-exchange resin was added and the reaction was stirred overnight or until all precipitate disappeared (if any appeared). The resin was filtered off and the clear solution was evaporated to dryness. A minimal amount of acetonitrile was added to redissolve the POM and the solution was added dropwise to an excess of diethylether. The precipitate was collected by centrifugation and subsequently the remaining solid was washed with water and diethylether and dried at air for several days.

CuAAC coupling of alkyne-substrates to compound 3 using method B

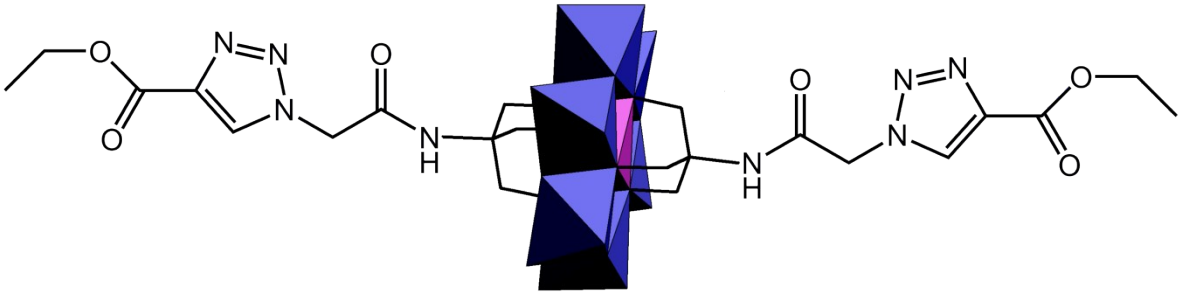
The synthesis of compounds 4a-4e was performed following method B, using 0.05 mmol (1 eq.) of compound **3**, 0.20 mmol (4 eq.) of alkyne-substrate, 0.025 mmol (0.5 eq.) of $CuSO_4 \cdot 5H_2O$ and 0.10 mmol (2 eq.) of sodium ascorbate in a total volume of approximately 14 ml of dry DMF.

Compound 4a: $(C_{16}H_{36}N)_3$-$[MnMo_6O_{18}((OCH_2)_3C_{11}H_9N_4O)_2]$



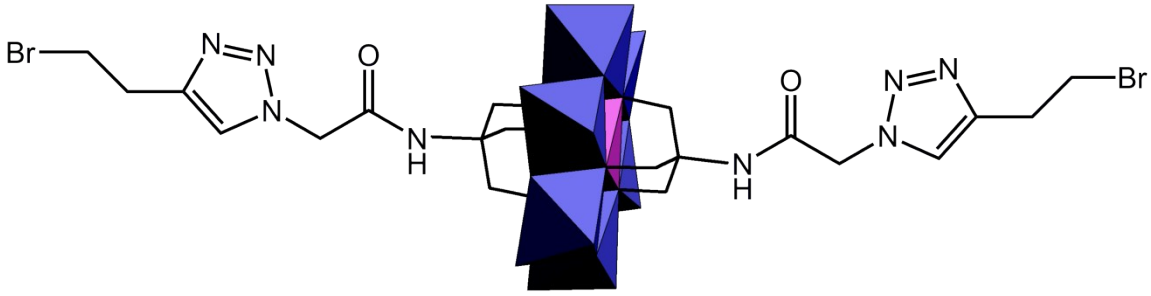
Yield: 104 mg (92%). ^{1}H NMR (600 MHz, DMSO-d6): δ = 64.60 ppm (br, 12H, O-C**H$_2$**-C), 8.54 ppm (s, 2H, C**H$_{triazole}$**), 8.43 ppm (s, 2H, -N**H**), 7.87 ppm (d, 4H, C**H$_{arom,ortho}$**), 7.43 ppm (t, 4H, C**H$_{arom,meta}$**), 7.32 ppm (t, 2H, C**H$_{arom,para}$**), 5.48 ppm (s, 4H, CO-C**H$_2$**-N), 3.15 ppm (m, 24H, **H$_{TBA}$**), 1.56 ppm (m, 24H, **H$_{TBA}$**), 1.31 ppm (m, 24H, **H$_{TBA}$**), 0.93 ppm (t, 36H, **H$_{TBA}$**). ^{13}C NMR (150 MHz, DMSO-d6): δ = 166.2 ppm (NH-**C**O), 146.0 ppm (CH=**C**-C$_{arom}$), 130.8 ppm (C-**C$_{arom}$**-CH$_{arom}$), 128.7 ppm (**C**H$_{arom,meta}$), 127.6 ppm (**C**H$_{arom,para}$), 125.0 ppm (**C**H$_{arom,ortho}$), 122.9 ppm (N-**C**H=C), 57.5 ppm (**C$_{TBA}$**), 48.9 (CO-**C**H$_2$-N), 23.0 ppm (**C$_{TBA}$**), 19.2 ppm (**C$_{TBA}$**), 13.5 ppm (**C$_{TBA}$**). IR: $\tilde{\nu}$ = 3289 (w), 3249 (w), 3087 (w), 2959 (m), 2873 (w), 1702 (m), 1569 (m), 1467 (m), 1378 (w), 1257 (w), 1042 (m), 939 (s), 914 (s), 898 (s), 767 (m), 661 (vs), 565 (s), 462 (m), 413 (m). Elemental analysis (%) for $C_{76}H_{138}MnMo_6N_{11}O_{26}$ (2052.7 g mol^{-1}): calcd. C 40.52, H 6.17, N 6.84; found: C 39.89, H 5.92, N 6.62.

Compound 4b: $(C_{16}H_{36}N)_3$-$[MnMo_6O_{18}((OCH_2)_3C_8H_9N_4O_2)_2]$



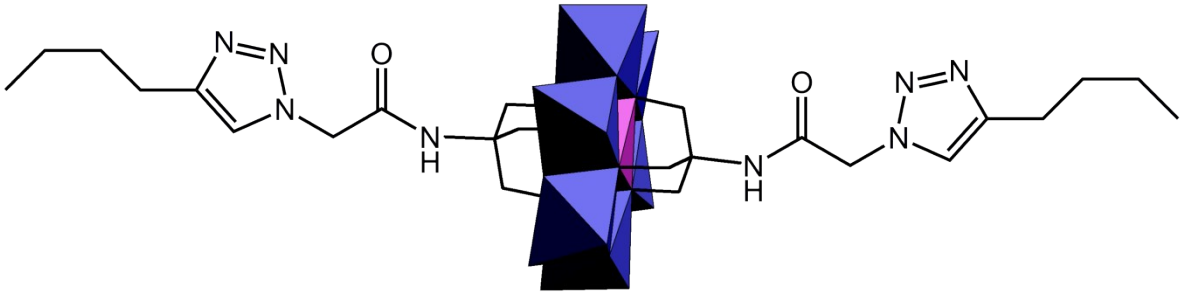
Yield: 102 mg (91%). ^{1}H NMR (600 MHz, DMSO-d6): δ = 64.53 ppm (br, 12H, O-C**H$_2$**-C), 8.69 ppm (s, 2H, C**H$_{triazole}$**), 8.43 ppm (s, 2H, -N**H**), 5.50 ppm (s, 4H, C**H$_2$**-N), 4.31 ppm (q, 4H, C**H$_2$**-CH_3) 3.16 ppm (m, 24H, **H$_{TBA}$**), 1.57 ppm (m, 24H, **H$_{TBA}$**), 1.30 ppm (m, 30H, **H$_{TBA}$** + CH_2-C**H$_3$**), 0.93 ppm (t, 36H, **H$_{TBA}$**). ^{13}C NMR (150 MHz, DMSO-d6): δ = 165.7 ppm (NH-**C**O), 160.1 ppm (**C**O-O-CH_2), 138.4 ppm (CH=**C**-CO), 130.6 ppm (N-**C**H=C), 60.3 ppm (O-**C**H_2-CH_3), 57.5 ppm (**C$_{TBA}$**), 49.0 (CO-**C**H_2-N), 23.0 ppm (**C$_{TBA}$**), 19.2 ppm (**C$_{TBA}$**), 14.0 ppm (CH_2-**C**H_3), 13.5 ppm (**C$_{TBA}$**). IR: $\tilde{\nu}$ = 3298 (w), 2962 (m), 2874 (m), 1720 (m), 1694 (m), 1556 (m), 1467 (m), 1378 (m), 1232 (m), 1208 (m), 1110 (m), 1042 (m), 940 (s), 914 (s), 898 (s), 660 (vs), 565 (s), 459 (m), 411 (m). Elemental analysis (%) for $C_{70}H_{138}MnMo_6N_{11}O_{30}$ (2044.6 g mol^{-1}): calcd. C 37.46, H 6.20, N 6.86; found: C 37.10, H 6.41, N 6.43.

Compound 4c: $(C_{16}H_{36}N)_3$-$[MnMo_6O_{18}((OCH_2)_3C_7H_8N_4OBr)_2]$



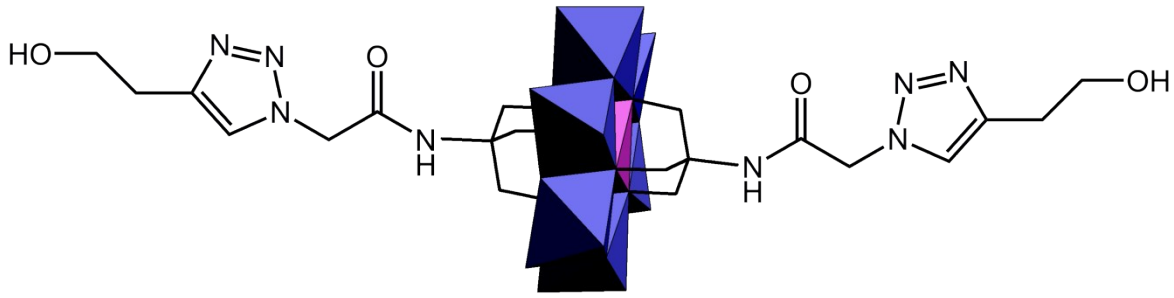
Yield: 100 mg (87%). ^{1}H NMR (600 MHz, DMSO-d6): δ = 64.54 ppm (br, 12H, O-C**H$_2$**-C), 8.35 ppm (s, 2H, -N**H**), 7.95 ppm (s, 2H, C**H$_{triazole}$**), 5.38 ppm (s, 4H, CO-C**H$_2$**-N), 3.72 ppm (t, 4H, CH_2-C**H$_2$**-Br), 3.17 ppm (m, 28H, **H$_{TBA}$** + C-C**H$_2$**-CH_2), 1.57 ppm (m, 24H, **H$_{TBA}$**), 1.31 ppm (m, 24H, **H$_{TBA}$**), 0.93 ppm (t, 36H, **H$_{TBA}$**). ^{13}C NMR (150 MHz, DMSO-d6): δ = 166.1 ppm (NH-**C**O), 143.7 ppm (CH=**C**-CO), 124.0 ppm (N-**C**H=C), 57.5 ppm (**C$_{TBA}$**), 48.9 ppm (CO-**C**H_2-N), 32.3 ppm (C-**C**H_2-CH_2), 29.0 ppm (CH_2-**C**H_2-Br), 23.0 ppm (**C$_{TBA}$**), 19.2 ppm (**C$_{TBA}$**), 13.5 ppm (**C$_{TBA}$**). IR: $\tilde{\nu}$ = 3294 (w), 2960 (m), 2874 (m), 1698 (m), 1557 (m), 1483 (m), 1464 (m), 1380 (m), 1259 (m), 1109 (m), 1047 (m), 940 (s), 919 (s), 900 (s), 660 (vs), 562 (s), 459 (m), 412 (m). Elemental analysis (%) for $C_{68}H_{136}MnMo_6N_{11}O_{26}Br_2$ (2314.4 g mol^{-1}): calcd. C 35.29, H 5.92, N 6.66; found: C 35.28, H 6.08, N 6.38.

Compound 4d: $(C_{16}H_{36}N)_3$-$[MnMo_6O_{18}((OCH_2)_3C_9H_{13}N_4O)_2]$



Yield: 90 mg (81%). ^{1}H NMR (600 MHz, DMSO-d6): δ = 64.22 ppm (br, 12H, O-C**H$_2$**-C), 8.31 ppm (s, 2H, -N**H**), 7.78 ppm (s, 2H, C**H$_{triazole}$**), 5.35 ppm (s, 4H, CO-C**H$_2$**-N), 3.17 ppm (m, 24H, **H$_{TBA}$**), 2.60 ppm (t, 4H, C-C**H$_2$**-CH$_2$), 1.57 ppm (m, 28H, **H$_{TBA}$** + CH$_2$-C**H$_2$**-CH$_2$), 1.31 ppm (m, 28H, H$_{TBA}$ + CH$_2$-C**H$_2$**-CH$_3$), 0.94 ppm (t, 36H, **H$_{TBA}$**), 0.89 ppm (t, 6H, CH$_2$-C**H$_3$**). ^{13}C NMR (150 MHz, DMSO-d6): δ = 166.3 ppm (NH-**C**O), 146.5 ppm (CH=**C**-CO), 123.2 ppm (N-**C**H=C), 57.5 ppm (**C$_{TBA}$**), 48.7 ppm (CO-**C**H$_2$-N), 31.0 ppm (C-**C**H$_2$-CH$_2$), 24.5 ppm (CH$_2$-**C**H$_2$-CH$_2$), 23.0 ppm (**C$_{TBA}$**), 21.6 ppm (CH$_2$-**C**H$_2$-CH$_3$), 19.2 ppm (**C$_{TBA}$**), 13.6 ppm (CH$_2$-**C**H$_3$), 13.5 ppm (**C$_{TBA}$**). IR: $\tilde{\nu}$ = 3300 (s), 3247 (s), 3085 (s), 2960 (m), 2872 (m), 1696 (m), 1567 (m), 1464 (m), 1379 (m), 1258 (m), 1109 (m), 1035 (m), 939 (s), 915 (s), 899 (s), 658 (vs), 564 (s), 460 (m), 412 (m). Elemental analysis (%) for $C_{72}H_{146}MnMo_6N_{11}O_{26}$ (2212.7 g mol^{-1}): calcd. C 39.08, H 6.65, N 6.96; found: C 38.25, H 6.55, N 6.54.

Compound 4e: $(C_{16}H_{36}N)_3$-$[MnMo_6O_{18}((OCH_2)_3C_7H_9N_4O_2)_2]$



Yield: 99 mg (91%). ^{1}H NMR (600 MHz, DMSO-d6): δ = 64.55 ppm (br, 12H, O-C**H$_2$**-C), 8.34 ppm (s, 2H, -N**H**), 7.89 ppm (s, 2H, C**H$_{triazole}$**), 5.35 ppm (s, 4H, CO-C**H$_2$**-N), 4.75 ppm (s, 2H, CH$_2$-O**H**) 3.75 ppm (t, 4H, CH$_2$-C**H$_2$**-OH), 3.16 ppm (m, 24H, **H$_{TBA}$**), 2.74 ppm (br, 4H, C-C**H$_2$**-CH$_2$), 1.57 ppm (m, 24H, **H$_{TBA}$**), 1.31 ppm (m, 24H, **H$_{TBA}$**), 0.94 ppm (t, 36H, **H$_{TBA}$**). ^{13}C NMR (150 MHz, DMSO-d6): δ = 166.2 ppm (NH-**C**O), 144.0 ppm (CH=**C**-CO), 123.8 ppm (N-**C**H=C), 60.3 ppm (CH$_2$-**C**H$_2$-OH), 57.5 ppm (**C$_{TBA}$**), 48.7 ppm (CO-**C**H$_2$-N), 29.0 ppm (C-**C**H$_2$-CH$_2$), 23.0 ppm (**C$_{TBA}$**), 19.3 ppm (**C$_{TBA}$**), 13.6 ppm (**C$_{TBA}$**). IR: $\tilde{\nu}$ = 3411 (w), 3243 (w), 3070 (w), 2961 (m), 2874 (m), 1705 (m), 1569 (m), 1482 (m), 1381 (m), 1256 (m), 1111 (m), 1028 (m), 940 (s), 919 (s), 902 (s), 658 (vs), 565 (s), 460 (m), 413 (m). Elemental analysis (%) for $C_{68}H_{138}MnMo_6N_{11}O_{28}$ (2188.6 g mol^{-1}): calcd. C 37.32, H 6.36, N 7.04; found: C 36.14, H 6.30, N 6.53.

NMR data of compound 1, 2, 3, 4a-e

Figure S3: ^{1}H NMR spectrum of compound 1 in D_2O at 400 MHz.

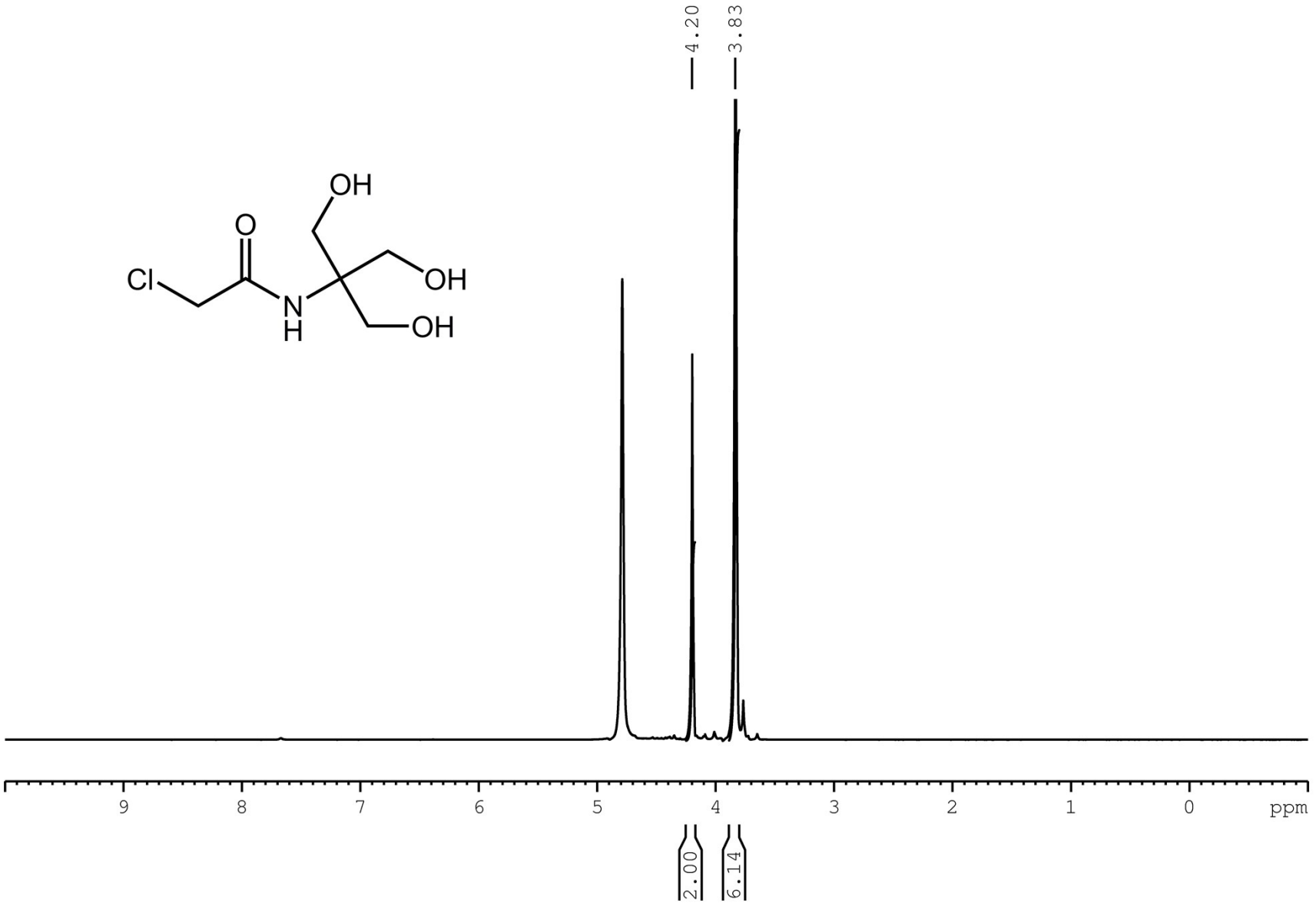


Figure S4: ^{13}C NMR spectrum of compound 1 in D_2O at 100 MHz.

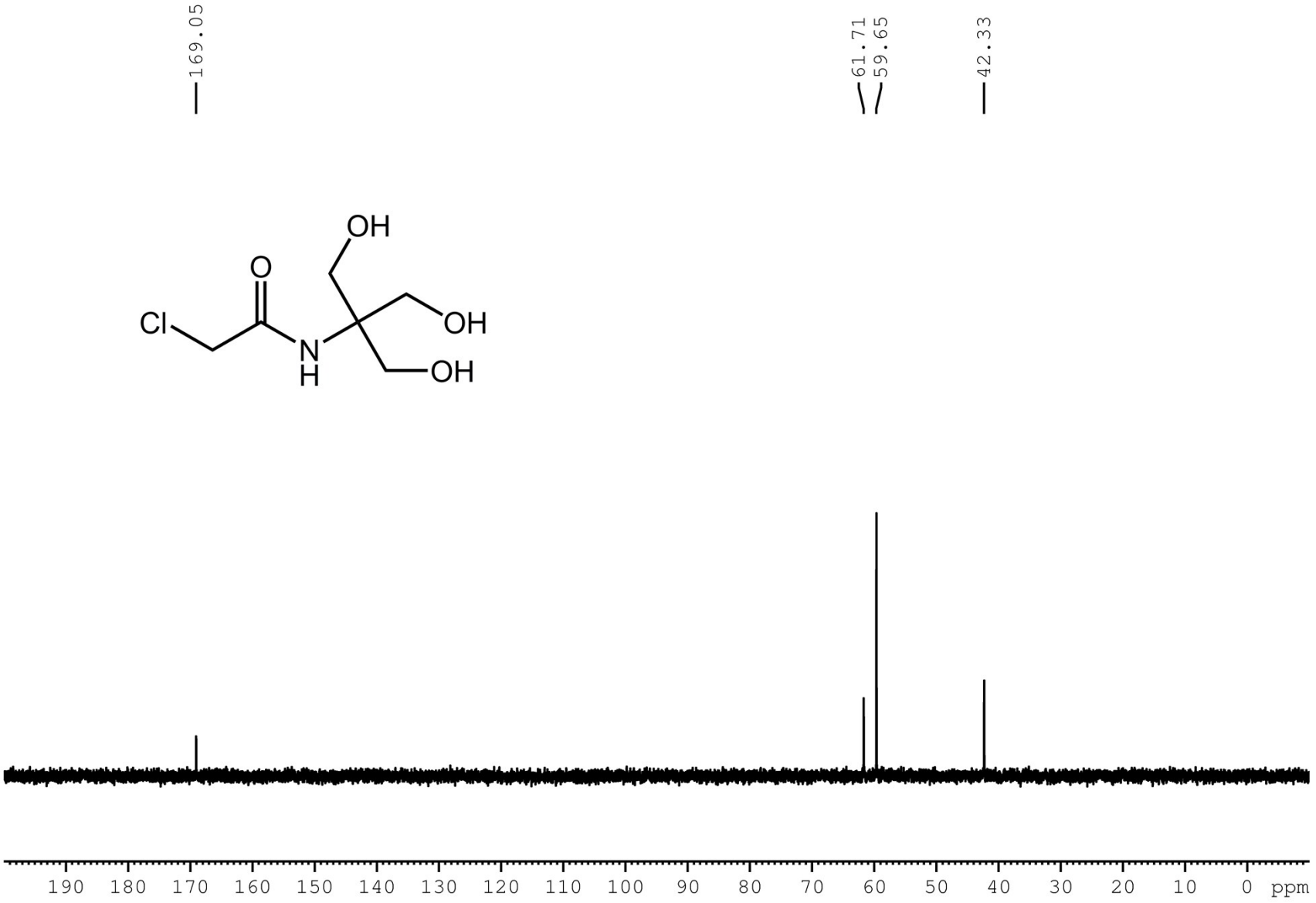


Figure S5: ^{1}H-^{13}C HSQC NMR spectrum of compound 1 in D_2O at 400-100 MHz.

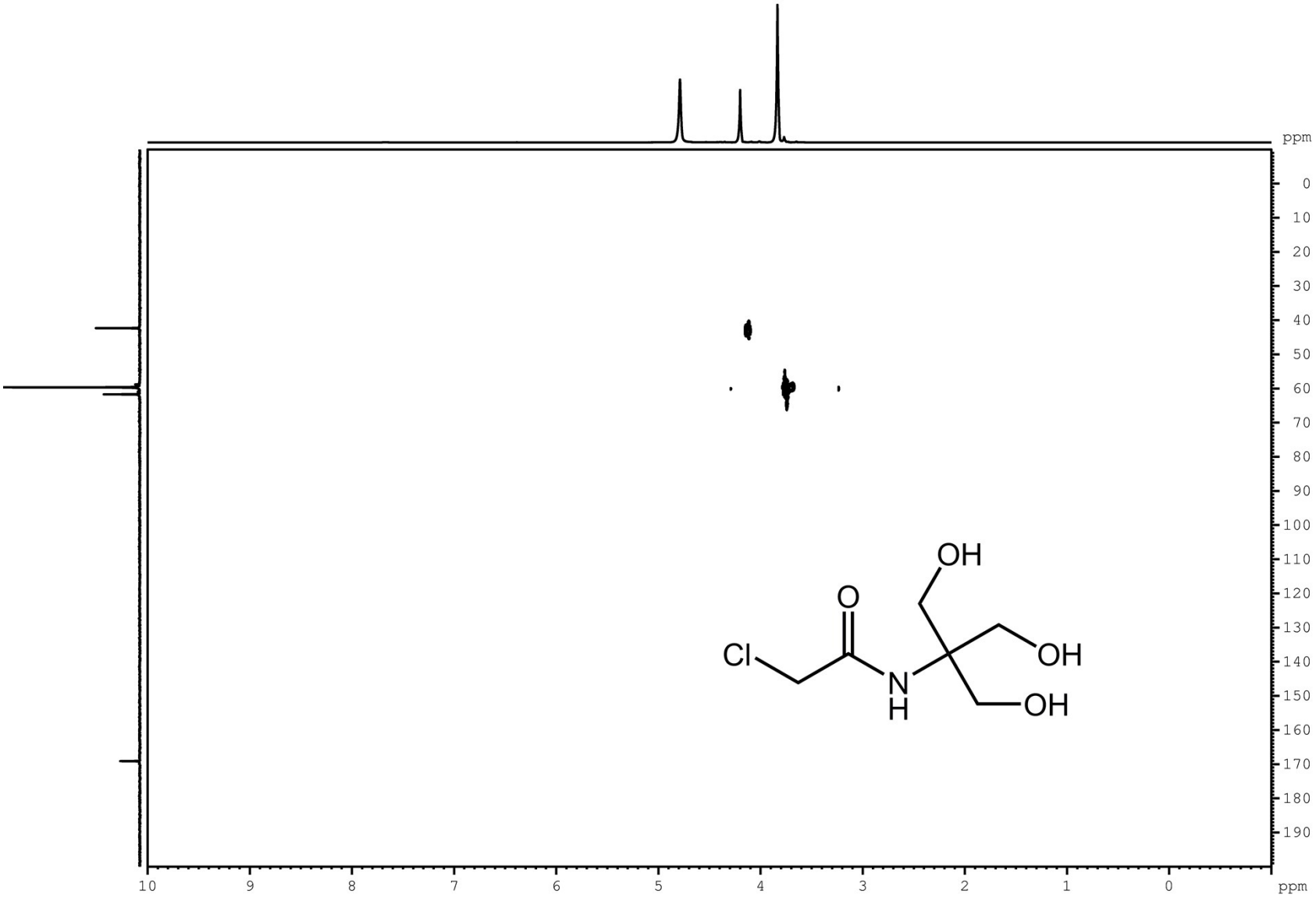


Figure S6: ^{1}H NMR spectrum of compound 2 in CD_3CN at 300 MHz.

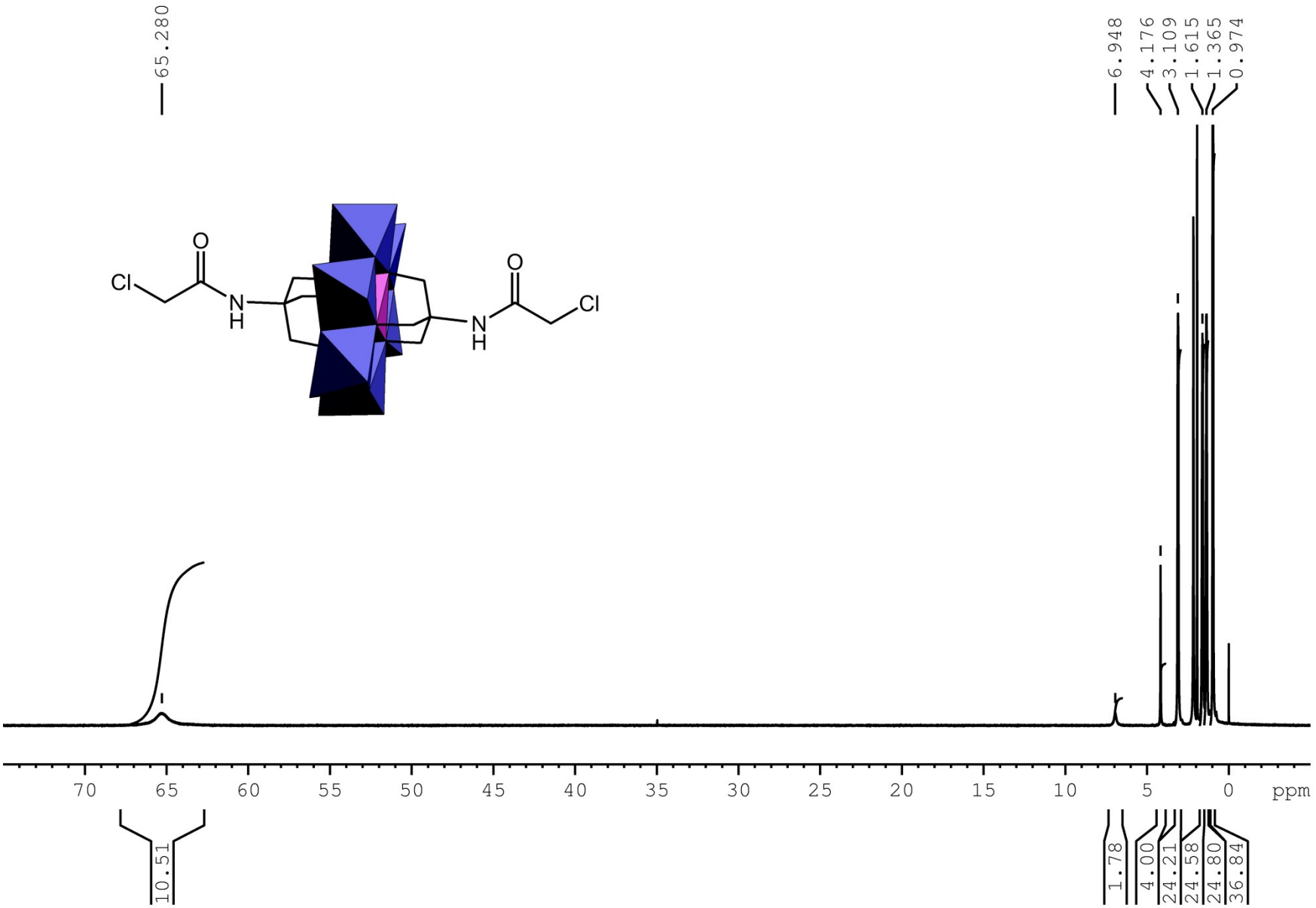


Figure S7: Detail (-1 to 10 ppm) of the ^{1}H NMR spectrum of compound 2 in CD_3CN at 300 MHz.

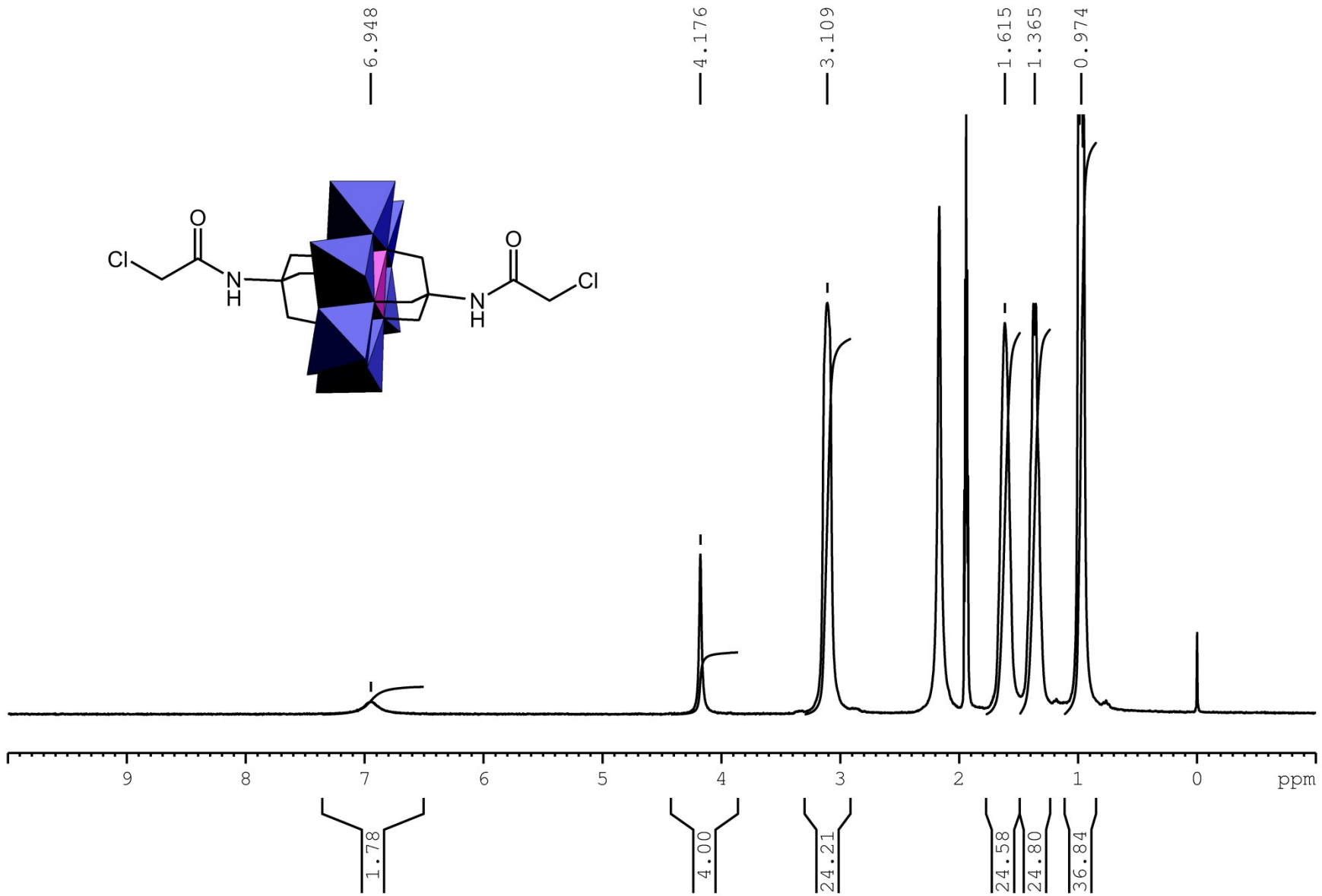


Figure S8: ^{13}C NMR spectrum of compound 2 in CD_3CN at 150 MHz.

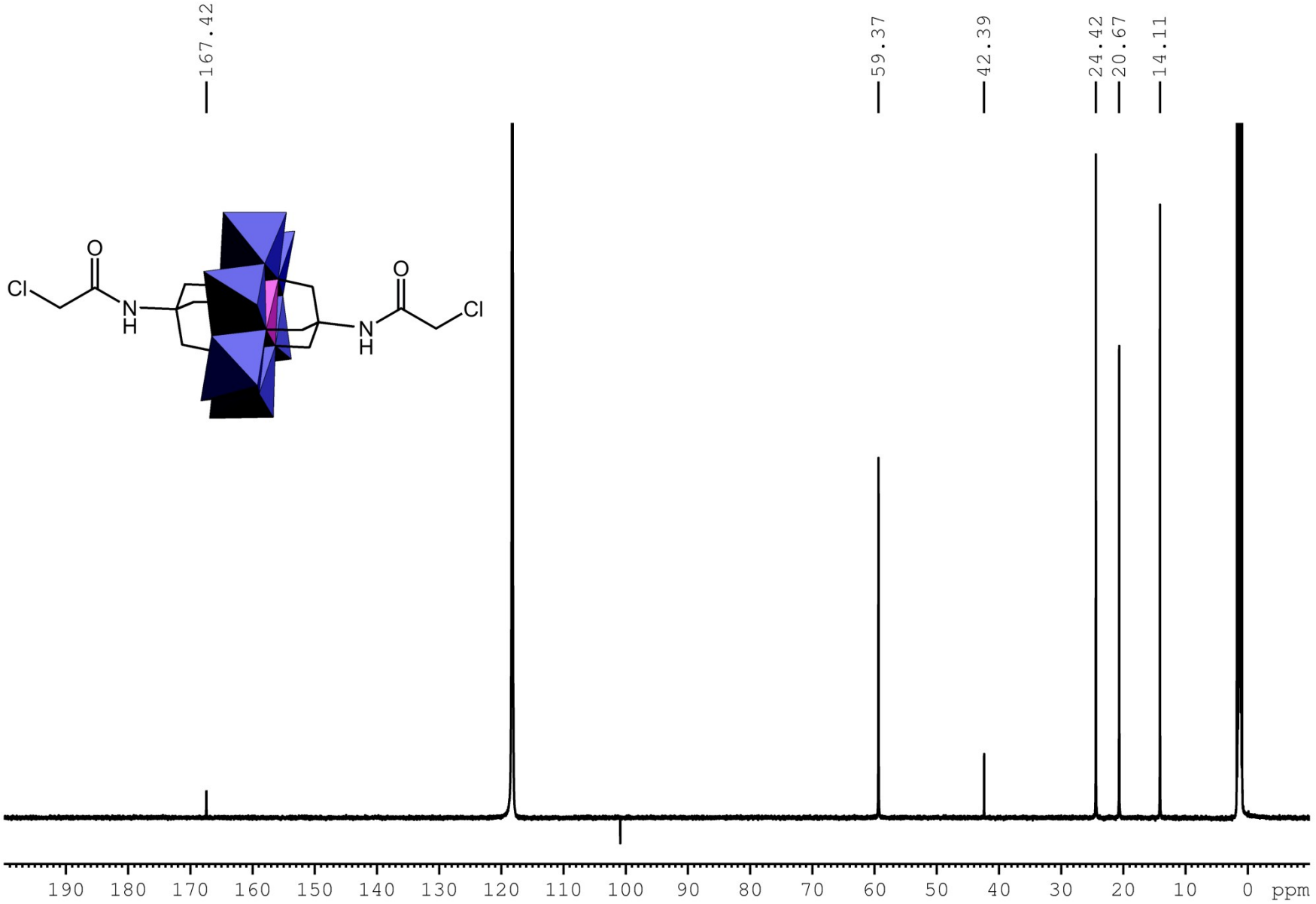


Figure S9: ^{1}H NMR spectrum of compound 3 in CD_3CN at 300 MHz.

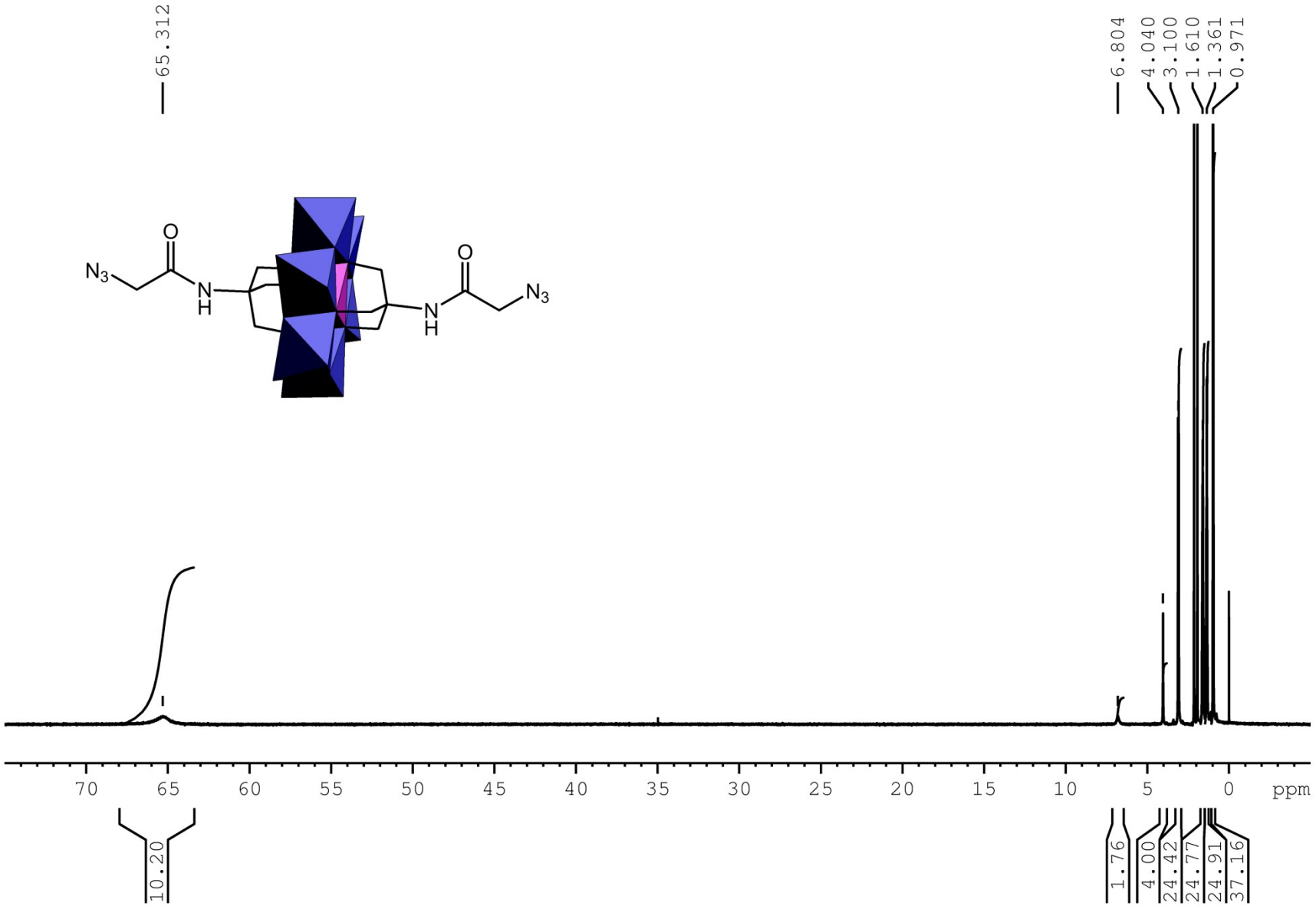


Figure S10: Detail (-1 to 10 ppm) of the ^{1}H NMR spectrum of compound 3 in CD_3CN at 300 MHz.

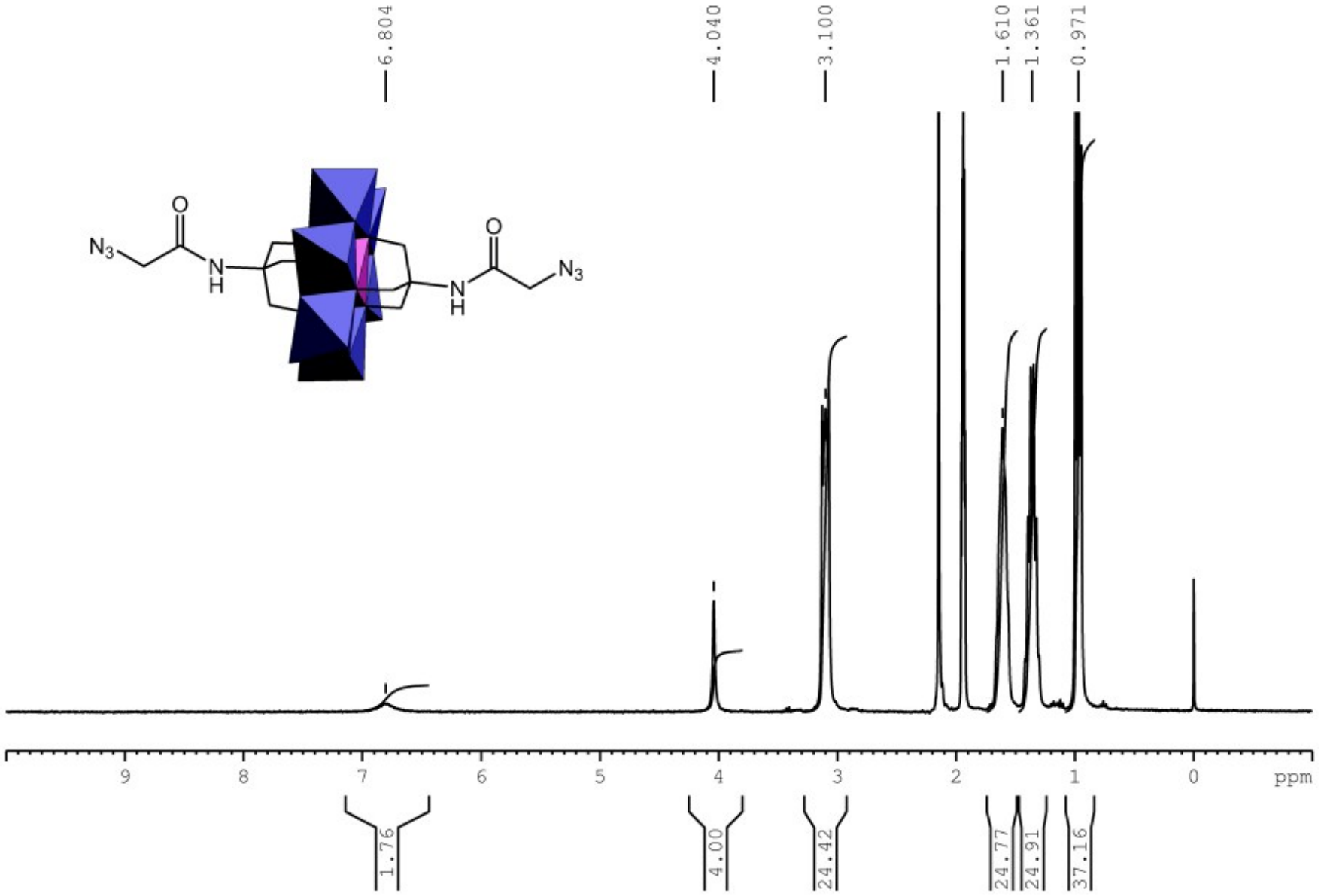


Figure S11: ^{13}C NMR spectrum of compound 3 in CD_3CN at 150 MHz.

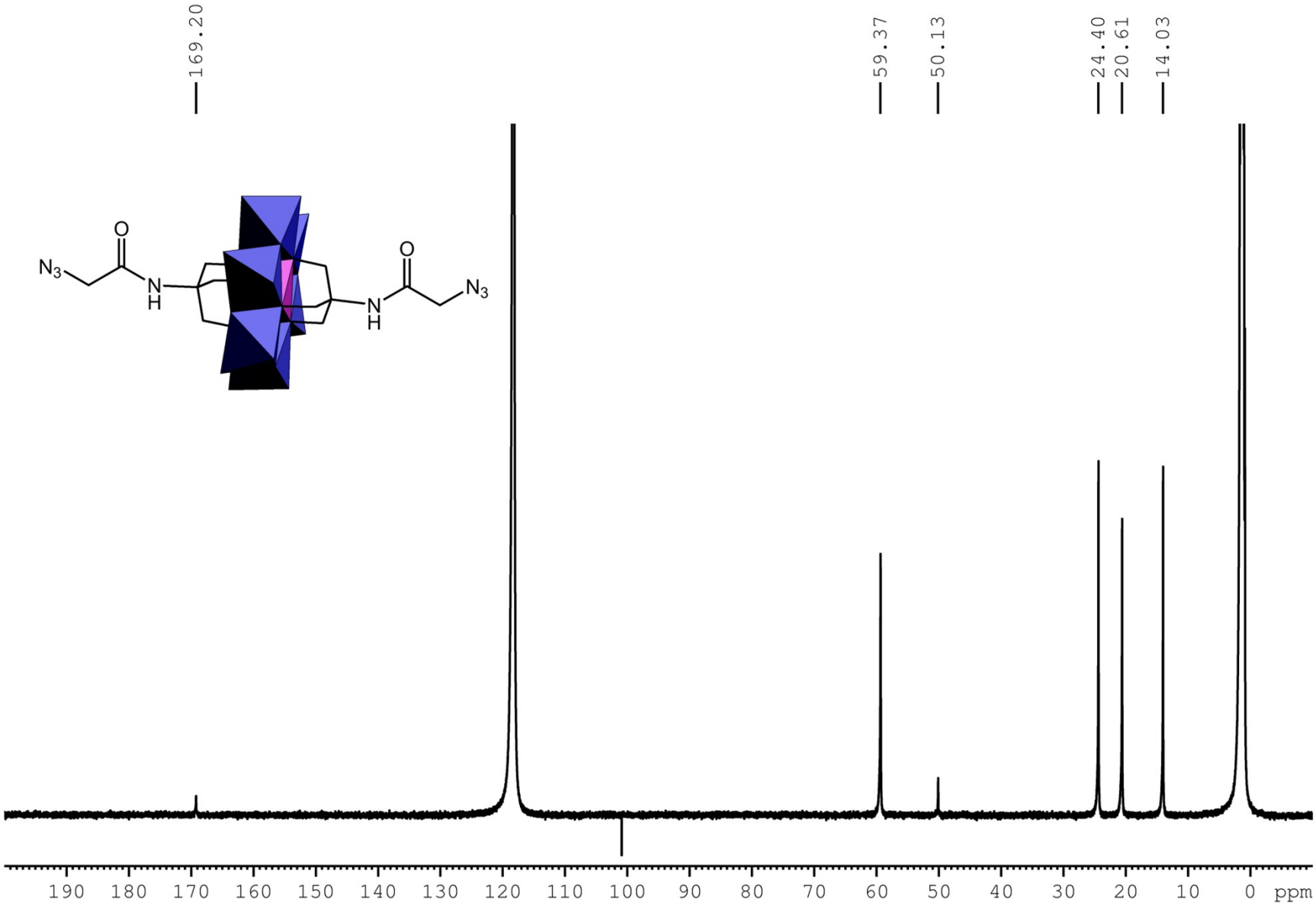


Figure S12: ^{1}H NMR spectrum of compound 4a in DMSO-d_6 at 600 MHz.

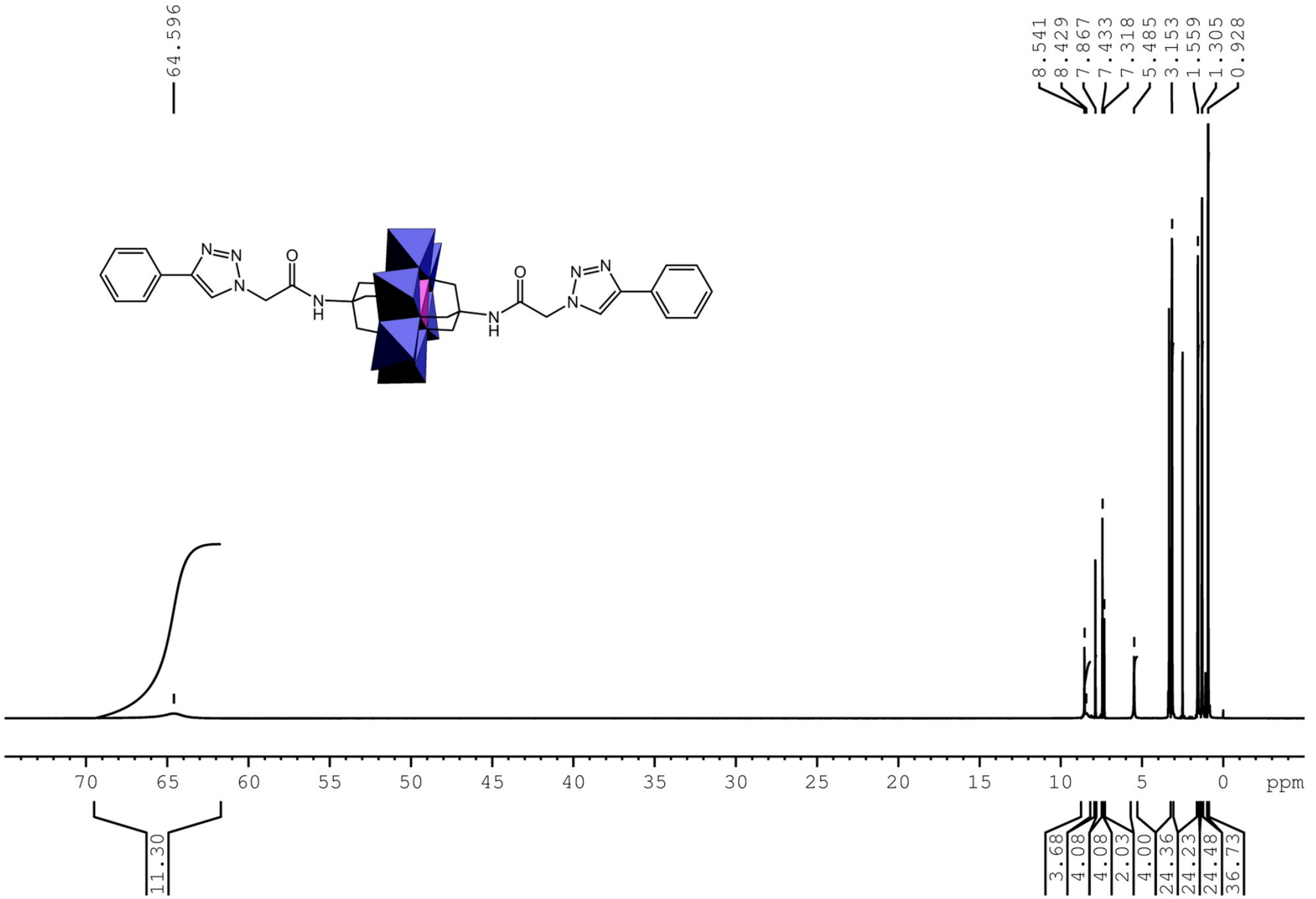


Figure S13: Detail (-1 to 10 ppm) of the ^{1}H NMR spectrum of compound 4a in DMSO-d_6 at 600 MHz.

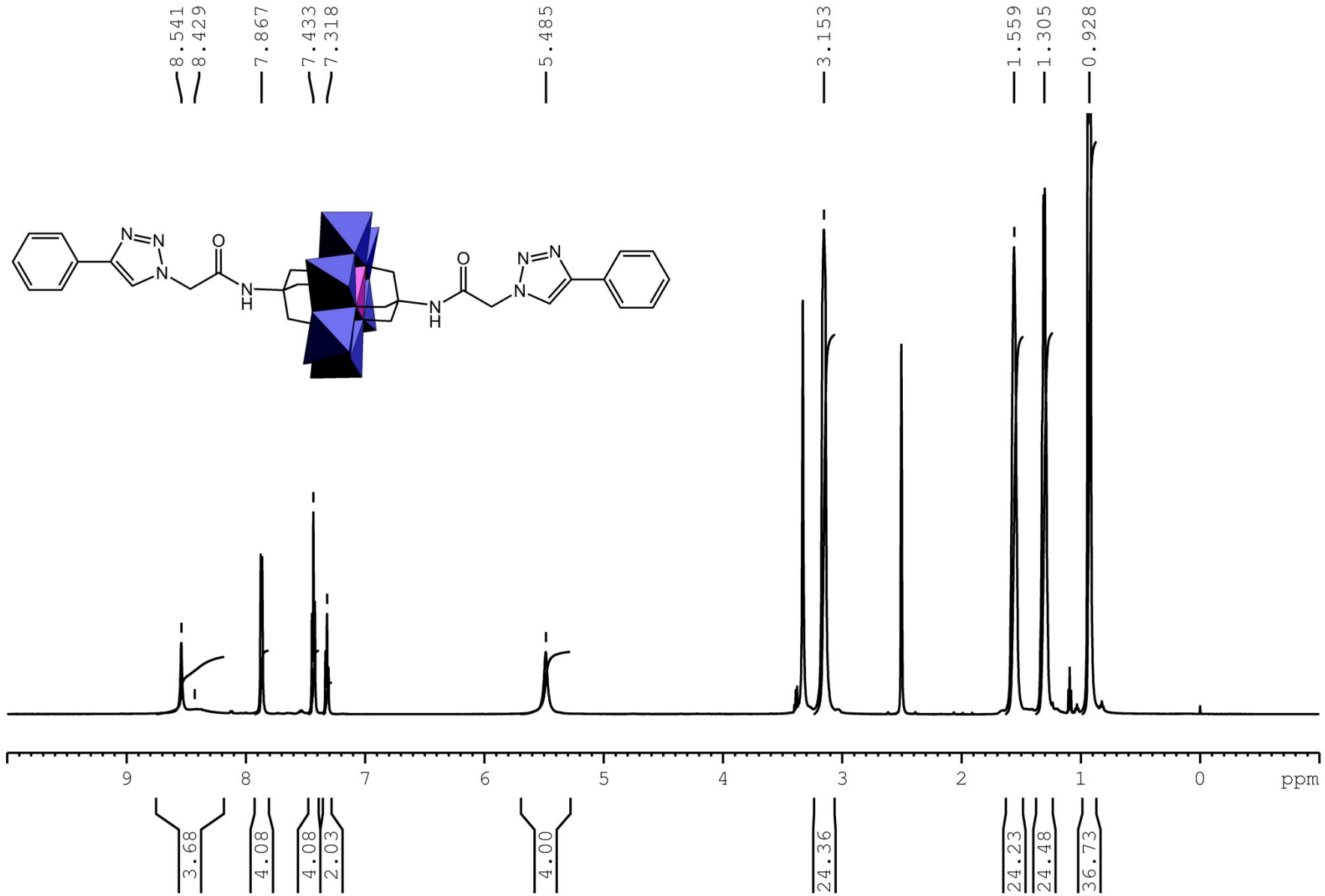


Figure S14: ^{13}C NMR spectrum of compound 4a in DMSO-d_6 at 150 MHz.

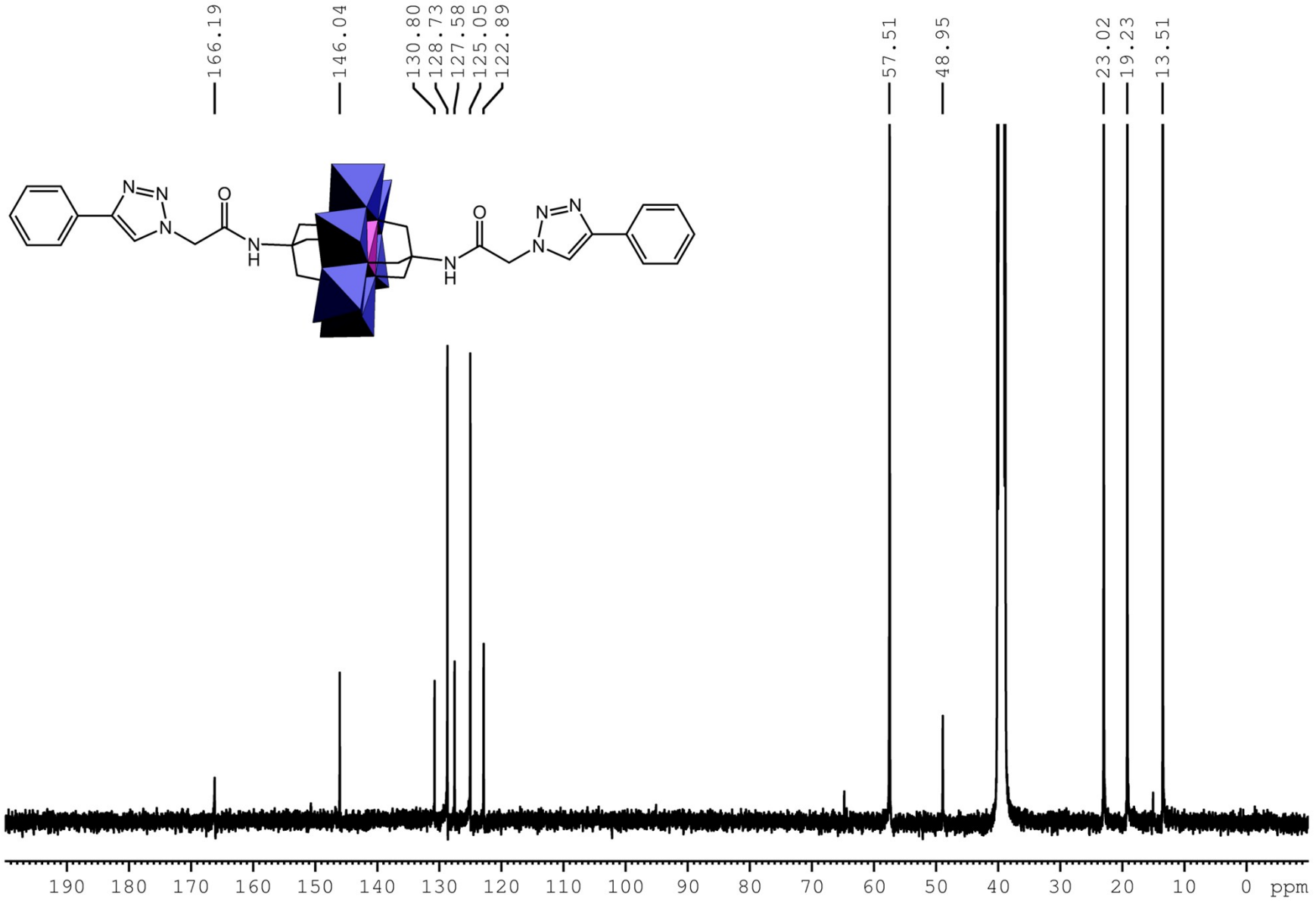


Figure S15: ^{1}H-^{13}C HSQC NMR spectrum of compound 4a in DMSO-d_6 at 400-100 MHz.

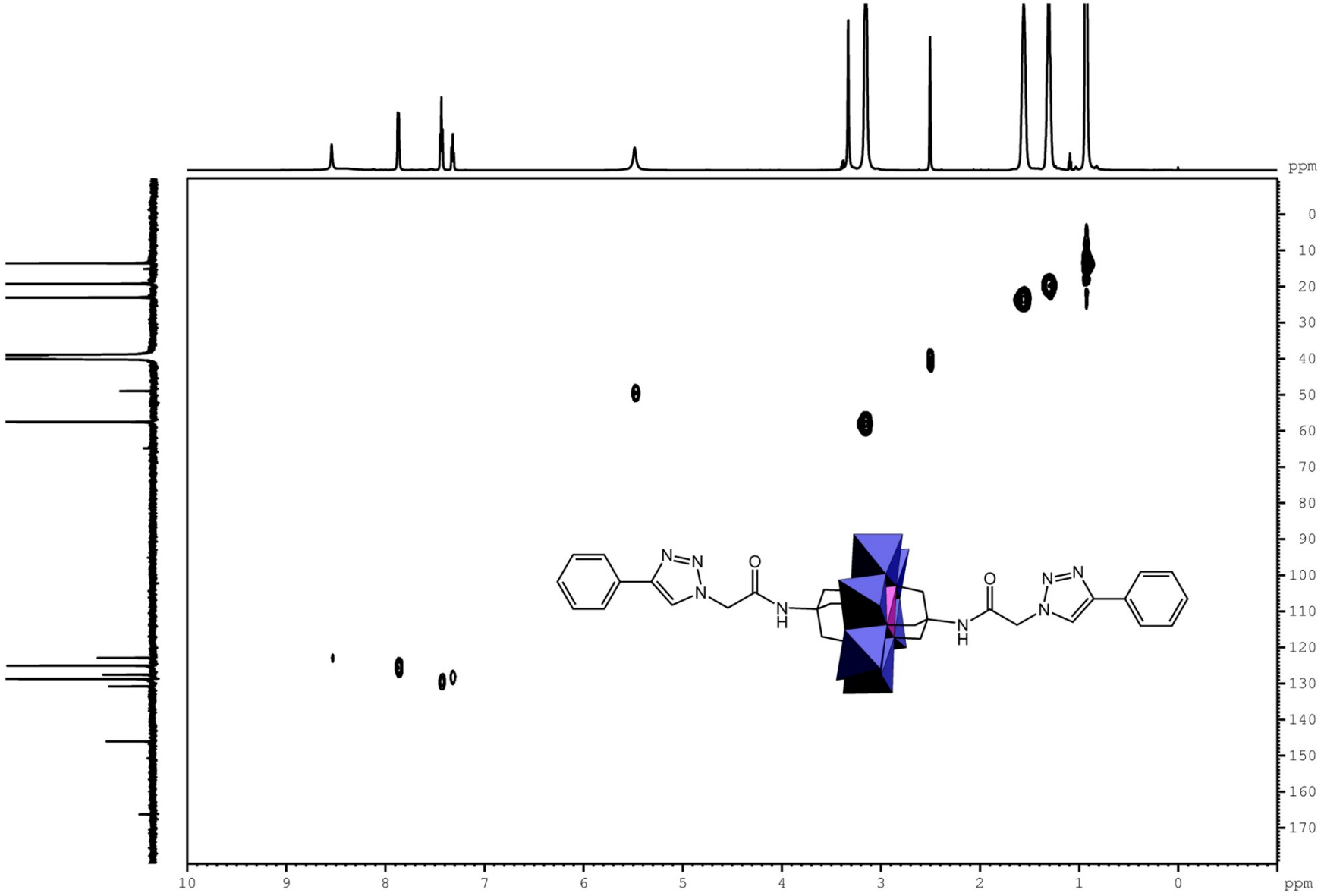


Figure S16: ^{1}H NMR spectrum of compound 4b in DMSO-d_6 at 600 MHz.

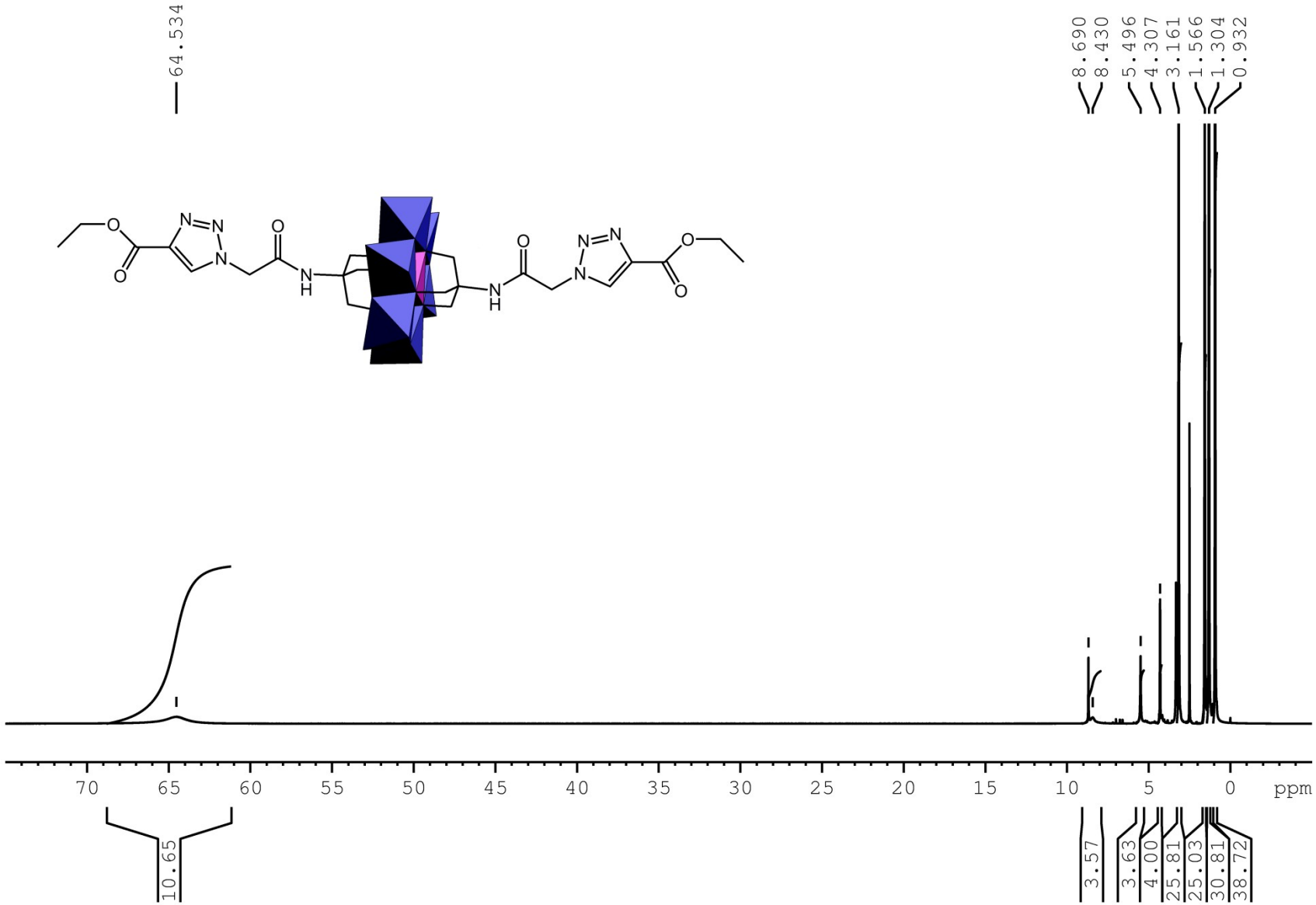


Figure S17: Detail (-1 to 10 ppm) of the ^{1}H NMR spectrum of compound 4b in DMSO-d_6 at 600 MHz.

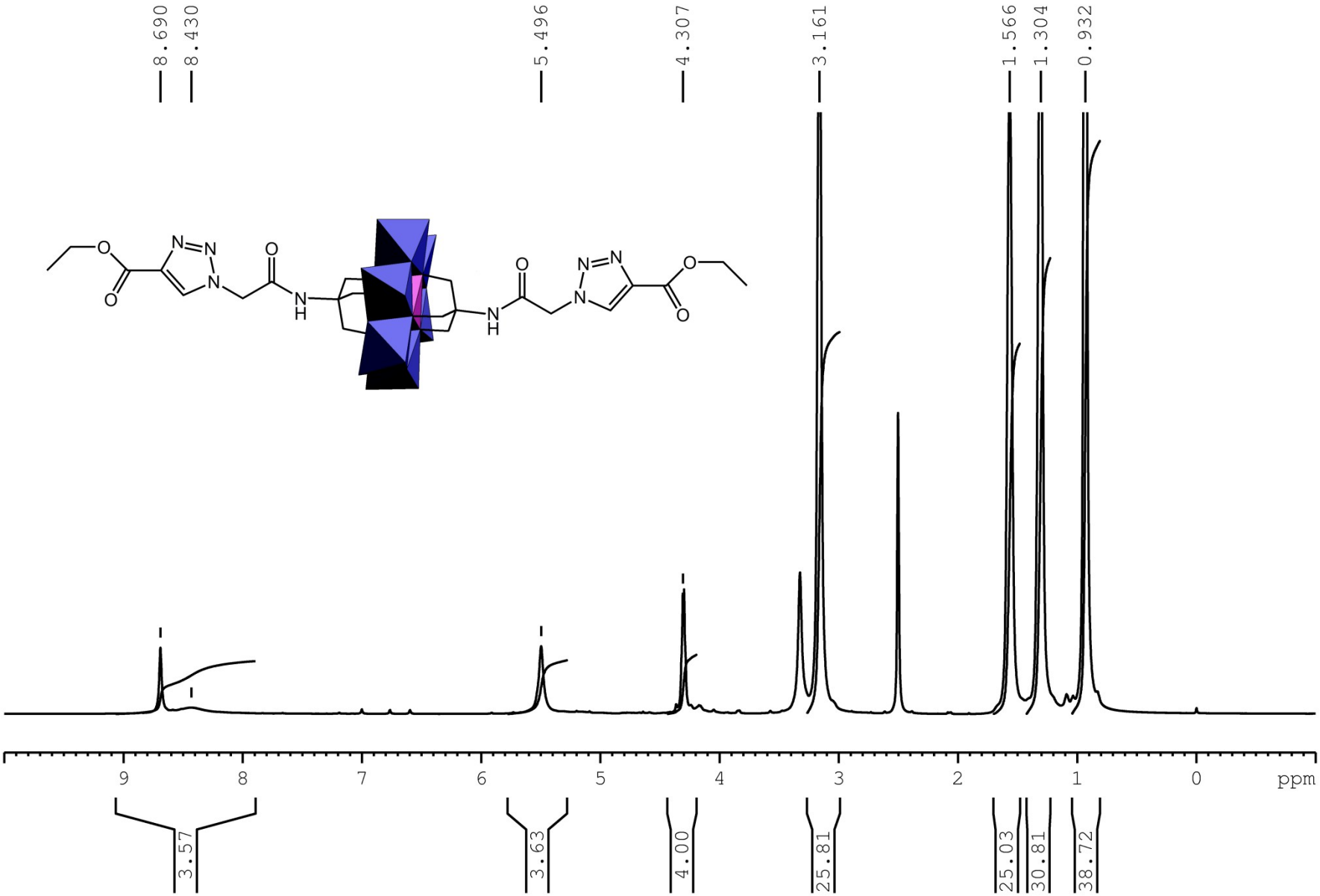


Figure S18: ^{13}C NMR spectrum of compound 4b in DMSO-d_6 at 150 MHz.

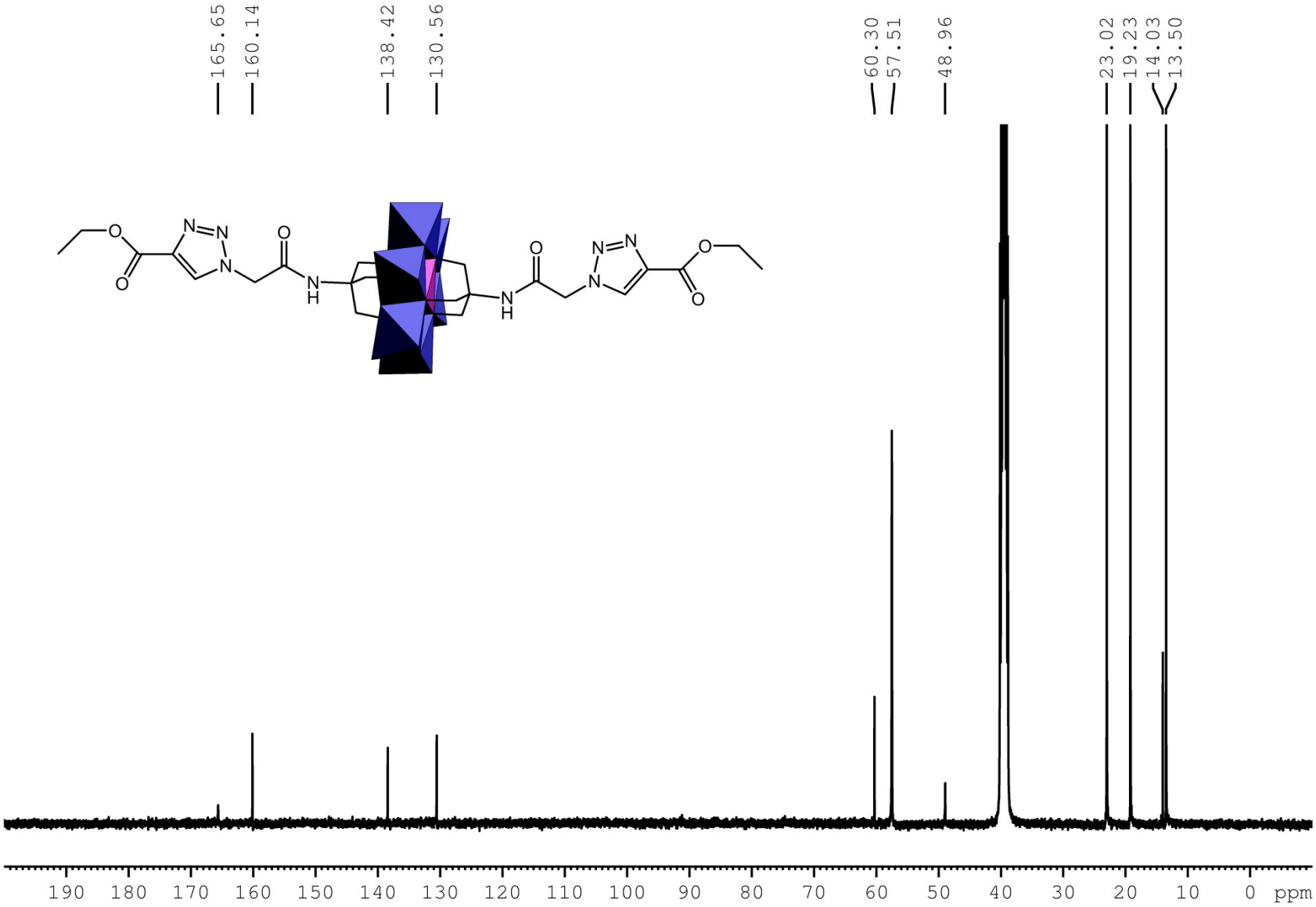


Figure S19: ^{1}H NMR spectrum of compound 4c in DMSO-d_6 at 600 MHz.

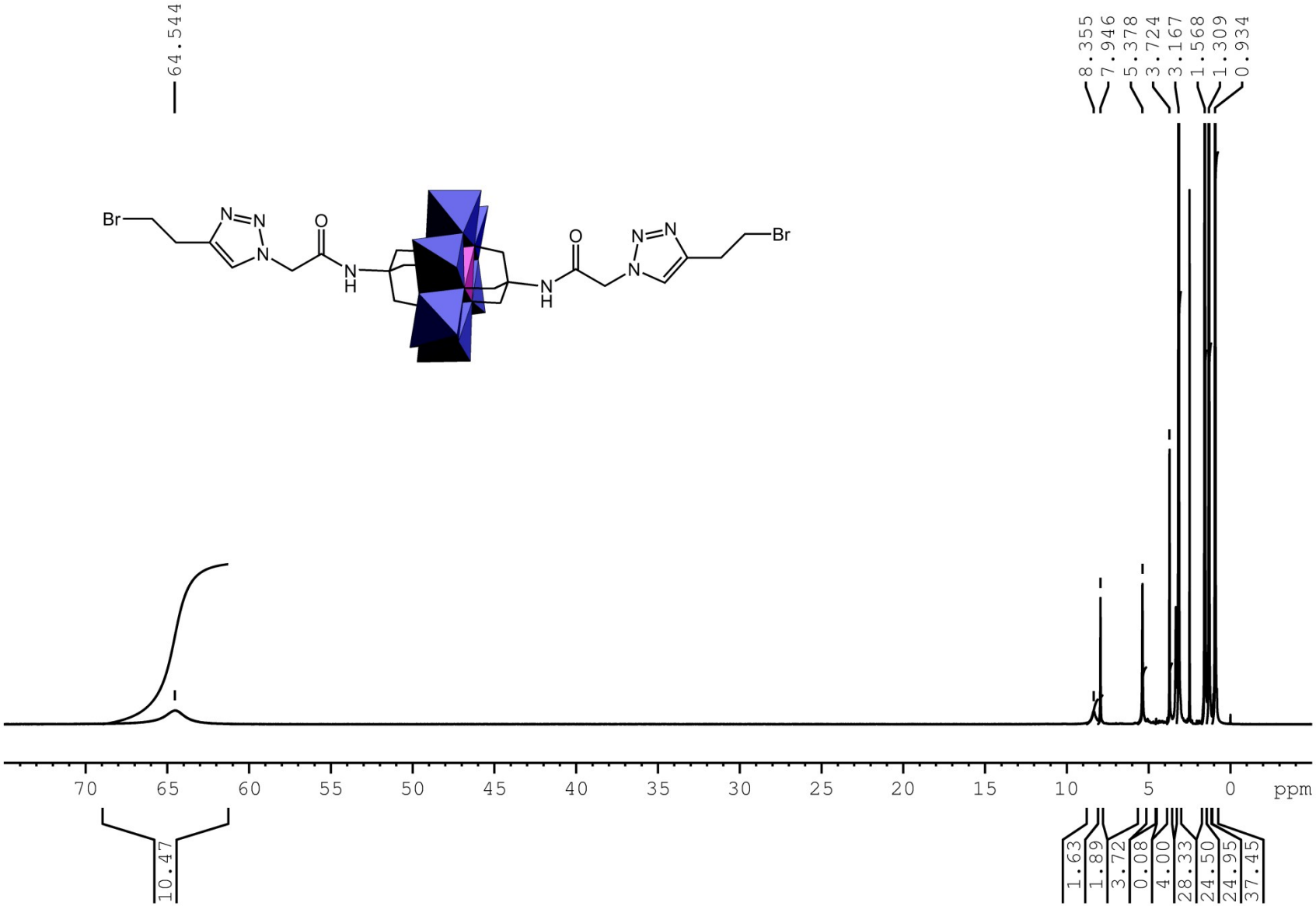


Figure S20: Detail (-1 to 10 ppm) of the ^{1}H NMR spectrum of compound 4c in DMSO-d_6 at 600 MHz.

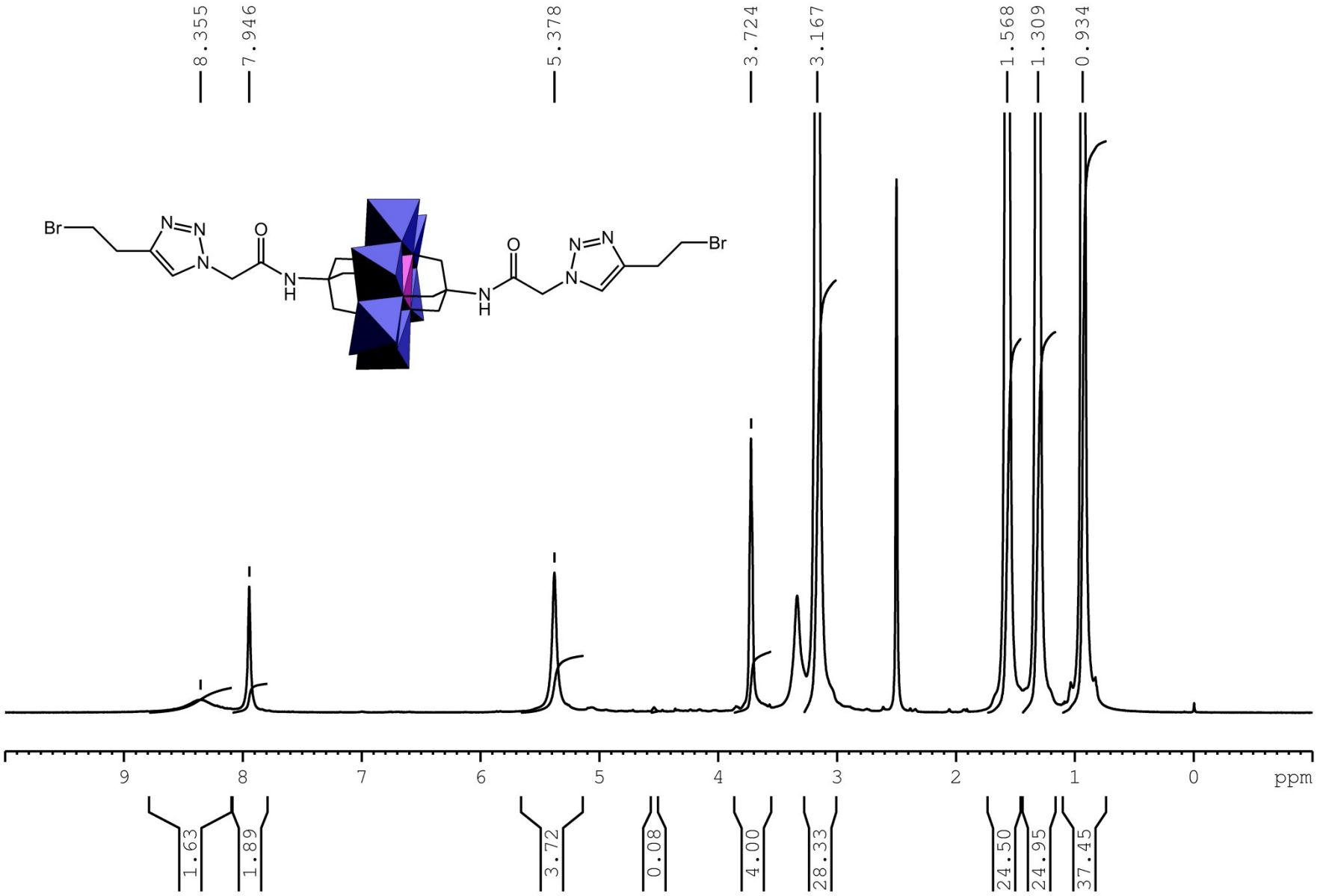


Figure S21: ^{13}C NMR spectrum of compound 4c in DMSO-d_6 at 150 MHz.

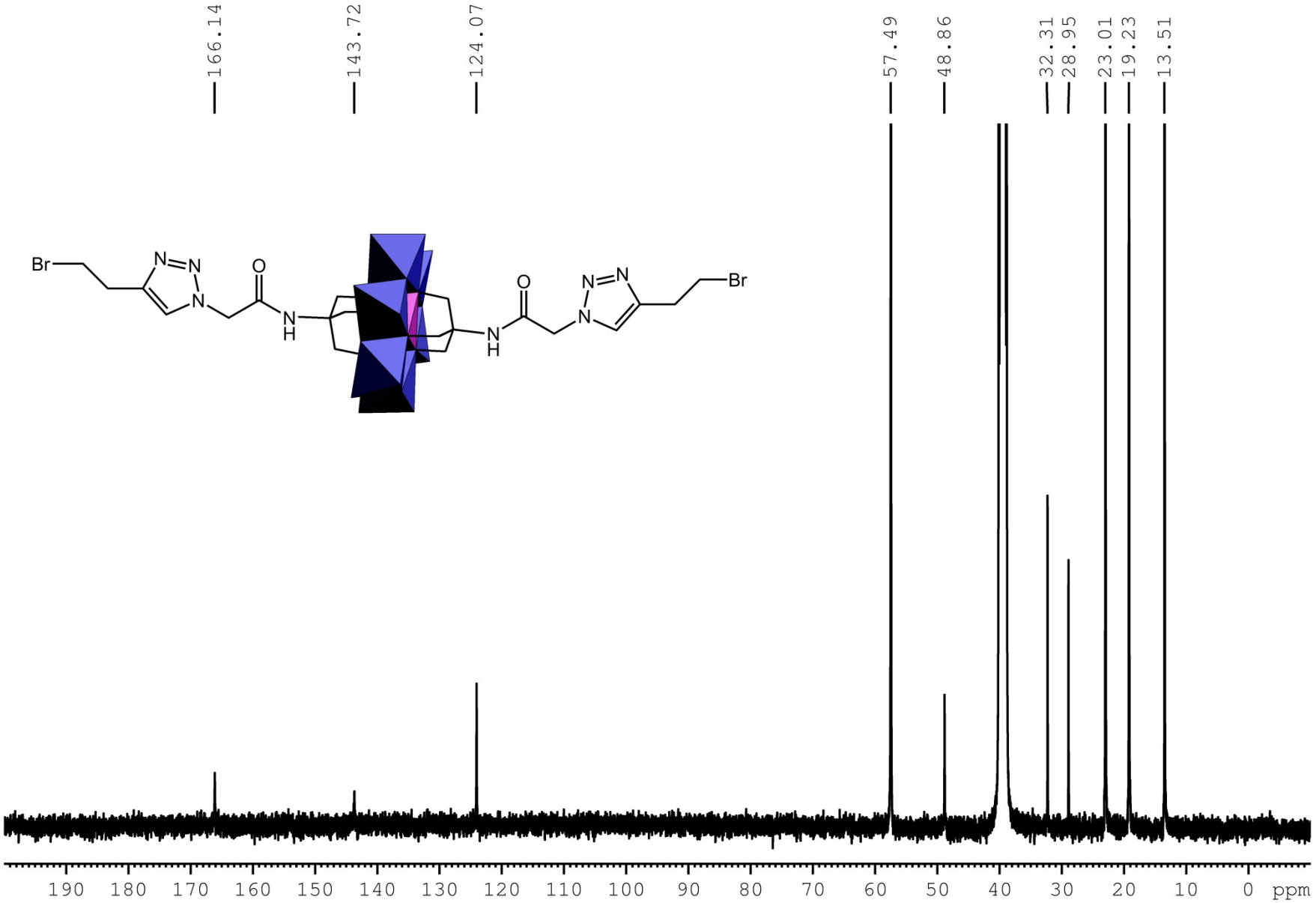


Figure S22: ^{1}H NMR spectrum of compound 4d in DMSO-d_6 at 600 MHz.

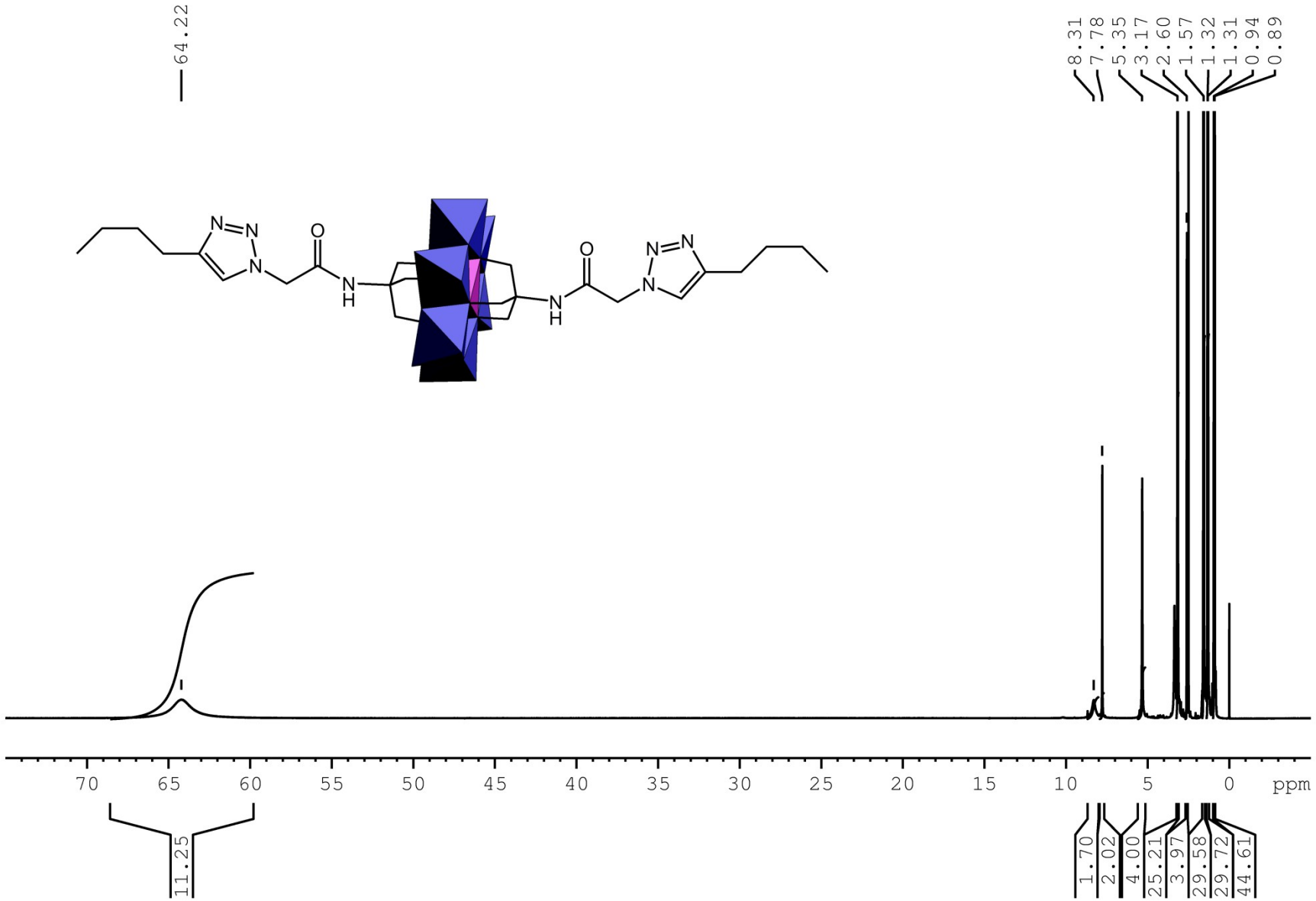


Figure S23: Detail (-1 to 10 ppm) of the ^{1}H NMR spectrum of compound 4d in DMSO-d_6 at 600 MHz.

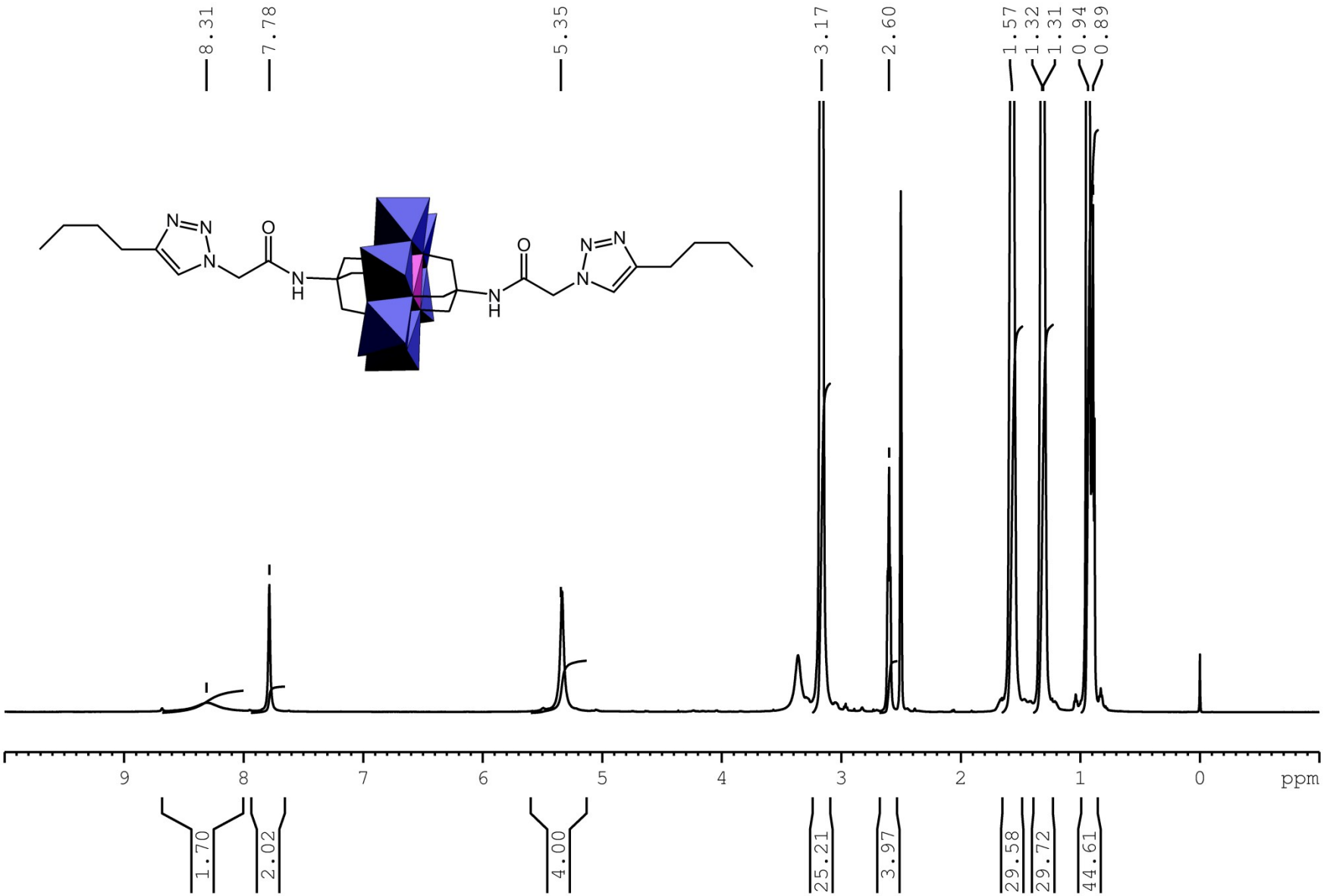


Figure S24: ^{13}C NMR spectrum of compound 4d in DMSO-d_6 at 150 MHz.

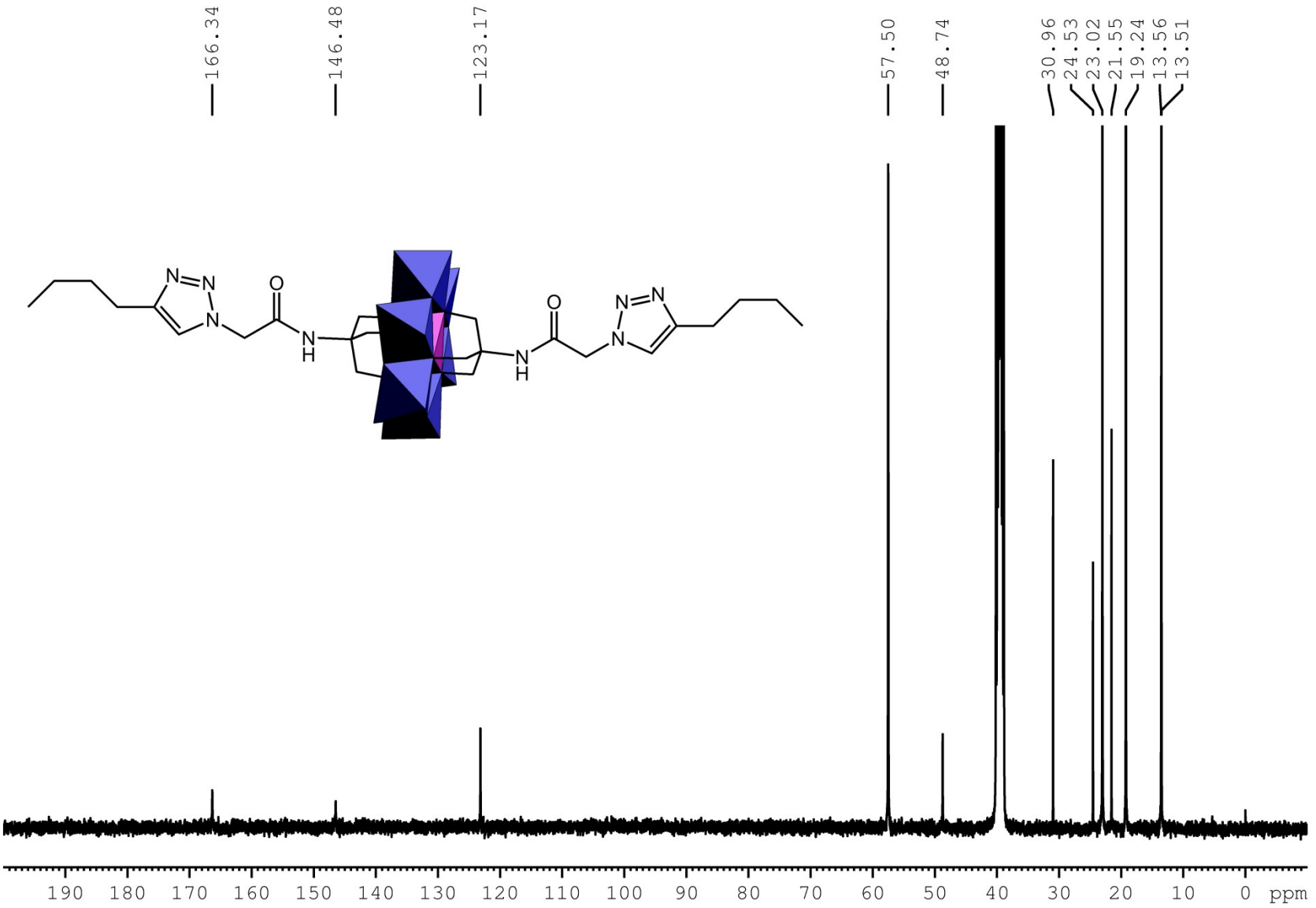


Figure S25: ^{1}H NMR spectrum of compound 1 in DMSO-d_6 at 600 MHz.

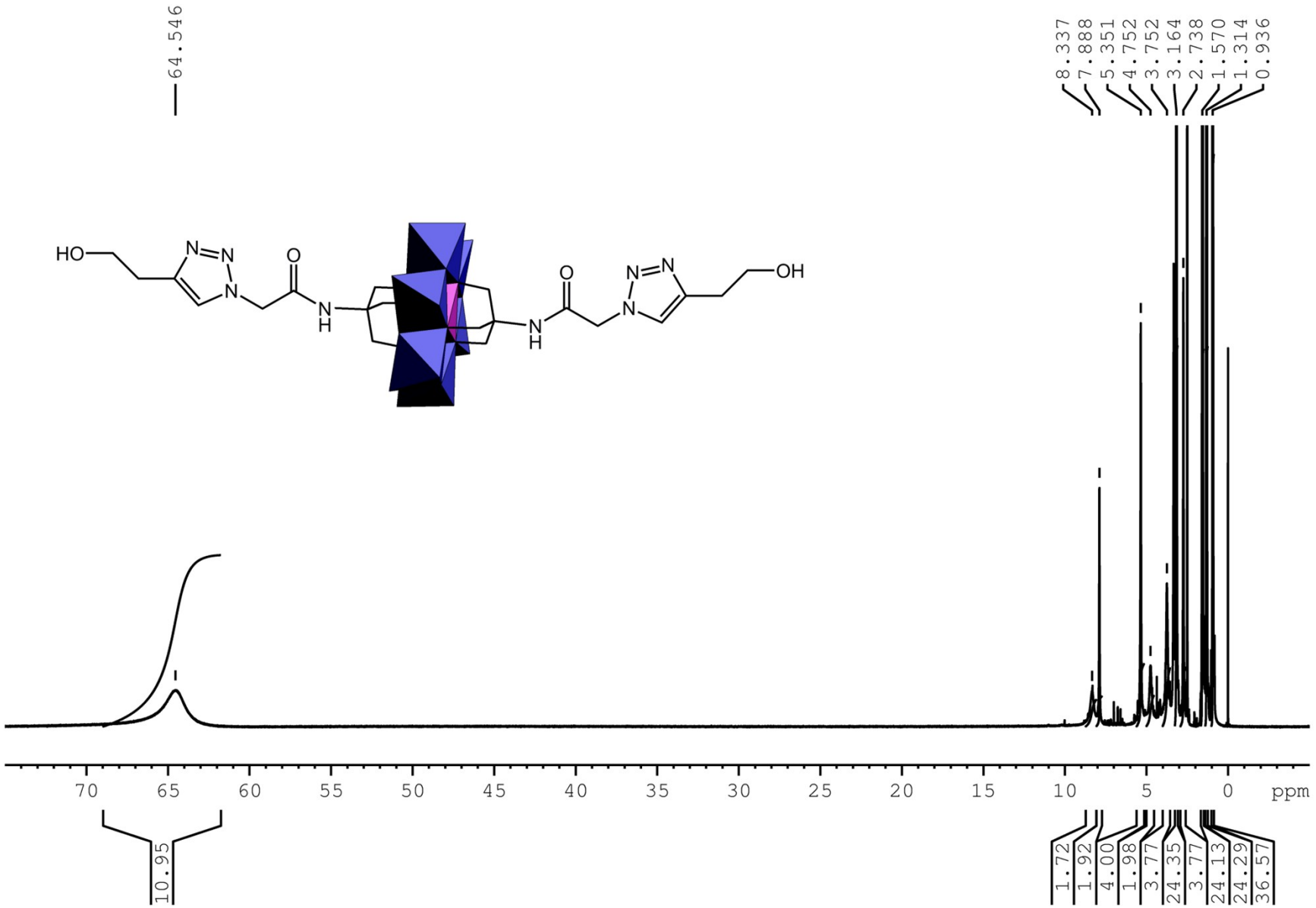


Figure S26: Detail (-1 to 10 ppm) of the ^{1}H NMR spectrum of compound 4e in DMSO-d_6 at 600 MHz.

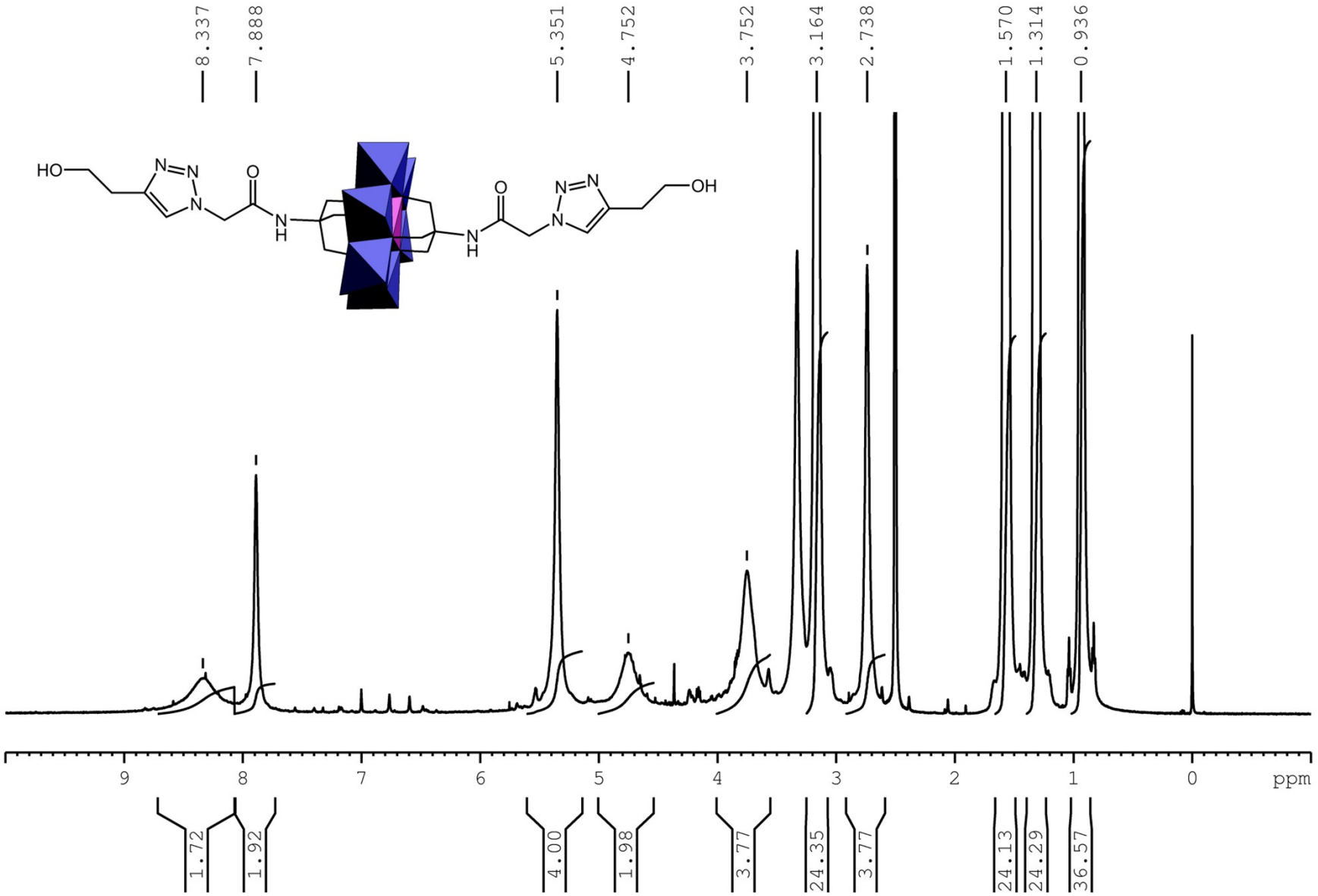
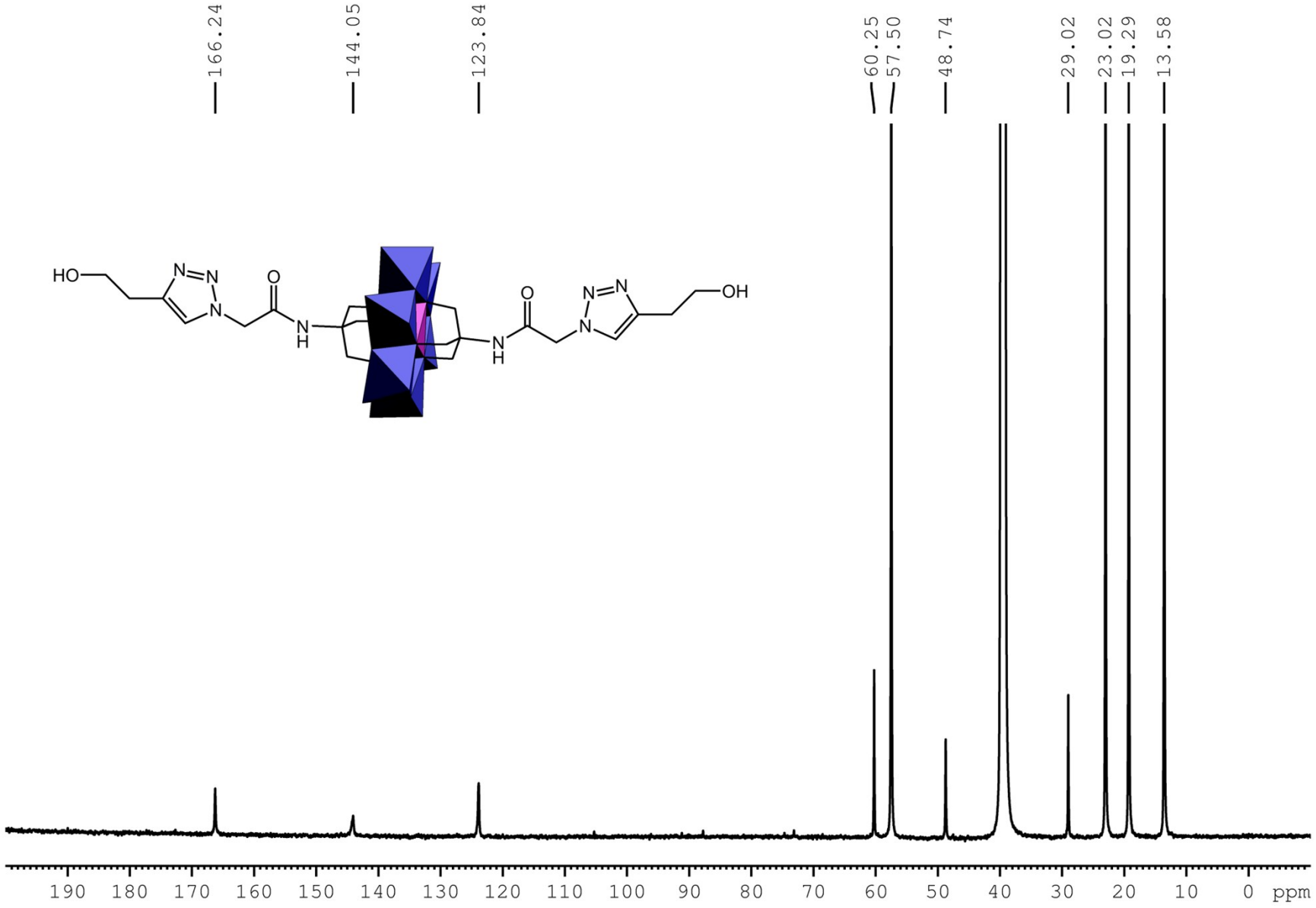


Figure S27: ^{13}C NMR spectrum of compound 4e in DMSO-d_6 at 150 MHz.



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