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Supporting Information

Synthesis and Characterization of Amide Linked Triazolyl Glycolipids as Molecular Hydrogelators and Organogelators

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Part I. Synthesis and characterizations of compounds 8-24

Synthesis of compound 8:

Compound **6** (75 mg, 0.20 mmol) was dissolved in acetonitrile (5 mL). 1-octyne (0.030 mL, 0.20 mmol) was added to this solution followed by the addition of CuI (8 mg, 0.041 mmol) and TEA (0.145 mL, 1.03 mmol). The reaction mixture was stirred for 24 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent from pure DCM to 2% MeOH/DCM to obtain off-white solid (83 mg, 85%) as the desired product (R_f = 0.3 in 5% MeOH/DCM). m.p. 163.0-165.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.43 (d, J = 8.5 Hz, 1H), 7.76 (s, 1H), 7.51-7.43 (m, 2H), 7.42-7.34 (m, 3H), 5.62 (s, 1H), 5.31 (d, J = 5.6 Hz, 1H), 5.11 (d, J = 16.4 Hz, 1H), 5.07 (d, J = 16.4 Hz, 1H), 4.66 (d, J = 3.5 Hz, 1H), 4.19 (dd, J = 9.9, 4.7 Hz, 1H), 3.90-3.83 (m, 1H), 3.80-3.60 (m, 3H), 3.56-3.48 (m, 1H), 3.33 (s, 3H), 2.61 (t, J = 7.5 Hz, 2H), 1.64-1.52 (m, 2H), 1.38-1.21 (m, 6H), 0.86 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.5, 137.7, 128.8, 128.0, 126.4, 123.2, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 54.8, 54.3, 51.3, 31.0, 28.9, 28.2, 24.9, 22.0, 13.9; LCMS (ESI+) calcd for $C_{24}H_{35}N_4O_6$ $[M+H]^+$, 475.2 found 475.2.

Synthesis of compound 9:

Compound **6** (100 mg, 0.27 mmol) was dissolved acetonitrile (5 mL). To this solution 1-undecyne (0.030 mL, 0.31 mmol) was added followed by adding a pinch of CuI (8 mg, 0.041 mmol) and DIEA (0.19 mL, 1.1 mmol). Reaction was stirred for 24 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography from pure DCM to 2% MeOH/DCM to obtain yellow

solid (114 mg, 81%) as the desired product (R_f = 0.4 in 5% MeOH/DCM). m.p. 168.0-170.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.44 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H), 7.52-7.33 (m, 5H), 5.63 (s, 1H), 5.31 (d, J = 5.3 Hz, 1H), 5.09 (s, 2H), 4.67 (d, J = 3.4 Hz, 1H), 4.24-4.14 (m, 1H), 3.92-3.83 (m, 1H), 3.82-3.59 (m, 3H), 3.57-3.47 (m, 1H), 3.34 (s, 3H), 2.61 (t, J = 7.2 Hz, 2H), 1.59 (m, 2H), 1.37-1.17 (m, 12H), 0.85 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.5, 137.7, 128.8, 128.0, 126.4, 123.2, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 54.8, 54.3, 51.3, 31.2, 28.93, 28.88, 28.7, 28.6, 28.5, 24.9, 22.0, 13.9; LCMS (ESI+) calcd for $C_{27}H_{41}N_4O_6$ $[M+H]^+$, 517.2 found 517.2.

Synthesis of compound 10:

Compound **6** (100 mg, 0.27 mmol) was dissolved in acetonitrile (5 mL). To this solution 1-dodecyne (0.051 g, 0.31 mmol) was added followed by adding a pinch of CuI (8 mg, 0.041 mmol) and DIEA (0.19 mL, 1.1 mmol). Reaction was stirred for 24 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent from pure DCM to 2% MeOH/DCM to obtain off-white solid (94 mg, 78%) as the desired product (R_f = 0.4 in 5% MeOH/DCM). m.p. 175.0-177.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.41 (m, 3H), 7.38-7.31 (m, 3H), 6.42 (d, J = 8.8 Hz, 1H), 5.52 (s, 1H), 5.05 (s, 2H), 4.66 (d, J = 3.7 Hz, 1H), 4.30-4.15 (m, 2H), 3.89-3.81 (m, 1H), 3.79-3.69 (m, 2H), 3.59-3.51 (m, 1H), 3.34 (s, 3H), 2.72 (t, J = 7.6 Hz, 2H), 1.72-1.61 (m, 2H), 1.38-1.22 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.5, 137.7, 128.9, 128.0, 126.4, 123.2, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 54.8, 54.3, 51.3, 31.2, 28.9, 28.7, 28.6, 28.5, 24.9, 22.0, 13.9; LCMS (ESI+) calcd for $C_{28}H_{43}N_4O6$ $[M+H]^+$, 531.3 found 531.3.

Synthesis of compound 11:

Compound **6** (100 mg, 0.27 mmol) and 1-hexadecyne (102.7 mg, 0.41 mmol) were dissolved in the acetonitrile (6 mL). CuI (11 mg, 0.055 mmol) and DIEA (0.24 mL, 1.37 mmol) were added to the reaction mixture. Reaction was stirred at room temperature for 24 hours. Solvent was removed under reduced pressure and then workup was performed using EtOAc (60 mL)/water (10 mL) to give the crude, which was purified by column chromatography using the eluent from 20% to 80% EtOAc/hexane to obtain white solid (127 mg, 77%) as the desired product (R_f = 0.45 in 80% EtOAc/hexane). m.p. 178.5-180.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 3H), 7.39-7.33 (m, 3H), 6.38 (d, *J* = 8.8 Hz, 1H), 5.53 (s, 1H), 5.07 (s, 2H), 4.66 (d, *J* = 3.7 Hz, 1H), 4.29-4.16 (m, 2H), 3.89-3.82 (m, 1H), 3.80-3.70 (m, 2H), 3.58-3.51 (m, 1H), 3.35 (s, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.72-1.61 (m, 2H), 1.38-1.20 (m, 22H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + d_6-DMSO) δ 165.3, 136.8, 128.3, 127.3, 125.8, 101.1, 98.1, 81.3, 68.1, 67.6, 61.9, 54.5, 54.1, 51.5, 31.0, 28.8, 28.7, 28.6, 28.53, 28.45, 28.4, 24.8, 21.8, 13.3; LCMS (ESI+) calcd for $C_{32}H_{51}N_4O_6$ $[M+H]^+$, 587.4 found 587.4.

Synthesis of compound 12

Compound **6** (171.6 mg, 0.471 mmol) and 1,7-octadiyne (20 mg, 25 uL, 0.188 mmol) were dissolved in the acetonitrile (6 mL). CuI (14.0 mg, 0.075 mmol) and DIEA (0.16 mL, 0.942 mmol) were added to the reaction mixture. Reaction was stirred at room temperature for 36 hours. Solvent was removed under reduced pressure and then workup was performed using $CHCl_3$ (60 mL)/water (5 mL) to give the crude, which was purified by column chromatography using the eluent from 1% to 3% MeOH/DCM to afford monomer **12** (white solid, 71 mg, 79%) as the desired product. R_f=0.5 in 5% MeOH/DCM. m.p. 175.0-177.0 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.44 (d, *J* =

8.5 Hz, 1H), 7.78 (s, 1H), 7.49-7.43 (m, 2H), 7.42-7.34 (m, 3H), 5.62 (s, 1H), 5.31 (d, *J* = 5.6 Hz, 1H), 5.09 (s, 2H), 4.66 (d, *J* = 3.6 Hz, 1H), 4.19 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.90-3.80 (m, 1H), 3.79-3.60 (m, 3H), 3.56-3.48 (m, 1H), 3.33 (s, 3H), 2.73 (t, *J* = 2.7 Hz, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.19 (dt, *J* = 7.5, 2.7 Hz, 2H), 1.72-1.63 (m, 2H), 1.53-1.44 (m, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.2, 137.7, 128.8, 128.0, 126.4, 123.3, 100.9, 98.5, 84.3, 81.7, 71.2, 67.9, 67.5, 62.5, 54.8, 54.3, 51.3, 28.0, 27.4, 24.3, 17.4; LCMS (ESI+) calcd for $C_{24}H_{31}N_4O_6$ $[M+H]^+$, 471.2 found 471.2.

Synthesis of compound 13:

Compound **6** (100 mg, 0.27 mmol) was dissolved in THF:*t*-BuOH:H_2O (6 mL, v/v/v 1:1:1). To this solution 6-chloro-1-hexyne (0.033 mL, 0.27 mmol) was added followed by adding $CuSO_4$ (9 mg, 0.055 mmol) and L-ascorbic acid sodium salt (21 mg, 0.108 mmol). Reaction was stirred for 12 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent from pure DCM to 2% MeOH/DCM to obtain off-white solid (113 mg, 86%) as the desired product (R_f = 0.4 in 5% MeOH/DCM). m.p. 134.0-136.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.45 (d, *J* = 8.5 Hz, 1H), 7.80 (s, 1H), 7.48-7.44 (m, 2H), 7.40-7.36 (m, 3H), 5.62 (s, 1H), 5.31 (d, *J* = 5.6 Hz, 1H), 5.11 (d, *J* = 16.3 Hz, 1H), 5.07 (d, *J* = 16.3 Hz, 1H), 4.66 (d, *J* = 3.6 Hz, 1H), 4.19 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.90-3.82 (m, 1H), 3.79-3.60 (m, 5H), 3.56-3.48 (m, 1H), 3.33 (s, 3H), 2.65 (t, *J* = 7.1 Hz, 2H), 1.81-1.66 (m, 4H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.1, 137.7, 128.9, 128.0, 126.4, 123.4, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 54.8, 54.4, 51.4, 45.1, 31.5, 26.2, 24.1; LCMS (ESI+) calcd for $C_{22}H_{30}ClN_4O_6$ $[M+H]^+$, 481.1 found 481.1.

Synthesis of compound 14:

Compound **6** (100 mg, 0.274 mmol) and phenylacetylene (0.046 mL, 0.412 mmol) were dissolved in the acetonitrile (6 mL). To this solution, CuI (10.5 mg, 0.055 mmol) and DIEA (0.24 mL, 1.37 mmol) were added and the reaction mixture was stirred at room temperature for 24 hours. Solvent was removed under reduced pressure and then workup was performed using EtOAc (60 mL)/water (10 mL) to give the crude, which was purified by column chromatography using the eluent from 20% EtOAc/hexane to 80% EtOAc/hexane to obtain white solid (101 mg, 80%) as the desired product (R_f = 0.5 in 80% EtOAc/hexane), m.p. 237.0-239.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.54 (d, J = 8.6 Hz, 1H), 8.50 (s, 1H), 7.89-7.83 (m, 2H), 7.50-7.42 (m, 4H), 7.41-7.31 (m, 4H), 5.63 (s, 1H), 5.34 (d, J = 5.6 Hz, 1H), 5.23 (d, J = 16.4 Hz, 1H), 5.19 (d, J = 16.4 Hz, 1H), 4.68 (d, J = 3.6 Hz, 1H), 4.19 (dd, J = 9.8, 4.7 Hz, 1H), 3.92-3.84 (m, 1H), 3.78-3.61 (m, 3H), 3.57-3.50 (m, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.6, 146.0, 130.7, 137.7, 128.9, 128.0, 127.8, 126.4, 125.1, 122.9, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 54.8, 54.4, 51.6; LCMS (ESI+) calcd for $C_{24}H_{27}N_4O_6$ $[M+H]^+$, 467.2 found 467.2.

Synthesis of compound 15:

Compound **6** (75 mg, 0.20 mmol) and 5-phenyl-1-pentyne (0.032 mL, 0.20 mmol) were dissolved in acetonitrile (6 mL). To this solution CuI (8 mg, 0.041 mmol) and TEA (0.14 mL, 1.037 mmol) were added and the reaction mixture was stirred at room temperature for 24 hours. Solvent was removed under reduced pressure and then workup was performed using EtOAc (60 mL)/water (10 mL) to give the crude, which was purified by column chromatography using the eluent from 20% to 80% EtOAc/hexane to obtain off-white solid (91 mg, 87%) as the desired product (R_f = 0.4 in 5% MeOH/DCM). m.p. 173.0-175.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.44 (d, J = 8.5 Hz,

1H), 7.81 (s, 1H), 7.49-7.43 (m, 2H), 7.41-7.34 (m, 3H), 7.32-7.25 (m, 2H), 7.24-7.14 (m, 3H), 5.62 (s, 1H), 5.31 (d, *J* = 5.3 Hz, 1H), 5.12 (d, *J* = 16.2 Hz, 1H), 5.07 (d, *J* = 16.2 Hz, 1H), 4.66 (d, *J* = 3.6 Hz, 1H), 4.21-4.15 (m, 1H), 3.90-3.83 (m, 1H), 3.79-3.59 (m, 3H), 3.55-3.48 (m, 1H), 3.33 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 4H), 1.90 (pentet, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.7, 146.2, 141.8, 137.7, 128.8, 128.3, 128.2, 128.0, 126.4, 125.7, 123.4, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 54.8, 54.3, 51.4, 34.5, 30.7, 24.4; LCMS (ESI+) calcd for $C_{27}H_{33}N_4O_6$ $[M+H]^+$, 509.2 found 509.2.

Synthesis of compound 16:

Compound **6** (100 mg, 0.27 mmol) was dissolved in *t*-BuOH:H_2O (5 mL, v/v 1:1). To this solution N,N-dimethyl propargyl amine (0.029 mL, 0.27 mmol) was added followed by adding $CuSO_4$•$5H_2O$ (13 mg, 0.054 mmol) and L-ascorbic acid sodium salt (21 mg, 0.108 mmol). Reaction was stirred for 12 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent 88:10:2 (DCM: MeOH: aq.NH_3) to obtain off-white solid (97 mg, 79%) as the desired product (R_f = 0.4 in DCM: MeOH: aq.NH_3 = 88:10:2). m.p. 220.0-222.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.45 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.49-7.43 (m, 2H), 7.41-7.35 (m, 3H), 5.62 (s, 1H), 5.31 (br s, 1H), 5.16 (d, *J* = 16.3 Hz, 1H), 5.12 (d, *J* = 16.3 Hz, 1H), 4.66 (d, *J* = 3.6 Hz, 1H), 4.19 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.90-3.83 (m, 1H), 3.79-3.60 (m, 3H), 3.56-3.47 (m, 3H), 3.33 (s, 3H), 2.16(s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.7, 143.3, 137.7, 128.8, 128.0, 126.4, 125.2, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 54.8, 54.4, 53.5, 51.4, 44.5; LCMS (ESI+) calcd for $C_{21}H_{30}N_5O_6$ $[M+H]^+$, 448.2 found 448.2.

Synthesis of compound 17:

Compound **6** (100 mg, 0.27 mmol) was dissolved *t*-BuOH:H_2O (5 mL, v/v 1:1). 1,1-dimethyl-2-propynol (0.031 mL, 0.32 mmol) , $CuSO_4 \cdot 5H_2O$ (13 mg, 0.054 mmol) and L-ascorbic acid sodium salt (21 mg, 0.108 mmol) were added to the reaction mixture. Reaction was stirred at room temperature for 24 hours. Then solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent from pure DCM to 5% MeOH/DCM to obtain off-white solid (98 mg, 72%) as the desired product (R_f = 0.2 in 5% MeOH/DCM). m.p. 230.0-232.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.46 (d, *J* = 8.5 Hz, 1H), 7.80 (s, 1H), 7.49-7.43 (m, 2H), 7.41-7.36 (m, 3H), 5.62 (s, 1H), 5.31 (d, *J* = 5.4 Hz, 1H), 5.15-5.06 (m, 3H), 4.66 (d, *J* = 3.6 Hz, 1H), 4.19 (dd, *J* = 9.9, 4.7 Hz, 1H), 3.91-3.83 (m, 1H), 3.79-3.60 (m, 3H), 3.56-3.48 (m, 1H), 3.33 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.9, 155.6, 137.7, 129.0, 128.1, 126.5, 121.9, 101.0, 98.6, 81.8, 68.0, 67.6, 67.1, 62.6, 54.9, 54.4, 51.4, 30.7; LCMS (ESI+) calcd for $C_{21}H_{29}N_4O_7$ $[M+H]^+$, 449.2 found 449.1.

Synthesis of compound 18:

Compound **6** (100 mg, 0.27 mmol) was dissolved in THF:*t*-BuOH:H_2O (6 mL, v/v/v 1:1:1). To this solution 3-butyne-1-ol (0.020 mL, 0.27 mmol) was added followed by adding $CuSO_4$ (9 mg, 0.055 mmol) and L-ascorbic acid sodium salt (21 mg, 0.108 mmol). Reaction was stirred for 12 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent from pure DCM to 5% MeOH/DCM to obtain off-white solid (99 mg, 84%) as the desired product (R_f = 0.2 in 5% MeOH/DCM). m.p. 268.0-270.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.46 (d, *J* = 8.5 Hz, 1H), 7.86 (s, 1H), 7.50-7.42 (m, 2H), 7.42-7.32 (m, 3H), 5.62 (s, 1H), 5.31 (d, *J* = 5.6 Hz, 1H),

5.13 (d, *J* = 16.4 Hz, 1H), 5.09 (d, *J* = 16.4 Hz, 1H), 4.72 (s, 1H), 4.66 (d, *J* = 3.5 Hz, 1H), 4.18 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.90-3.81 (m, 1H), 3.79-3.58 (m, 5H), 3.56-3.48 (m, 1H), 3.33 (s, 3H), 2.80 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.7, 137.7, 128.9, 128.0, 126.4, 100.9, 98.5, 81.7, 68.0, 67.5, 62.5, 60.3, 59.7, 54.9, 54.4, 51.5, 29.1; LCMS (ESI+) calcd for $C_{20}H_{27}N_4O_7$ $[M+H]^+$, 435.2 found 435.1.

Synthesis of compound 19:

Compound **6** (0.1 g, 0.27 mmol) was dissolved in *t*-BuOH:H_2O (5 mL, v/v 1:1). To this solution 4-pentyne-1-ol (0.028 mL, 0.29 mmol) was added followed by adding $CuSO_4 \bullet 5H_2O$ (9 mg, 0.054 mmol) and L-ascorbic acid sodium salt (21 mg, 0.108 mmol). Reaction was stirred for 12 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent from pure DCM to 5% MeOH/DCM to obtain off-white solid (91 mg, 77%) as the desired product (R_f = 0.2 in 5% MeOH/DCM). m.p. 270.0-272.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.44 (d, *J* = 8.5 Hz, 1H), 7.77 (s, 1H), 7.48-7.43 (m, 2H), 7.41-7.36 (m, 3H), 5.62 (s, 1H), 5.31 (d, *J* = 5.6 Hz, 1H), 5.11 (d, *J* = 16.2 Hz, 1H), 5.06 (d, *J* = 16.2 Hz, 1H), 4.65 (d, *J* = 3.6 Hz, 1H), 4.46 (t, *J* = 5.2 Hz, 1H), 4.19 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.90-3.82 (m, 1H), 3.78-3.59 (m, 3H), 3.55-3.48 (m, 1H), 3.47-3.40 (m, 2H), 3.33 (s, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.78-1.69 (m, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.4, 137.7, 128.9, 128.0, 126.4, 123.3, 100.9, 98.5, 81.7, 68.0, 67.5, 62.5, 60.0, 54.8, 54.4, 51.4, 32.3, 21.6; LCMS (ESI+) calcd for $C_{21}H_{29}N_4O_7$ $[M+H]^+$, 449.2 found 449.1.

Synthesis of compound 20:

Compound **6** (100 mg, 0.27 mmol) was dissolved in *t*-BuOH:H_2O (5 mL, v/v 1:1). To this solution 1-ethynyl-1-cyclohexanol (0.038 mL, 0.29 mmol) followed by adding $CuSO_4 \bullet 5H_2O$ (13 mg, 0.054 mmol) and L-ascorbic acid sodium salt (21 mg, 0.108 mmol) were added to the reaction mixture. Reaction was stirred for 12 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography using eluent from pure DCM to 5% MeOH/DCM to obtain off-white solid (103 mg, 78%) as the desired product (R_f = 0.4 in 5% MeOH/DCM). m.p. 144.0-146.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.45 (d, J = 8.5 Hz, 1H), 7.81 (s, 1H), 7.51-7.42 (m, 2H), 7.41-7.33 (m, 3H), 5.62 (s, 1H), 5.13 (d, J = 16.4 Hz, 1H), 5.08 (d, J = 16.4 Hz, 1H), 4.66 (d, J = 3.6 Hz, 1H), 4.19 (dd, J = 9.8, 4.7 Hz, 1H), 3.91-3.82 (m, 1H), 3.78-3.60 (m, 3H), 3.57-3.48 (m, 1H), 3.33 (s, 3H), 1.92-1.80 (m, 2H), 1.75-1.59 (m, 4H), 1.58-1.37 (m, 3H), 1.34-1.22 (m, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.7, 155.5, 137.7, 128.9, 128.0, 126.4, 122.3, 100.9, 98.5, 81.7, 79.1, 68.0, 67.5, 62.5, 54.8, 54.4, 51.4, 37.8, 25.2, 21.6; LCMS (ESI+) calcd for $C_{24}H_{33}N_4O_7$ $[M+H]^+$, 489.2 found 489.2.

Synthesis of compound 21:

Compound **6** (100 mg, 0.27 mmol) was dissolved in acetonitrile (5 mL). To this solution 10-undecyn-1-ol (50 mg, 0.29 mmol) was added followed by adding a pinch of CuI (10.5 mg, 0.055 mmol) and DIEA (0.23 mL, 1.35 mmol). Reaction was stirred for 24 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography eluent from pure DCM to 5% MeOH/DCM to obtain light brown solid (132 mg, 88%) as the desired product (R_f = 0.2 in 5%

MeOH/DCM). m.p: 168.0-170.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.43 (d, J = 8.5 Hz, 1H), 7.76 (s, 1H), 7.48-7.43 (m, 2H), 7.41-7.35 (m, 3H), 5.62 (s, 1H), 5.11 (d, J = 16.3 Hz, 1H), 5.06 (d, J = 16.3 Hz, 1H), 4.66 (d, J = 3.6 Hz, 1H), 4.19 (dd, J = 9.8, 4.7 Hz, 1H), 3.90-3.82 (m, 1H), 3.79-3.60 (m, 3H), 3.57-3.49 (m, 1H), 3.42-3.34 (m, 5H), 2.60 (t, J = 7.5 Hz, 2H), 1.63-1.52 (m, 2H), 1.44-1.35 (m, 2H), 1.33-1.22 (m, 10H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.5, 137.7, 128.8, 128.0, 126.4, 123.2, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 60.7, 54.8, 54.3, 51.3, 32.5, 28.97, 28.95, 28.9, 28.7, 28.5, 25.4, 24.9; LCMS (ESI+) calcd for $C_{27}H_{41}N_4O_7$ $[M+H]^+$, 533.3 found 533.3.

Synthesis of compound 22:

Compound **6** (100 mg, 0.27 mmol) was dissolved in *t*-BuOH:H_2O (5 mL, v/v 1:1). To this solution 6-heptynoic acid (0.041 mL, 0.32 mmol) was added followed by $CuSO_4 \cdot 5H_2O$ (13 mg, 0.054 mmol) and L-ascorbic acid sodium salt (21 mg, 0.108 mmol) were added to the reaction mixture. Reaction was stirred for 12 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography from pure DCM to 10% MeOH/DCM to obtain light brown solid (96 mg, 72%) as the desired product (R_f = 0.2 in 10% MeOH/DCM). m.p. 224.0-226.0 ºC; ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.93 (br s, 1H), 8.44 (d, J = 8.5 Hz, 1H), 7.77 (s, 1H), 7.51-7.33 (m, 5H), 5.62 (s, 1H), 5.29 (s, 1H), 5.09 (s, 2H), 4.65 (d, J = 3.2 Hz, 1H), 4.19 (dd, J = 9.8, 4.7 Hz, 1H), 3.90-3.81 (m, 1H), 3.79-3.58 (m, 3H), 3.56-3.48 (m, 1H), 3.33 (s, 3H, covered by the moisture in d_6-DMSO), 2.62 (t, J = 6.8 Hz, 2H), 2.23 (t, J = 6.8 Hz, 2H), 1.66-1.48 (m, 4H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 174.3, 165.7, 146.3, 137.7, 128.8, 128.0, 126.4, 123.2, 100.9, 98.5, 81.7, 67.9, 67.5,

62.5, 54.8, 54.3, 51.3, 33.4, 28.4, 24.6, 24.0; LCMS (ESI+) calcd for $C_{23}H_{31}N_4O_8$ $[M+H]^+$, 491.2 found 491.2.

Synthesis of compound 23:

Compound **6** (100 mg, 0.27 mmol) was dissolved in acetonitrile (5 mL). To this solution 10-undecyn-1-ol (65 mg, 0.35 mmol) was added followed by adding a pinch of CuI (10.5 mg, 0.055 mmol) and DIEA (0.23 mL, 1.35 mmol). Reaction was stirred for 24 hours at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography from pure DCM to 10% MeOH/DCM to obtain light brown solid (98 mg, 65%) as the desired product (R_f = 0.25 in 10% MeOH/DCM). m.p. 160.0-162.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.90 (br s, 1H), 8.44 (d, J = 8.5 Hz, 1H), 7.76 (s, 1H), 7.49-7.43 (m, 2H), 7.41-7.35 (m, 3H), 5.62 (s, 1H), 5.32 (s, 1H), 5.10 (d, J = 16.3 Hz, 1H), 5.06 (d, J = 16.3 Hz, 1H), 4.65 (d, J = 3.5 Hz, 1H), 4.18 (dd, J = 9.9, 4.7 Hz, 1H), 3.90-3.82 (m, 1H), 3.79-3.59 (m, 3H), 3.56-3.48 (m, 1H), 3.33 (s, 3H, covered by the moisture in d_6-DMSO), 2.62 (t, J = 7.5 Hz, 2H), 2.18 (s, 2H), 1.64-1.53 (m, 2H), 1.52-1.42 (m, 2H), 1.36-1.19 (m, 8H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.6, 137.7, 128.9, 128.0, 126.4, 126.3, 123.2, 100.9, 98.5, 81.7, 67.9, 67.5, 62.5, 60.7, 54.8, 54.4, 51.3, 32.5, 28.98, 28.95, 28.7, 28.6, 25.5, 24.9; LCMS (ESI+) calcd for $C_{27}H_{39}N_4O_8$ $[M+H]^+$, 547.3 found 547.3.

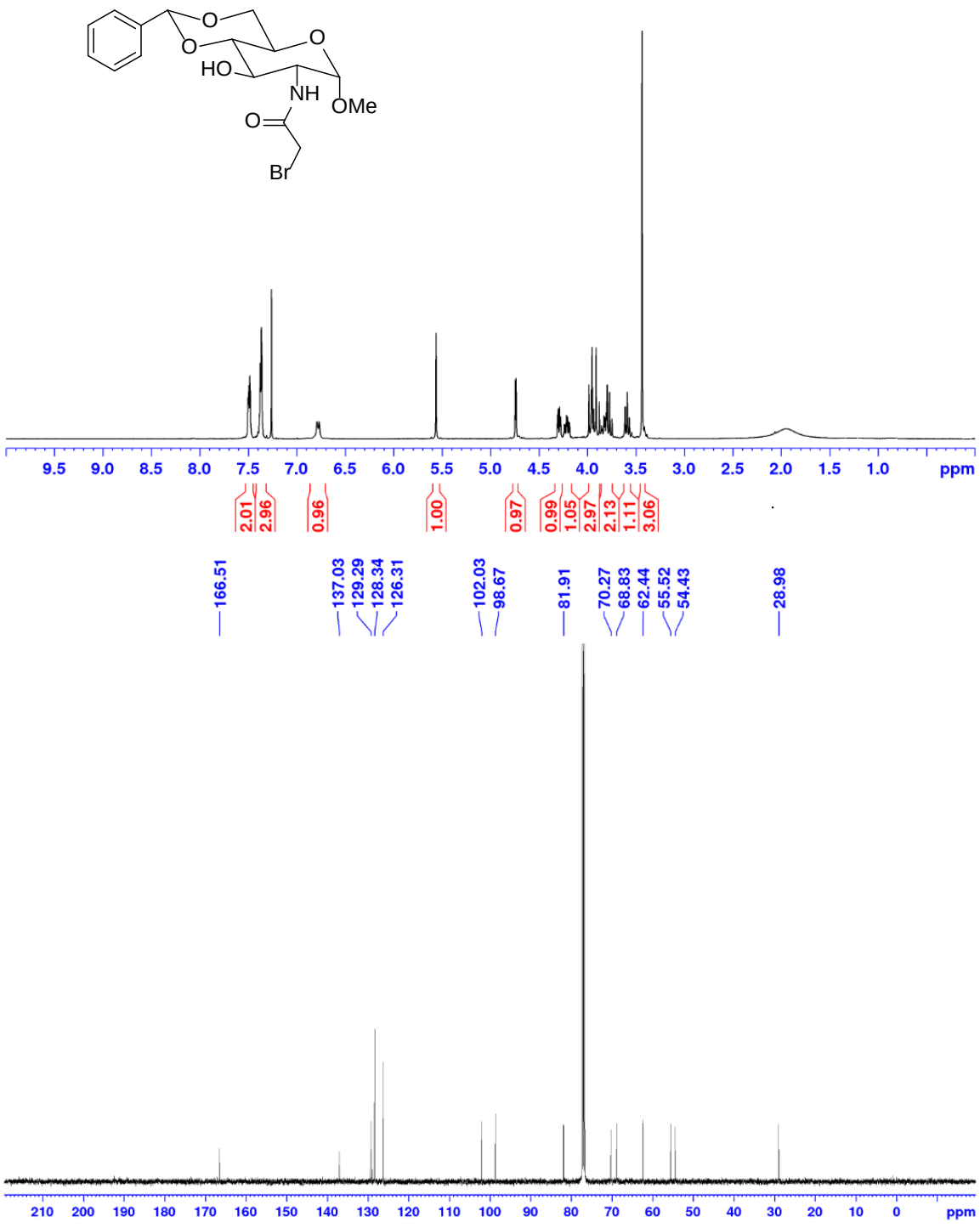
Synthesis of compound 24

Compound **6** (205 mg, 0.564 mmol) was dissolved in 6 mL of THF:*t*-BuOH:H_2O (6 mL, v/v/v 1:1:1). To this solution 1, 7-octadiyne (40 mg, 0.376 mmol) was added followed by adding $CuSO_4$ (24 mg, 0.154 mmol) and L-ascorbic acid sodium salt (59 mg, 0.30 mmol). Reaction was stirred

for 2 days at room temperature. After complete disappearance of starting material solvent was removed under reduced pressure. Crude product was purified by column chromatography from pure DCM to 15% MeOH/DCM to obtain both the monomer and dimer. Dimer was obtained as a white solid (154 mg, 51 %). Monomer **12** was obtained as a white solid (60 mg, 20%). The pure dimer was obtained as a white solid (154 mg, 51%, R_f = 0.3 in 20% MeOH/DCM). m.p. 240.0-242.0 ºC. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.44 (d, J = 8.6 Hz, 2H), 7.77 (s, 2H), 7.50-7.42 (m, 4H), 7.41-7.34 (m, 6H), 5.62 (s, 2H), 5.30 (d, J = 5.5 Hz, 2H), 5.08 (s, 4H), 4.66 (d, J = 3.2 Hz, 2H), 4.18 (dd, J = 9.8, 4.5 Hz, 2H), 3.91-3.81 (m, 2H), 3.79-3.58 (m, 6H), 3.56-3.48 (m, 2H), 3.36 (s, 6H, covered by the moisture in d_6-DMSO), 2.70- 2.60 (m, 4H), 1.70-1.58 (m, 4H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 165.8, 146.4, 137.7, 128.9, 128.0, 126.4, 123.3, 100.9, 98.5, 81.7, 68.0, 67.5, 62.5, 54.8, 54.4, 51.4, 28.5, 24.7; LCMS (ESI+) calcd for $C_{40}H_{51}N_8O_{12}$ $[M+H]^+$, 835.4 found 835.3.

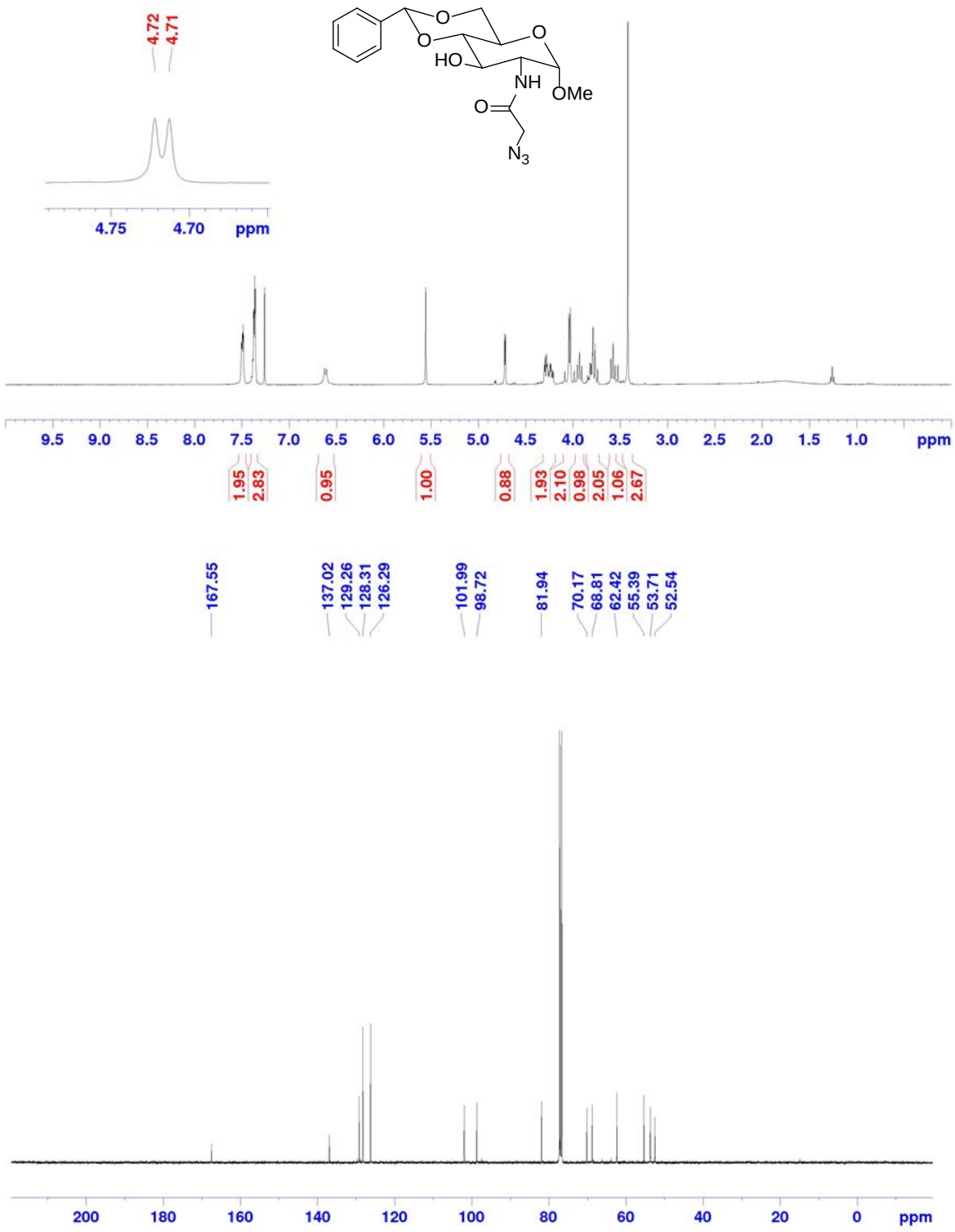
Part II. Copies of ^{1} and ^{13}C NMR spectra of compounds **5-24**

Compound 5:



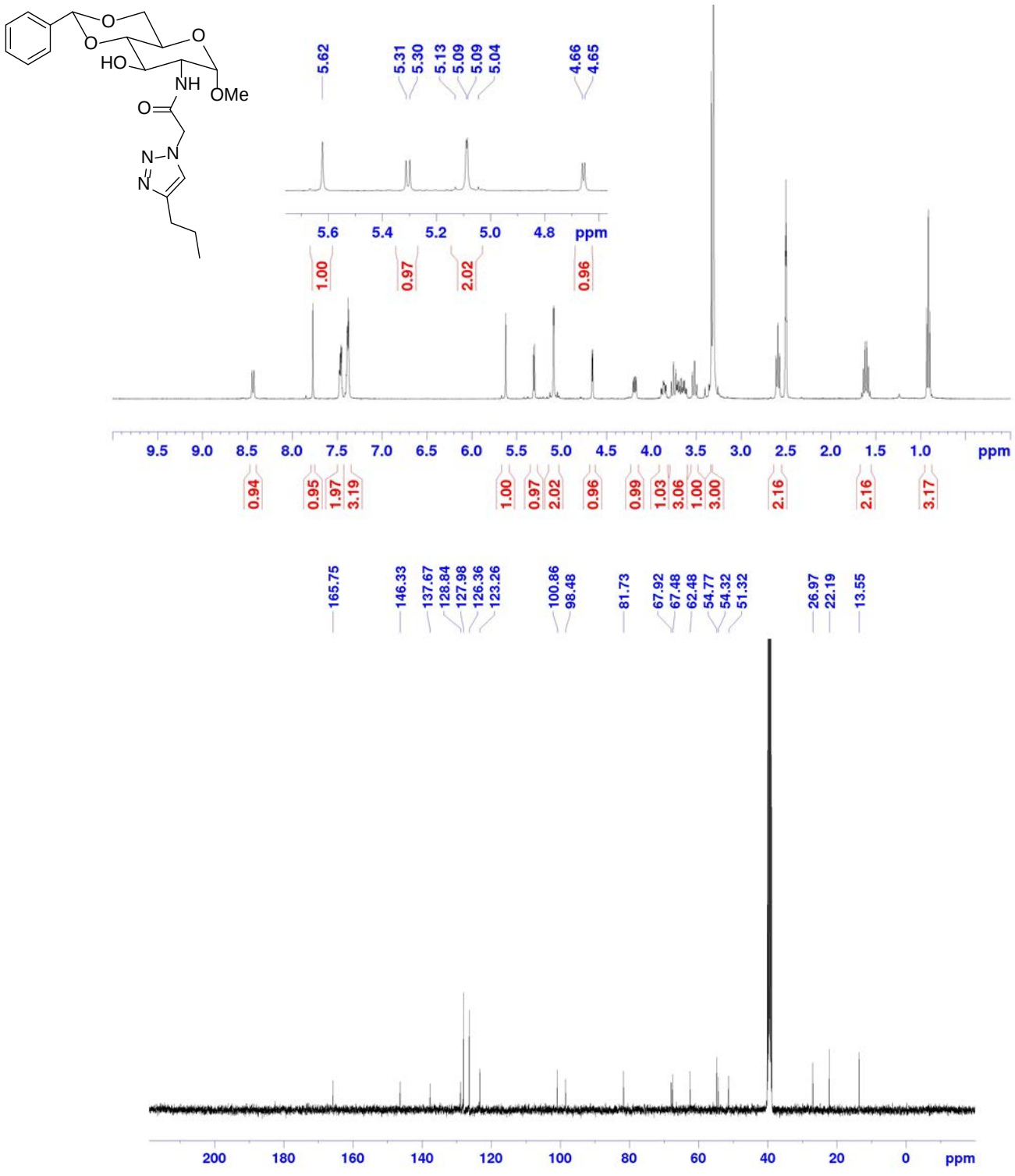
^{1}H NMR and ^{13}C NMR spectra for compound **5** in $CDCl_3$

Compound 6:



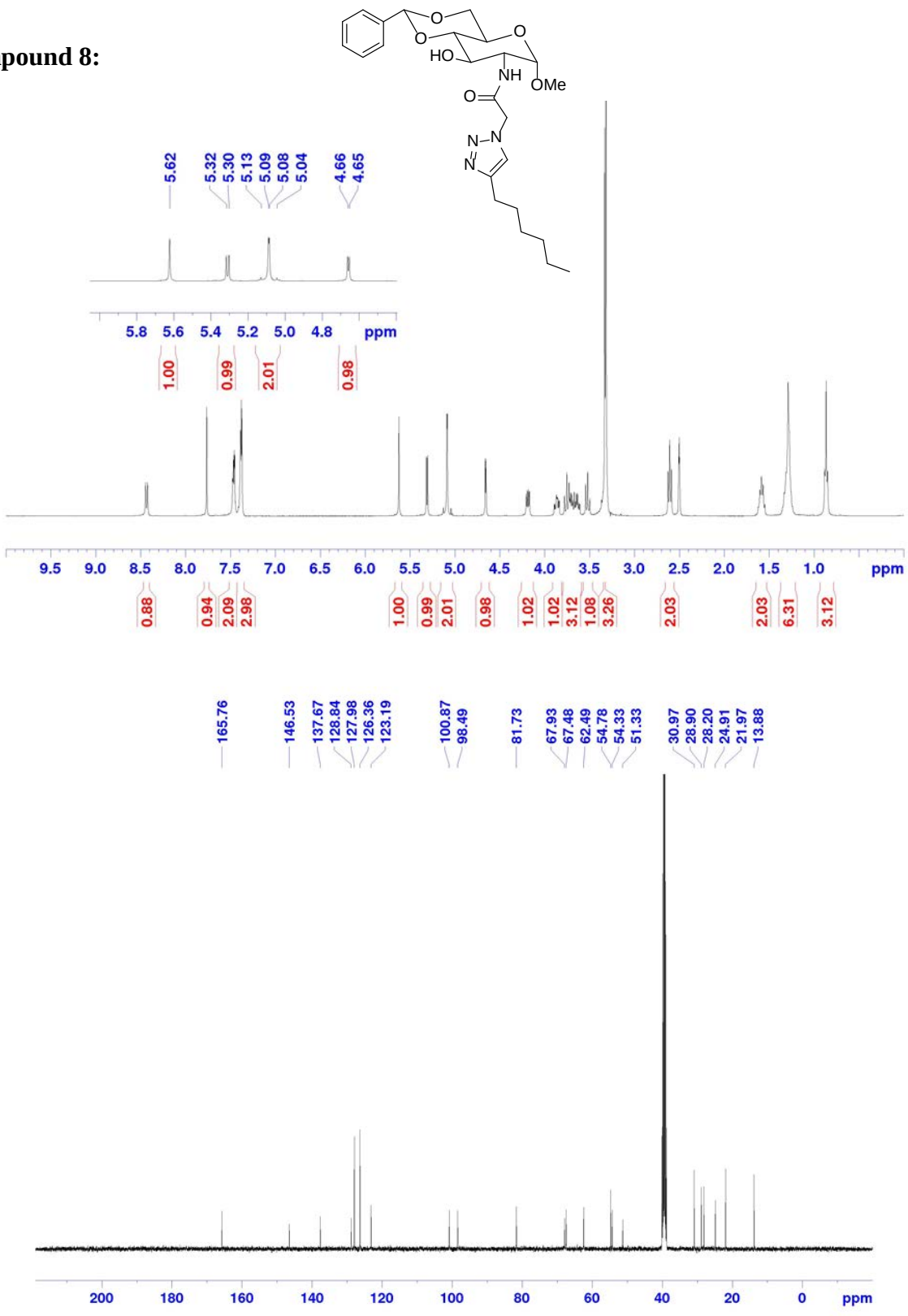
^{1}H NMR and ^{13}C NMR spectra for compound **6** in $CDCl_3$

Compound 7:



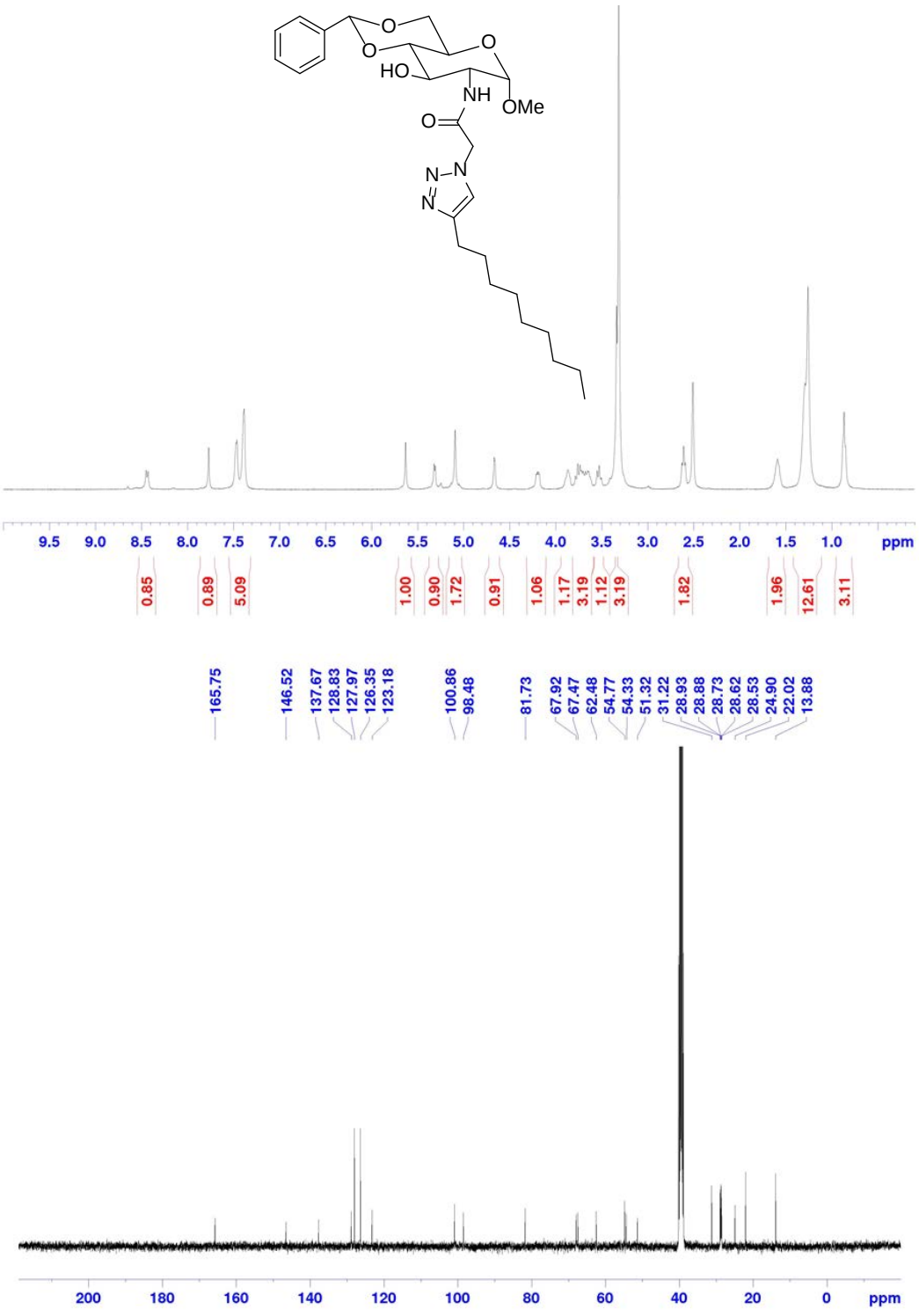
^{1}H NMR and ^{13}C NMR spectra for compound **7** in d_6-DMSO

Compound 8:



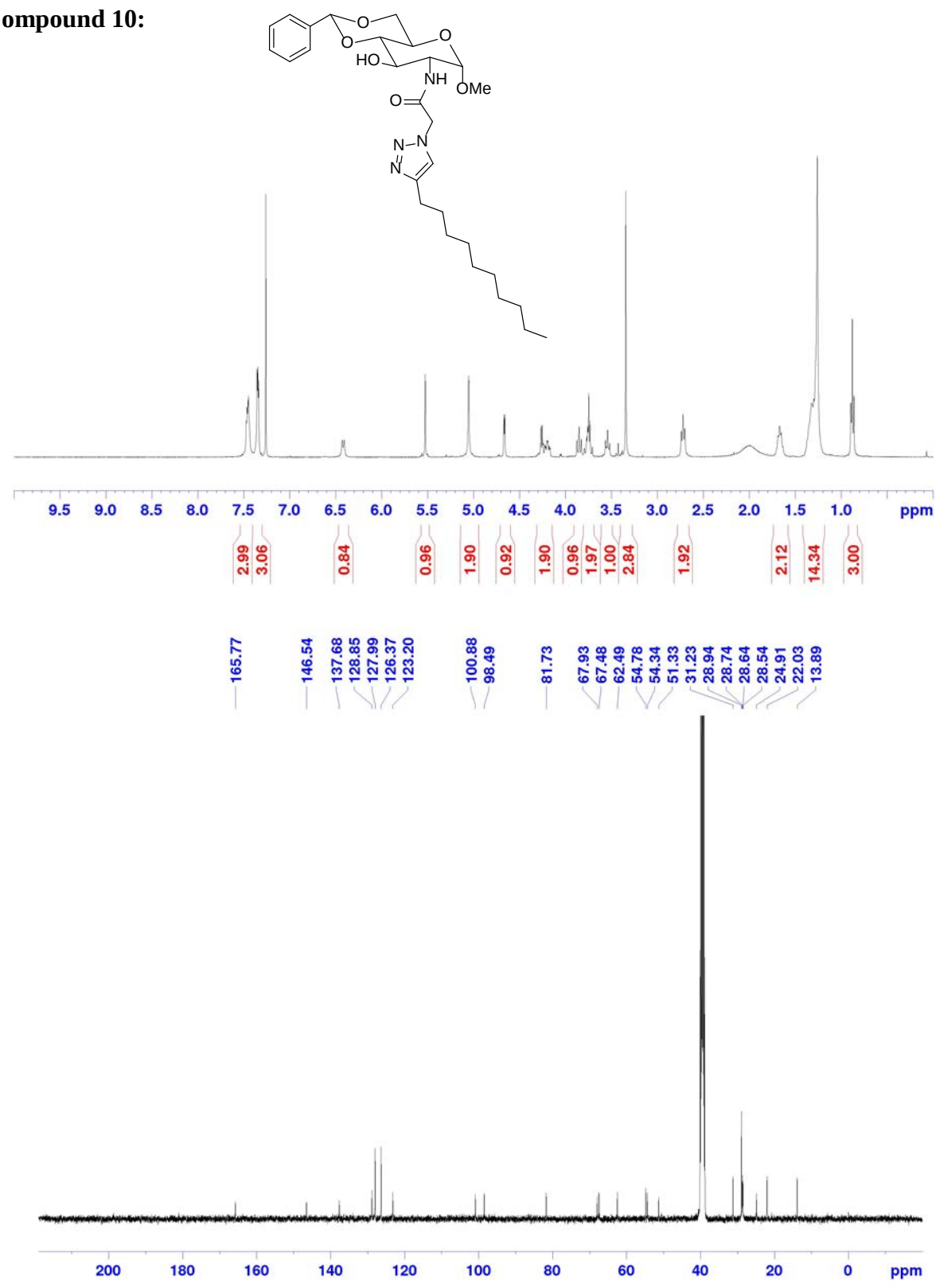
^{1}H NMR and ^{13}C NMR spectra for compound **8** in d_6-DMSO

Compound 9:



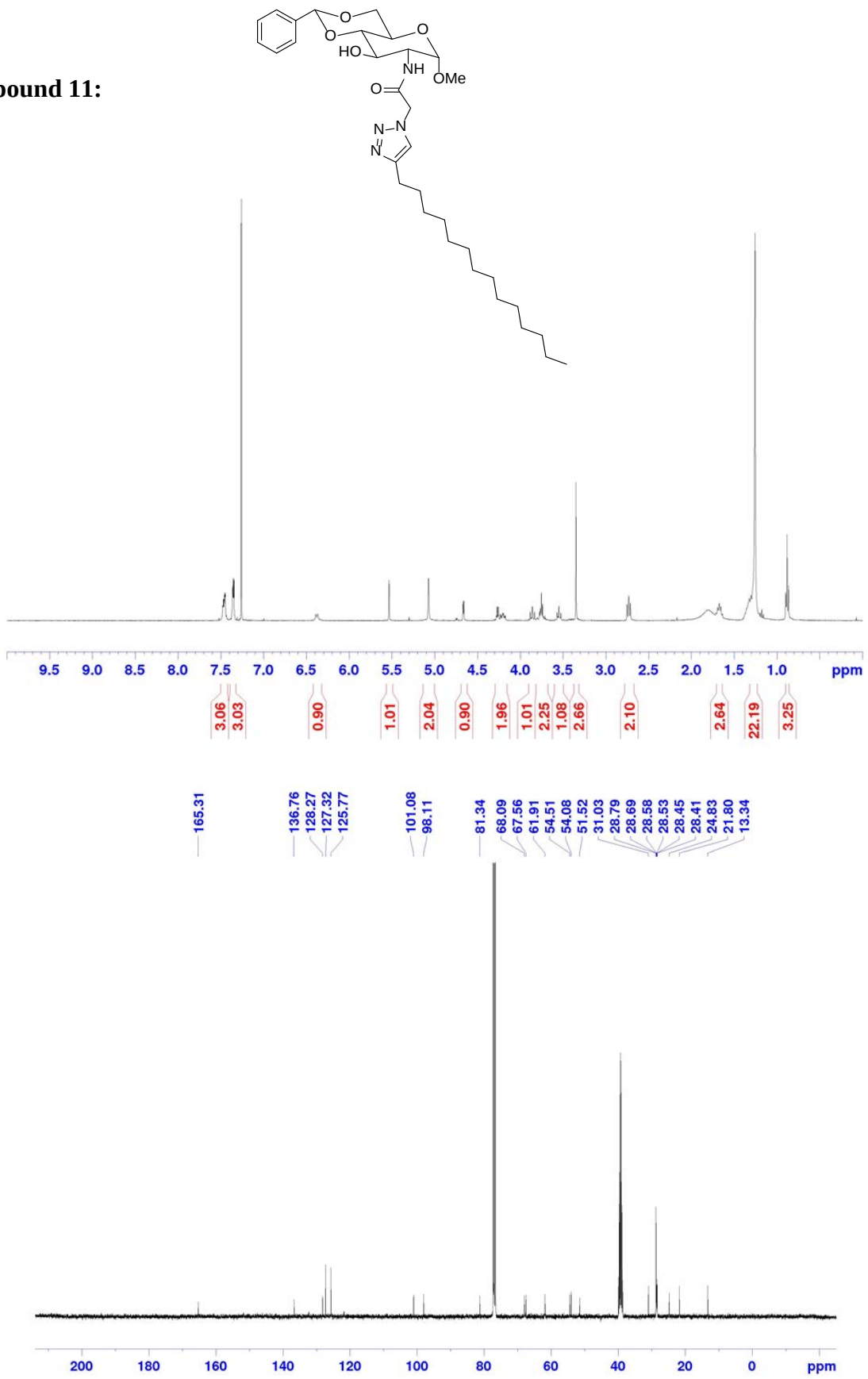
^{1}H NMR and ^{13}C NMR spectra for compound **9** in d_6-DMSO

Compound 10:



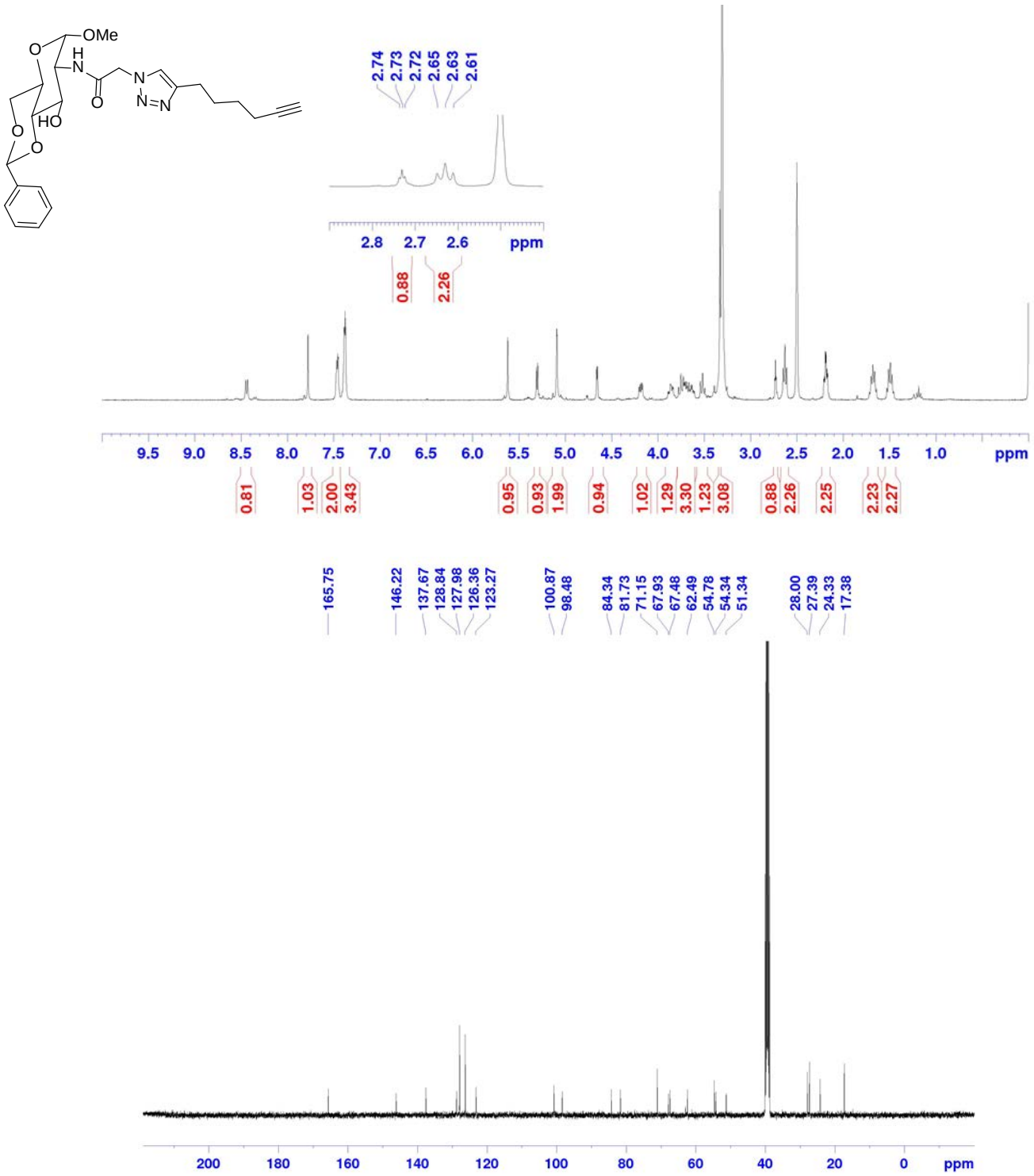
^{1}H NMR spectrum in $CDCl_3$ and ^{13}C NMR spectrum in d_6-DMSO for compound **10**

Compound 11:



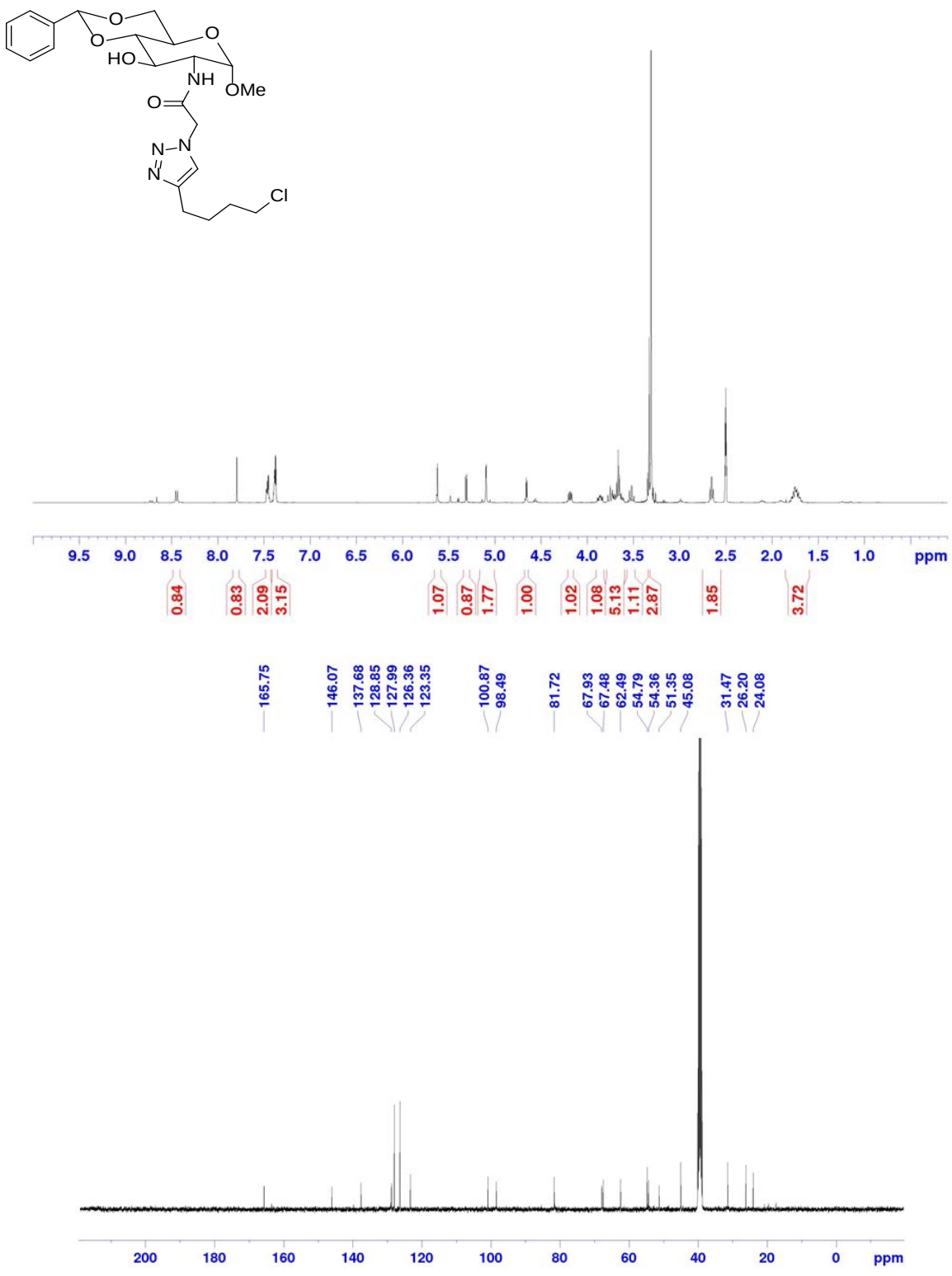
^{1}H NMR spectrum in $CDCl_3$ and ^{13}C NMR spectrum in $CDCl_3$ and d_6-DMSO for compound **11**

Compound 12:



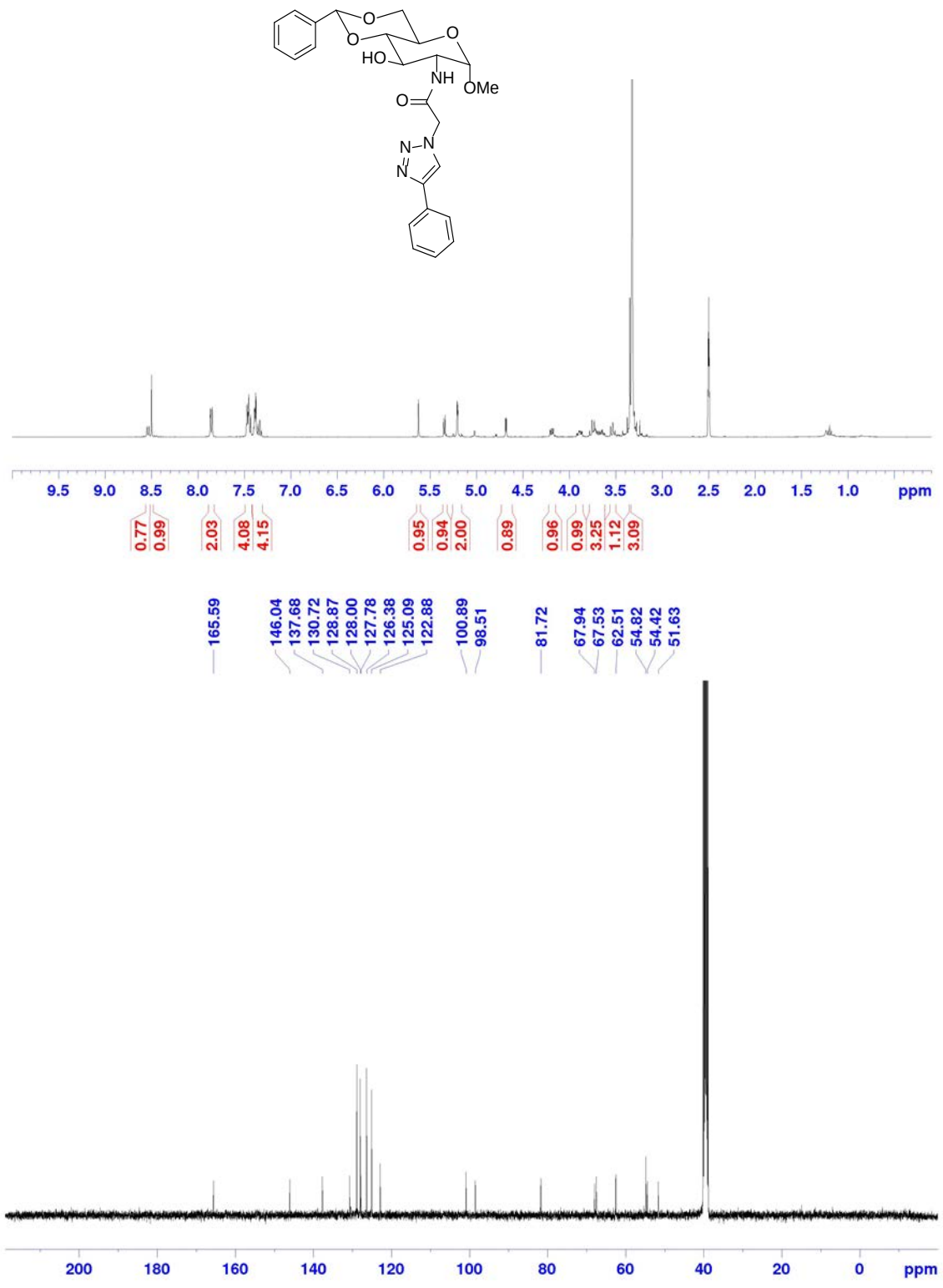
^{1}H NMR and ^{13}C NMR spectra for compound **12** in d_6-DMSO

Compound 13:



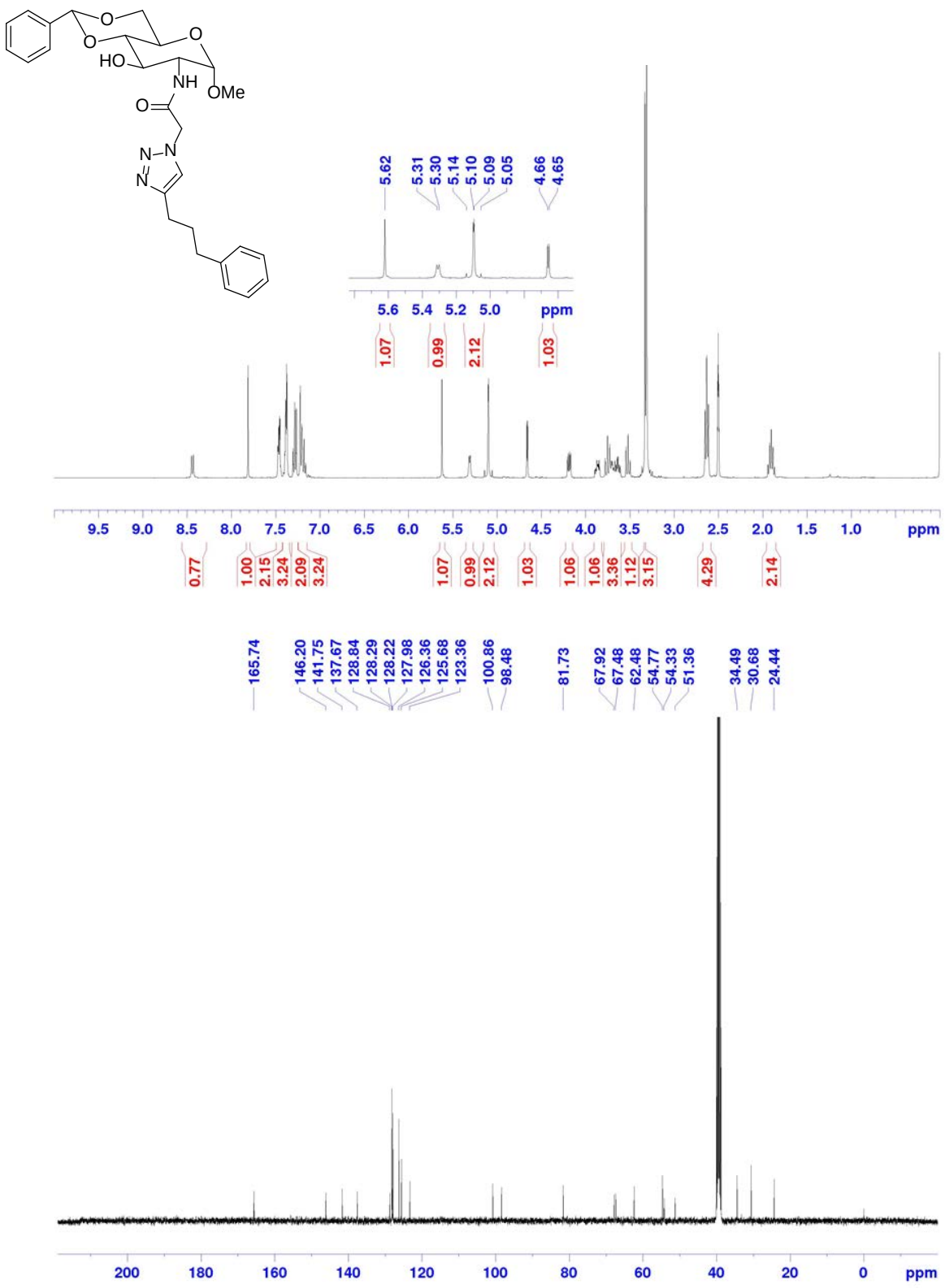
^{1}H NMR and ^{13}C NMR spectra for compound **13** in d_6-DMSO

Compound 14:



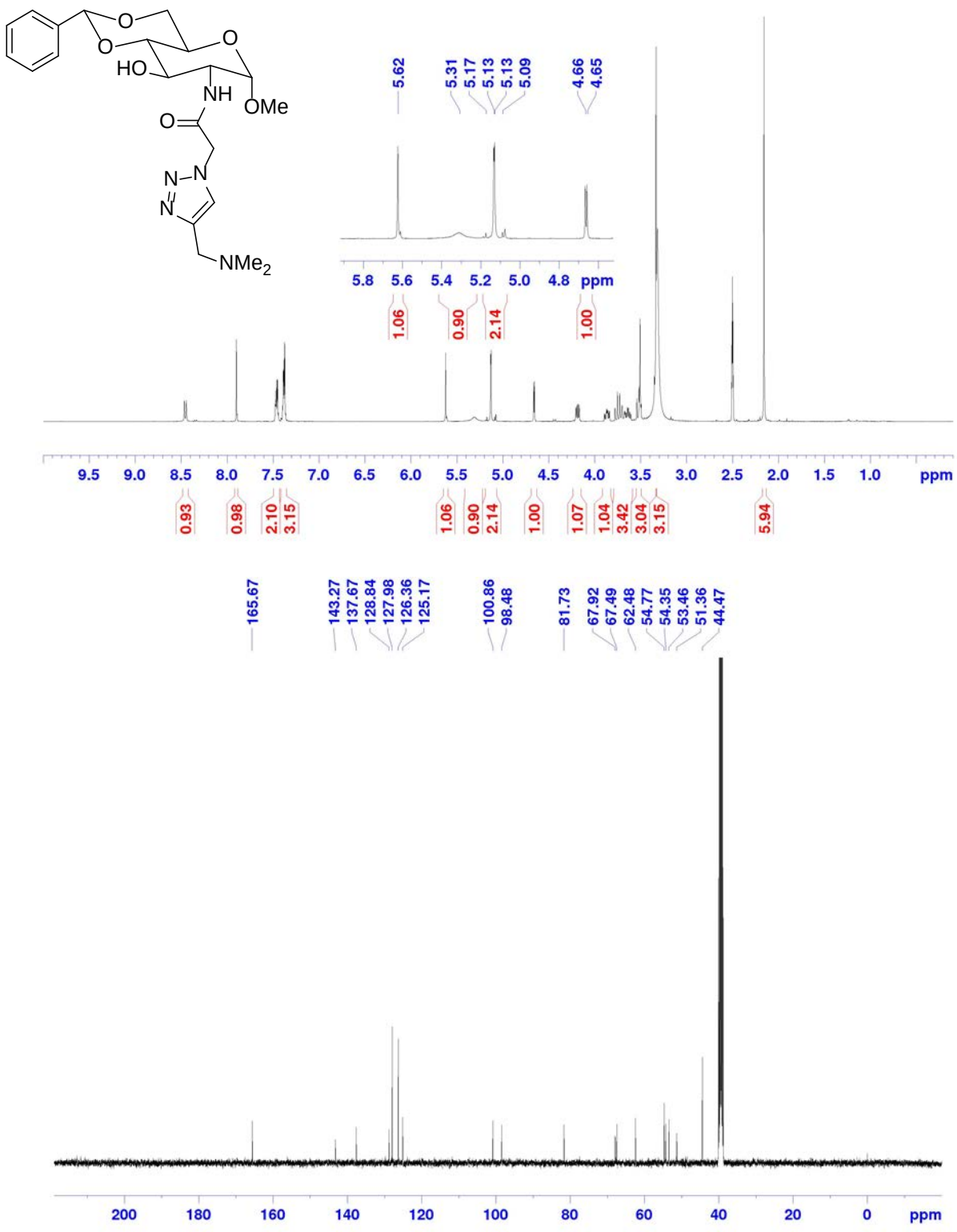
^{1}H NMR and ^{13}C NMR spectra for compound **14** in d_6-DMSO

Compound 15:



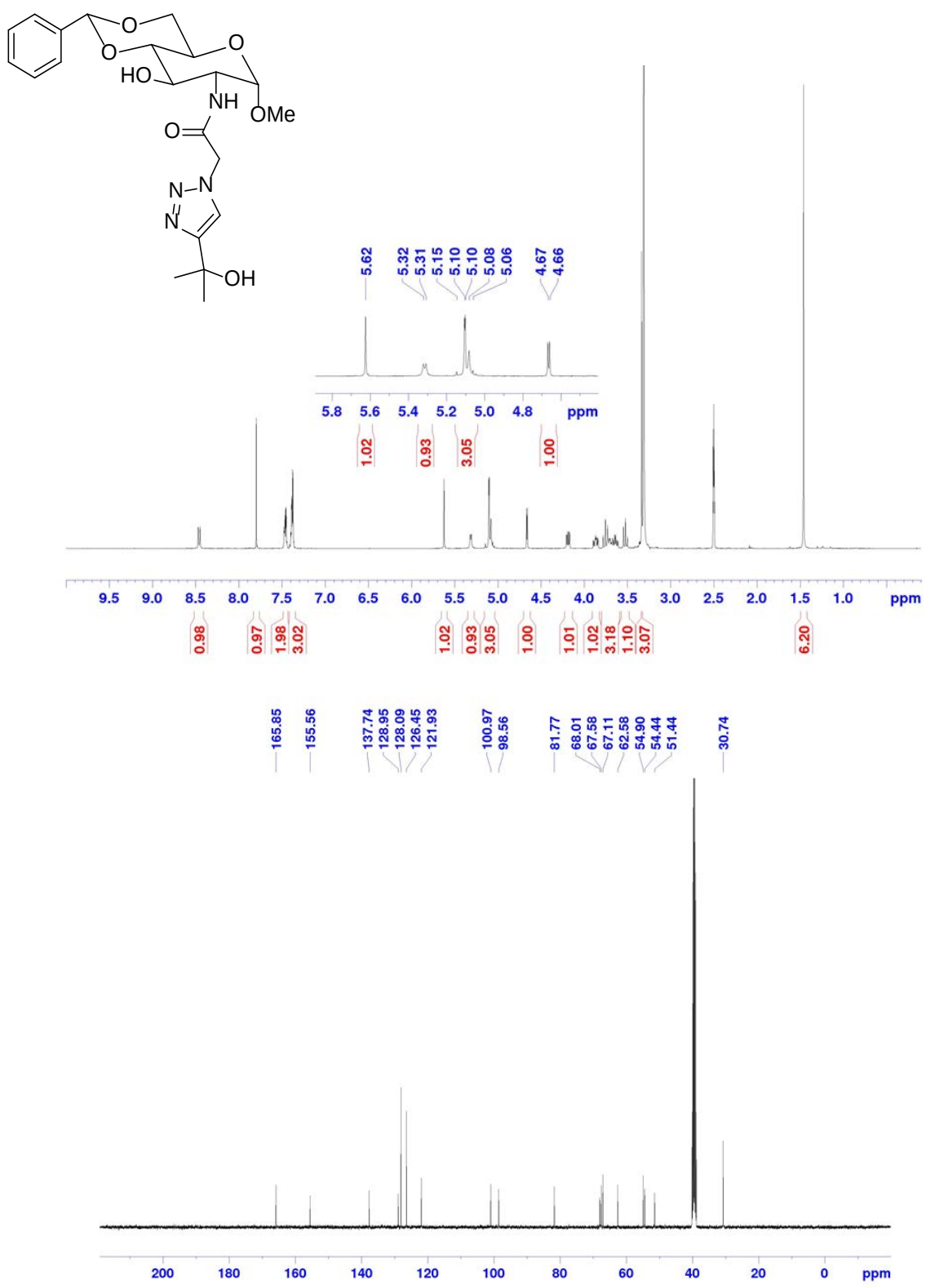
^{1}H NMR and ^{13}C NMR spectra for compound **15** in d_6-DMSO

Compound 16:



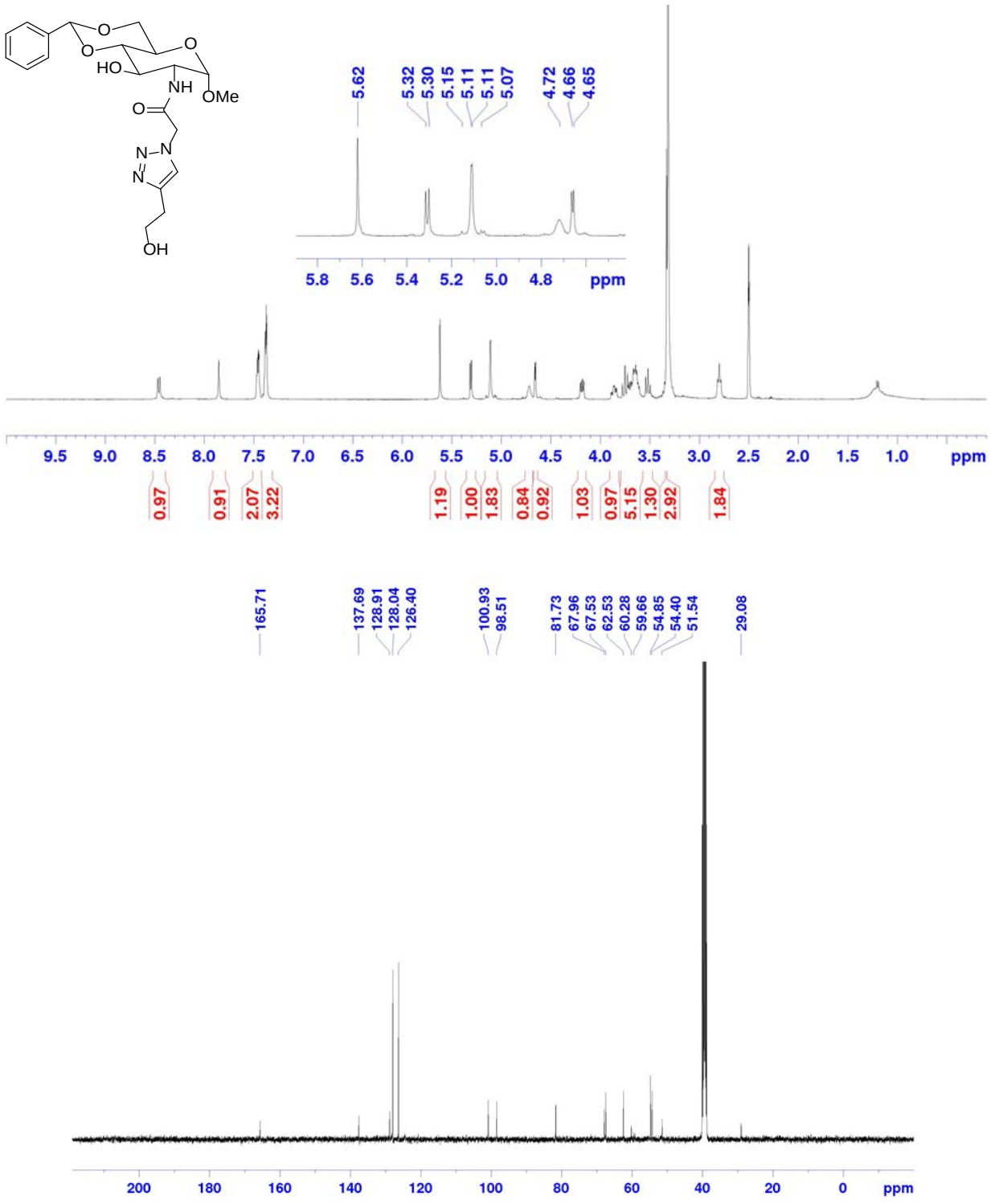
^{1}H NMR and ^{13}C NMR spectra for compound **16** in d_6-DMSO

Compound 17:



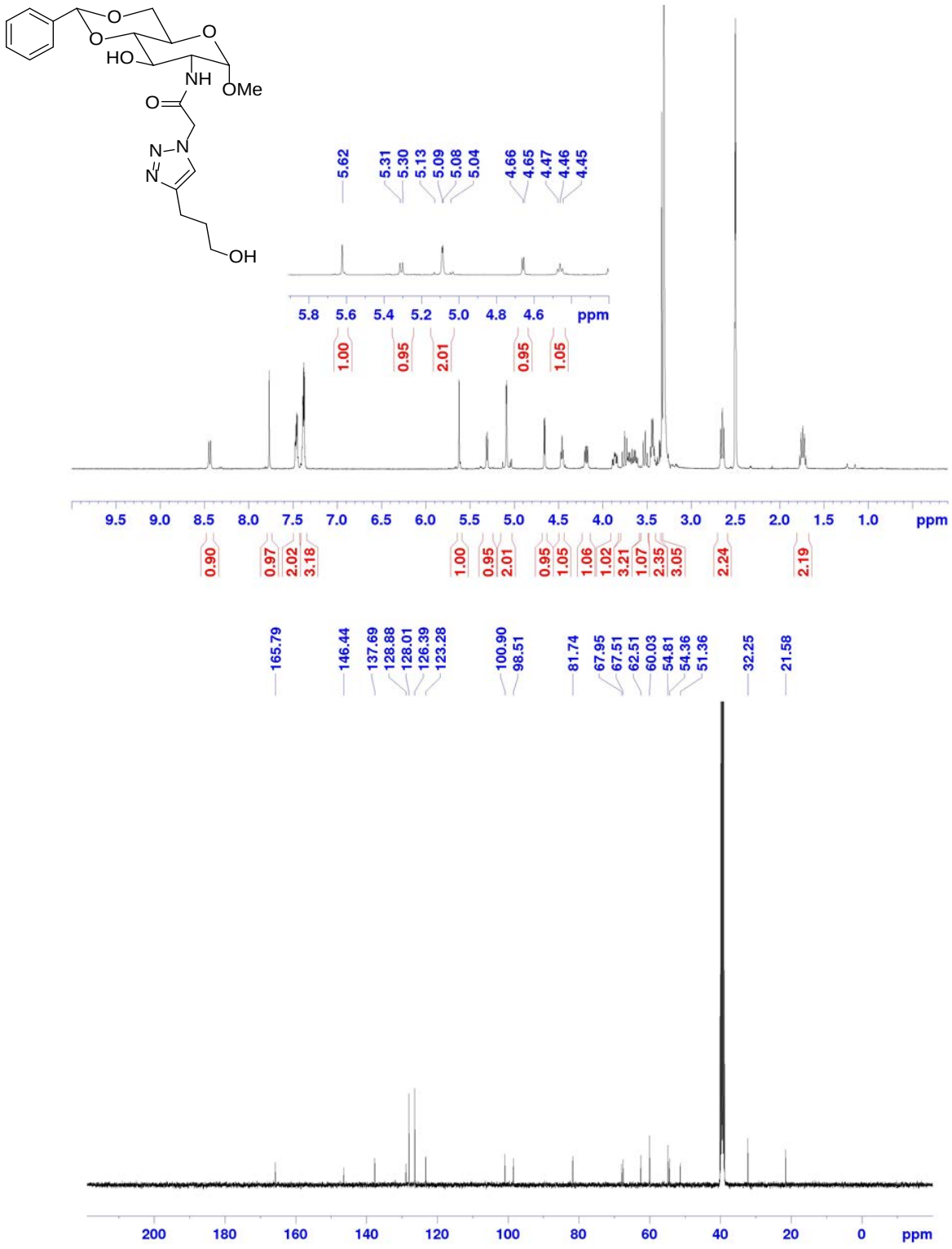
^{1}H NMR and ^{13}C NMR spectra for compound **17** in d_6-DMSO

Compound 18:



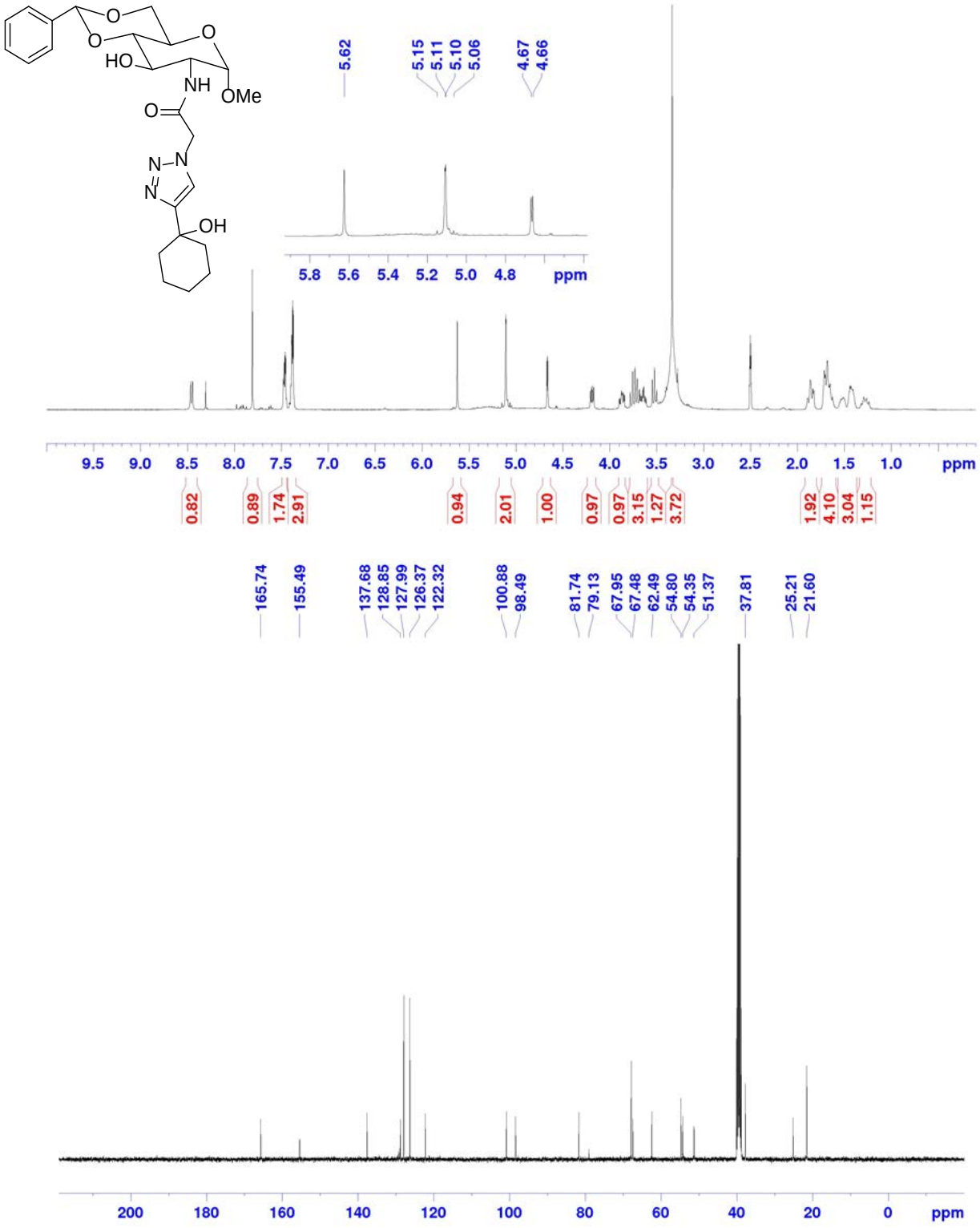
^{1}H NMR and ^{13}C NMR spectra for compound **18** in d_6-DMSO

Compound 19:



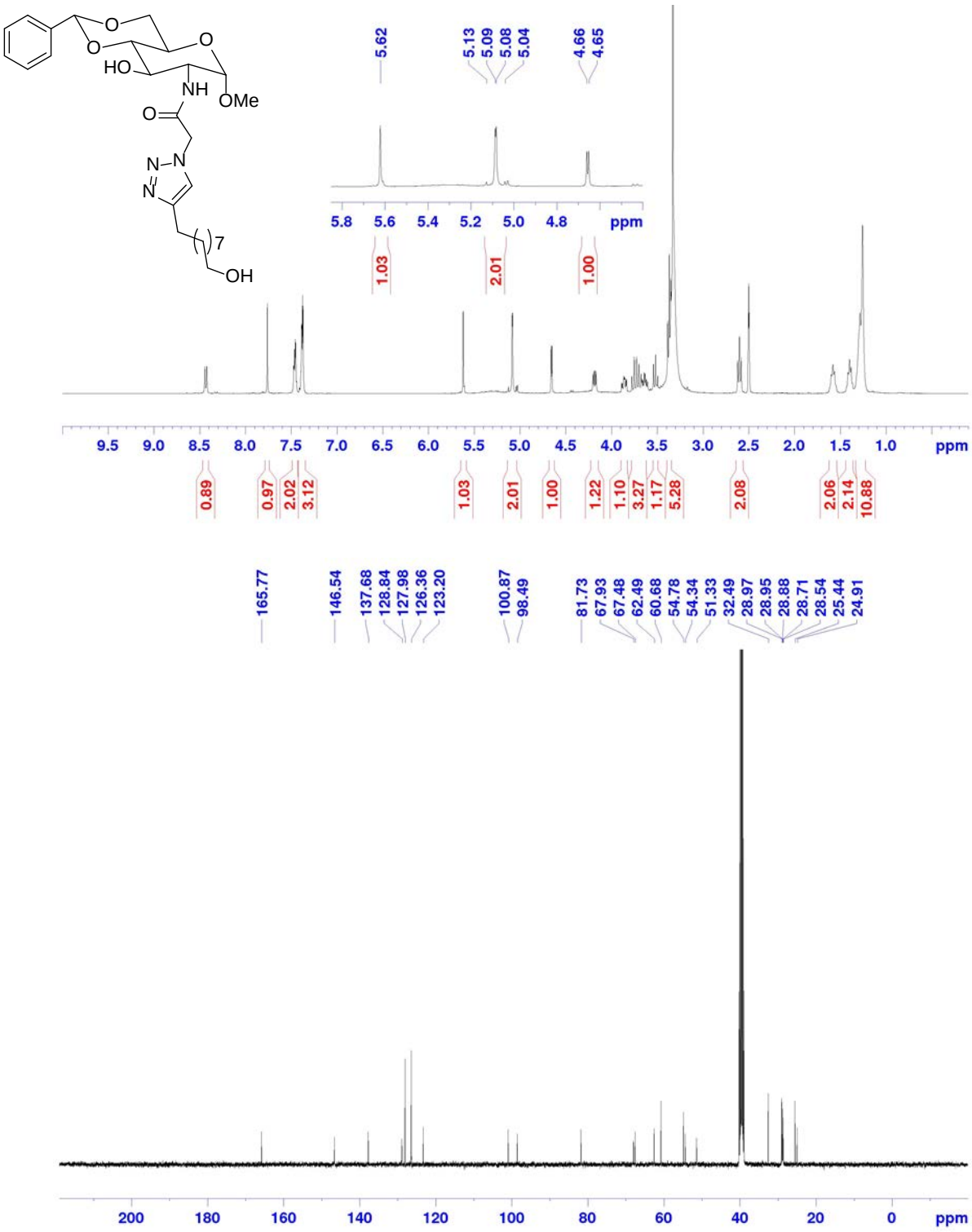
^{1}H NMR and ^{13}C NMR spectra for compound **19** in d_6-DMSO

Compound 20:



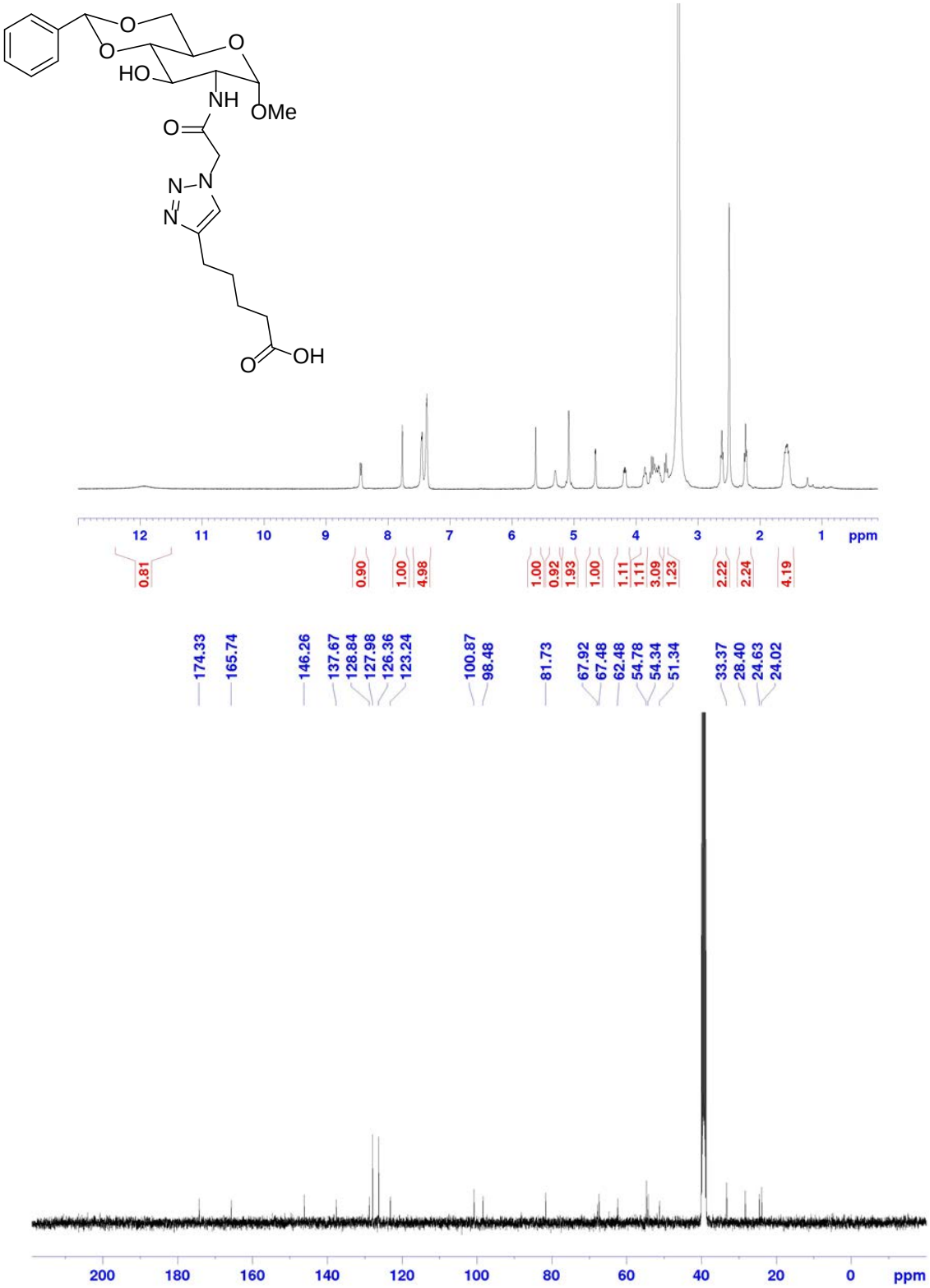
^{1}H NMR and ^{13}C NMR spectra for compound **20** in d_6-DMSO

Compound 21:



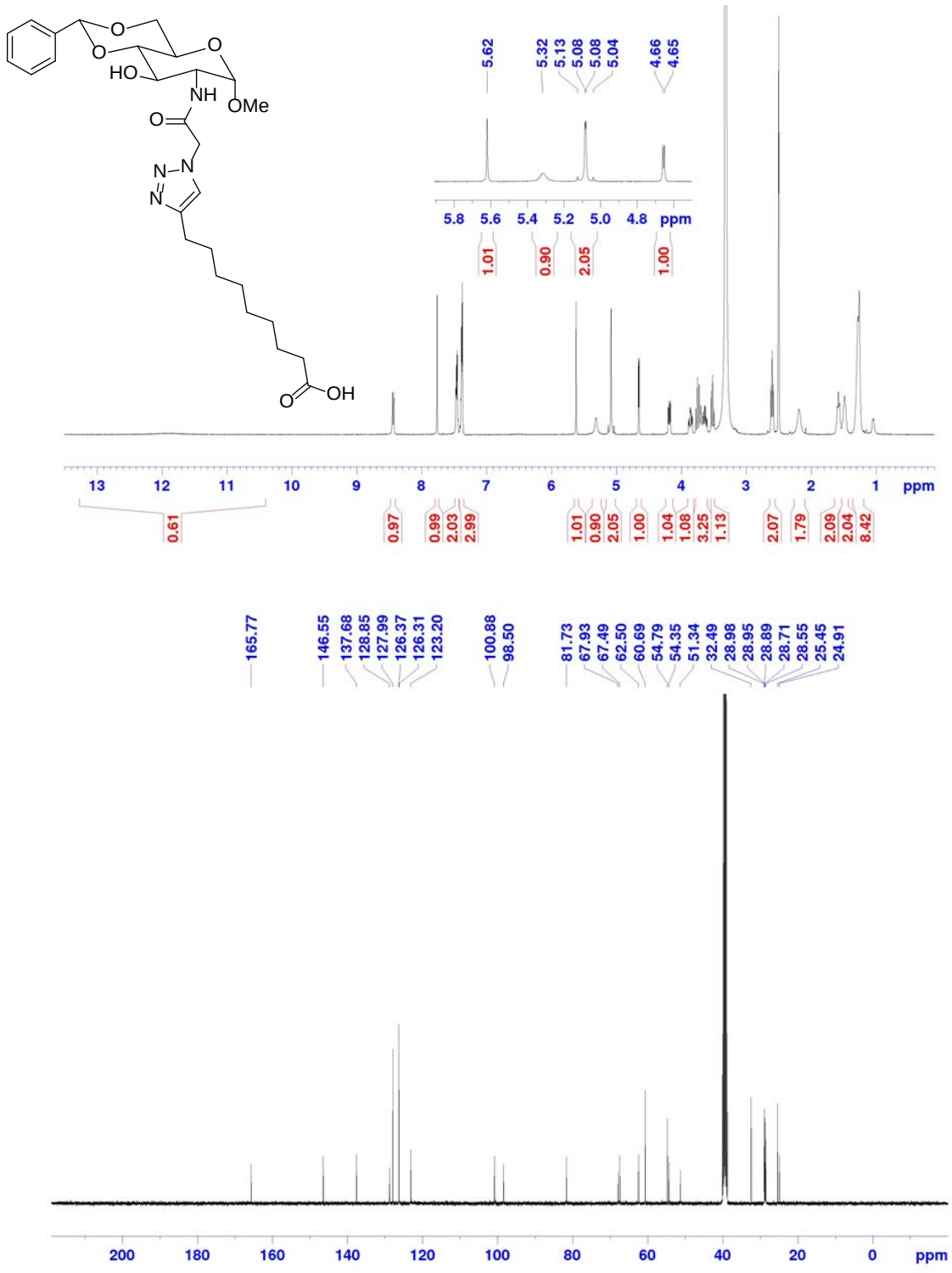
^{1}H NMR and ^{13}C NMR spectra for compound **21** in d_6-DMSO

Compound 22:



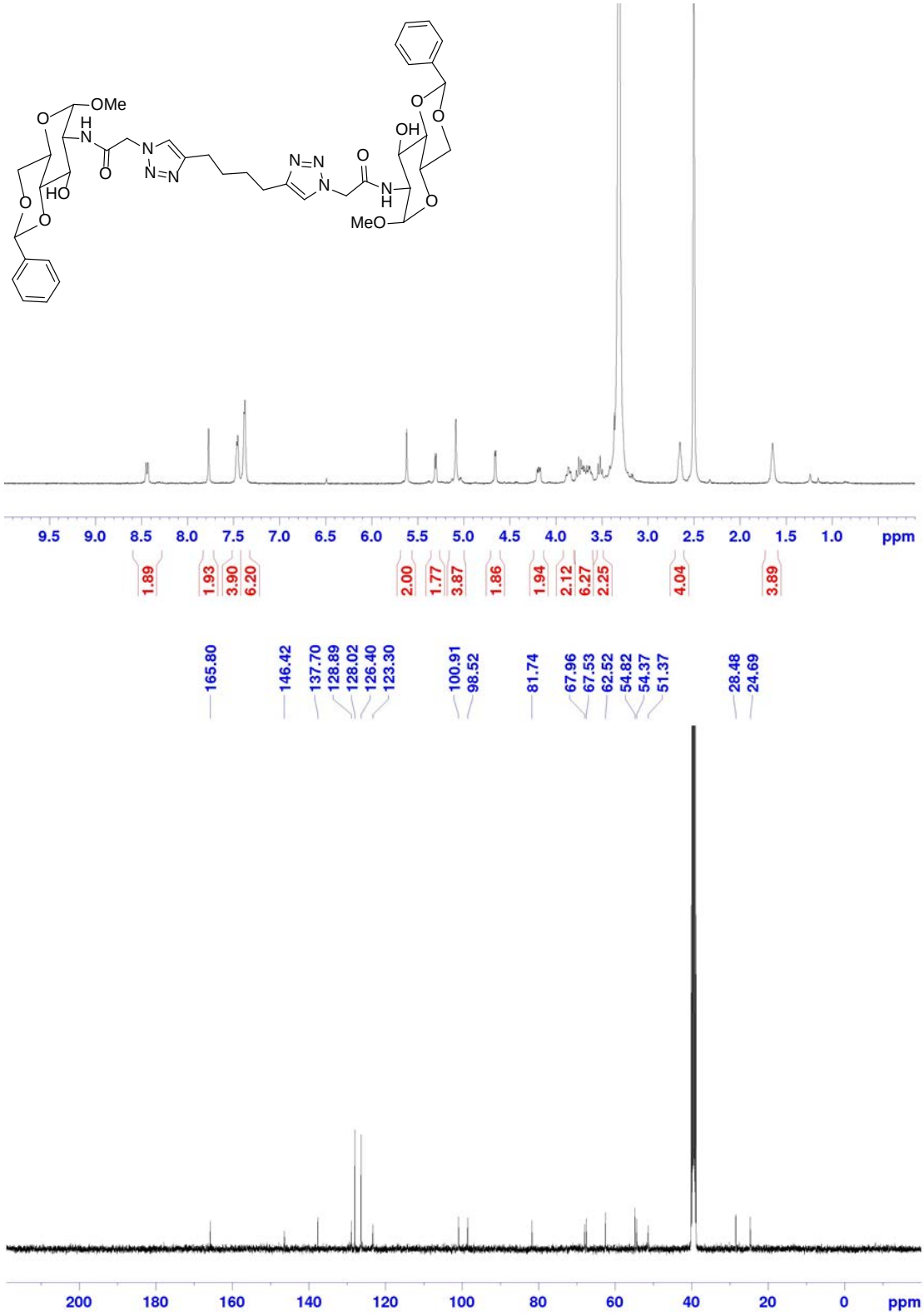
^{1}H NMR and ^{13}C NMR spectra in d_6-DMSO for compound **22**

Compound 23:



^{1}H NMR and ^{13}C NMR spectra for compound **23** in d_6-DMSO

Compound 24:



^{1}H NMR and ^{13}C NMR spectra for compound **24** in d_6-DMSO

Part III. Further gelator characterizations

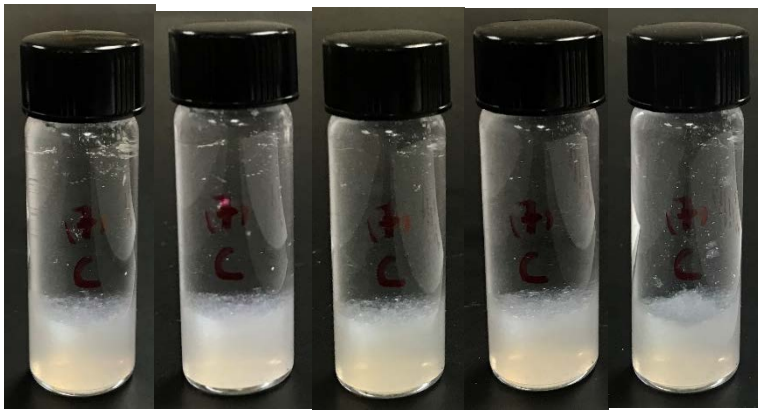
Table S1. Gelation properties in a mixture of DMSO:H_2O at different volume ratio

Ratio of DMSO/H_2O	1:9	1:11	1:13	1:15	1:17	1:19	1:21
7	G 4.0	G 3.3	G 2.9	G 2.5	G 2.2	G 2.0	G 1.8
9	P						
13	G 4.0	G 3.3	G 2.9				
15	G 4.0	G 3.3	G 2.9				
16	P						
21	G 4.0						
22	UG						
23	G 4.0	G 3.3	G 2.9				

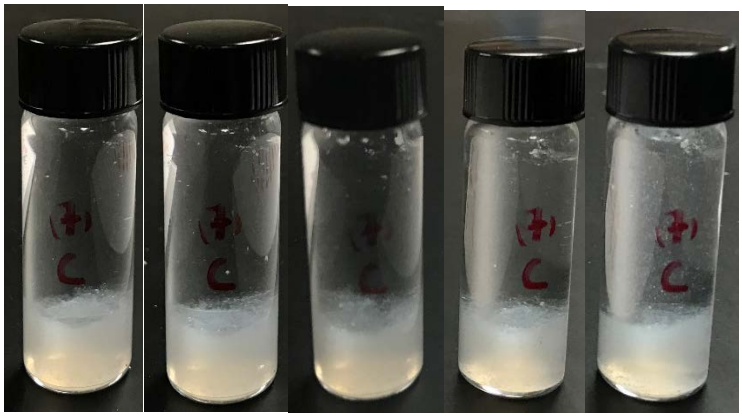
The gelation concentration is included after the letter G in mg/mL unit.

Chloramphenicol encapsulation and release

Photos were taken at different time points are shown in Figure S1. The drug release profile at different time course was measured by UV spectroscopy and was plotted as shown in Figure 5 in the main text and Figure S2.



0 hr 2 hrs 4 hrs 6 hrs 8 hrs

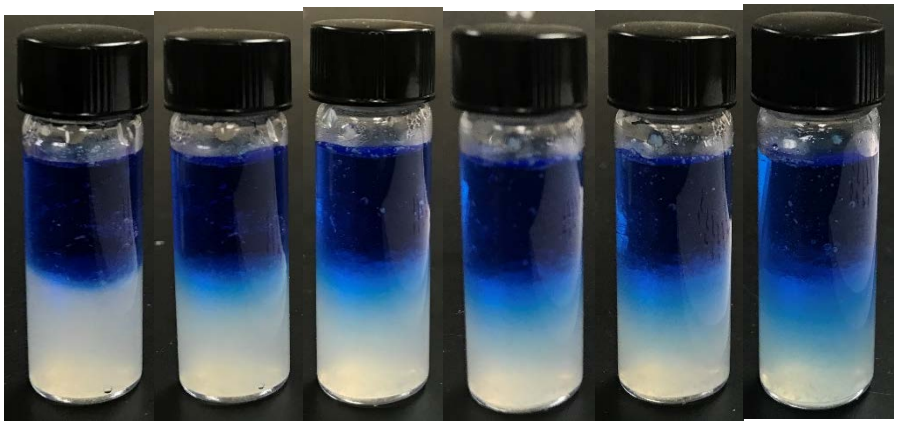


12 hrs 16 hrs 20 hrs 24 hrs 36 hrs

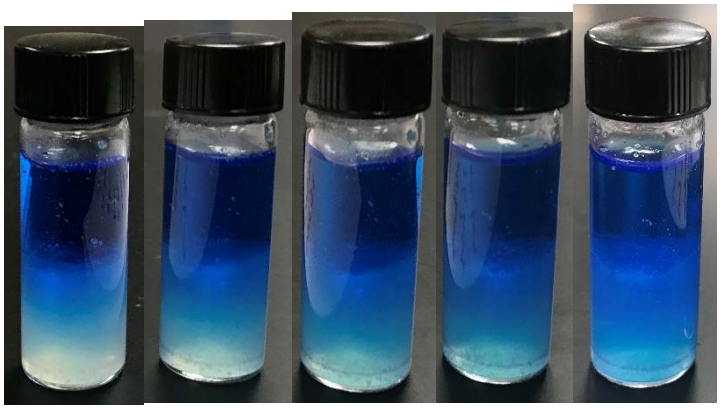
Figure S1. Photos of the gels with aqueous phase at different time periods of chloramphenicol release study. Gel was formed by compound **7** (2 mg) in water (1.4 mL) with chloramphenicol (0.25 mg), water (3 mL) was added on top of the gel. Chloramphenicol control was prepared by dissolving chloramphenicol (0.25 mg) in water (3 mL).

Dye diffusion and absorption studies

Toluidine blue dye was selected for the diffusion study with the hydrogel formed by compound **13**. A hydrogel was prepared in a 1 dram vial by compound **13** (5 mg) with water (2 mL) at its MGC (2.5 mg/mL). After a stable gel was formed and the gel was left at room temperature for 2 hours, toluidine blue aqueous solution (2 mL, 0.1 mM) was added dropwise onto the top of the gel. Photographs were taken at different time course are shown in Figure S3.



0 hr 2 hrs 4hrs 6 hrs 8 hrs 12 hrs



16 hrs 24 hrs 36 hrs 48 hrs 64 hrs

Figure S2. Photos at different time periods of toluidine blue absorption study.