SUPPLEMENTARY DATA

A new Class of cationic Cyclodextrins: Synthesis and chemico-physical Properties

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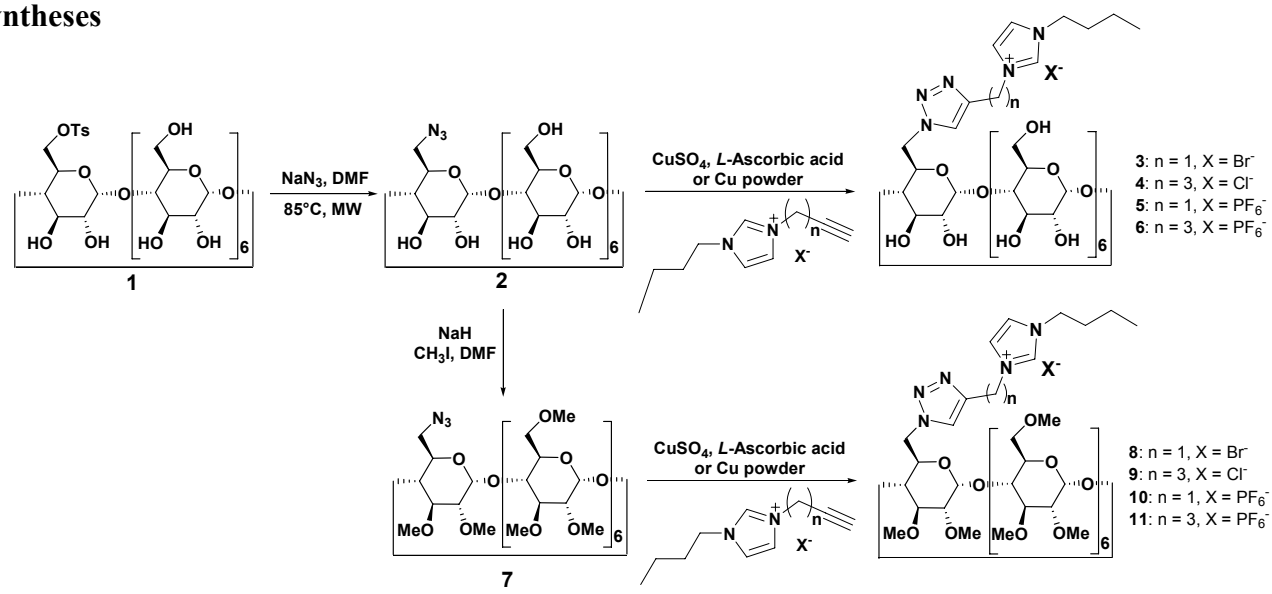
Table of contents

Syntheses



Scheme 2.

6^{I}-azido-6^{I}-deoxy-β-CD (2). Sodium azide (454 mg, 6.98 mmol, 1.5 equiv.) was suspended in DMF (100 mL), and 6^{I}-*O*-tosyl-β-CD (**1**) (6 g, 4.65 mmol) was added. The mixture was irradiated with MW at 85 °C (200 W) for 30 min; then acetone was added and the formed precipitate was filtered. After crystallization from water-acetone 9:1, 4.07 g of pure **2** as a white powder were obtained (3.51 mmol, 75.5%). R_f (*i*-Prop-OH/H_2O/EtOAc/NH_3 5:3:1:1) = 0.49; mp decomposition over 221 °C; FTIR (KBr) ν/cm^{-1} = 3400, 2104 (N_3), 1663, 1437, 1412, 1333, 1300, 1157, 1030, 915. ^{1}H NMR (300 MHz, D_6-DMSO): δ 5.56-5.76 (m, 14H, 2,3-OH), 4.87-4.81 (br, 7H, 1-H), 4.4-4.56 (m, 6H, 6-OH), 3.48-3.81 (overlapped signals, 28H, 3,5,6-H), 3.23-3.44 (overlapped signals, 14H, 2,4-H). ^{13}C NMR (75 MHz, D_6-DMSO): δ 102.3-101.6 (1-CH), 83.0-81.4 (4-CH), 73.1-72.0 (2,3,5-CH), 70.2 (5-CH near 6-CH_2N_3), 60.2-59.8 (6-CH_2), 51.1 (6-CH_2N_3). MALDI-TOF MS $(M+K)^+$ *m/z* (%) calcd for $[C_{42}H_{69}KN_3O_{34}]$: 1198.34, found: 1198.59.

6^{I}-azido-6^{I}-deoxy-2^{I-VII},3^{I-VII},6^{II-VII}-*O*-permethyl-β-CD (7). Compound **2** (3 g, 2.59 mmol) was dissolved in 50 mL of anhydrous DMF and cooled to 0 °C in an ice bath. NaH was added (103.6 mmol, 40 equiv., 60% in mineral oils) and a white precipitate was formed. To this suspension 6.45 mL of MeI (103.6 mmol, 40 equiv., d = 2.28, 14.7 g) were added dropwise. The suspension was warmed to rt and kept in magnetical stirring for 3 h. The reaction mixture was filtered and the salts were washed with diethyl ether. The DMF was poured into water (100 mL) and extracted with diethyl ether (5 x 30 mL). the organic layers were collected, washed with brine solution, dried with anhydrous Na_2SO_4 and evaporated to give 3.8 g of crude product. The obtained product was purified by Flash Chromatography, using CH_2Cl_2, CH_2Cl_2/MeOH 99:1, 98:2, 95:5, 9:1, MeOH as eluents on 24g-silica gel column; 3.17 g of pure product as white powder were obtained (2.2 mmol, 85%). R_f ($CHCl_3$/CH_3OH 95:5) = 0.72; mp = 107 °C; FTIR (KBr) ν/cm^{-1} = 2930, 2836, 2101 (N_3), 1640, 1458, 1369, 1145, 1036, 970, 857, 756. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.14-5.09 (overlapped signals, 6H, 1-H), 5.05 (d, 1H, 1-H), 4.00-3.70 (overlapped signals, 15H, 5,6-H), 3.70-3.45 (overlapped signals, 80H, 3,4,6-H, 2,3,6-OCH_3), 3.18 (dd, 7H, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 99.5-98.5 (1-CH), 82.2-81.5 (2,3-CH), 80.5-80.2 (4-CH), 71.7-71.2 (6-CH_2), 71.1-70.97 (5-CH), 61.7-61.5 (3-OCH_3), 59.2-58.6 (2,6-OCH_3), 52.2 (6-CH_2N_3). ESI MS $(M+Na)^+$ *m/z* (%) calcd for $[C_{62}H_{109}N_3NaO_{34}]$: 1463.52, found: 1463.63.

1-butyl-3-propargylimidazolium bromide. 0.75 mL of 1-butylimidazole (0.708 g, 5.7 mmol, d = 0.945) were introduced in a 25 mL two-necked round-bottomed flask and cooled to 0 °C in an ice bath; 0.76 mL of propargyl bromide (0.814 g, 6.84 mmol, 1.2 equiv., d = 1.335, 80% in toluene) were added in nitrogen atmosphere. The reaction mixture was warmed to room temperature and irradiated with MW at 60 °C for 0.5 h (mean power 50 W). The crude mixture was washed with cyclohexane and dried under vacuum to give 1.17 g of ionic liquid (4.8 mmol, 84.3%) as a deliquescent solid. FTIR (film) ν/cm^{-1} = 3076, 2961, 2874, 2124 (alkyne), 1560, 1464, 1441, 1356, 1339, 1161, 1115, 1024, 951, 864, 754. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.43 (s, 1H, H-Im), 7.66 (s, 1H, *J* = 1.5 Hz, H-Im), 7.51 (s, 1H, *J* = 1.5 Hz, H-Im), 5.44 (d, 2H, *J* = 2.7 Hz, -C*H*$_2$C≡CH), 4.34 (t, 2H, -C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.75 (t, 1H, *J* = 2.7 Hz, -CH$_2$C≡C*H*), 1.9 (m, 2H, -CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.38 (m, 2H, -CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.96 (t, 3H, -CH$_2$CH$_2$CH$_2$*CH*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.8 (2-CH Im), 122.6 (4-CH Im), 122.0 (5-CH Im), 77.9 (-CH$_2$*C*≡CH), 74.2 (-CH$_2$C≡*C*H), 49.8 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 39.6 (-*C*H$_2$C≡CH), 31.8 (-CH$_2$*C*H$_2$CH$_2$CH$_3$), 19.1 (-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.2 (-CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI MS $(M-Br)^+$ *m/z* (%) calcd for $C_{10}H_{15}N_2^+$: 163.24, found: 163.50.

1-butyl-3-propargylimidazolium hexafluorophosphate. In a 25 mL two-necked round-bottomed flask, 1.06 mL of 1-butylimidazole (1 g, 8.053 mmol, d = 0.945), 0.985 mL of propargyl bromide (1.32 g, 8.86 mmol, 1.1 equiv., d = 1.34, 80% in toluene) and 1.482 g of potassium hexafluorophosphate (8.05 mmol, 1 equiv.) were introduced in nitrogen atmosphere. The

reaction mixture was irradiated with MW at 60 °C for 1 h (mean power 40 W). The crude mixture was washed with acetone, filtered on a celite pad and dried under vacuum. The ionic liquid obtained was washed with water and cyclohexane to give 1.62 g of ionic liquid as a brown liquid (5.26 mmol, 65.3%).
FTIR (film) ν/cm^{-1} = 3291, 3162, 2966, 2139 (alkyne), 1611, 1566, 1468, 1445, 1341, 1161, 1111, 839, 741. ^{1}H NMR (300 MHz, acetone-D$_6$): δ 9.20 (s, 1H, H-Im), 7.85 (s, 1H, H-Im), 7.83 (s, 1H, H-Im), 5.30 (d, 2H, J = 2.4 Hz, -CH_2C≡CH), 4.37 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 3.36 (t, 1H, J = 2.7 Hz, -CH$_2$C≡CH), 1.95 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.38 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.95 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, acetone-D$_6$): δ 137.9 (2-CH Im), 123.8 (4-CH Im), 123.3 (5-CH Im), 78.6 (-CH$_2$$C$≡CH), 75.6 (-CH$_2$C≡$C$H), 50.5 (-$CH_2CH_2CH_2CH_3$), 39.8 (-$CH_2$C≡CH), 32.6 (-CH$_2$$CH_2CH_2CH_3$), 19.9 (-CH$_2CH_2$$CH_2CH_3$), 13.6 (-CH$_2CH_2CH_2$$CH_3$). ESI MS (M-PF$_6$)$^+$ *m/z* (%) calcd for [C$_{10}$H$_{15}$N$_2$]$^+$: 163.24, found: 163.0.

1-butyl-3-(4-pentynyl)imidazolium chloride. 1.06 mL of 1-butylimidazole (1 g, 8.05 mmol, d = 0.945) were introduced in a 25 mL two-necked round-bottomed flask and cooled to 0 °C in an ice bath; 1.02 mL of 5-chloro-1-pentyne (991 mg, 9.66 mmol, 1.2 equiv., d = 0.968) were added in nitrogen atmosphere. The reaction mixture was warmed to room temperature and irradiated with MW at 110 °C for 1 h (mean power 120 W). The crude mixture was washed with cyclohexane and dried under vacuum to give 1.71 g of ionic liquid as a brown liquid (7.55 mmol, 94%).
FTIR (film) ν/cm^{-1} = 3096, 2963, 2936, 2874, 2123 (alkyne), 1654, 1564, 1464, 1334, 1163, 1111, 1028, 951, 861, 754. ^{1}H NMR (300 MHz, CDCl$_3$): δ 10.97 (s, 1H, H-Im), 7.39 (s, 1H, J = 1.5 Hz, H-Im), 7.30 (s, 1H, J = 1.5 Hz, H-Im), 4.57 (t, 2H, -CH_2CH$_2$CH$_2$C≡CH), 4.37 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 2.36 (m, 2H, -CH$_2$CH$_2$CH_2C≡CH), 2.22 (m, 2H, -CH$_2$CH_2CH$_2$C≡CH), 2.08 (t, 1H, J = 2.9 Hz, -CH$_2$CH$_2$CH$_2$C≡CH), 1.92 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.42 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.98 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): δ 136.3 (2-CH Im), 122.3 (4-CH Im), 122.0 (5-CH Im), 81.3 (-CH$_2$CH$_2$CH$_2$$C$≡CH), 70.2 (-CH$_2CH_2CH_2$C≡$C$H), 49.3 (-$CH_2CH_2CH_2$C≡CH), 48.2 (-$CH_2CH_2CH_2CH_3$), 31.7 (-CH$_2$$CH_2CH_2CH_3$), 28.2 (-CH$_2$$CH_2CH_2$C≡CH), 19.0 (-CH$_2CH_2$$CH_2$C≡CH), 15.0 (-CH$_2CH_2$$CH_2CH_3$), 13.0 (-CH$_2CH_2CH_2$$CH_3$). ESI MS (M-Cl)$^+$ *m/z* (%) calcd for C$_{12}$H$_{19}$N$_2^+$: 191.29, found: 191.5.

1-butyl-3-(4-pentynyl)imidazolium hexafluorophosphate. 1.06 mL of 1-butylimidazole (1 g, 8.05 mmol, d = 0.945) were introduced in a 25 mL two-necked round-bottomed flask and cooled to 0 °C in an ice bath; 1.02 mL of 5-chloro-1-pentyne (991 mg, 9.66 mmol, 1.2 equiv., d = 0.968) and 1.48 g of potassium hexafluorophosphate (8.05 mmol, 1 equiv.) were added in nitrogen atmosphere. The reaction mixture was warmed to room temperature and irradiated with MW at 110 °C for 1 h (mean power 110 W). The crude mixture was washed with acetone, filtered on a celite pad and dried under vacuum. The ionic liquid obtained was washed with water and cyclohexane to give 1.54 g of ionic liquid as a brown oil (4.58 mmol, 57%). FTIR (film) ν/cm^{-1} = 3295, 3164, 2964, 2878, 2120 (alkyne), 1709, 1611, 1566, 1468, 1366, 1161, 1111, 1028, 861, 777, 752. ^{1}H NMR (300 MHz, acetone-D$_6$): δ 9.03 (s, 1H, H-Im), 7.77 (2H, H-Im), 4.46 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 4.35 (t, 2H, -CH_2CH$_2$CH$_2$C≡CH), 2.08 (t, 1H, J = 2.9 Hz, -CH$_2$CH$_2$CH$_2$C≡CH), 2.33 (m, 2H, -CH$_2$CH$_2$CH_2C≡CH), 2.26 (m, 2H, -CH$_2$CH_2CH$_2$C≡CH), 1.93 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.38 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.94 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, acetone-D$_6$): δ 137.5 (2-CH Im), 123.62 (4-CH Im), 123.60 (5-CH Im), 82.7 (-CH$_2$CH$_2$CH$_2$$C$≡CH), 71.4 (-CH$_2CH_2CH_2$C≡$C$H), 50.3 (-C$H_2CH_2CH_2$C≡CH), 49.4 (-$CH_2CH_2CH_2CH_3$), 32.6 (-CH$_2$$CH_2CH_2CH_3$), 29.3 (-CH$_2CH_2CH_2$C≡CH), 19.9 (-CH$_2CH_2$$CH_2$C≡CH), 15.7 (-CH$_2CH_2$$CH_2CH_3$), 13.6 (-CH$_2CH_2CH_2$$CH_3$). ESI MS (M-PF$_6$)$^+$ *m/z* (%) calcd for [C$_{12}$H$_{19}$N$_2$]$^+$: 191.29, found: 191.4

1-butyl-3-[1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-ylmethyl]imidazolium bromide (8). Yellow powder; R$_f$ (CHCl$_3$/CH$_3$OH 8:2) = 0.4; mp 107 °C; FTIR (KBr) ν/cm^{-1} = 2930, 2836, 2100, 1749.6, 1650, 1455, 1369.6, 1165, 1109, 968.4, 951, 856.5, 835.3, 754.3, 706. ^{1}H NMR (300 MHz, CD$_3$OD): δ 9.16 (br s, 1H, H-Im), 8.20 (br s, 1H, H-Tz), 7.70 (br, 2H, H-Im), 5.59 (br s, 2H, Tz-CH$_2$-Im), 5.4-5.1 (overlapped signals, 7H, 1-H), 5.1-4.85 (m, 2H, 6-CH_2-Tz), 4.25 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 4.1 (br m, 1H, 5-H near 6-CH_2-Tz), 4.0-3.7 (overlapped signals, 14H, 5,6-H), 3.7-3.45 (overlapped signals, 57H, 3,4,6-H, 2,3-OCH$_3$), 3.45-3.25 (overlapped signals, 18H, 6-OCH$_3$), 3.25-3.0 (overlapped signals, 10H, 2,6-H), 1.9 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.4 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 1.0 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, CD$_3$OD): δ 137.5 (CH Im), 128 (CH Tz), 124.1 (CH Im), 123.8 (CH Im), 99.5-98.9 (1-CH), 83.5-82.1 (2,4-CH), 81-78.9 (3-CH), 72.7-72.5 (6-CH$_2$), 72.5-71.3 (5-CH), 62-58.4 (-OMe), 52.2 (6-CH$_2$-Tz), 50.6 (-CH$_2$CH$_2$CH$_2$CH$_3$), 44.9 (Tz-CH$_2$-Im), 32.8 (-CH$_2$$CH_2CH_2CH_3$), 20.2 (-CH$_2CH_2$$CH_2CH_3$), 13.5 (-CH$_2CH_2CH_2$$CH_3$). ESI MS (M+H)$^+$ *m/z* (%) calcd for [C$_{72}$H$_{124}$BrN$_5$O$_{34}$]: 1683.67, found: 1683.84 (5%); (M-Br)$^+$ calcd for [C$_{72}$H$_{124}$N$_5$O$_{34}$]$^+$: 1603.77, found: 1603.89 (100%).

1-butyl-3-[3-(1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-yl)propyl]imidazolium chloride (9). Yellow powder; R$_f$ (CHCl$_3$/CH$_3$OH 8:2) = 0.35; mp 84 °C; FTIR (KBr) ν/cm^{-1} = 2930, 2835.7, 1645, 1564, 1458, 1369, 1161, 1088, 1037, 968, 912, 856, 754, 704. ^{1}H NMR (300 MHz, CD$_3$OD): δ 9.1 (br s, 1H, H-Im), 7.82 (br s, 1H, H-Tz), 7.71 (d, 1H, H-Im), 7.69 (d, 1H, H-Im), 5.42-5.11 (7H, 1-H), 5.00-4.85 (m, 2H, 6-CH_2-Tz), 4.32 (t, 2H, Im-CH_2CH$_2$CH$_2$-Tz), 4.24 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 4.08 (br m, 1H, 5-H near 6-CH_2-Tz), 4.0-3.7 (overlapped signals, 13H, 5,6-H), 3.7-3.40 (overlapped signals, 59H, 3,4,6-H, 2,3-OCH$_3$), 3.40-3.25 (18H, 6-OCH$_3$), 3.25-3.0 (overlapped signals, 9H, 2,6-H), 2.78 (t, 2H, Im-CH$_2$CH$_2$CH_2-Tz), 2.29 (t, 2H, Im-CH$_2$CH_2CH$_2$-Tz), 1.89 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.38 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 1.0 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, CD$_3$OD): δ 137.5 (CH Im), 126 (CH Tz), 123.9 (CH Im), 123.8 (CH Im), 99.65-99.17 (1-CH), 83.7-82.5 (2,4-CH), 81.2-79.3 (3-CH), 72.9-72.5 (6-CH$_2$), 72.5-71.8 (5-CH), 62.1-58.6 (-OMe), 52.2 (6-CH$_2$-Tz), 50.7 (Im-CH$_2$CH$_2$CH$_2$-Tz), 50.1 (-CH$_2$CH$_2$CH$_2$CH$_3$), 33.05 (-CH$_2$$CH_2CH_2CH_3$), 30.8 (Im-CH$_2$$CH_2CH_2$-Tz), 22.9 (Im-CH$_2CH_2$$CH_2$-Tz), 20.5 (-CH$_2CH_2$$CH_2CH_3$), 13.8 (-CH$_2CH_2CH_2$$CH_3$). ESI MS (M-Cl)$^+$ *m/z* (%) calcd for [C$_{74}$H$_{128}$N$_5$O$_{34}$]$^+$: 1631.82, found: 1632.46 (71%); (M+Na-Cl)$^{2+}$ calcd for [C$_{74}$H$_{128}$N$_5$NaO$_{34}$]$^{2+}$: 827.40, found: 827.66 (100%).

1-butyl-3-[1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-ylmethyl]imidazolium hexafluorophosphate (10). Yellow powder; R_f ($CHCl_3$/CH_3OH 95:5) = 0.23; mp 97 °C; FTIR (KBr) ν/cm^{-1} = 2930, 2835.7, 1645, 1564, 1458, 1369, 1161, 1088, 1037, 968, 912, 856, 754, 704. ^{1}H NMR (300 MHz, CD_3OD): δ 9.01 (br s, 1H, H-Im), 8.19 (br s, 1H, H-Tz), 7.66 (br, 2H, H-Im), 5.57 (br s, 2H, Tz-CH_2-Im), 5.40-5.10 (overlapped signals, 7H, 1-H), 5.02-4.93 (m, 2H, 6a,b -CH_2-Tz), 4.24 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 4.10 (br m, 1H, 5-H near 6-CH_2-Tz), 4.0-3.7 (overlapped signals, 13H, 5,6-H), 3.7-3.45 (overlapped signals, 60H, 3,4,6-H, 2,3-OCH_3), 3.45-3.25 (overlapped signals, 18H, 6-OCH_3), 3.25-3.0 (overlapped signals, 9H, 2,6-H), 1.89 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.37 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.99 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, CD_3OD): δ 138.3, 137.3 (CH Im), 128.1 (CH Tz), 124.0, 123.7 (CH Im), 99.7-99.1 (1-CH), 83.5-82.4 (2,4-CH), 81.0-79.7 (3-CH), 72.6-72.2 (6-CH_2), 72.2-72.0 (5-CH), 71.5 (5-CH near 6-CH_2-Tz), 62.1-58.6 (-OMe), 52.4 (6-CH_2-Tz), 50.8 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 45.0 (Tz-CH_2-Im), 33.0 (-CH$_2$*C*H$_2$CH$_2$CH$_3$), 20.4 (-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.7 (-CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI MS (M-PF_6)$^+$ *m/z* (%) calcd for [$C_{72}H_{124}N_5O_{34}$]$^+$: 1603.77, found: 1603. 97.

1-butyl-3-[3-(1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-yl)propyl]imidazolium hexafluorophosphate (11). Yellow powder; R_f ($CHCl_3$/ CH_3OH 8:2) = 0.63; mp 95 °C; FTIR (KBr) ν/cm^{-1} = 2934, 2837, 1643, 1460, 1369, 1196, 1163, 1109, 1036, 970, 845, 706. ^{1}H NMR (300 MHz, CD_3OD): δ 8.96 (br s, 1H, H-Im), 7.82 (br s, 1H, H-Tz), 7.67 (m, 2H, H-Im), 5.41, 5.30-5.10 (7H, 1-H), 5.00, 4.80 (m, 2H, 6-CH_2-Tz), 4.29 (t, 2H, Im-CH_2CH$_2$CH$_2$-Tz), 4.22 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 4.09 (br m, 1H, 5-H near 6-CH_2-Tz), 4.05-3.7 (overlapped signals, 12H, 5,6-H), 3.7-3.45 (overlapped signals, 58H, 3,4,6-H, 2,3-OCH_3), 3.40-3.25 (overlapped signals, 20H, 6-H, 6-OCH_3), 3.25-3.0 (overlapped signals, 9H, 2,6-H), 2.78 (t, 2H, Im-CH$_2$CH$_2$CH_2-Tz), 2.29 (t, 2H, Im-CH$_2$CH_2CH$_2$-Tz), 1.89 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.38 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.99 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, CD_3OD): δ 137.2 (CH Im), 126 (CH Tz), 123.83 (CH Im), 123.78 (CH Im), 99.66-99.23 (1-CH), 83.6-82.5 (2,4-CH), 81.1-79.7 (3-CH), 72.8-72.4 (6-CH_2), 72.5-71.7 (5-CH), 62.1-58.6 (-OMe), 52.2 (6-CH_2-Tz), 50.7 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 50.1 (Im-*C*H$_2$CH$_2$CH$_2$-Tz), 33.0 (-CH$_2$*C*H$_2$CH$_2$CH$_3$), 30.8 (Im-CH$_2$*C*H$_2$CH$_2$-Tz), 23.0 (Im-CH$_2$CH$_2$*C*H$_2$-Tz), 20.5 (-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.8 (-CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI MS (M-PF_6)$^+$ *m/z* (%) calcd for [$C_{74}H_{128}N_5O_{34}$]$^+$: 1631.82, found: 1632.38.

1-butyl-3-[1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-yl methyl]imidazolium bromide (3). White powder; R_f (*i*-Prop-OH/H_2O/EtOAc/NH_3 5:3:1:1) = 0.33; mp dec. 210 °C; FTIR (KBr) ν/cm^{-1} = 3350, 2921, 2851, 1645, 1412, 1369, 1238, 1157, 1080, 1032, 1005, 947, 845, 754. ^{1}H NMR (300 MHz, D_2O): δ 8.98 (br s, 1H, H-Im), 8.21 (br s, 1H, H-Tz), 7.58 (d, 1H, H-Im), 7.55 (d, 1H, H-Im), 5.57 (br s, 2H, Tz-CH_2-Im), 5.2-4.9 (overlapped signals, 7H, 1-H overlaps with m, 1H, 6a-CH_2-Tz), 4.65 (m, 1H, 6b-CH_2-Tz), 4.22 (t, 2H, 1-H overlaps with br m, 1H, 5-H near 6-CH_2-Tz), 4.0-3.7 (overlapped signals, 23H, 3,5,6-H), 3.7-3.40 (overlapped signals, 14H, 2,4-H), 2.80 (dd, 2H, 6-H), 1.86 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.31 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.92 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, D_2O): δ 140.9 (CH Im), 127.3 (CH Tz), 123.2 (CH Im), 122.8 (CH Im), 102.4-101.8 (1-CH), 83.5-81.2 (4-CH), 73.5-71.8 (2,3,5-CH), 70.8 (5-CH near 6-CH_2-Tz), 60.7-59.5 (6-CH_2), 51.8 (6-CH_2-Tz), 49.9 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 44.0 (Tz-CH_2-Im), 31.6 (-CH$_2$*C*H$_2$CH$_2$CH$_3$), 19.2 (-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.05 (-CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI MS (M-Br)$^+$ *m/z* (%) calcd for [$C_{52}H_{84}N_5O_{34}$]$^+$: 1323.24, found: 1323.12 (35%); (M+Na-Br)$^{2+}$ calcd for [$C_{52}H_{84}N_5NaO_{34}$]$^{2+}$: 673.11, found: 672.92 (100%).

1-butyl-3-[3-(1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-yl) propyl]imidazolium chloride (4). Pale-yellow powder; R_f (*i*-Prop-OH/H_2O/EtOAc/NH_3 5:3:1:1) = 0.37; mp > 350 °C; FTIR (KBr) ν/cm^{-1} = 3350, 2919, 2851, 1648, 1541, 1457, 1375, 1159, 1080, 1030, 1001, 947, 754. ^{1}H NMR (300 MHz, D_2O): δ 8.96 (br s, 1H, H-Im), 7.86 (br s, 1H, H-Tz), 7.49 (d, 1H, H-Im), 7.46 (d, 1H, H-Im), 5.2-4.9 (overlapped signals, 7H, 1-H overlaps with m, 1H, 6a-CH_2-Tz), 4.60 (m, 1H, 6b-CH_2-Tz), 4.29 (t, 2H, Im-CH_2CH$_2$CH$_2$-Tz), 4.20 (t, 2H, 1-H overlaps with br m, 1H, 5-H near 6-CH_2-Tz), 4.0-3.7 (overlapped signals, 23H, 3,5,6-H), 3.7-3.40 (overlapped signals, 14H, 2,4-H), 3.12-2.80 (dd, 2H, 6-H), 2.79 (t, 2H, Im-CH$_2$CH$_2$CH_2-Tz), 2.30 (t, 2H, Im-CH$_2$CH_2CH$_2$-Tz), 1.84 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.33 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.93 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, D_2O): δ 140.2 (CH Im), 126 (CH Tz), 122.7 (CH Im), 122.6 (CH Im), 102.5-101.8 (1-CH), 83.6-81.2 (4-CH), 73.5-71.8 (2,3,5-CH), 71.0 (5-CH near 6-CH_2-Tz), 60.7-59.3 (6-CH_2), 51.5 (6-CH_2-Tz), 49.6 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 49.3 (Im-*C*H$_2$CH$_2$CH$_2$-Tz), 31.6 (-CH$_2$*C*H$_2$CH$_2$CH$_3$), 29.9 (Im-CH$_2$*C*H$_2$CH$_2$-Tz), 21.9 (Im-CH$_2$CH$_2$*C*H$_2$-Tz), 19.2 (-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.0 (-CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI MS (M-Cl)$^+$ *m/z* (%) calcd for [$C_{54}H_{88}N_5O_{34}$]$^+$:1351.29, found: 1351.57.

1-butyl-3-[1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-yl methyl]imidazolium hexafluorophosphate (5). Pale-yellow powder; R_f (*i*-Prop-OH/H_2O/EtOAc/NH_3 5:3:1:1) = 0.38; mp dec. 212 °C; FTIR (KBr) ν/cm^{-1} = 3360, 2932, 1650, 1560, 1458, 1340, 1161, 1080, 1028, 947, 843, 754. ^{1}H NMR (300 MHz, CD_3OD): δ 9.01 (br s, 1H, H-Im), 8.20 (br s, 1H, H-Tz), 7.67 (br, 1H, H-Im), 7.65 (br, 1H, H-Im), 5.56 (br s, 2H, Tz-CH_2-Im), 5.2-4.8 (overlapped signals, 7H, 1-H overlaps with m, 1H, 6a-CH_2-Tz), 4.7 (m, 1H, 6b-CH_2-Tz), 4.24 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 4.14 (br m, 1H, 5-H near 6-CH_2-Tz), 4.0-3.7 (overlapped signals, 23H, 3,5,6-H), 3.7-3.30 (overlapped signals, 14H, 2,4-H), 3.15-2.95 (dd, 2H, 6-H), 1.89 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.40 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.99 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, CD_3OD): δ 141.8, 137.5 (CH Im), 127.3 (CH Tz), 123.9 (CH Im), 104.0-103.8 (1-CH), 85.1-82.9 (4-CH), 74.8-73.4 (2,3,5-CH), 72.0 (5-CH near 6-CH_2-Tz), 62.0-61.8 (6-CH_2), 52.7 (6-CH_2-Tz), 50.8 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 45.2 (Tz-CH_2-Im), 33.0 (-CH$_2$*C*H$_2$CH$_2$CH$_3$), 20.4 (-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.8 (-CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI MS (M-PF_6)$^+$ *m/z* (%) calcd for [$C_{52}H_{84}N_5O_{34}$]$^+$: 1323.24, found: 1323.72.

1-butyl-3-[3-(1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-yl) propyl]imidazolium hexafluorophosphate (6). Yellow powder; R_f (*i*-Prop-OH/H_2O/EtOAc/NH_3 5:3:1:1) = 0.39; mp dec. 222 °C; FTIR (KBr) ν/cm^{-1} = 3360, 2934, 1684, 1635, 1568, 1458, 1339, 1159, 1080, 1028, 947, 843, 754. ^{1}H NMR (300 MHz, CD_3OD): δ 8.98 (br s, 1H, H-Im), 7.86 (br s, 1H, H-Tz),

7.65 (br, 2H, H-Im), 5.1-4.8 (m, 7H, 1-H overlaps with m, 1H, 6a-CH_2-Tz), 4.60 (m, 1H, 6b-CH_2-Tz), 4.31 (t, 2H, Im-CH_2CH$_2$CH$_2$-Tz), 4.24 (t, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 4.12 (br m, 1H, 5-H near 6-CH_2-Tz), 4.0-3.7 (overlapped signals, 23H, 3,5,6-H), 3.7-3.40 (overlapped signals, 14H, 2,4-H), 3.3-3.05 (dd, 2H, 6-H), 2.78 (t, 2H, Im-CH$_2$CH$_2$CH_2-Tz), 2.30 (t, 2H, Im-CH$_2$CH_2CH$_2$-Tz), 1.89 (m, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.37 (m, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.99 (t, 3H, -CH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (75 MHz, CD$_3$OD): δ 147.2, 137 (CH Im), 125.4 (CH Tz), 123.8 (CH Im), 104-103 (1-CH), 85-82 (4-CH), 75-73 (2,3,5-CH), 72.0 (5-CH near 6-CH$_2$-Tz), 62-60 (6-CH$_2$), 52.4 (6-CH$_2$-Tz), 50.6 (-*C*H$_2$CH$_2$CH$_2$CH$_3$), 50.2 (Im-*C*H$_2$CH$_2$CH$_2$-Tz), 33.0 (-CH$_2$*C*H$_2$CH$_2$CH$_3$), 30.5 (Im-CH$_2$*C*H$_2$CH$_2$-Tz), 22.9 (Im-CH$_2$CH$_2$*C*H$_2$-Tz), 20.5 (-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.8 (-CH$_2$CH$_2$CH$_2$*C*H$_3$). ESI MS (M-PF$_6$)$^+$ *m/z* (%) calcd for [C$_{54}$H$_{88}$N$_5$O$_{34}$]$^+$: 1351.29, found: 1351.55.

NMR Spectra**6^{I}-azido-6^{I}-deoxy-β-CD (2)**

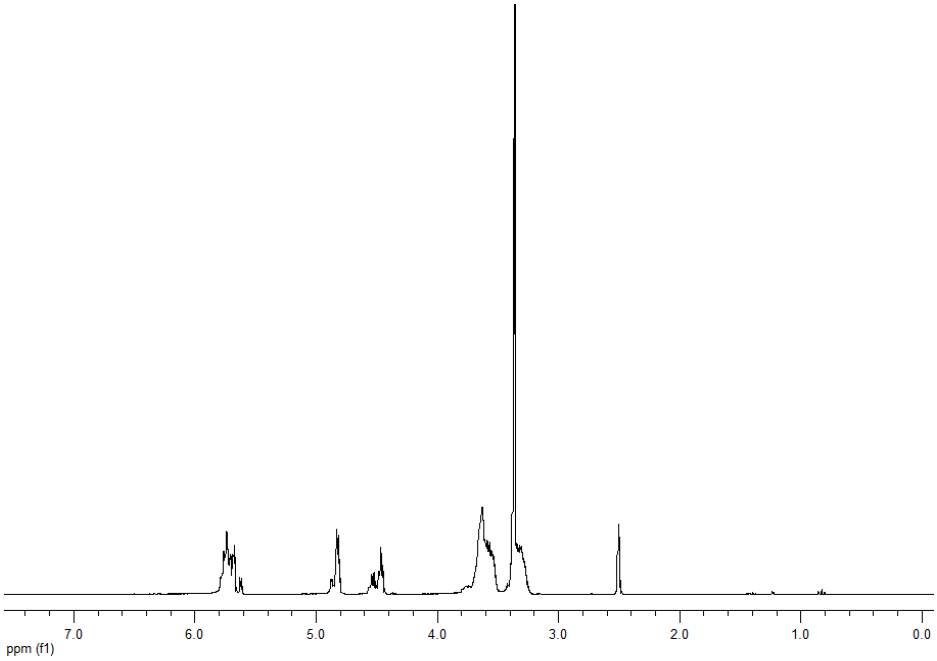


Fig. 1. ^{1}H NMR (300 MHz, DMSO-D_6) of **2**.

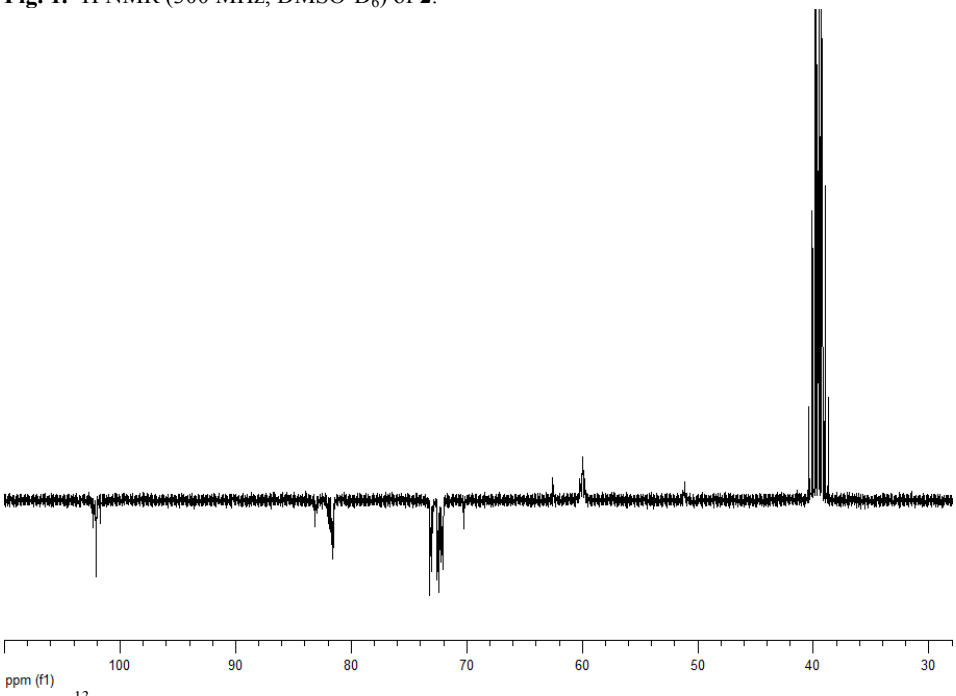


Fig. 2. ^{13}C APT NMR (75 MHz, DMSO-D_6) of **2**.

6^{I}-azido-6^{I}-deoxy-$2^{I\text{-}VII}$,$3^{I\text{-}VII}$,$6^{II\text{-}VII}$-permethyl-β-CD (7)

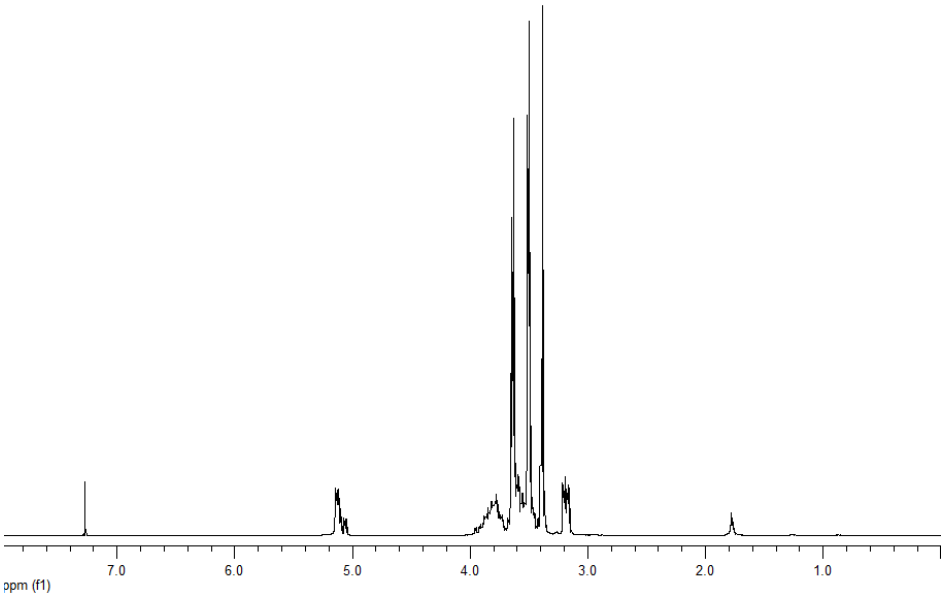


Fig. 3. ^{1}H NMR (300 MHz, $CDCl_3$) of **7**.

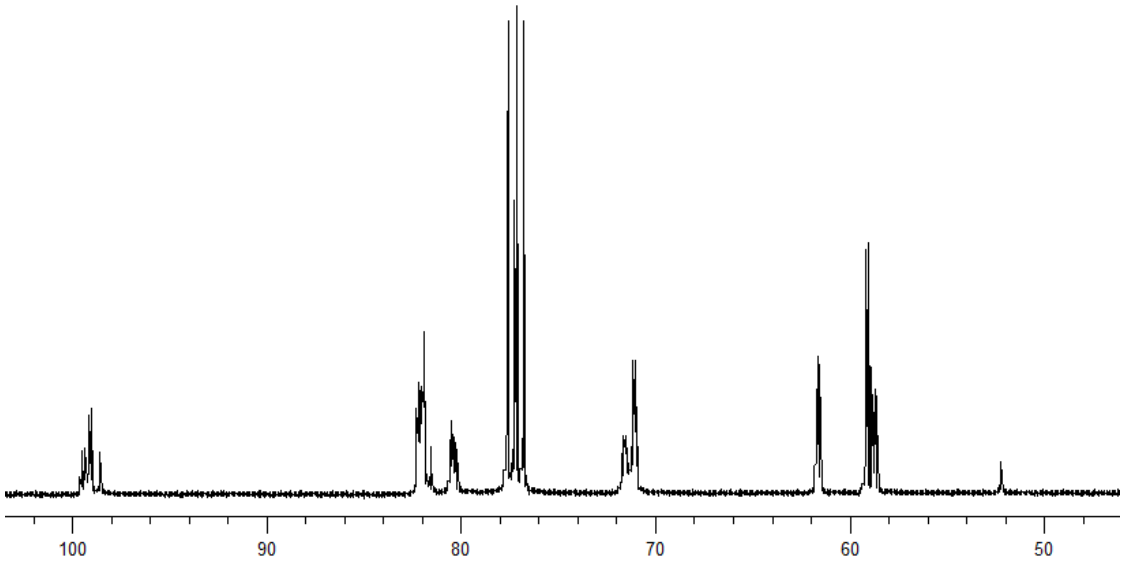


Fig. 4. ^{13}C NMR (75 MHz, $CDCl_3$) of **7**.

1-butyl-3-propargylimidazolium bromide.

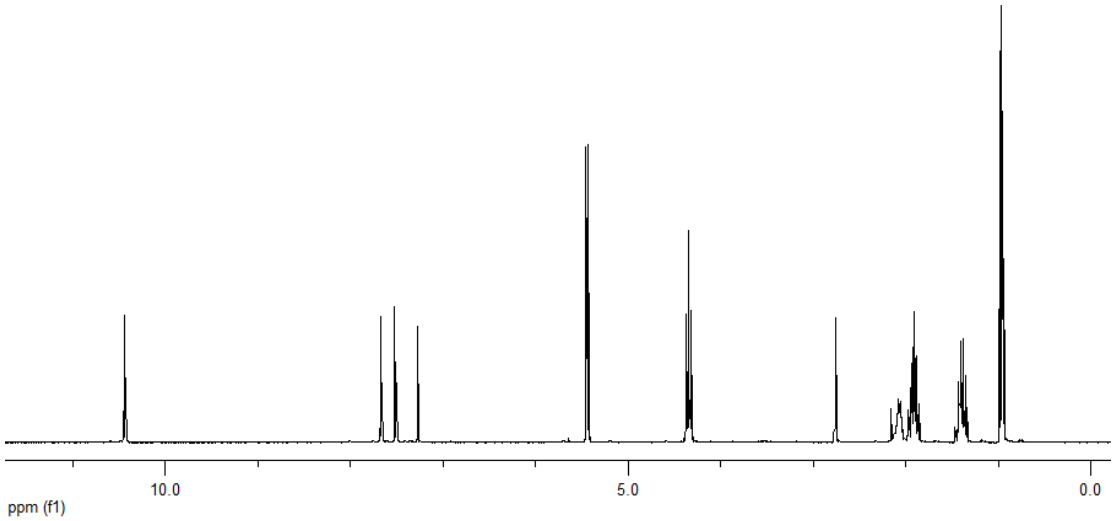


Fig. 5. ^{1}H NMR (300 MHz, $CDCl_3$) of BuPrImBr.

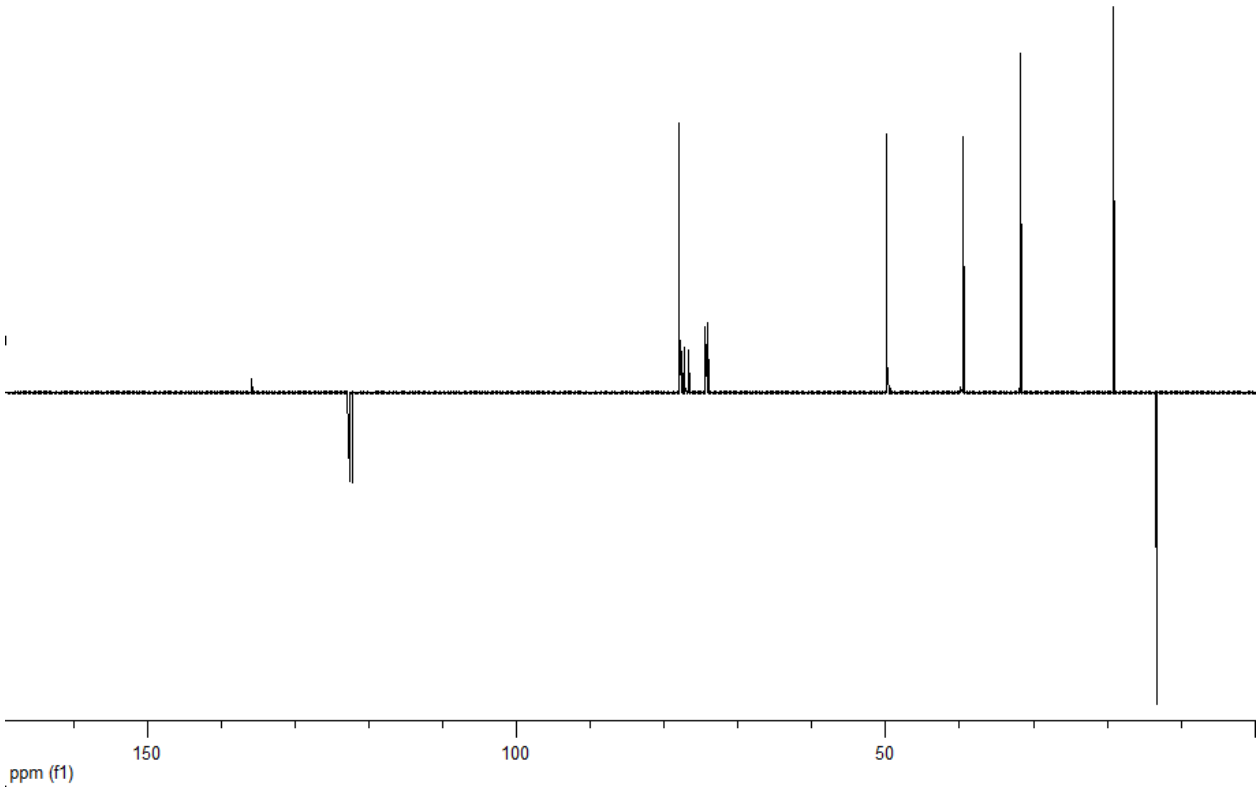


Fig. 6. ^{13}C NMR (75 MHz, $CDCl_3$) of BuPrImBr.

1-butyl-3-propargylimidazolium hexafluorophosphate.

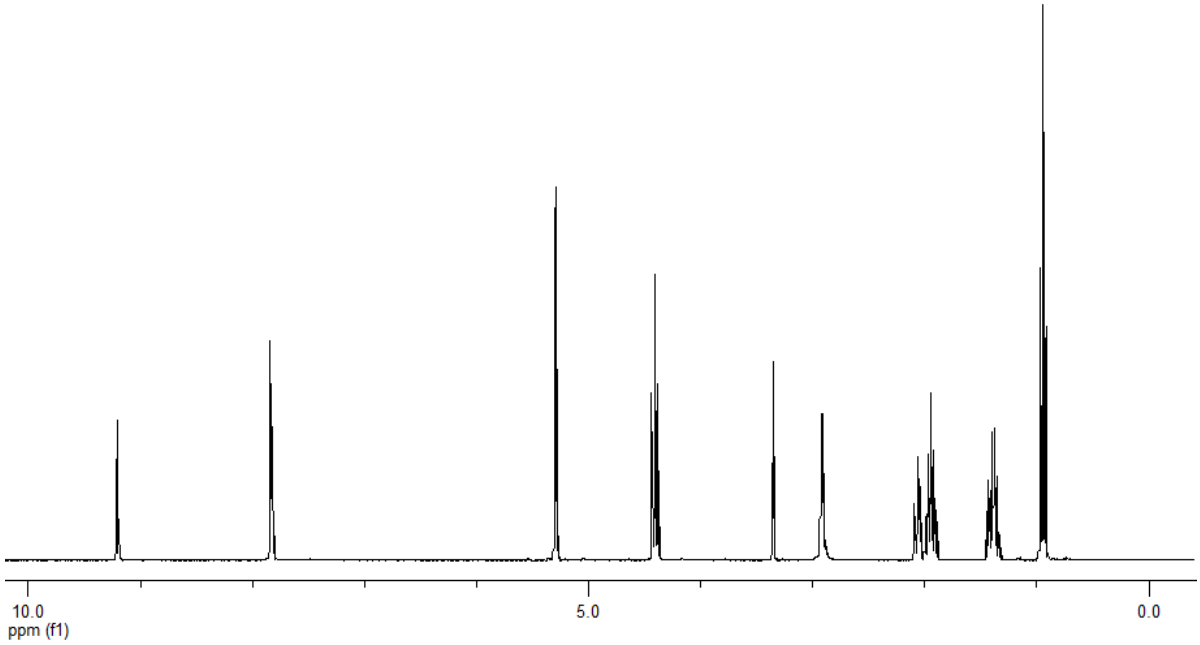


Fig. 7. ^{1}H NMR (300 MHz, acetone-D_6) of BuPrImPF$_6$.

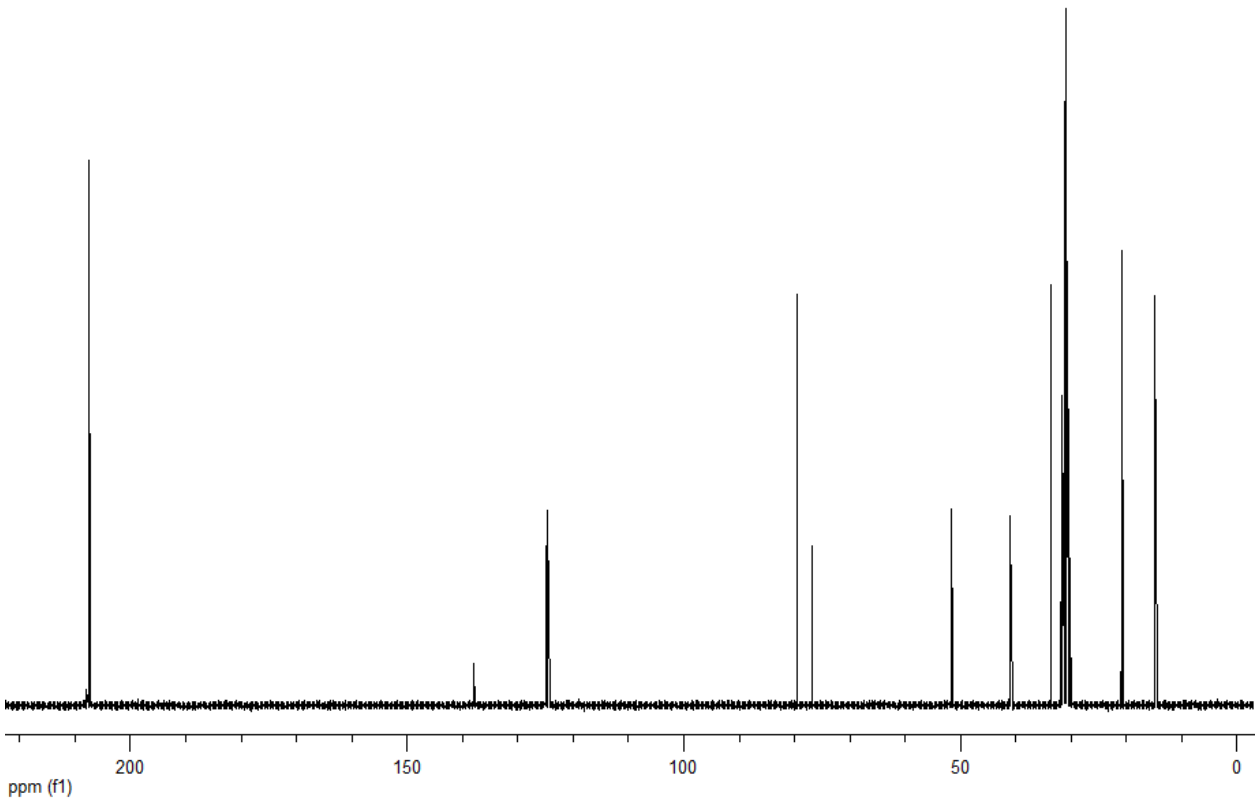


Fig. 8. ^{13}C NMR (75 MHz, acetone-D_6) of BuPrImPF$_6$.

1-butyl-3-(4-pentynyl)imidazolium chloride.

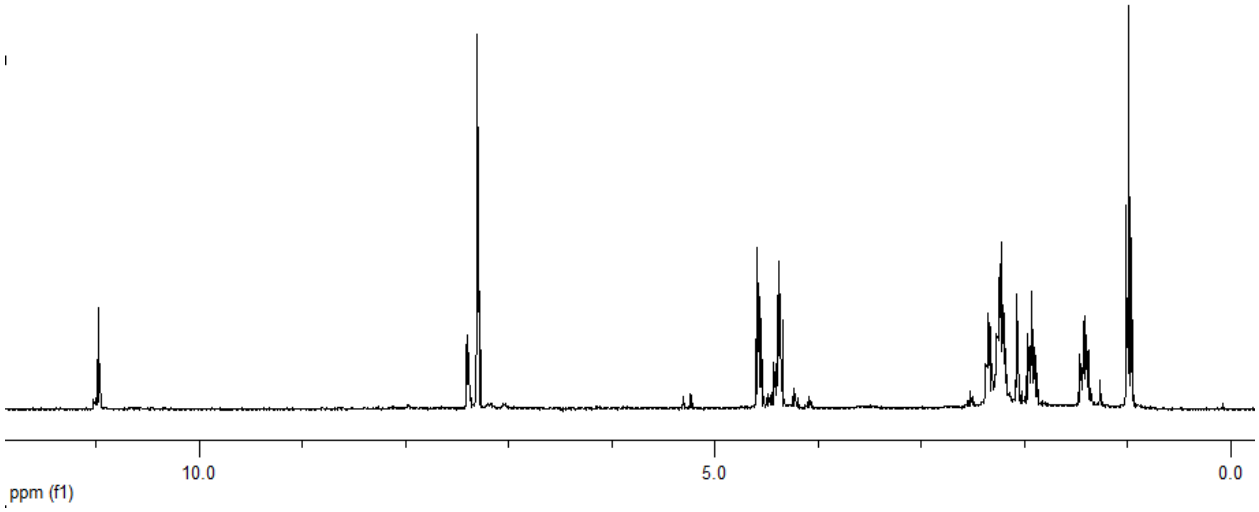


Fig. 9. ^{1}H NMR (300 MHz, $CDCl_3$) of BuPeImCl.

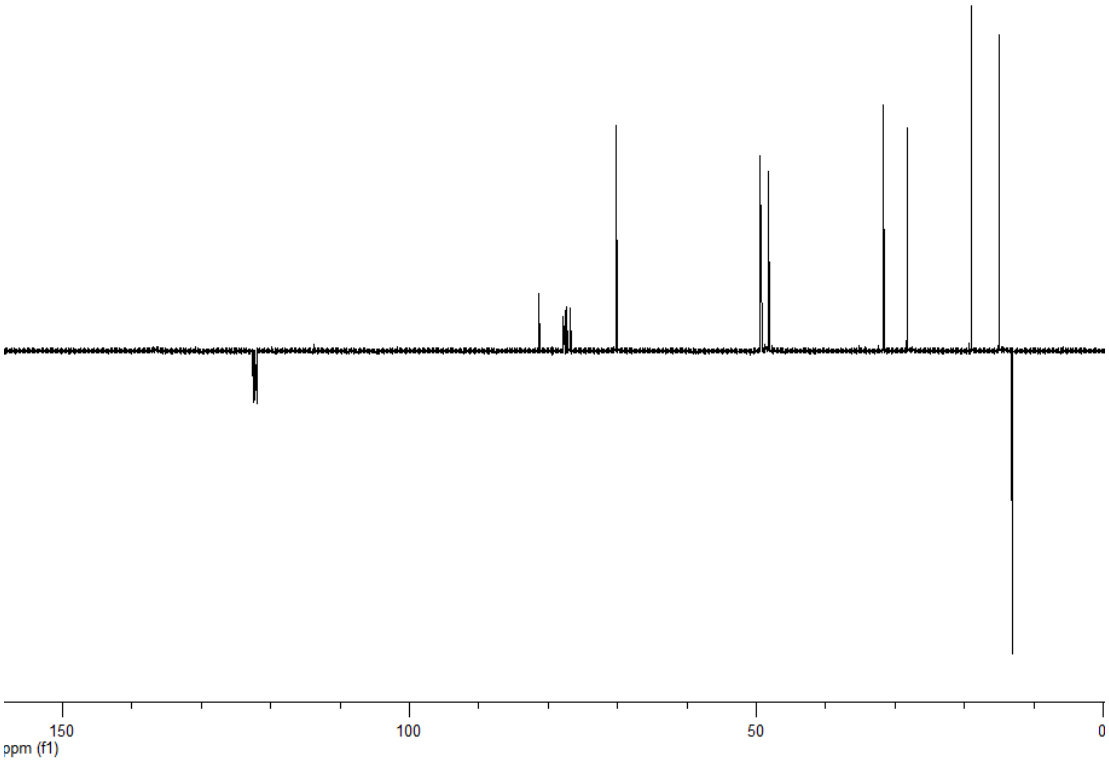


Fig. 10. ^{13}C APT NMR (75 MHz, $CDCl_3$) of BuPeImCl.

1-butyl-3-(4-pentynyl)imidazolium hexafluorophosphate.

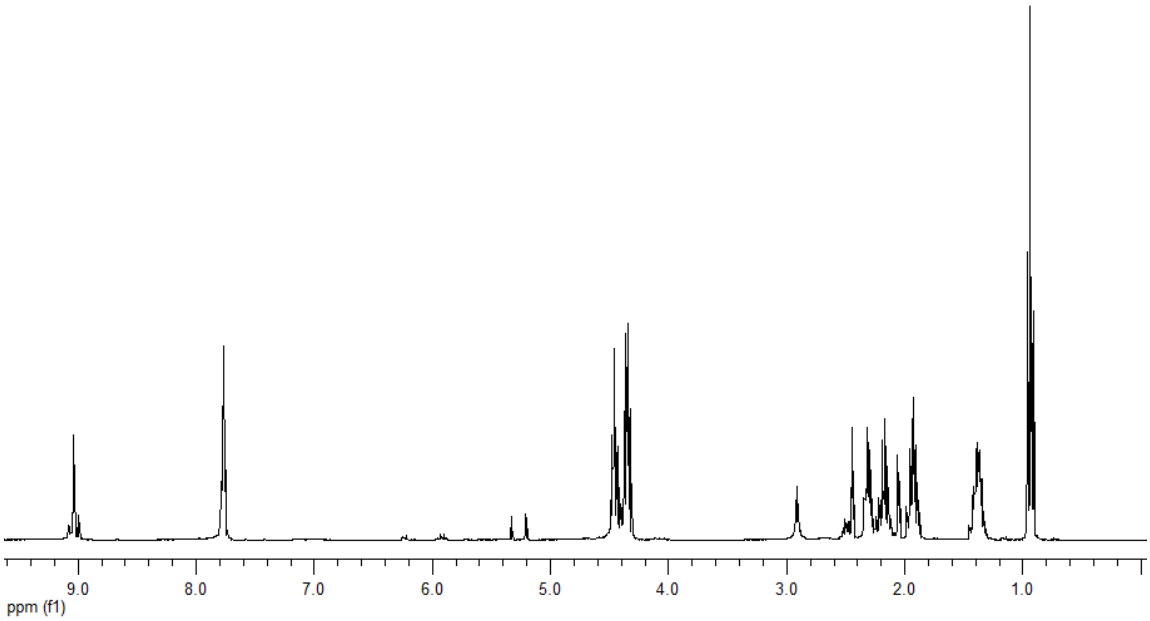


Fig. 11. ^{1}H NMR (300 MHz, acetone-D_6) of BuPeImPF$_6$.

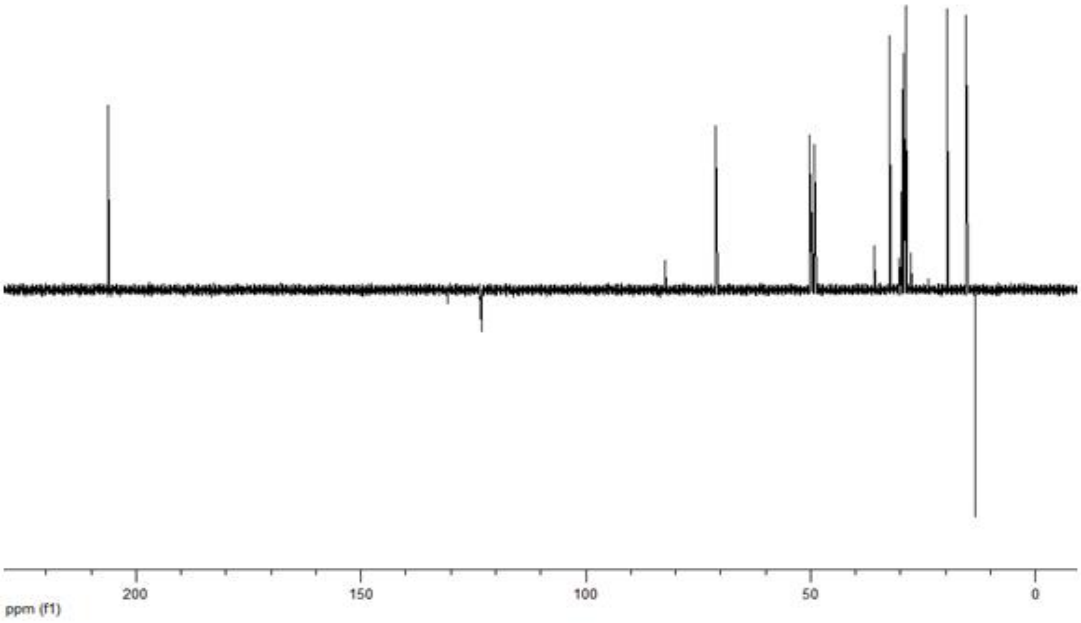


Fig. 12. ^{13}C NMR (75 MHz, acetone-D_6) of BuPeImPF$_6$.

1-butyl-3-[1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-ylmethyl]imidazolium bromide (8).

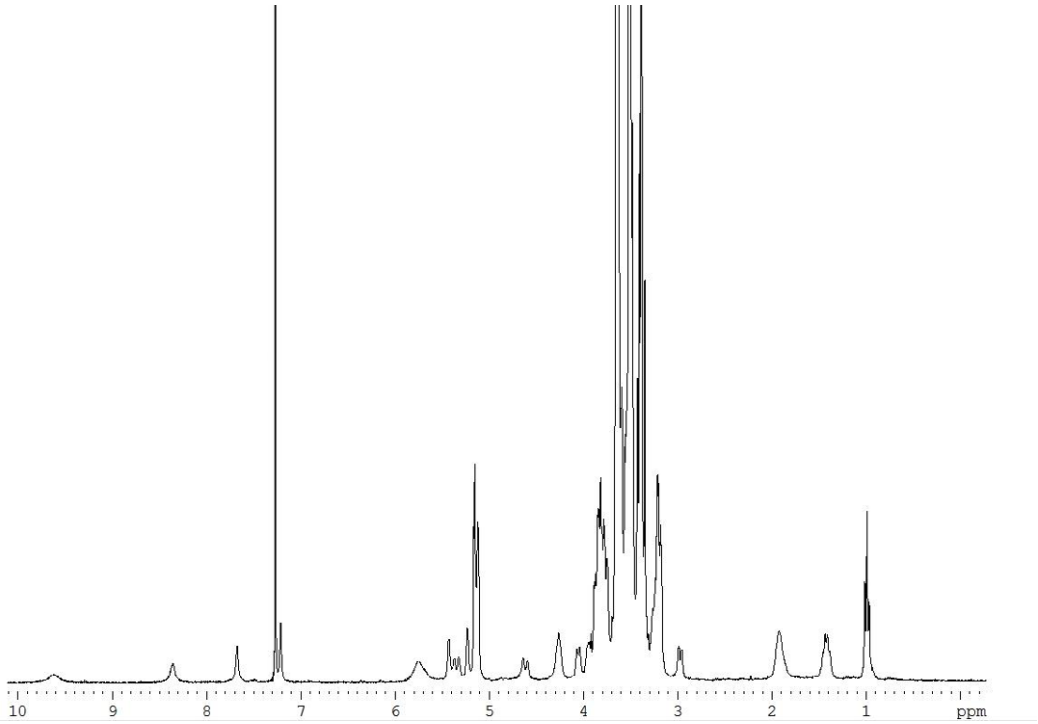


Fig. 13. ^{1}H NMR (300 MHz, $CDCl_3$) of **8**.

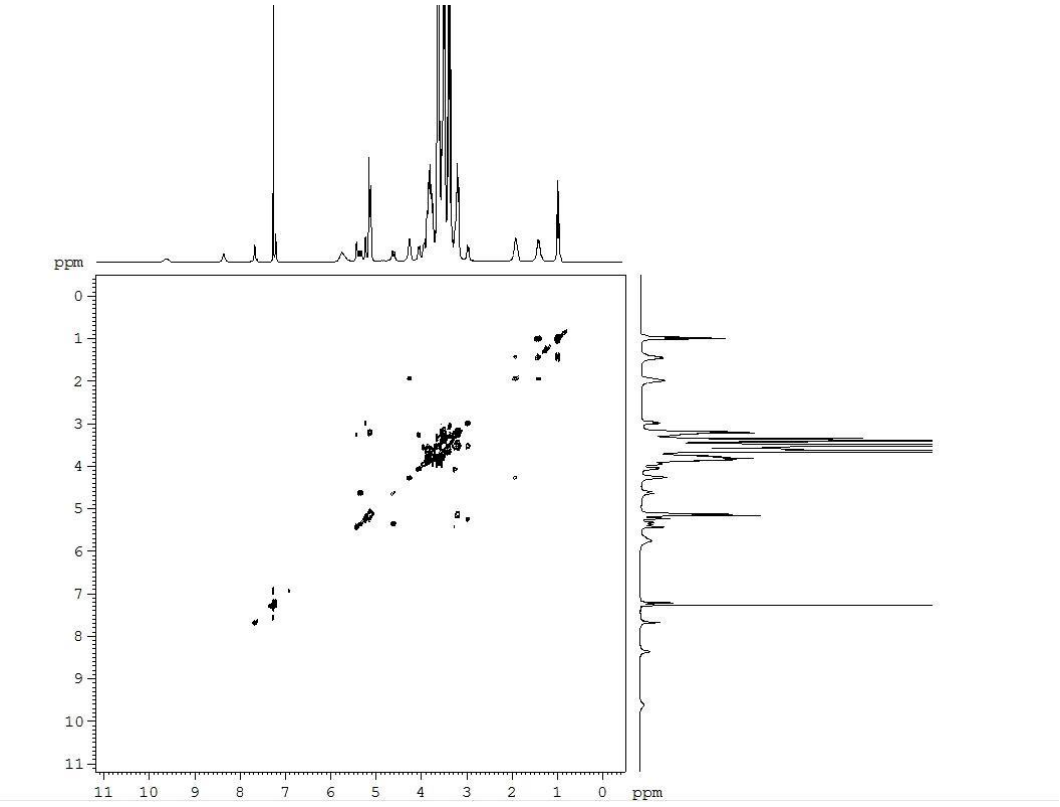


Fig. 14. ^{1}H-^{1}H COSY (300 MHz, $CDCl_3$) of **8**.

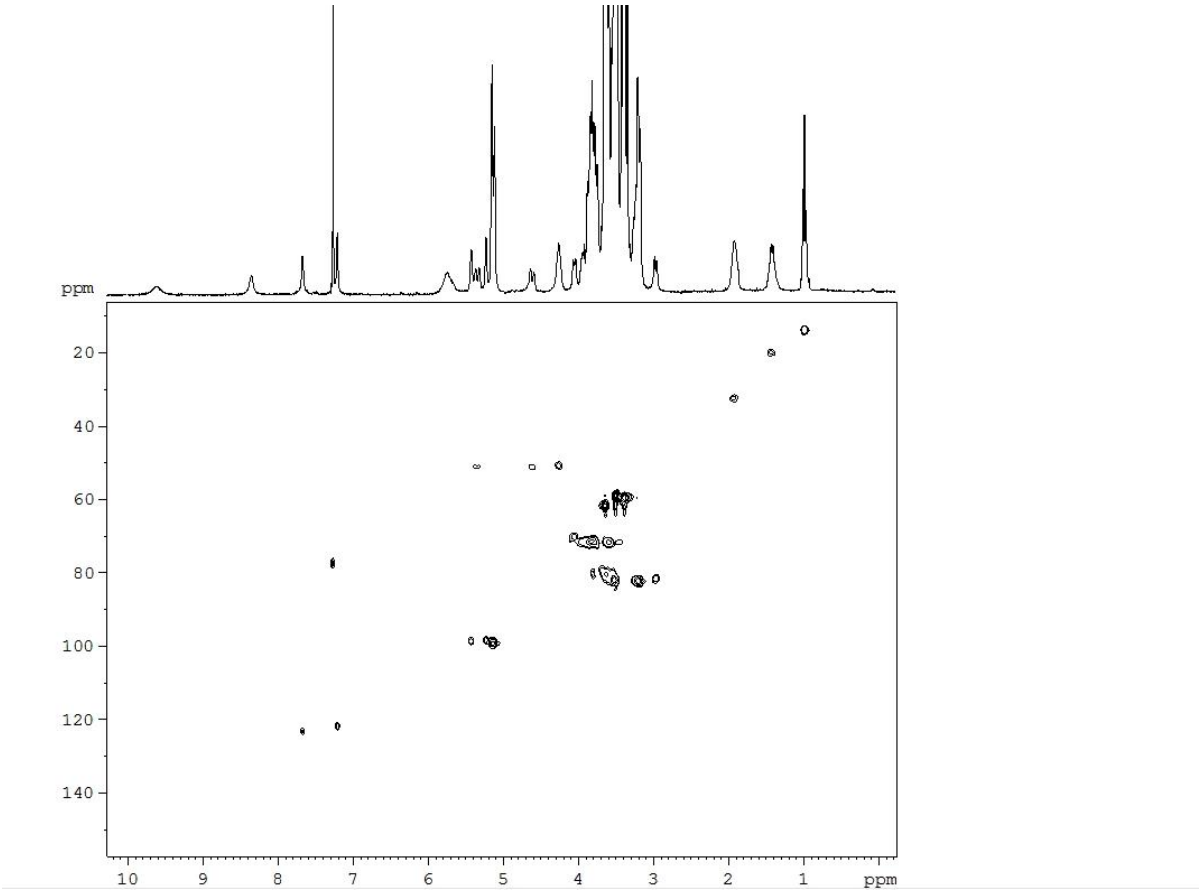


Fig. 15. ^{1}H-^{13}C HSQC (300/75 MHz, $CDCl_3$) of **8**.

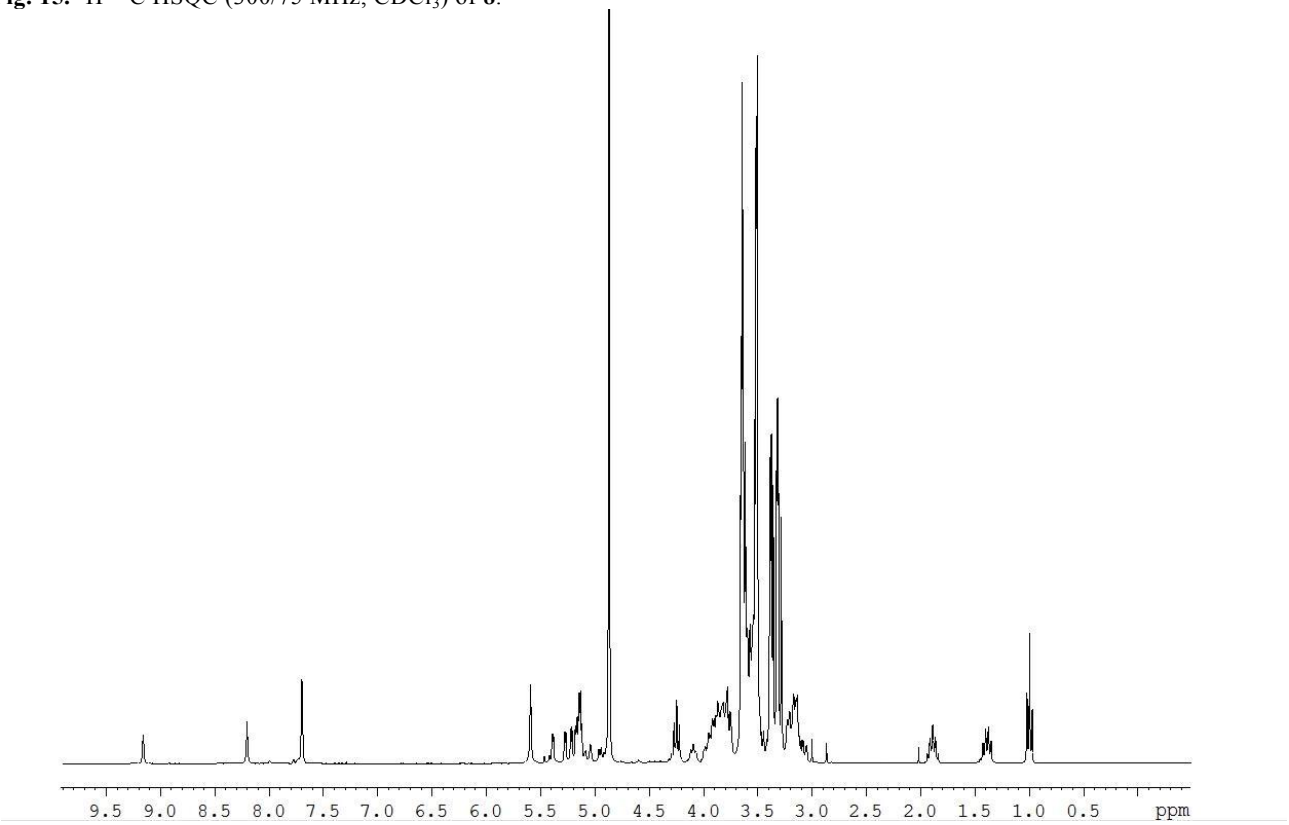


Fig. 16. ^{1}H NMR (300 MHz, CD_3OD) of **8**.

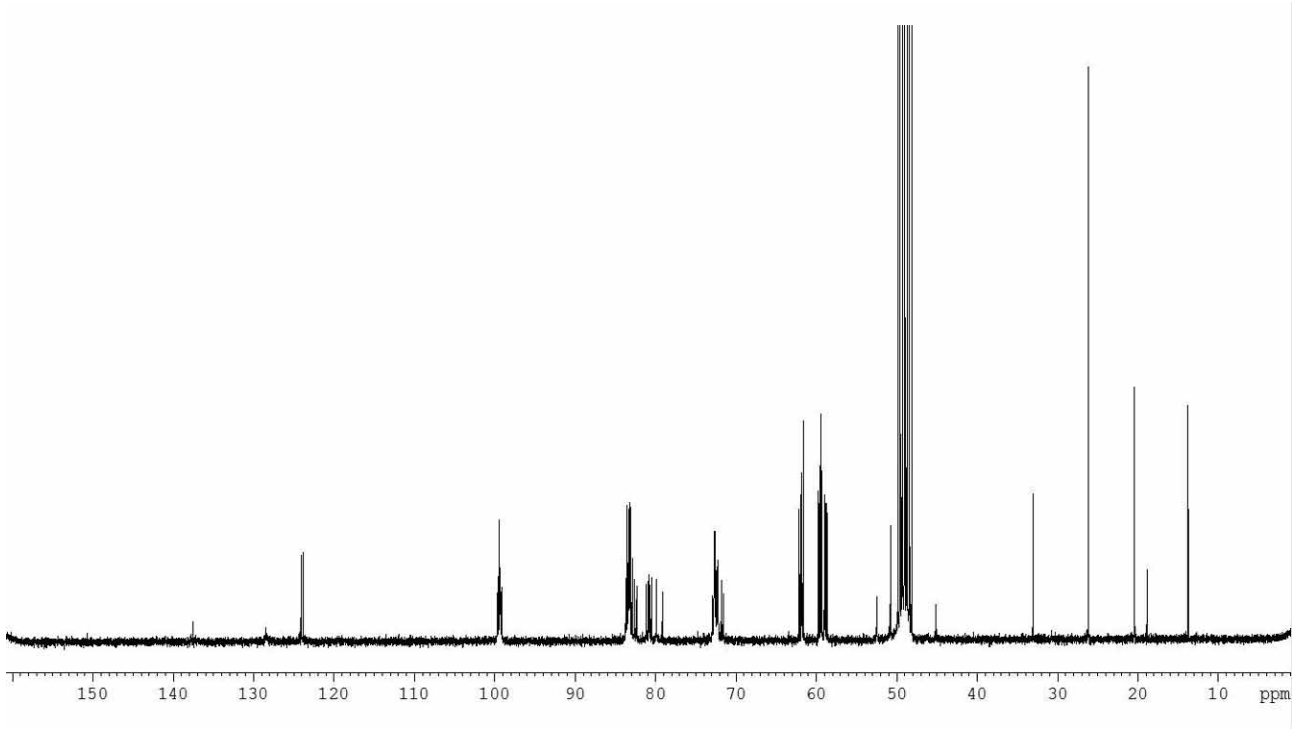


Fig. 17. ^{13}C NMR (75 MHz, CD_3OD) of **8**.

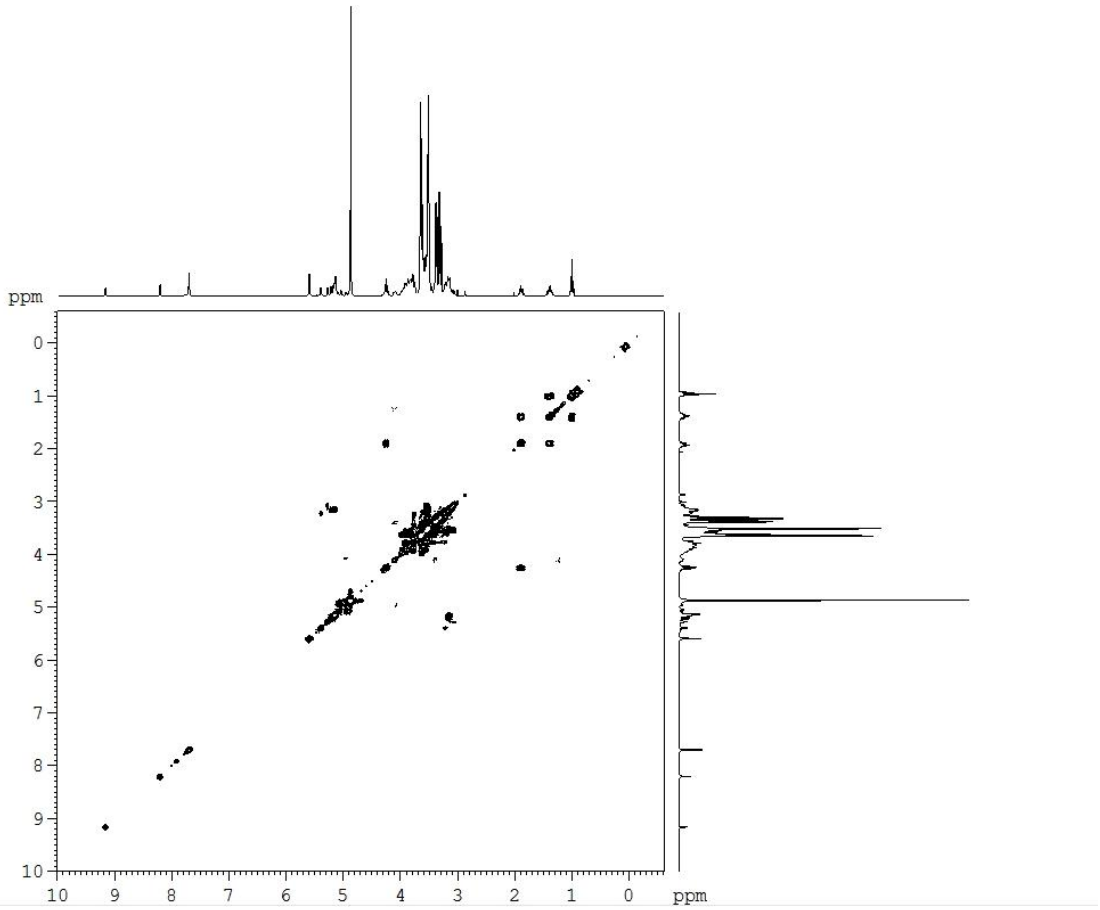


Fig. 18. ^{1}H-^{1}H COSY (300 MHz, CD_3OD) of **8**.

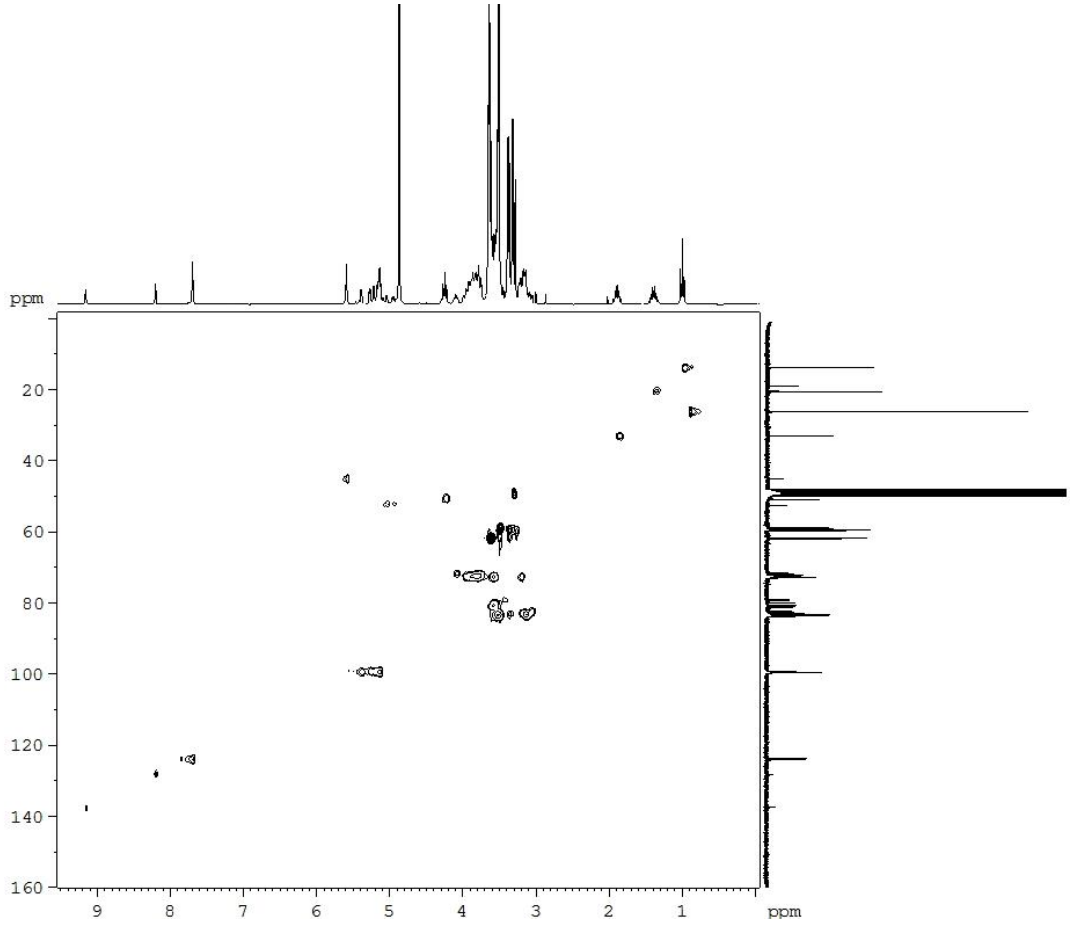


Fig. 19. ^{1}H-^{13}C HSQC (300/75 MHz, CD_3OD) of **8.**

1-butyl-3-[3-(1-(6^{I}-deoxy-6$^{II\text{-}VII}$,2$^{I\text{-}VII}$,3$^{I\text{-}VII}$-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-yl)propyl]imidazolium chloride (9)

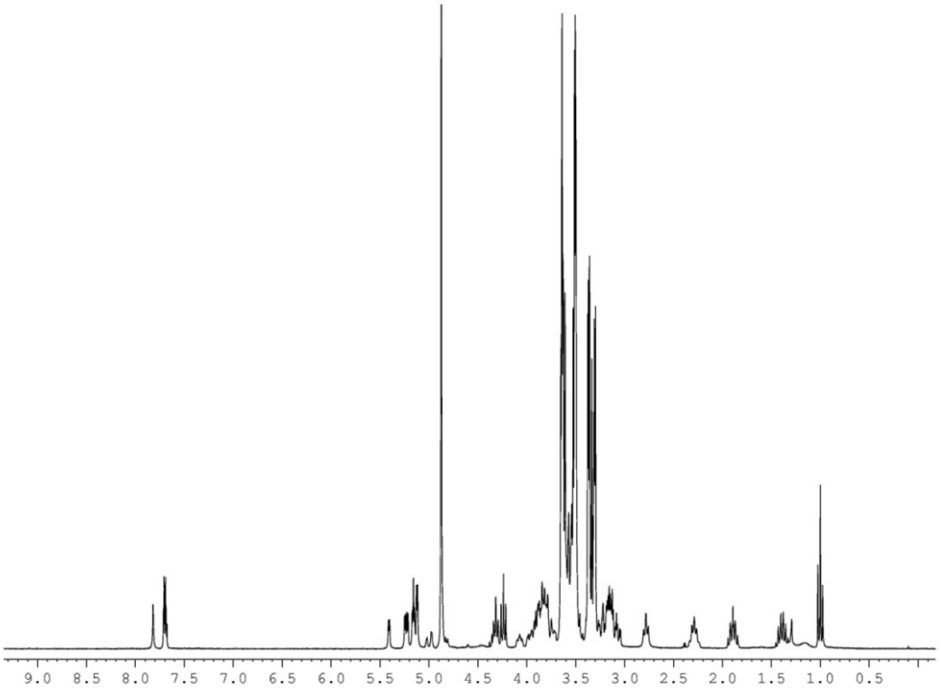


Fig. 20. ^{1}H NMR (300 MHz, CD_3OD) of **9**.

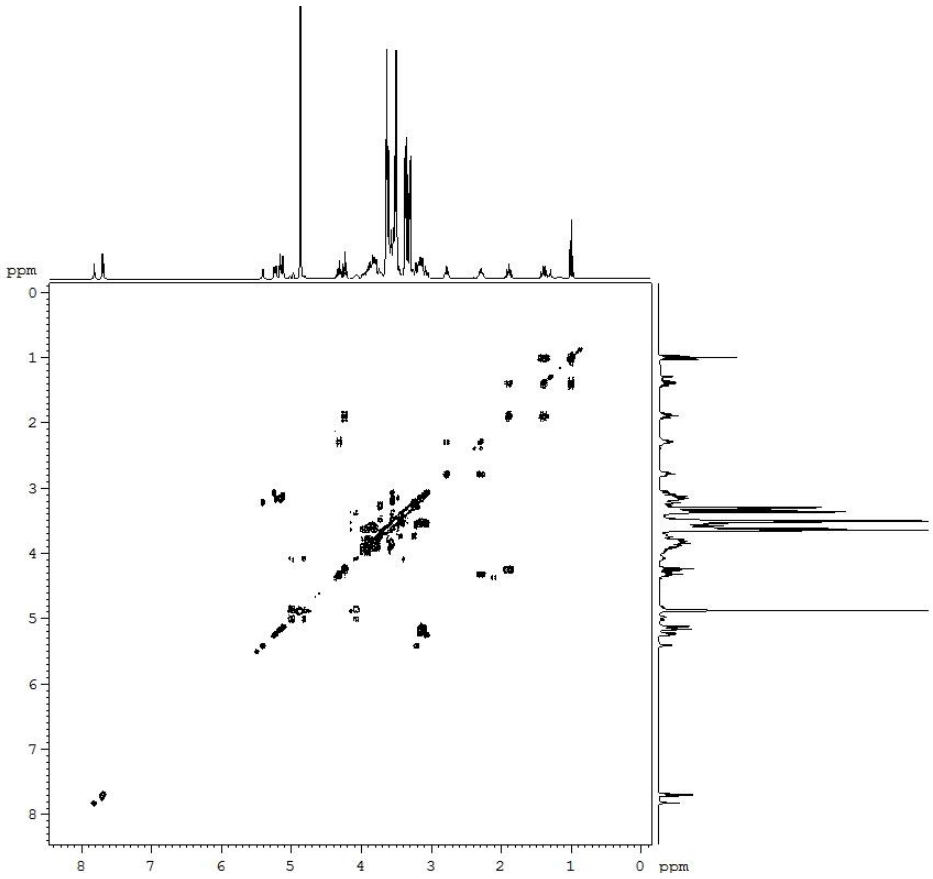


Fig. 21. ^{1}H-^{1}H COSY (300 MHz, CD_3OD) of **9**.

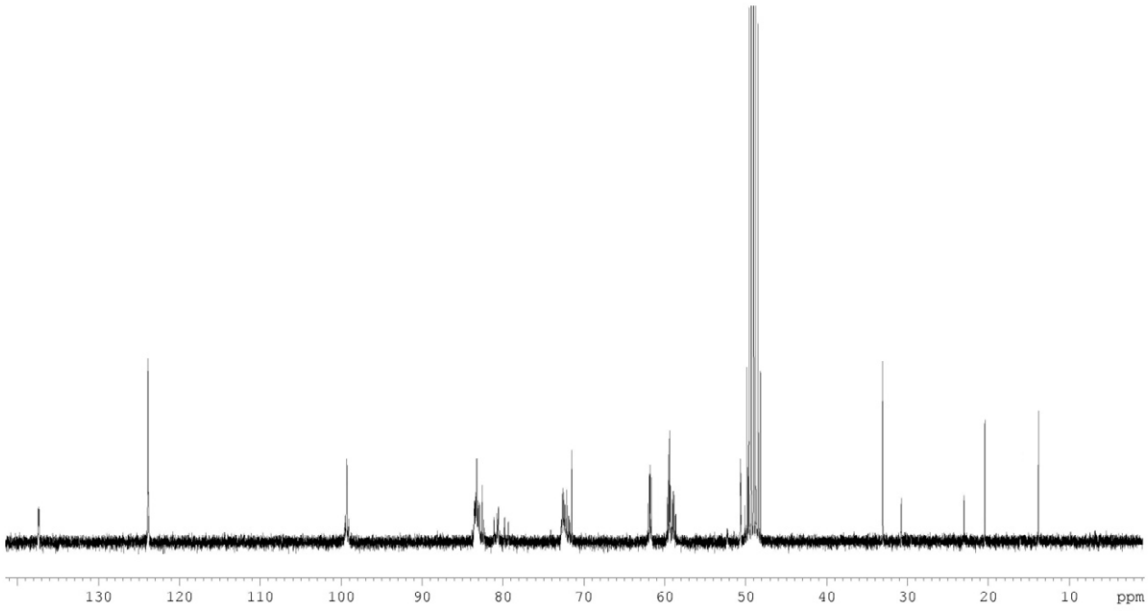


Fig. 22. ^{13}C APT NMR (75 MHz, CD_3OD) of **9.**

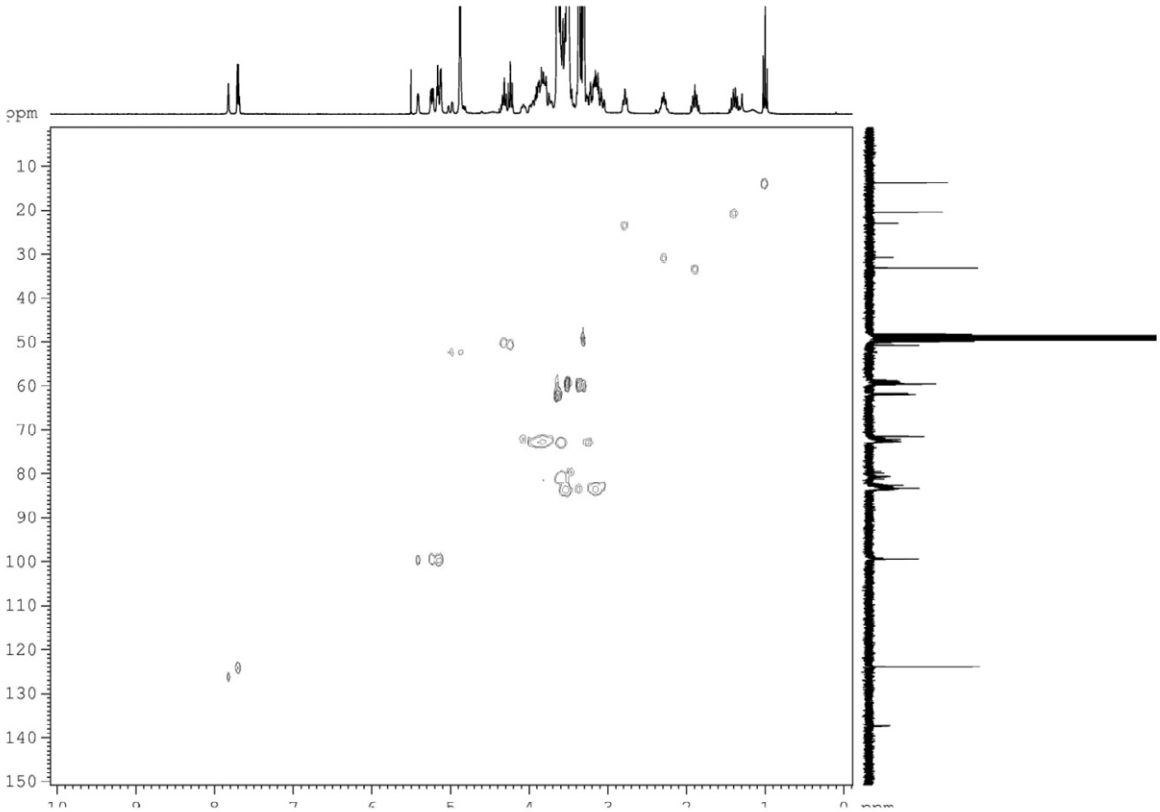


Fig. 23. ^{1}H-^{13}C HSQC (300/75 MHz, CD_3OD) of **9**.

1-butyl-3-[1-(6^{I}-deoxy-6$^{II\text{-}VII}$,2$^{I\text{-}VII}$,3$^{I\text{-}VII}$-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-ylmethyl]imidazolium hexafluorophosphate (10).

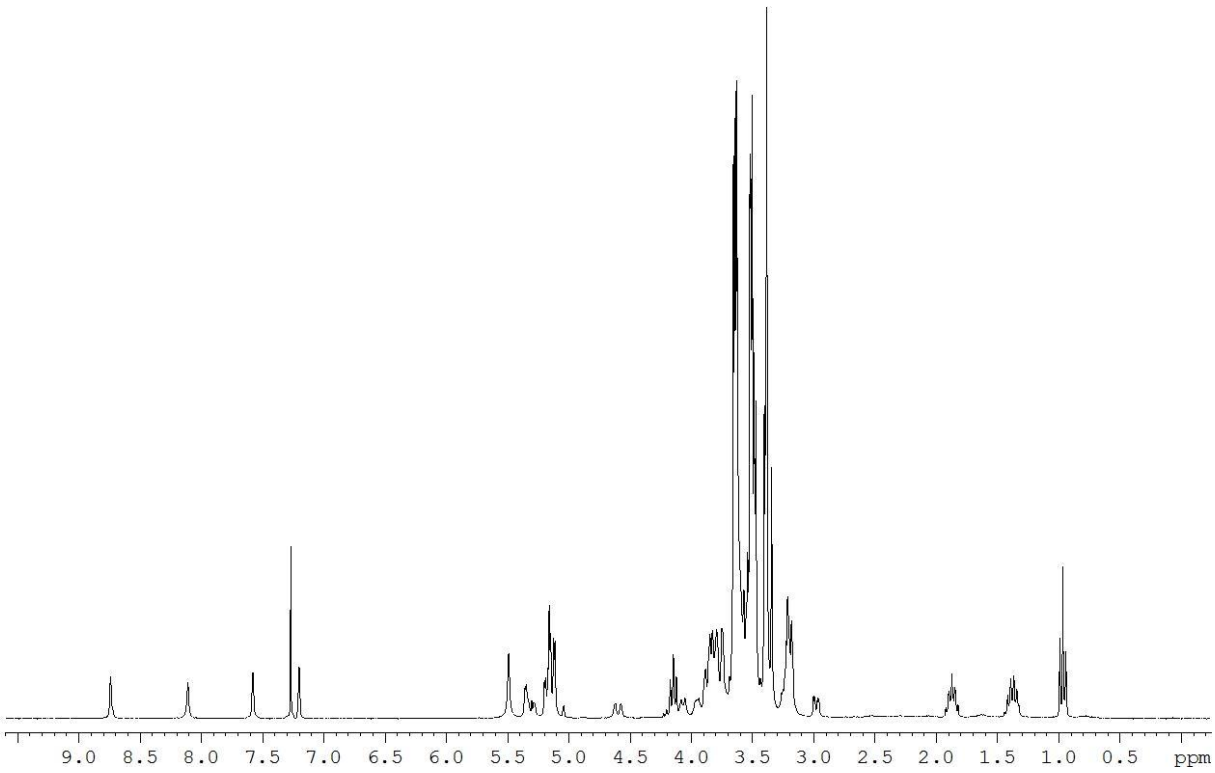


Fig. 24. ^{1}H NMR (300 MHz, $CDCl_3$) of **10**.

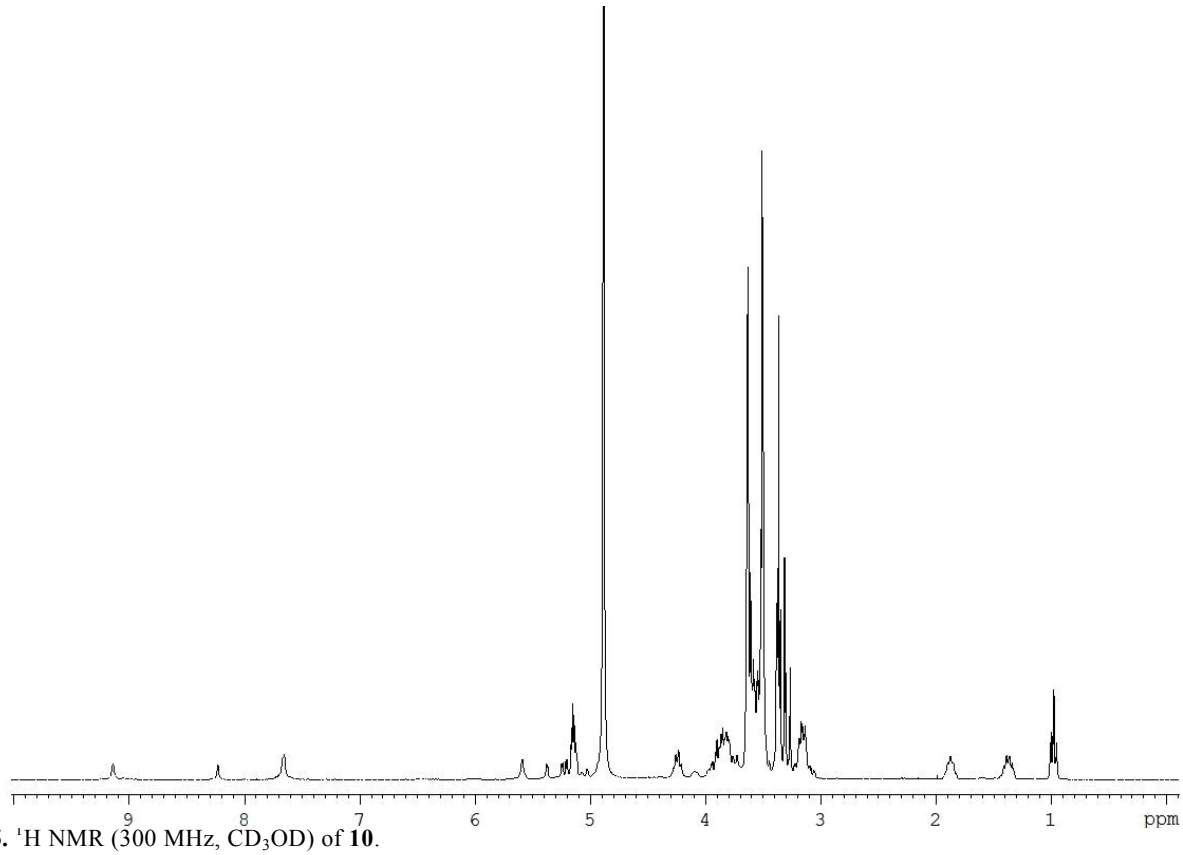


Fig. 25. ^{1}H NMR (300 MHz, CD_3OD) of **10**.

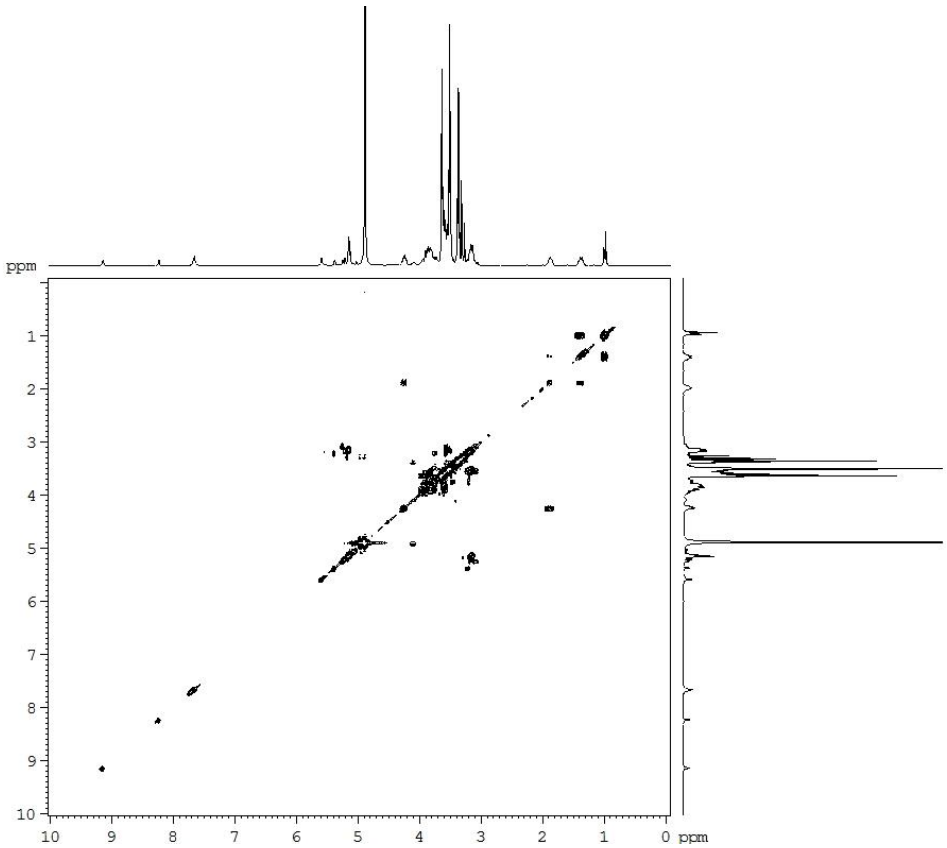


Fig. 26. ^{1}H-^{1}H COSY (300 MHz, CD_3OD) of **10**.

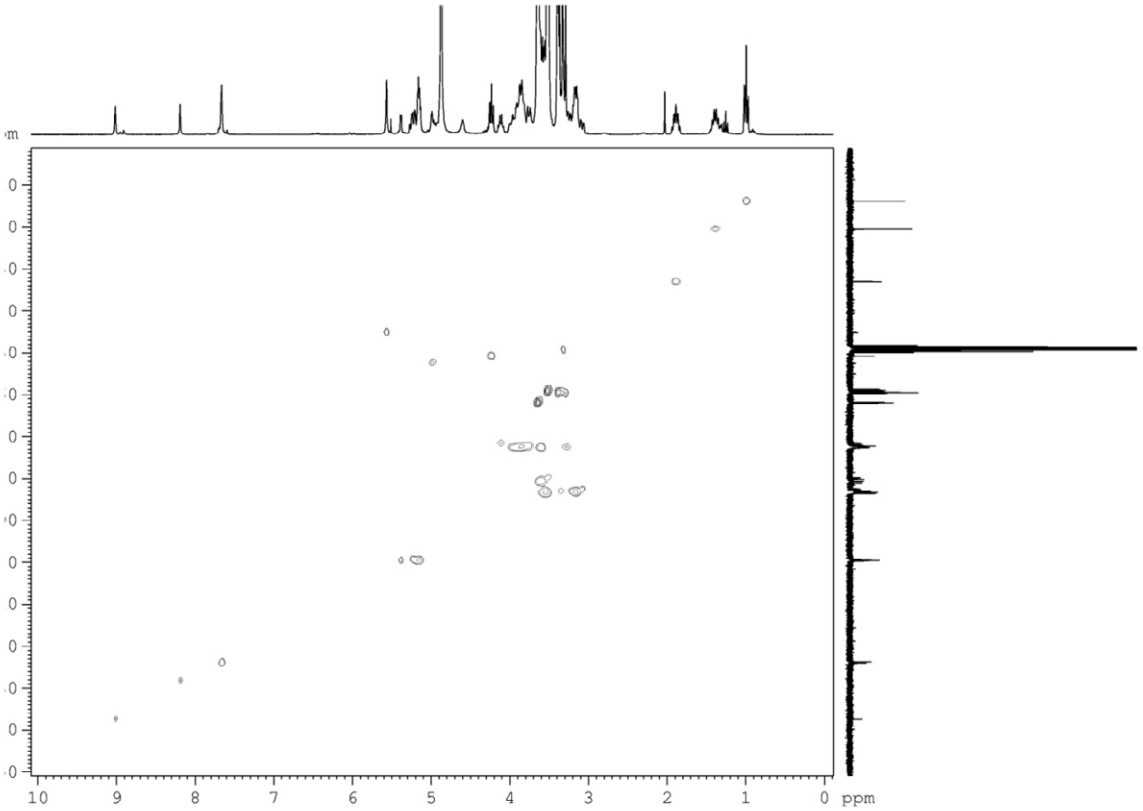


Fig. 27. ^{1}H-^{13}C HSQC (300/75 MHz, CD_3OD) of **10**.

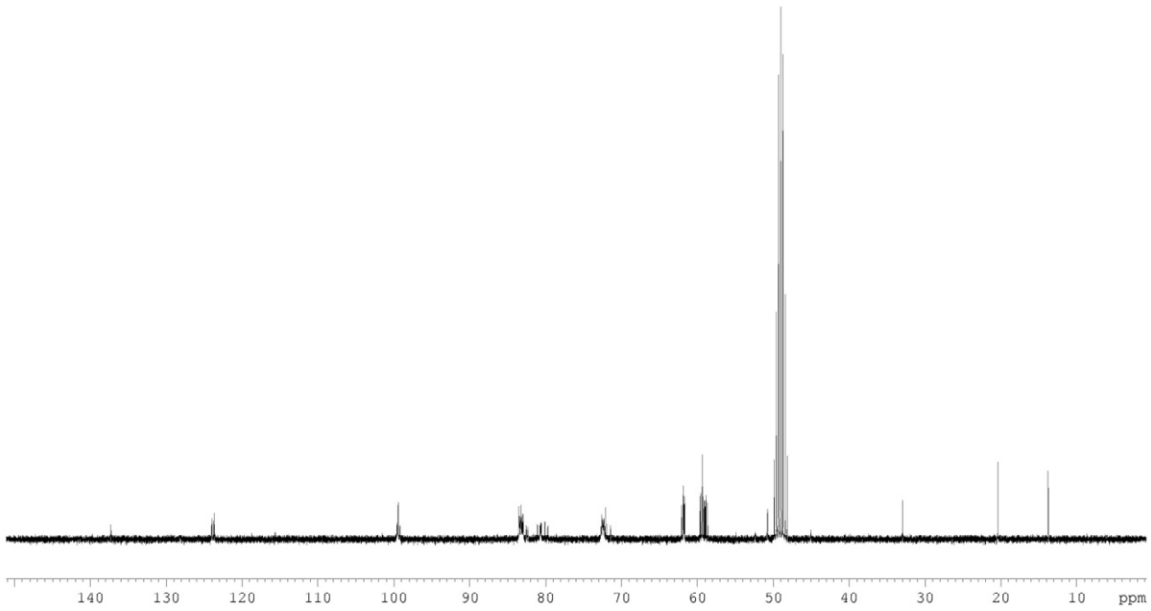


Fig. 28. ^{13}C NMR (75 MHz, CD_3OD) of **10**.

1-butyl-3-[3-(1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-yl)propyl]imidazolium hexafluorophosphate (11).

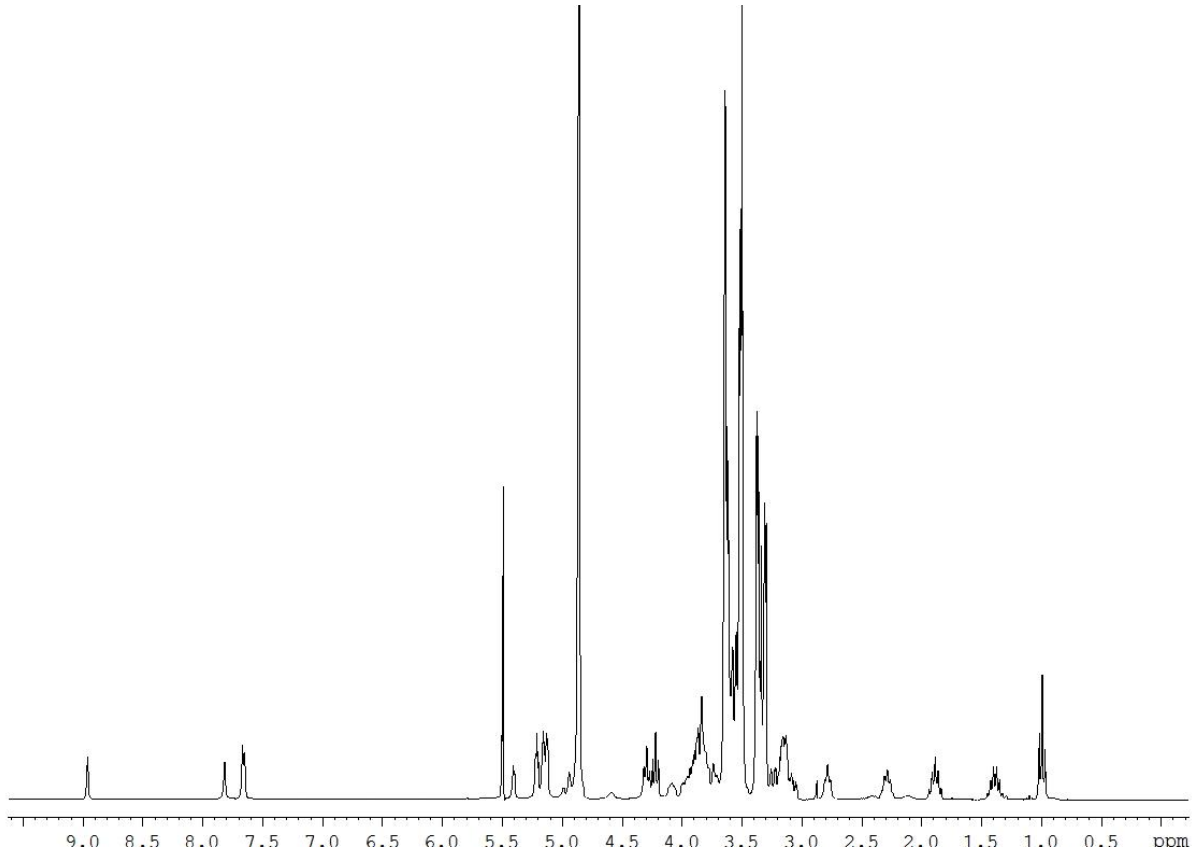


Fig. 29. ^{1}H NMR (300 MHz, CD_3OD) of **11**.

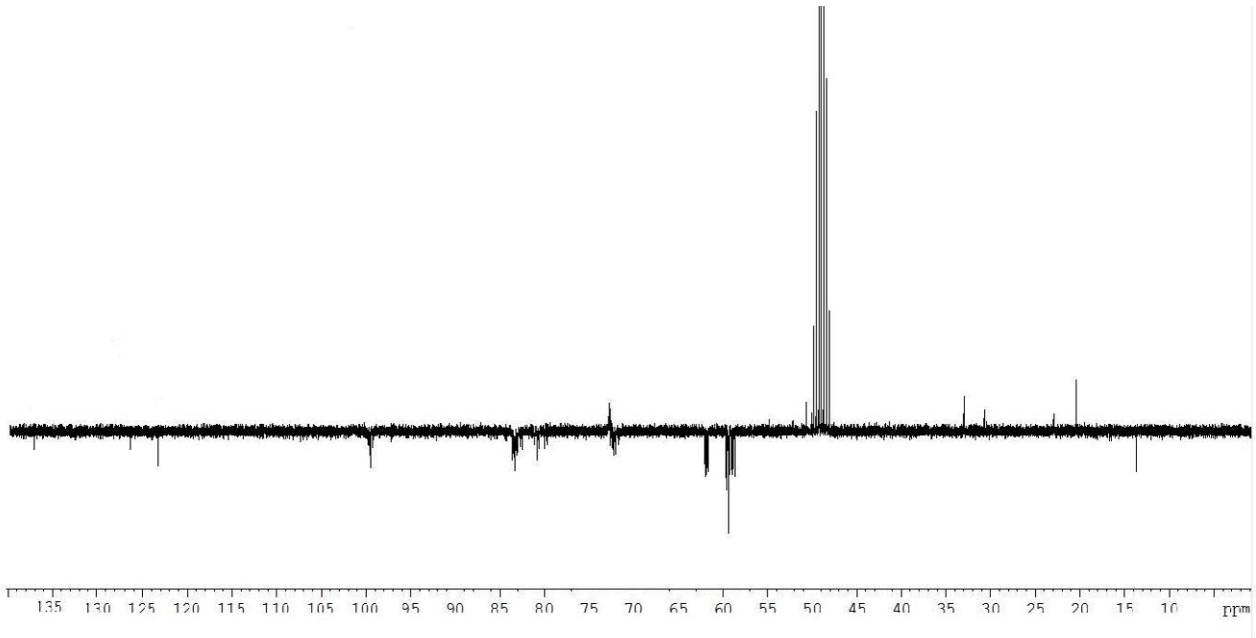


Fig. 30. ^{13}C APT NMR (75 MHz, CD_3OD) of **11**.

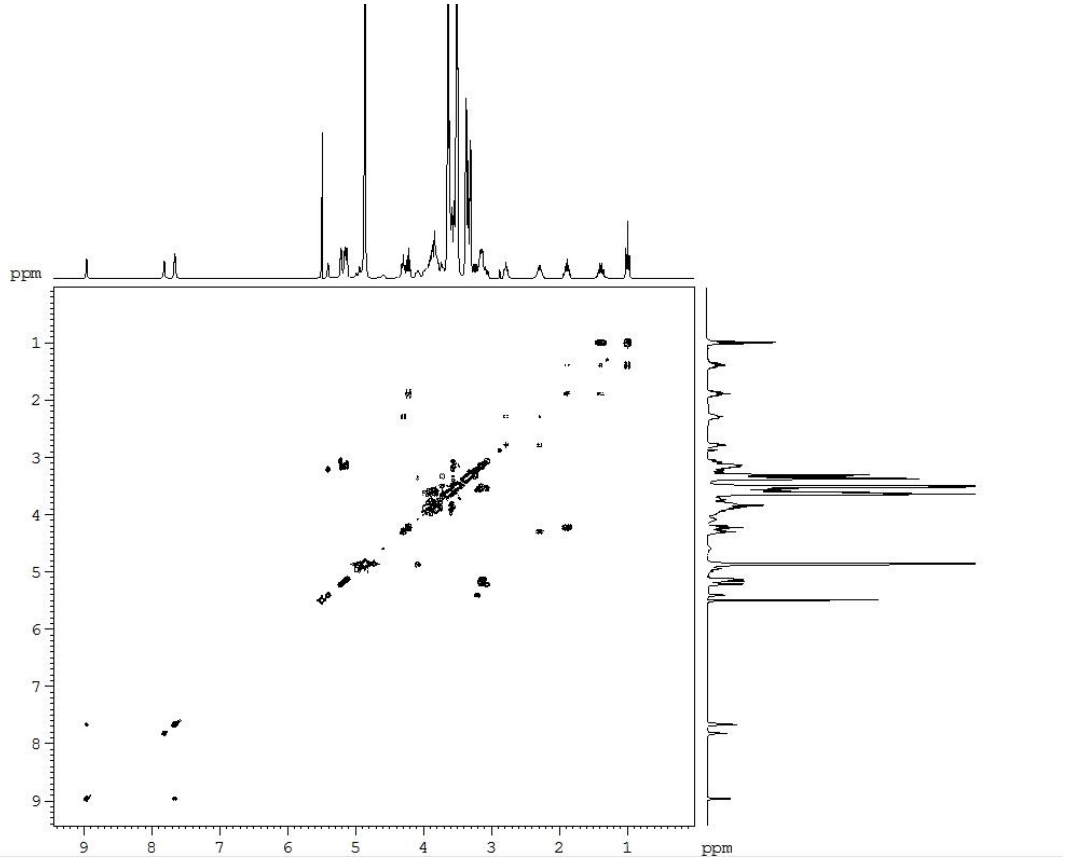


Fig. 31. ^{1}H-^{1}H COSY (300 MHz, CD_3OD) of **11**.

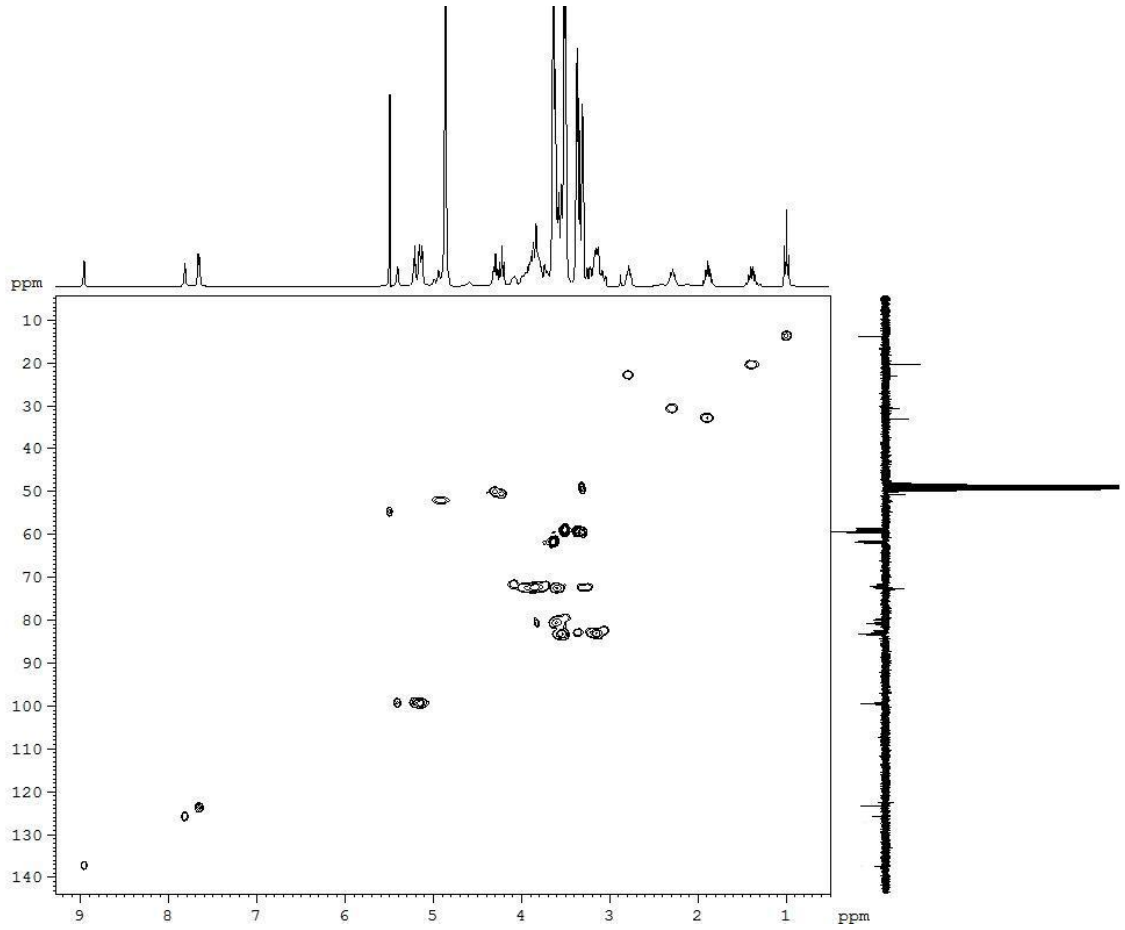


Fig. 32. ^{1}H-^{13}C HSQC (300/75 MHz, CD_3OD) of **11**.

1-butyl-3-[1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-yl methyl]imidazolium bromide (3).

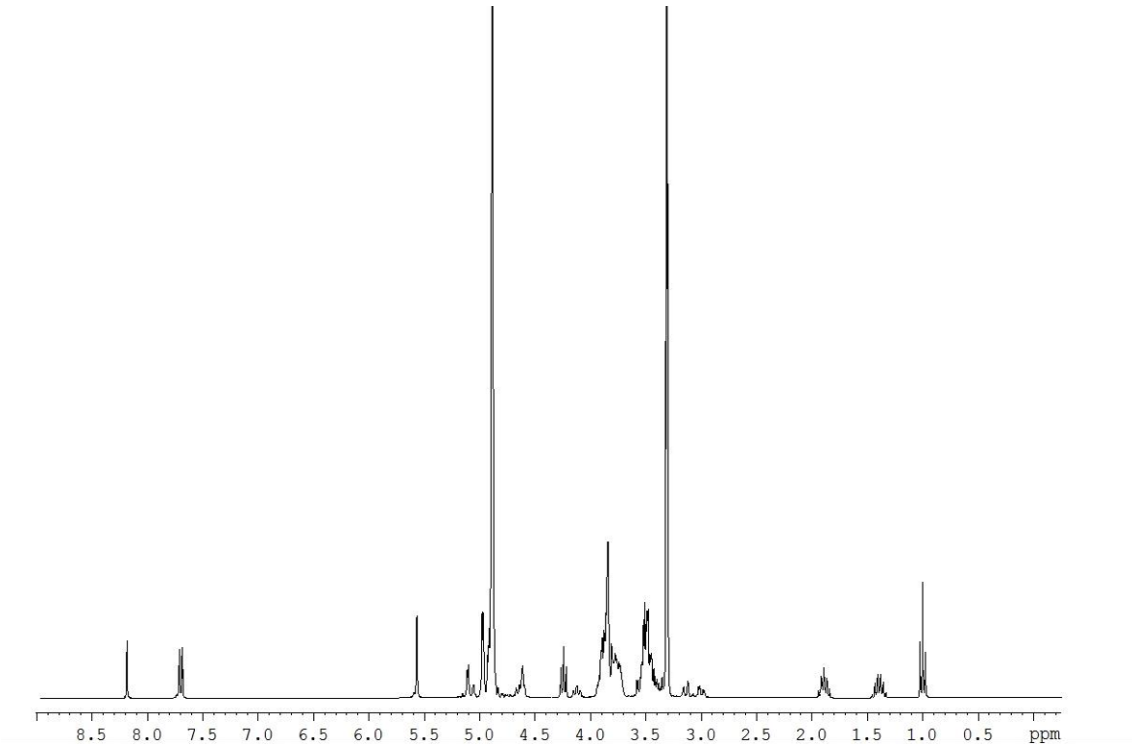


Fig. 33. ^{1}H NMR (300 MHz, CD_3OD) of **3**.

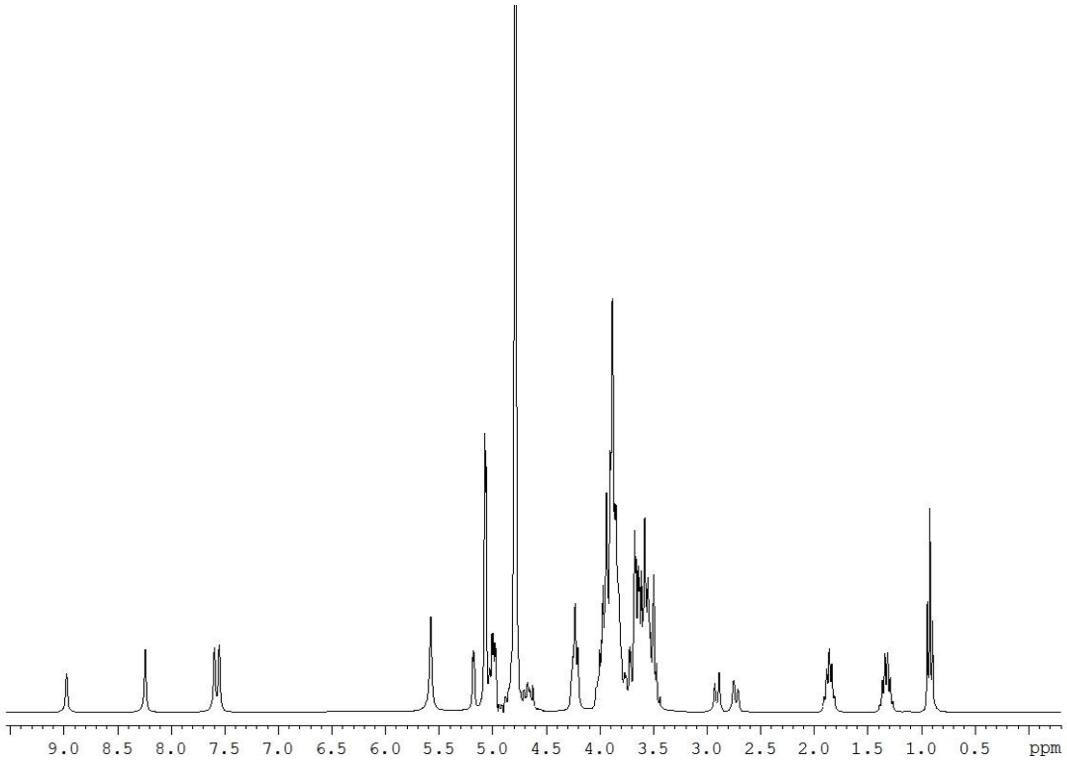


Fig. 34. ^{1}H NMR (300 MHz, D_2O) of **3**.

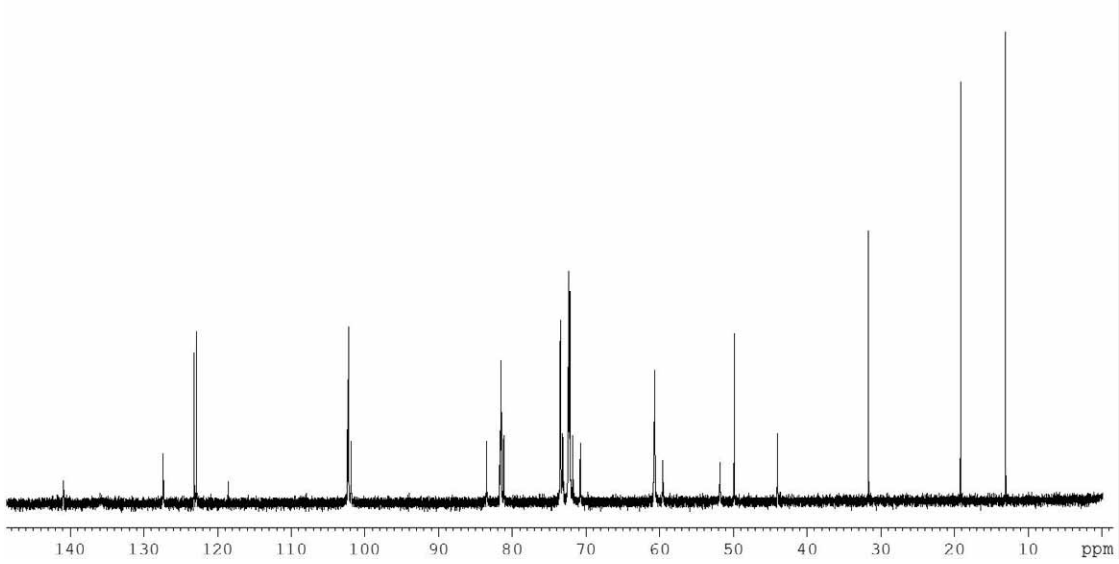


Fig. 35. ^{13}C NMR (75 MHz, D_2O) of **3**.

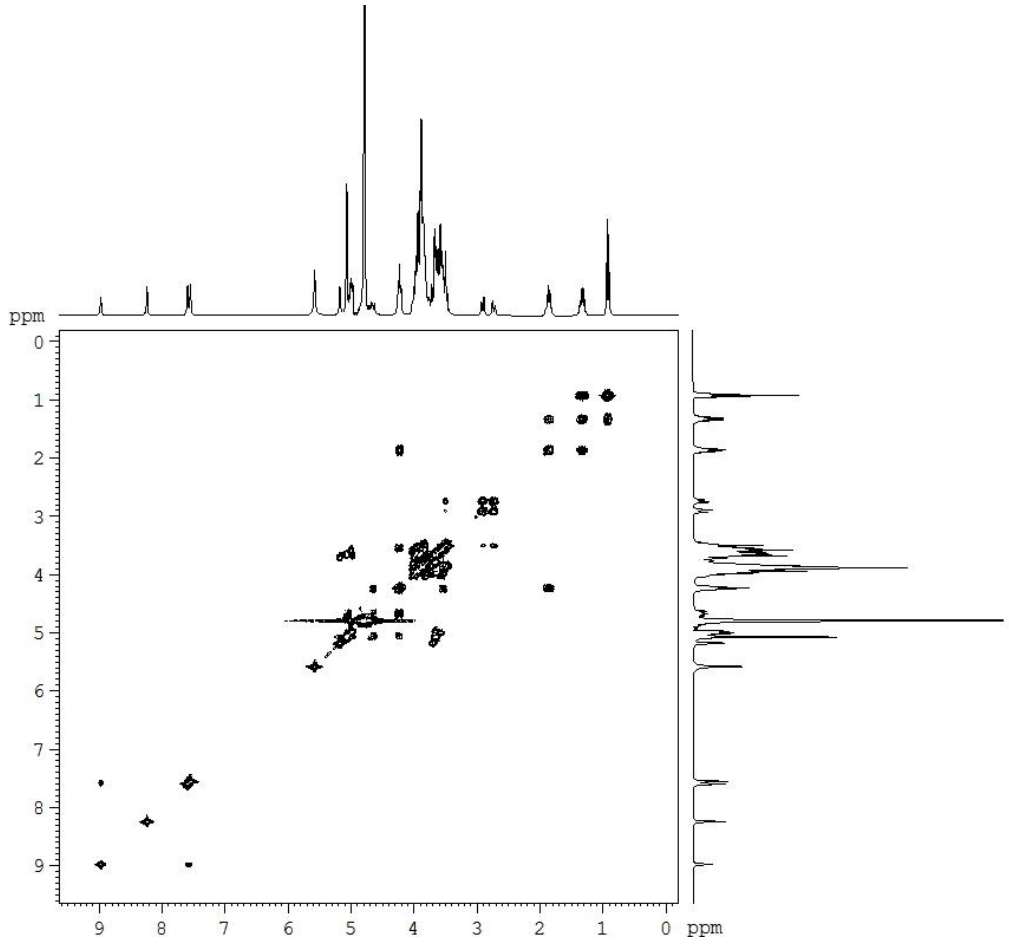


Fig. 36. ^{1}H-^{1}H COSY (300 MHz, D_2O) of **3**.

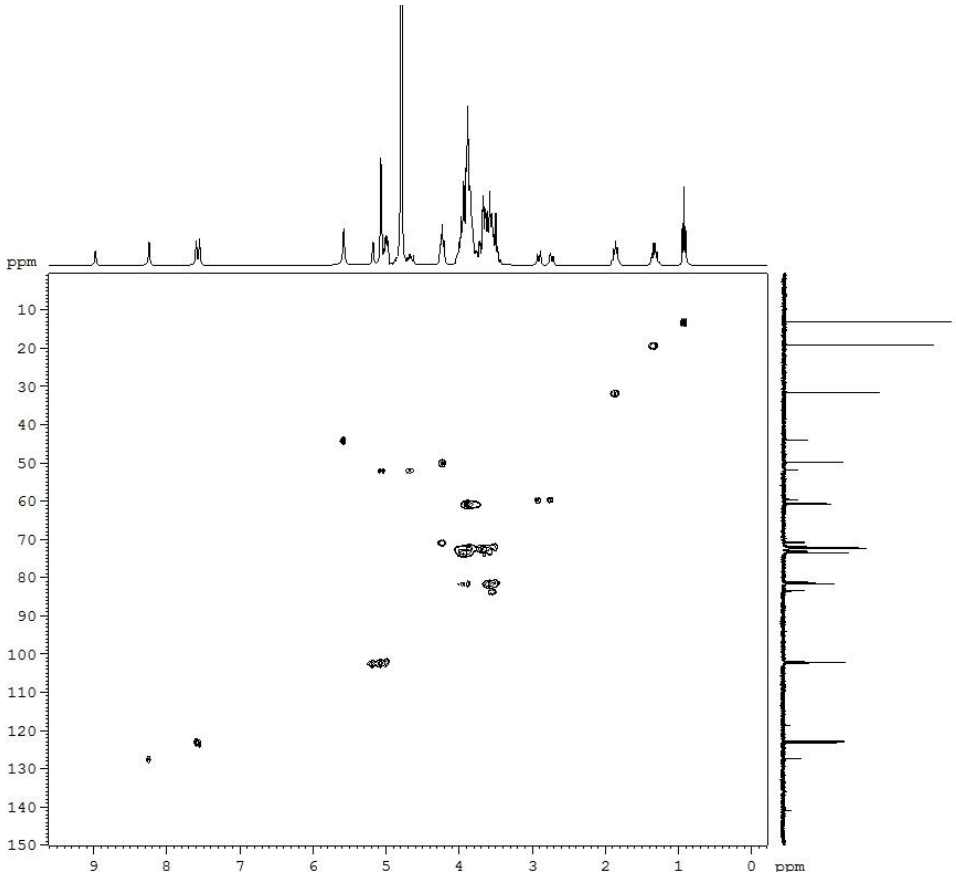


Fig. 37. ^{1}H-^{13}C HSQC (300/75 MHz, D_2O) of **3**.

1-butyl-3-[3-(1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-yl) propyl]imidazolium chloride (4).

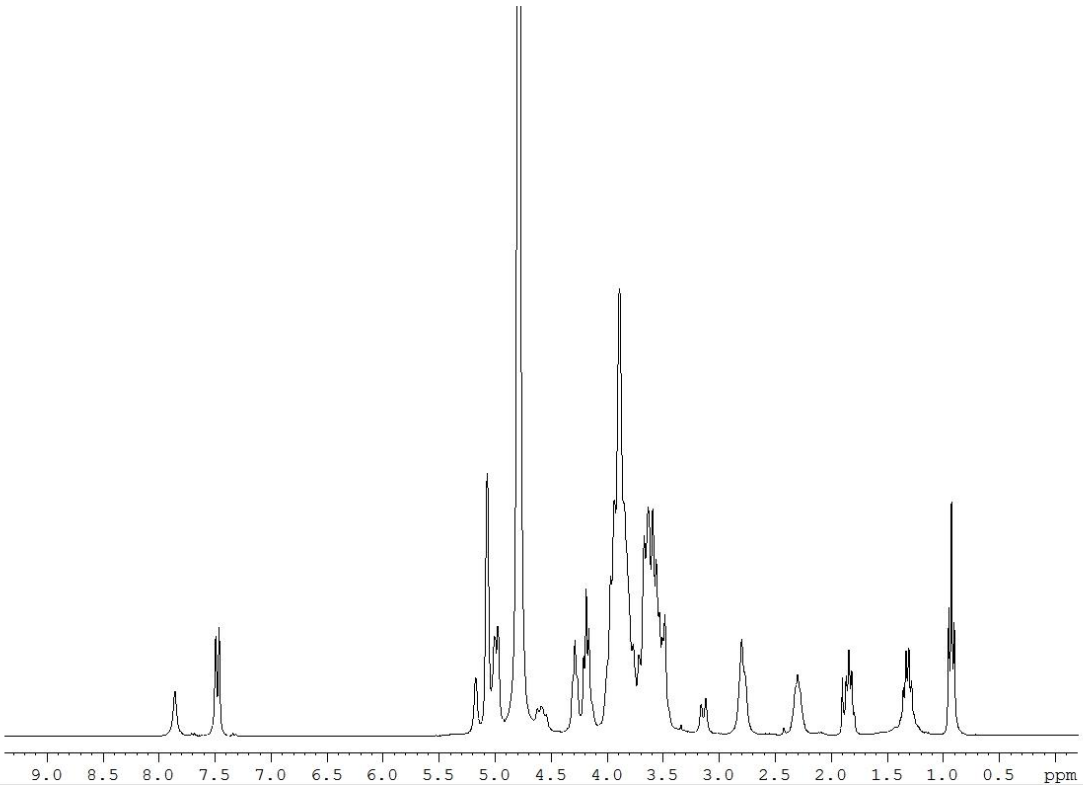


Fig. 38. ^{1}H NMR (300 MHz, D_2O) of **4**.

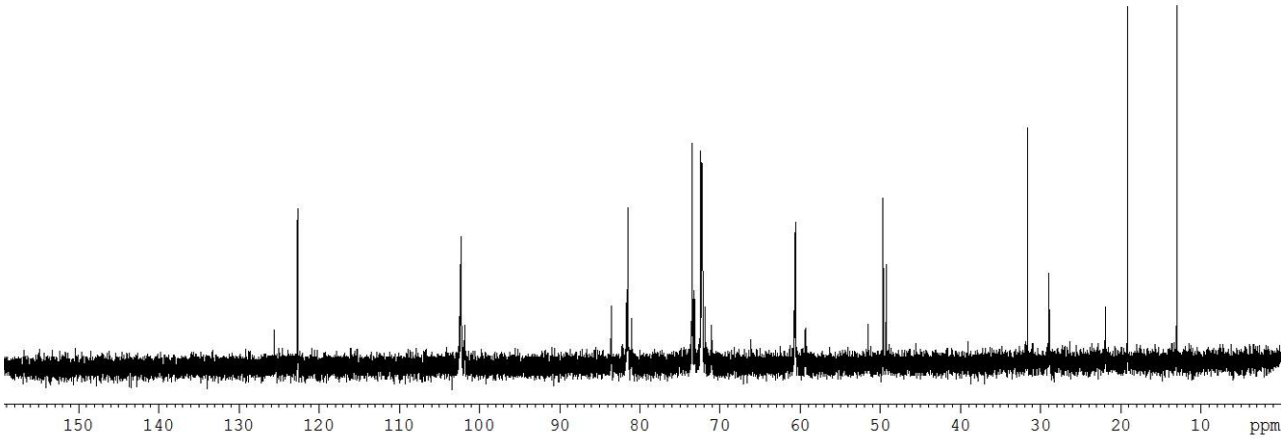


Fig. 39. ^{13}C NMR (75 MHz, D_2O) of **4**.

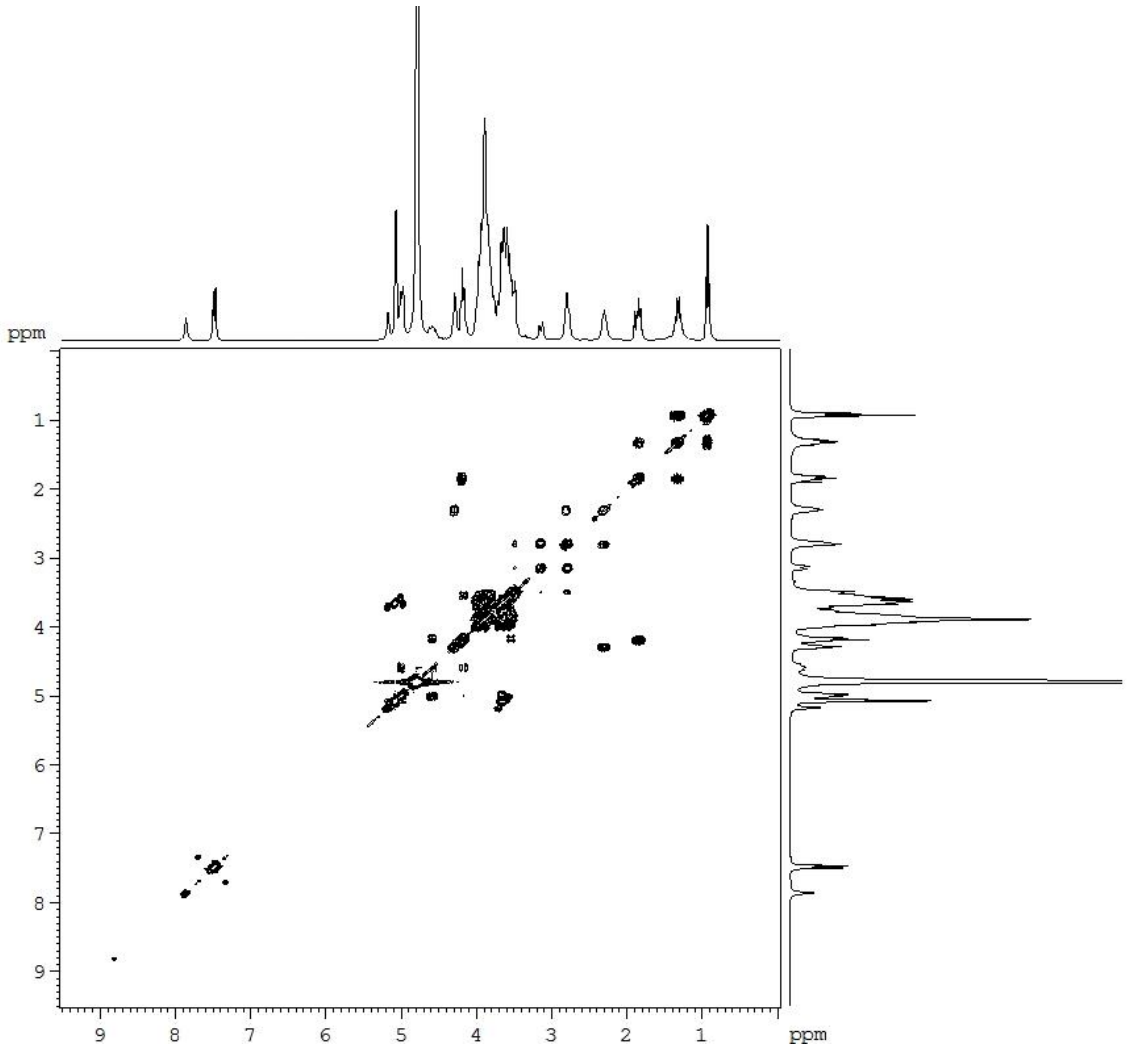


Fig. 40. ^{1}H-^{1}H COSY (300 MHz, D_2O) of **4**.

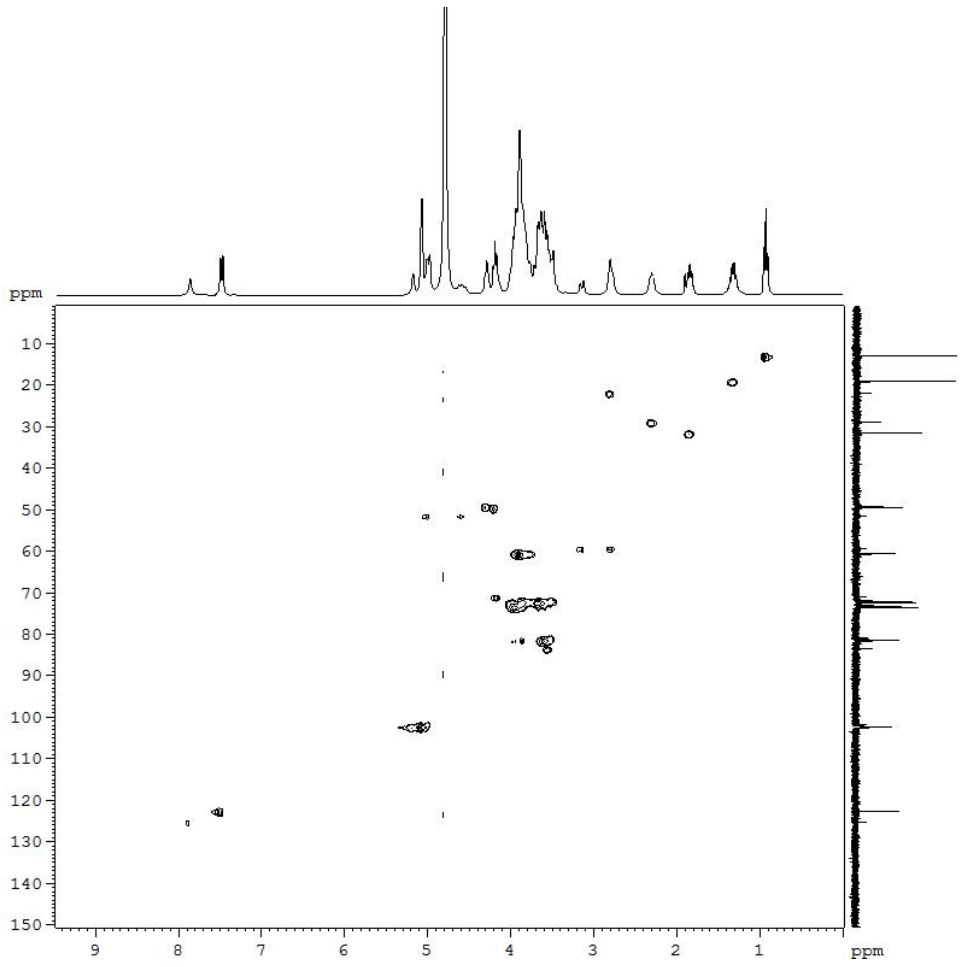


Fig. 41. ^{1}H-^{13}C HSQC (300/75 MHz, D_2O) of **4**.

1-butyl-3-[1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-ylmethyl]imidazolium hexafluorophosphate (5).

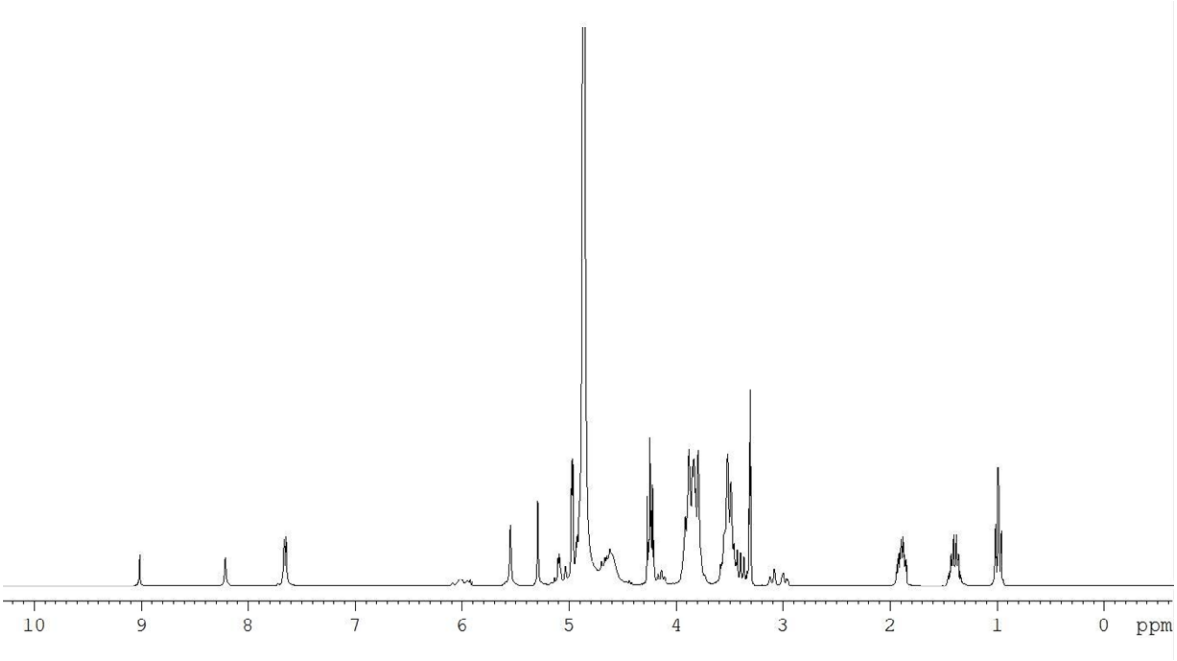


Fig. 42. ^{1}H NMR (300 MHz, CD_3OD) of **5**.

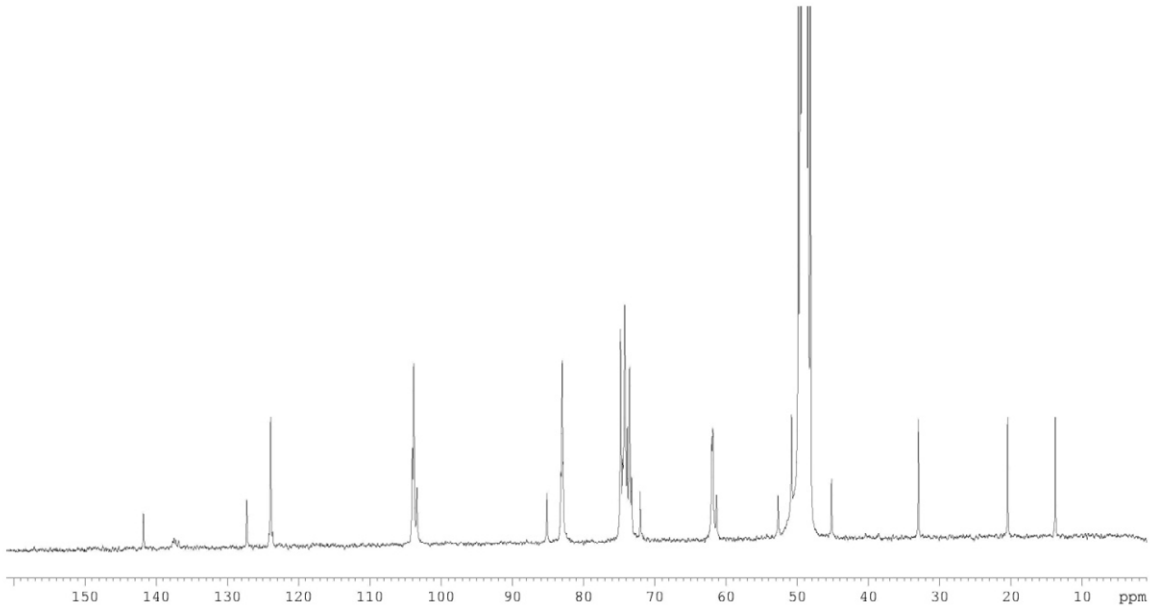


Fig. 43. ^{13}C NMR (75 MHz, CD_3OD) of **5**.

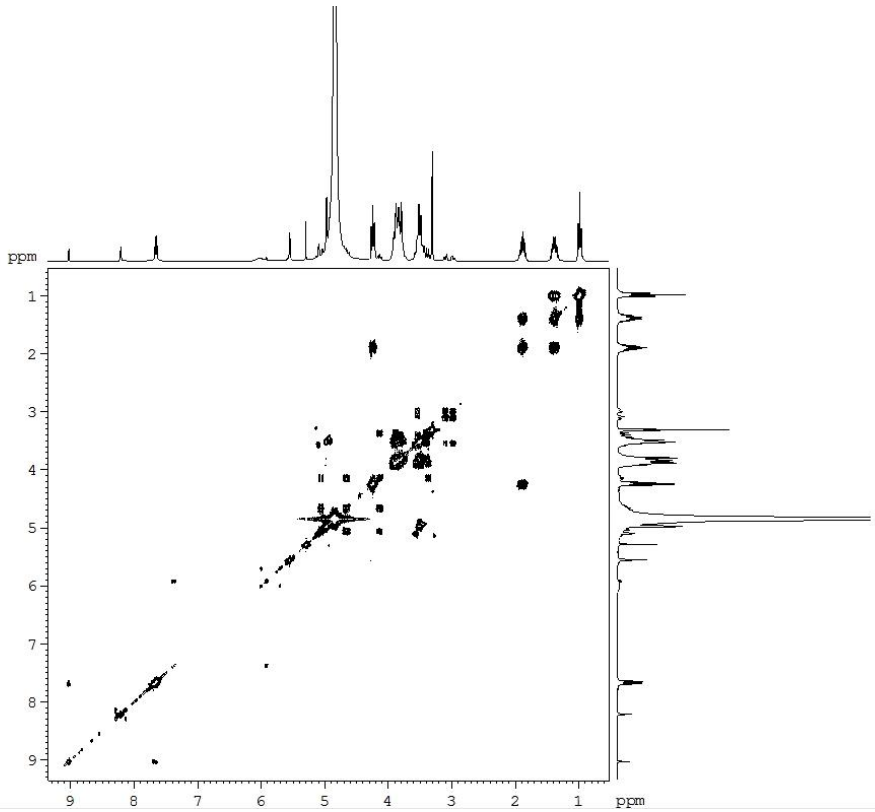


Fig. 44. ^{1}H-^{1}H COSY (300 MHz, CD_3OD) of **5**.

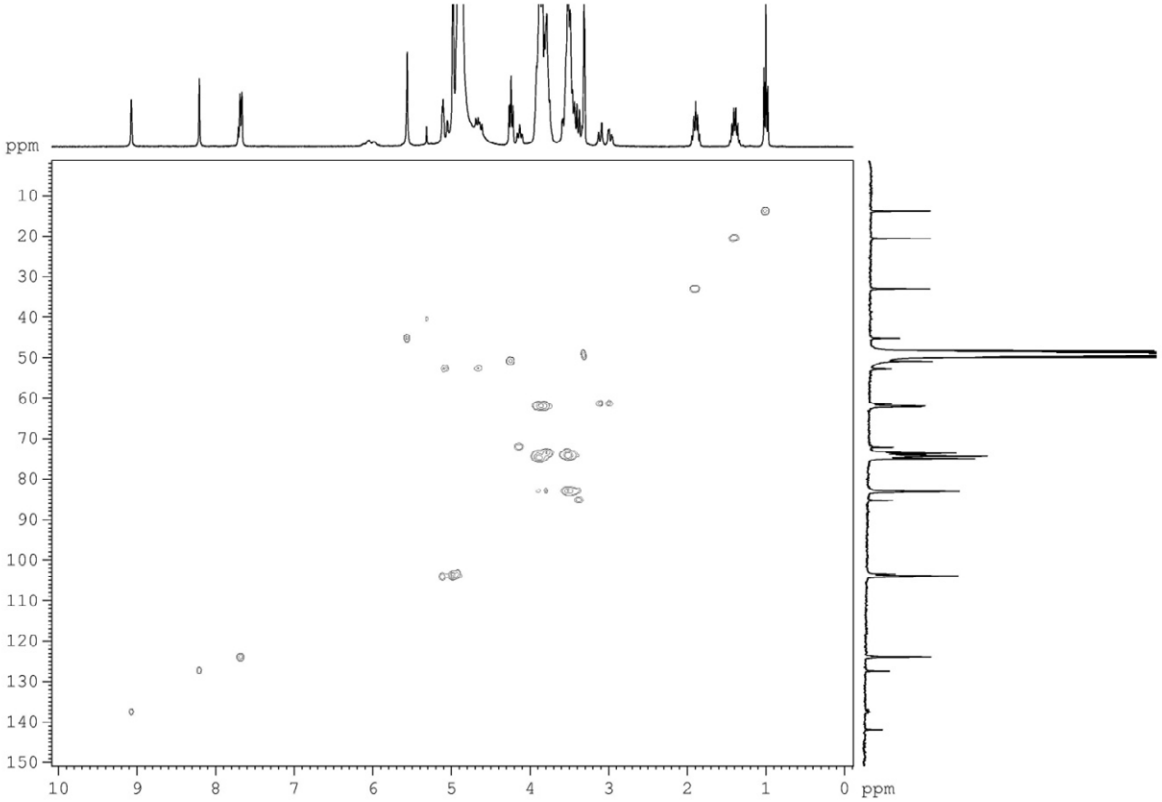


Fig. 45. ^{1}H-^{13}C HSQC (300/75 MHz, CD_3OD) of **5**.

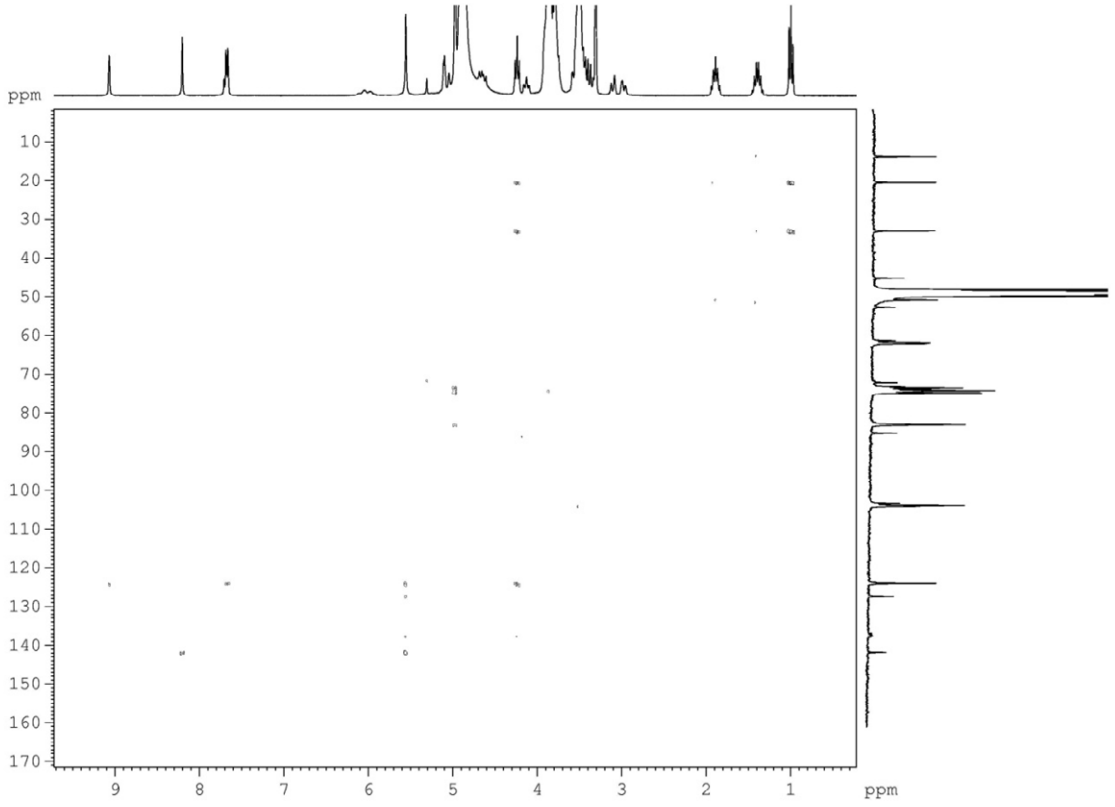


Fig. 46. ^{1}H-^{13}C HMBC (300/75 MHz, CD_3OD) ($J^{3}_{H\text{-}C}$ = 8 Hz) of **5**.

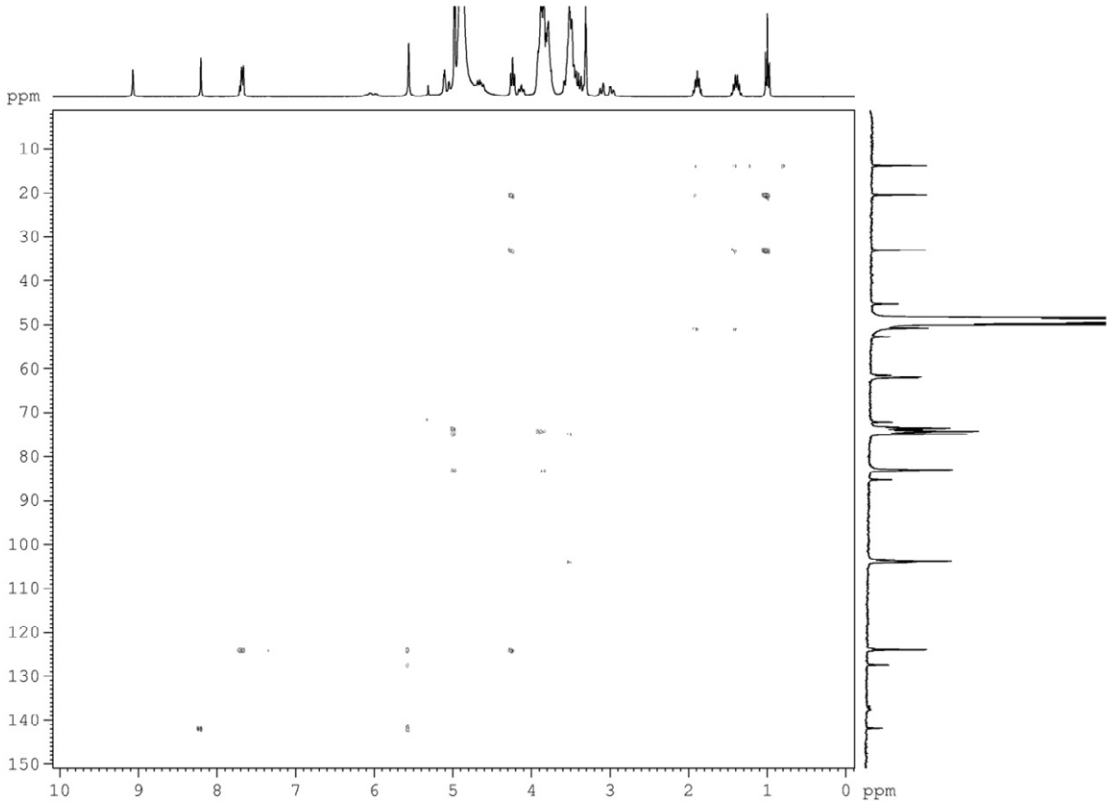


Fig. 47. ^{1}H-^{13}C HMBC (300/75 MHz, CD_3OD) ($J^{3}_{H\text{-}C}$ = 10 Hz) of **5**.

1-butyl-3-[3-(1-(6^{I}-deoxy-β-cyclodextrin-6^{I}-yl)triazol-4-yl) propyl]imidazolium hexafluorophosphate (6).

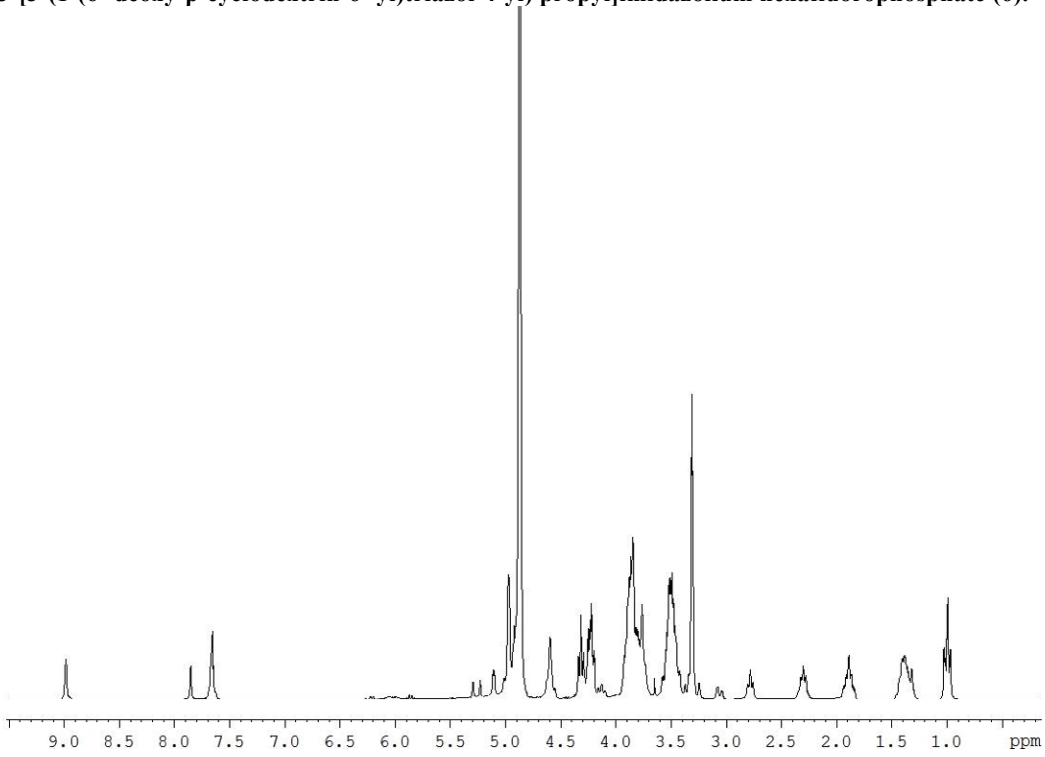


Fig. 48. ^{1}H NMR (300 MHz, CD_3OD) of **6**.

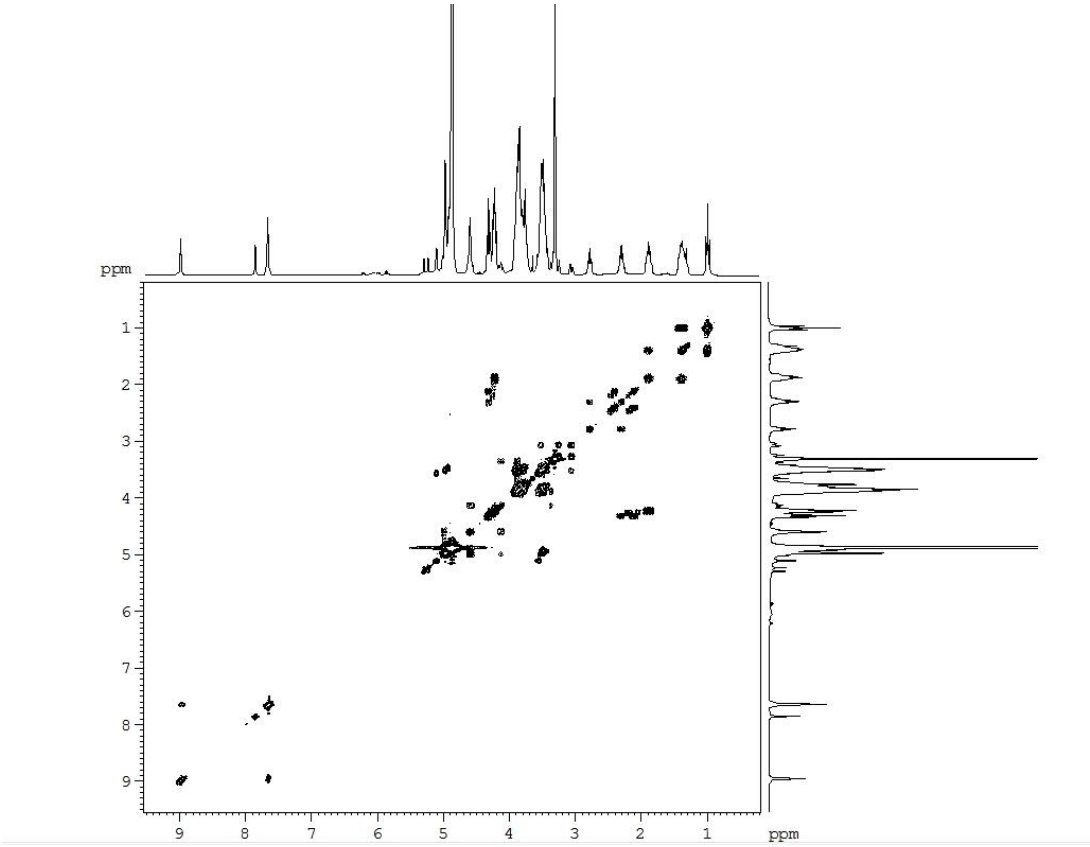


Fig. 49. ^{1}H-^{1}H COSY (300 MHz, CD_3OD) of **6**.

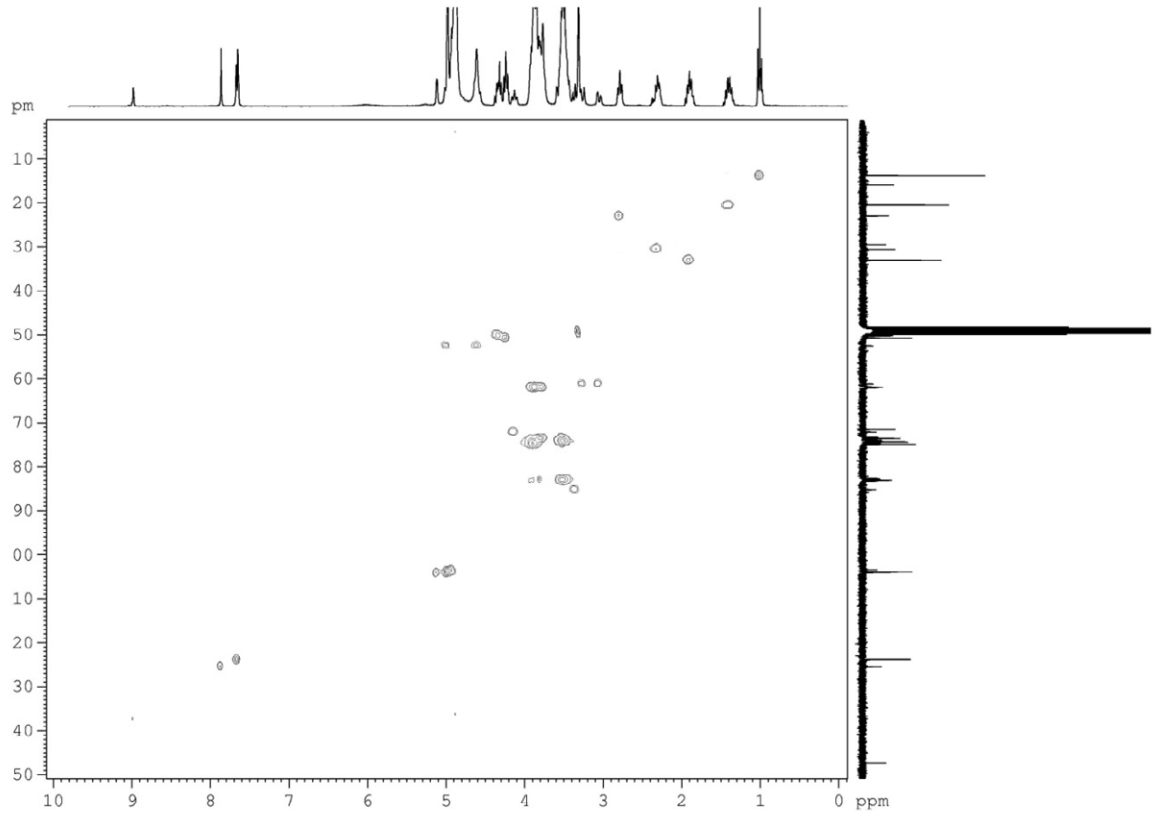


Fig. 50. ^{1}H-^{13}C HSQC (300/75 MHz, CD_3OD) of **6**.

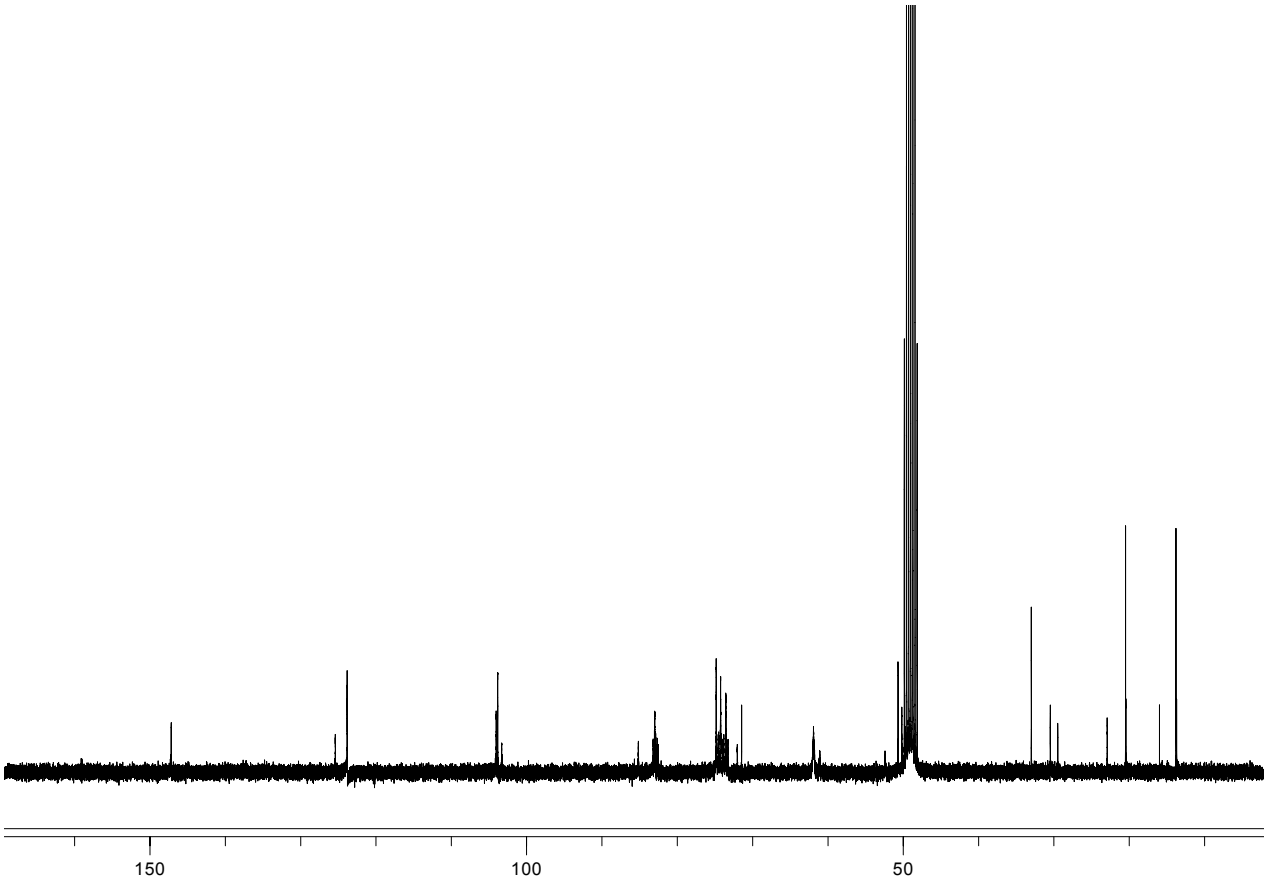


Fig. 51. ^{13}C NMR (75 MHz, CD_3OD) of **6**.

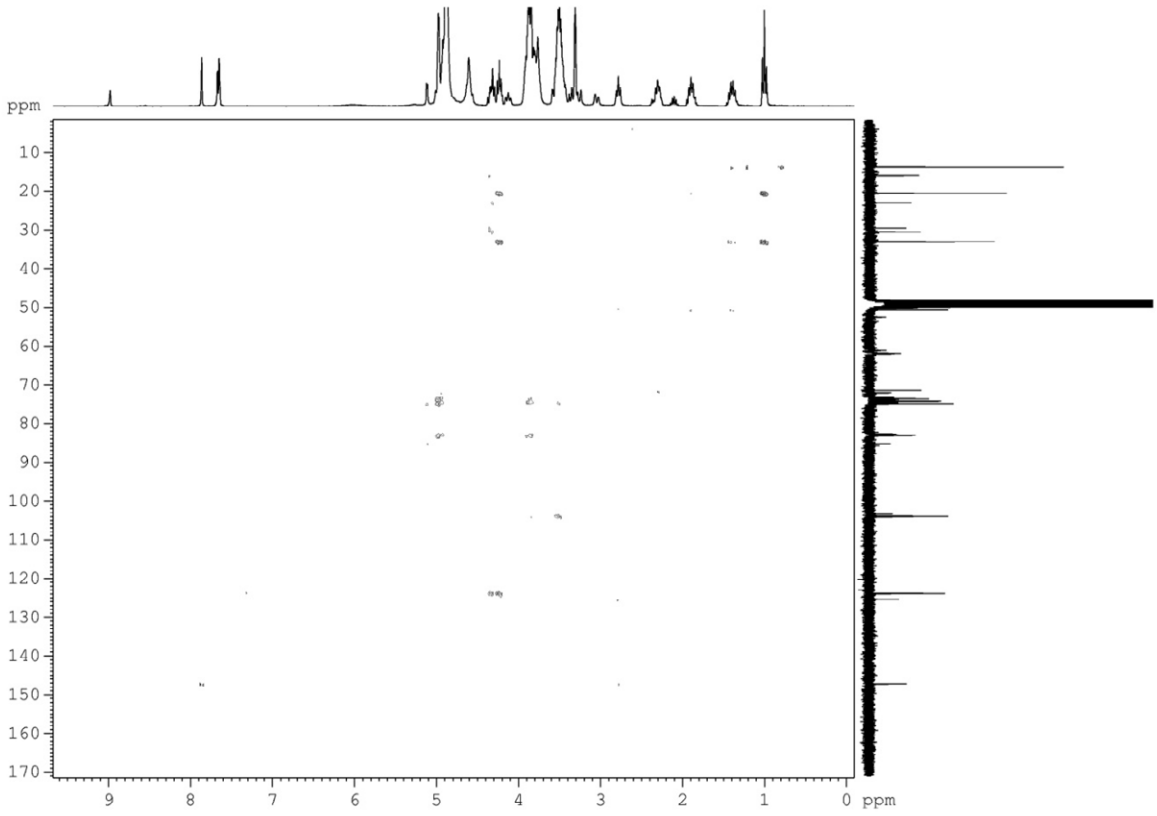


Fig. 52. ^{1}H-^{13}C HMBC (300/75 MHz, CD_3OD) ($J^{3}_{H\text{-}C}$ = 8 Hz) of **6**.

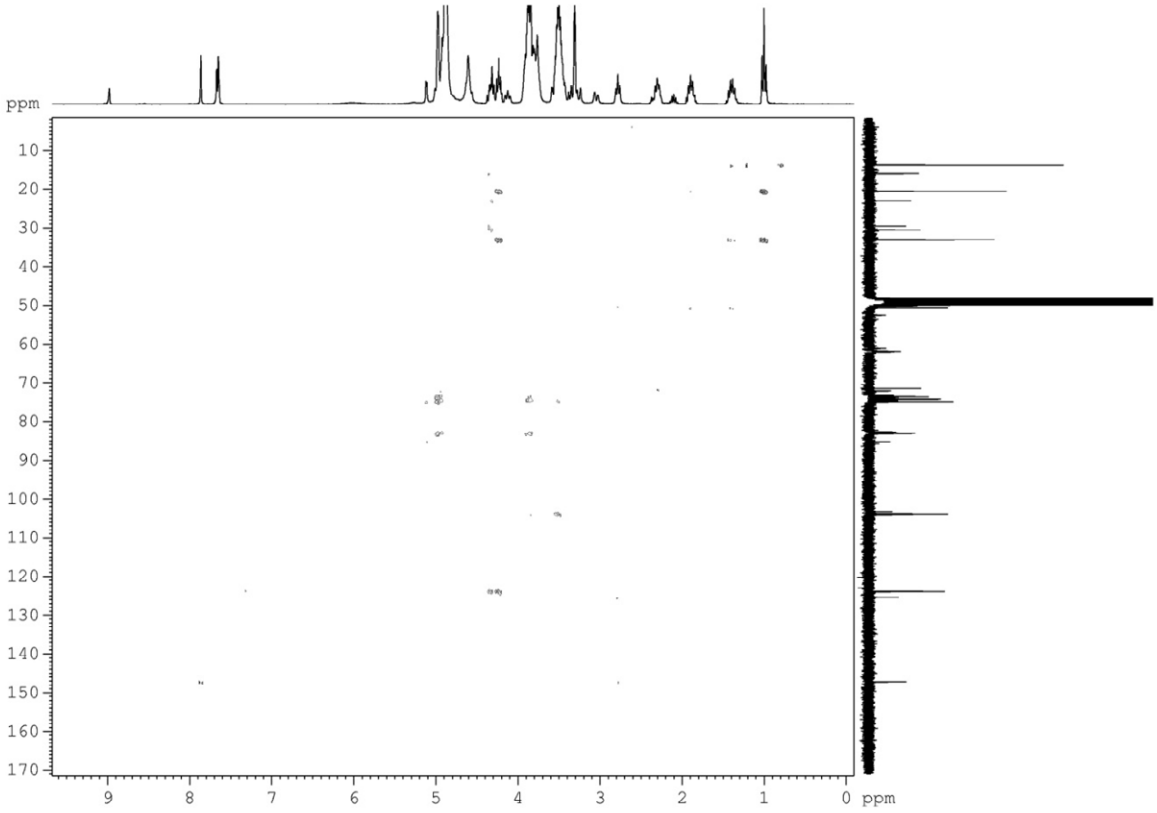
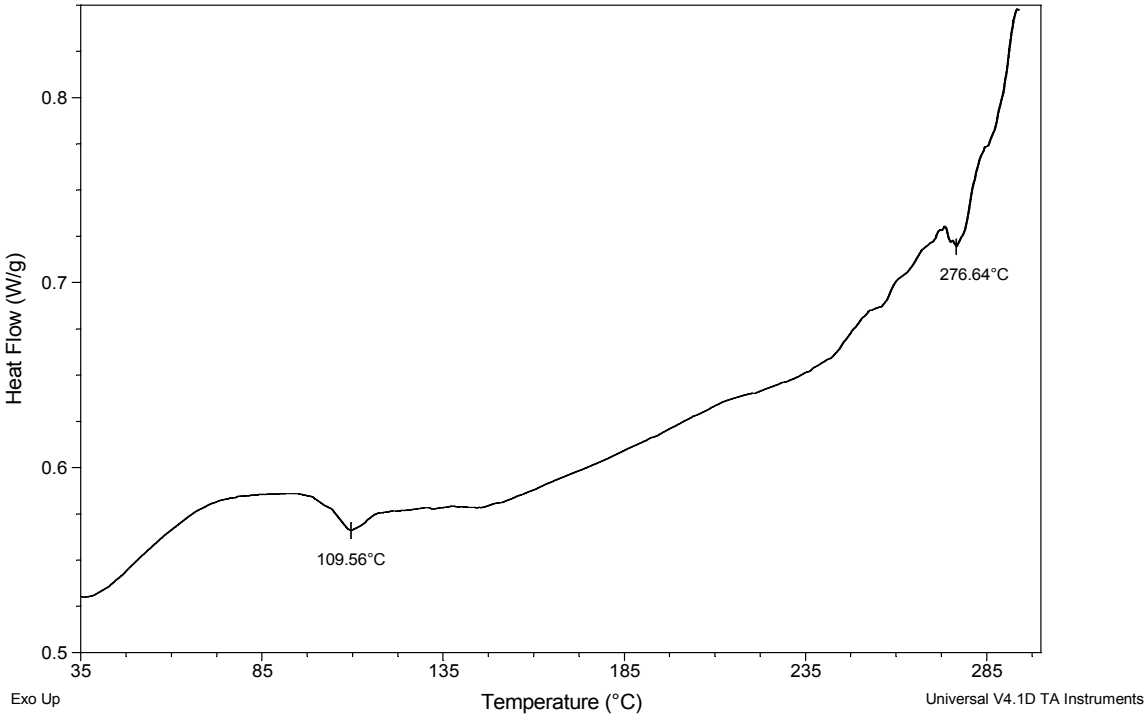


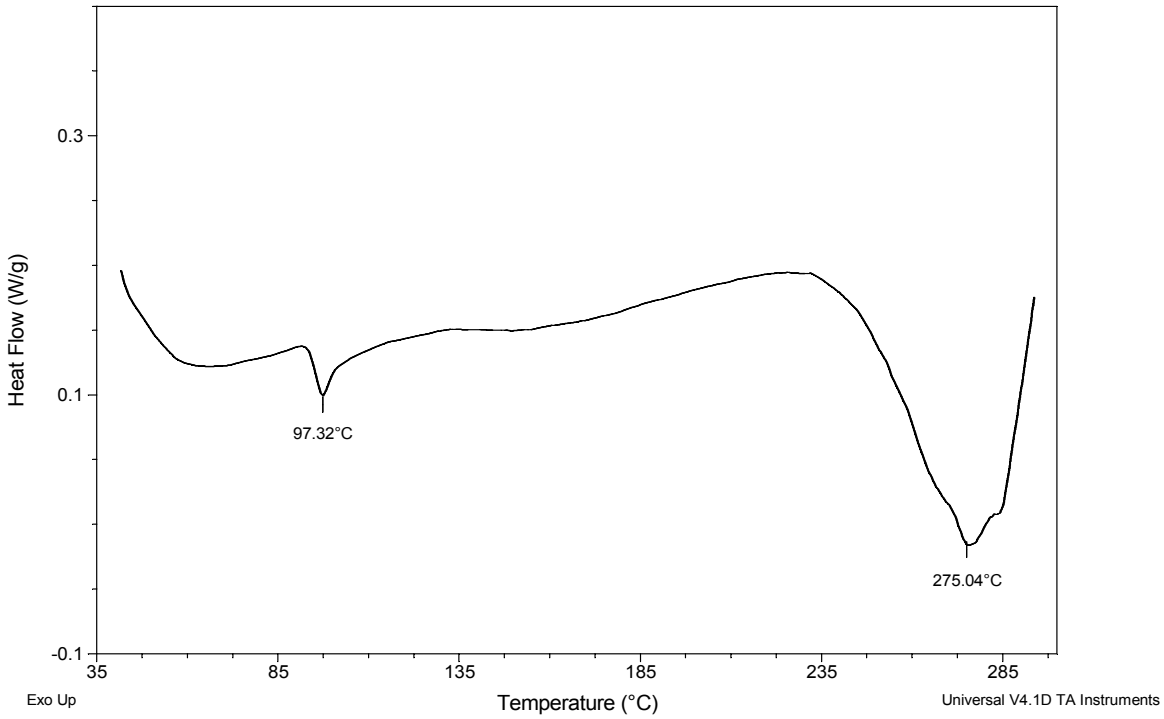
Fig. 53. ^{1}H-^{13}C HMBC (300/75 MHz, CD_3OD) ($J^{3}_{H\text{-}C}$ = 10 Hz) of **6**.

DSC analyses

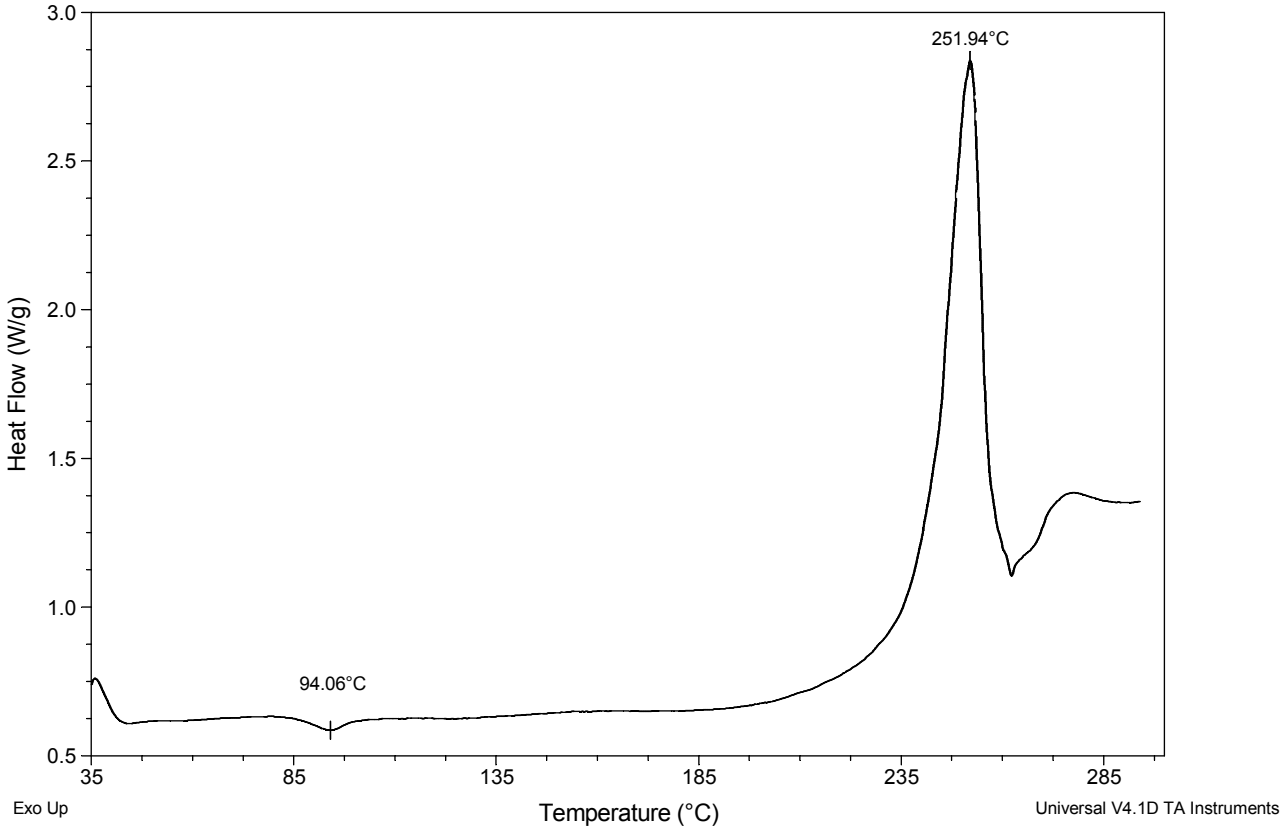
1-butyl-3-[1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-ylmethyl]imidazolium bromide (8).



1-butyl-3-[3-(1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-yl)propyl]imidazolium chloride (9).



1-butyl-3-[1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-ylmethyl]imidazolium hexafluorophosphate (10).



1-butyl-3-[3-(1-(6^{I}-deoxy-6^{II-VII},2^{I-VII},3^{I-VII}-*O*-permethyl-β-cyclodextrin-6^{I}-yl)triazol-4-yl)propyl]imidazolium hexafluorophosphate (11).