[1]Rotaxanes based on phosphorylated pillar[5]arenes

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Electronic Supplementary Information (48 pages)

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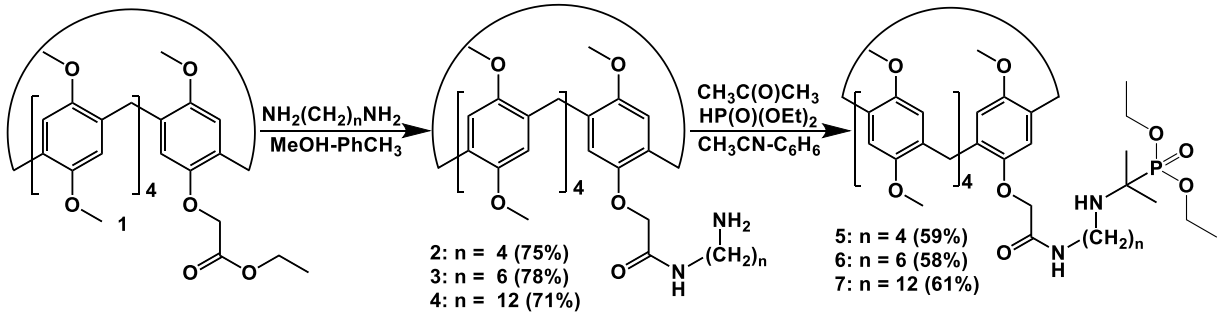
1. Materials and Methods

All chemicals were purchased from Acros (Fair Lawn, NJ, USA), and most of them were used as received without additional purification. Organic solvents were purified by standard procedures. ^{1}H, ^{13}C and 2D NOESY NMR spectra were obtained on a Bruker Avance-400 spectrometer (Bruker Corp., Billerica, MA, USA) ($^{13}C\{^{1}H\}$ - 100 MHz and ^{1}H and 2D NOESY - 400 MHz). The chemical shifts were determined against the signals of residual protons of deuterated solvent ($CDCl_3$, DMSO-d_6). The concentrations of the compounds were equal to 3-5% in all the records. Spectrum 400 (PerkinElmer) IR spectrometer, Bruker Ultraflex III MALDI-TOF (p-nitroaniline matrix, electrospray ionization with positive ions registration in the m/z range from 100 to 2800) were applied for the IR and mass spectra recording, respectively, and PerkinElmer 2400 Series II for elemental analysis. DataAnalysis 4.0 software (Bruker Daltonik GmbH, Bremen, Germany) was used for spectra analysis.

2. Synthesis



4-(Ethoxycarbonylmethoxy)-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (1) was synthesized according to the literature [S1]. Yield: 2.48 g (76%). M.p.: 209 °C (208-210 °C [S1]).

General procedure for the synthesis of the pillar[5]arenes 2-4.

In a round-bottom flask equipped with magnetic stirrer and reflux condenser with the calcium chloride tube, 0.2 g (0.24 mmol) of monoester **1** were dissolved in the solvents mixture (5 ml of methanol and 5 ml of toluene) and 0.73 mmol of corresponding amine (0.064 g of 1,4-butanediamine, 0.085 g of 1,6-hexanediamine, 0.150 g of 1,12-dodecanediamine) were added. The reaction mixture was refluxed for 52 hours. The resulting precipitate was dissolved in a minimal amount of chloroform and poured into an excess of the methanol. The formed precipitate was filtered off and dried under reduced pressure over phosphorus pentoxide.

4-[(*N*-{4'-Aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxy-pillar[5]arene (2).

Yield: 0.16 g (75%). M.p.: 227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.43 (m, 2H, -NHC$\underline{H_2}$-), -1.88 (m, 4H, -NHCH$_2$C$\underline{H_2}$C$\underline{H_2}$-), -0.53 (m, 2H, -NHCH$_2$CH$_2$CH$_2$C$\underline{H_2}$-), 0.45 (br.t., J = 5.6 Hz, 2H, -CH$_2$N$\underline{H_2}$), 3.74-3.80 (m, 37H, -CH$_2$- and -OCH$_3$), 4.57 (s, 2H, ArOCH$_2$-), 4.82 (br.t., J = 4.6 Hz, 1H, -C(O)NH-), 6.72-6.97 (m, 10H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.18, 22.71, 28.62, 28.71, 29.55, 29.77, 30.67, 37.96, 41.52, 55.23, 55.26, 55.42, 55.48, 55.53, 55.62, 55.68, 65.98, 112.47, 112.55, 112.63, 112.69, 112.96, 113.29, 113.49, 113.82, 113.86, 126.70, 126.87, 128.18, 128.67, 129.37, 129.78, 147.43, 150.05, 150.32, 150.67, 150.89, 167.24; IR ν: 1207, 1684, 3408, 3736 cm^{-1}; MS (m/z): (MALDI-TOF) Calcd. for $C_{50}H_{60}N_2O_{11}$ [M+H$^+$] 865.4, found: 865.6; Elemental analysis. Found (%): C, 69.87; H, 7.13; N, 3.30. $C_{50}H_{60}N_2O_{11}$. Calculated

(%):C, 69.43; H, 6.99; N, 3.24; ^{1}H-^{1}H NOESY NMR (most important cross-peaks): H^1/H^4, H^1/H^5, H^1/H^6, H^1/H^7, H^3/H^9.

4-[(*N*-{6'-Aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxy-pillar[5]arene (3).

Yield: 0.17 g (78%). M.p.: 218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: -1.99 (m, 2H, -NHC$\underline{H_2}$-), -1.80 (m, 2H, -NHCH$_2$C$\underline{H_2}$-), -0.70 (m, 2H, -NHCH$_2$CH$_2$C$\underline{H_2}$-), -0.56 (m, 2H, -NHCH$_2$CH$_2$CH$_2$C$\underline{H_2}$-), 1.12 (m, 4H, -C$\underline{H_2}$C$\underline{H_2}$NH$_2$), 1.81 (t, *J* = 6.6 Hz, 2H, -CH$_2$N$\underline{H_2}$), 3.74-3.81 (m, 37H, -CH$_2$- and -OCH$_3$), 4.60 (s, 2H, ArOCH$_2$-), 5.43 (m, 1H, -C(O)NH-), 6.77-6.98 (m, 10H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.80, 23.95, 26.81, 28.68, 28.93, 29.22, 29.64, 29.77, 33.60, 38.07, 42.22, 42.39, 55.09, 55.32, 55.43, 55.54, 55.76, 55.85, 55.94, 66.02, 112.08, 112.46, 112.75, 112.83, 112.97, 113.40, 113.67, 113.77, 114.04, 127.23, 127.60, 127.72, 128.02, 128.18, 128.29, 128.45, 128.95, 129.08, 147.04, 149.95, 150.20, 150.31, 150.51, 150.73, 150.77, 167.76; IR ν: 1206, 1686, 3414, 3608 cm^{-1}; MS (m/z): (MALDI-TOF) Calcd. for $C_{52}H_{64}N_2O_{11}$ [M+H$^+$] 893.5, found: 893.4; Elemental analysis. Found (%):C, 70.03; H, 7.49; N, 3.46. $C_{52}H_{64}N_2O_{11}$. Calculated (%): C, 69.93; H, 7.22; N, 3.14.; ^{1}H-^{1}H NOESY NMR (most important cross-peaks): H^1/H^4, H^1/H^5, H^1/H^6, H^1/H^7, H^1/H^8, H^1/H^9, H^3/H^{10}, H^3/H^{11}.

4-[(*N*-{12'-Aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxy-pillar[5]arene (4).

Yield: 0.17 g (71%). M.p.: 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.32 (m, 2H, -NHC$\underline{H_2}$-), -1.34 (m, 4H, -NHCH$_2$C$\underline{H_2}$C$\underline{H_2}$-), -0.09 (m, 2H, -NHCH$_2$CH$_2$CH$_2$C$\underline{H_2}$-), 0.75 (m, 2H, -NHCH$_2$CH$_2$CH$_2$CH$_2$C$\underline{H_2}$-), 1.15 (m, 2H, -NH(CH$_2$)$_5$C$\underline{H_2}$-), 1.33-1.48 (m, 12H, -CH$_2$(C$\underline{H_2}$)$_6$NH$_2$-), 2.73 (t, *J* = 7.0 Hz, 2H, -CH$_2$N$\underline{H_2}$), 3.72-3.79 (m, 37H, -CH$_2$- and -OCH$_3$), 4.58 (s, 2H, ArOCH$_2$), 5.10 (m, 1H, C(O)NH), 6.70-7.94 (m, 10H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 3.77, 26.72, 27.29, 28.37, 28.82, 28.96, 29.38, 30.11, 30.36, 30.65, 30.96, 34.04, 38.15, 55.26, 55.32, 55.44, 55.47, 55.52, 55.56, 55.67, 66.00, 112.49, 112.63, 112.84, 113.28, 113.42, 113.60, 113. 82, 113.98, 126.96, 127.21, 127.90, 128.02, 128.47, 129.15, 129.34, 150.07, 150.12, 150.25, 150.38, 150.47, 150.59, 150.65, 167.34; IR ν: 1207, 1684, 3413, 3615 cm^{-1}; MS (m/z): (MALDI-TOF) Calcd. for $C_{58}H_{76}N_2O_{11}$ [M+H$^+$] 977.5, found: 977.6; Elemental analysis. Found (%): C, 71.29; H, 7.84; N, 2.87. $C_{58}H_{76}N_2O_{11}$. Calculated (%): C, 72.05; H, 7.69; N, 2.89; ^{1}H-^{1}H NOESY NMR (most important cross-peaks): H^1/H^4, H^1/H^5, H^1/H^7, H^1/H^8, H^3/H^9, H^3/H^{10}, H^3/H^{11}.

General procedure for the synthesis of pillar[5]arenes 5-7.

In a round-bottom flask equipped with magnetic stirrer and the calcium chloride tube, 0.24 mmol of pillar[5]arenes **2-4** was dissolved in the solvents mixture (5 ml of acetonitrile and 5 ml of benzene), 1.4 mmol of acetone was added and refluxed for one hour. Then, 0.72 mmol of diethyl phosphite were added to the reaction mixture followed by its refluxing for 53 hours. The solvents were evaporated under reduced pressure. The resulting precipitate was dissolved in a minimal amount of the chloroform. An excess of diethyl phosphite was extracted with water (3×10 ml). The organic layer was dried over molecular sieves (3Å). Then the sieves were filtered off, and the solvent was evaporated under reduced pressure. The formed precipitate was dried under reduced pressure over phosphorus pentoxide.

4-[(*N*-[1-(O,O-Diethylphosphoryl)-1-methylethyl]-{4'-aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35- nonamethoxy-pillar[5]arene (5).

Yield: 0.15 g (59%). D.t.: 167 °C; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 30.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.16 (m, 2H, -C(O)NHC$\underline{H_2}$-), -1.51 (m, 2H, -C(O)NHCH$_2$C$\underline{H_2}$-), -0.07 (m, 2H,

-C(O)NHCH$_2$CH$_2$CH$_2$-), 1.16 (d, *J* = 15.6 Hz, 6H, -C(CH$_3$)$_2$), 1.23 (t, *J* = 7.0 Hz, 6H, -POCH$_2$CH$_3$), 1.96 (m, 2H, -C(O)NHCH$_2$CH$_2$CH$_2$CH$_2$-), 3.61-3.74 (m, 37H, -CH$_2$- и -OCH$_3$), 4.02 (m, 4H, -POCH$_2$CH$_3$), 4.32 (s, 1H, -CH$_2$NHC(CH$_3$)$_2$), 4.57 (s, 2H, ArOCH$_2$-), 5.03 (s, 1H, C(O)NH), 6.69-6.96 (m, 10H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 16.36, 22.16, 22.20, 22.78, 27.31, 27.65, 28.66, 28.73, 29.57, 29.79, 30.71, 32.60, 38.96, 40.56, 42.95, 56.79, 65.47, 68.08, 113.02, 113.63, 116.56, 126.74, 126.76, 128.38, 128.97, 129.67, 129.78, 131.48, 132.17, 133.59, 147.53, 149.23, 149.90, 150.15, 150.34, 150.68, 150.94, 169.75; IR ν: 1042, 1206, 1680, 3407, 3650 cm^{-1}; MS (m/z): (MALDI-TOF) Calcd. for $C_{57}H_{75}N_2O_{14}P$ [M+Na$^+$] 1045.5, found: 1066.2; Elemental analysis. Found (%): C, 65.87; H, 7.38; N, 2.55, P, 3.09. $C_{57}H_{75}N_2O_{14}P$. Calculated (%): C, 65.63; H, 7.25; N, 2.69, P, 2.97.

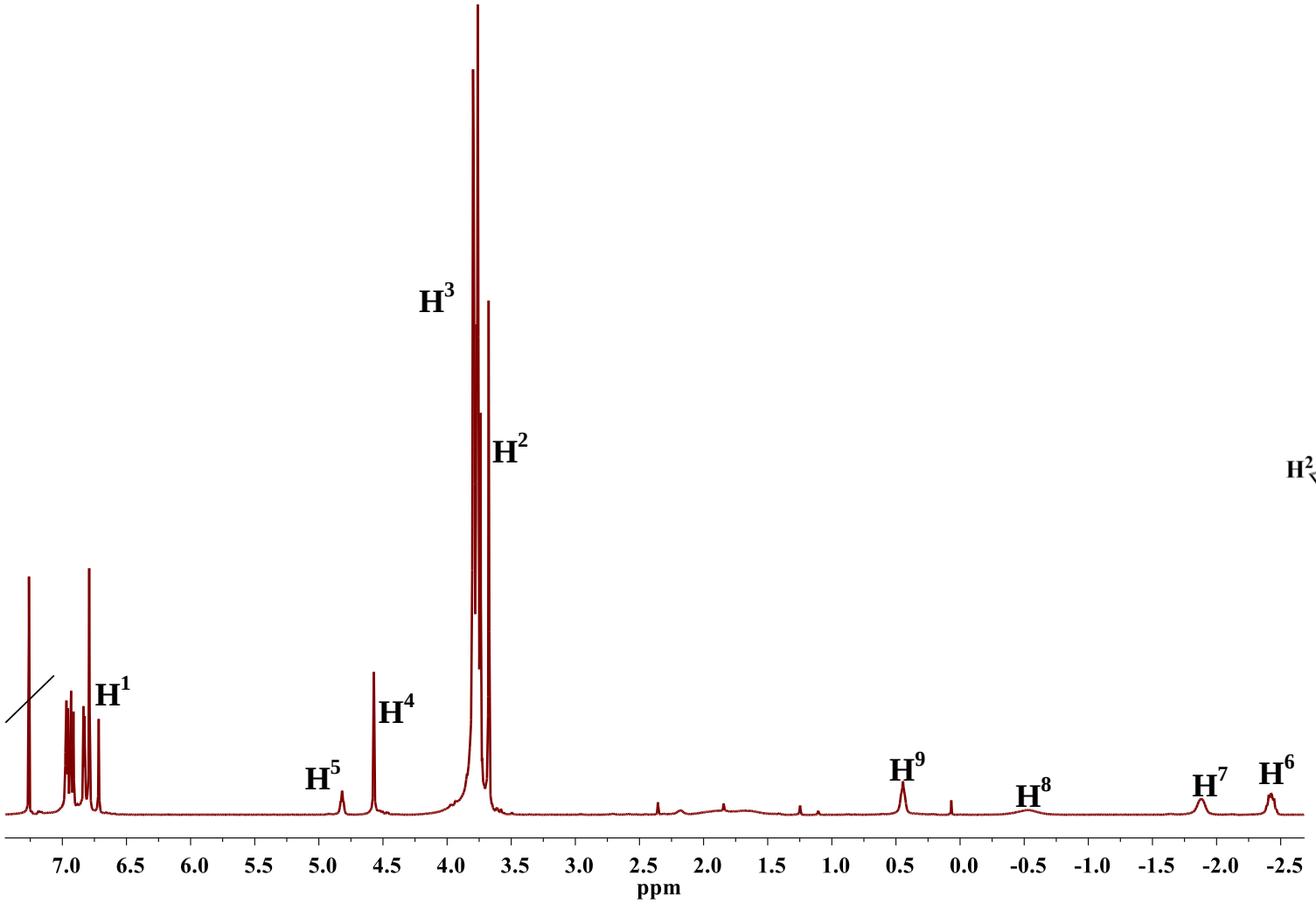
4-[(*N*-[1-(O,O-Diethylphosphryl)-1-methylethyl]-{6'-aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35- nonamethoxy-pillar[5]arene (6).

Yield: 0.15 г (58%). D.t.: 162 °C; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ: 31.3; ^{1}H NMR (400 MHz, CDCl$_3$) δ: -2.42 (m, 2H, -C(O)NHCH$_2$-), -1.82 (m, 2H, -C(O)NHCH$_2$CH$_2$-), -1.14 (m, 2H, -C(O)NHCH$_2$CH$_2$CH$_2$-), -0.54 (m, 2H, -C(O)NH(CH$_2$)$_3$CH$_2$-), 0.16 (m, 2H, -C(O)NH(CH$_2$)$_4$CH$_2$-), 1.16 (br.d., 6H, -C(CH$_3$)$_2$), 1.38 (t, *J* = 7.0 Hz, 6H, -POCH$_2$CH$_3$), 1.90 (m, 2H, -C(O)NH(CH$_2$)$_5$CH$_2$-), 3.67-3.77 (m, 37H, -CH$_2$- and -OCH$_3$), 4.17 (m, 4H, -POCH$_2$CH$_3$), 4.60 (s, 2H, ArOCH$_2$-), 4.92 (s, 1H, -CH$_2$NHC(CH$_3$)$_2$), 5.46 (s, 1H, C(O)NH), 6.70-6.99 (m, 10H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 16.78, 22.60, 23.53, 23.82, 26.25, 26.86, 28.07, 28.72, 29.37, 29.58, 29.74, 30.42, 30.82, 37.98, 38.12, 42.76, 42.85, 55.26, 55.52, 55.63, 55.89, 56.17, 62.03, 62.09, 66.00, 112.23, 112.58, 112.85, 113.49, 113.84, 114.41, 127.05, 128.05, 128.49, 129.27, 150.15, 150.26, 150.42, 150.62, 150.77, 150.90, 167.25, 167.88; IR ν: 1046, 1208, 1684, 3405, 3600 cm^{-1}; MS (m/z): (MALDI-TOF) Calcd. for $C_{59}H_{79}N_2O_{14}P$ [M+Na$^+$] 1093.5, found: 1094.4; Elemental analysis. Found (%): C, 66.44; H, 7.53; N, 2.71, P, 2.79. $C_{59}H_{79}N_2O_{14}P$. Calculated (%): C, 66.15; H, 7.43; N, 2.62, P, 2.89.

4-[(*N*-[1-(O,O-Diethylphosphoryl)-1-methylethyl]-{12'-aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35- nonamethoxy-pillar[5]arene (7).

Yield: 0.17 г (61%). D.p.: 158 °C; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ: 26.1; ^{1}H NMR (400 MHz, CDCl$_3$) δ: -1.36 (m, 4H, -C(O)NHCH$_2$CH$_2$-), -0.07 (m, 2H, -C(O)NHCH$_2$CH$_2$CH$_2$-), 0.76 (m, 2H, -C(O)NH(CH$_2$)$_3$CH$_2$-), 1.15 (m, 2H, -C(O)NH(CH$_2$)$_4$CH$_2$-), 1.39 (t, *J* = 7.2 Hz, 6H, -POCH$_2$CH$_3$), 1.50 (br.d., 6H, -C(CH$_3$)$_2$), 1.62 (m, 14H, -CH$_2$(CH$_2$)$_7$NHC(CH$_3$)$_2$), 3.72-3.79 (m, 37H, -CH$_2$- and -OCH$_3$), 4.23 (m, 4H, -POCH$_2$CH$_3$), 4.57 (s, 2H, ArOCH$_2$-), 5.06 (s, 1H, -CH$_2$NHC(CH$_3$)$_2$), 5.18 (s, 1H, C(O)NH), 6.70-6.93 (m, 10H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 16.36, 22.16, 23.84, 23.98, 26.87, 27.41, 29.49, 29.72, 32.60, 40.56, 42.39, 42.95, 55.13, 55.36, 55.45, 55.57, 55.79, 55.85, 55.94, 56.79, 65.47, 112.12, 112.48, 112.85, 112.93, 112.99, 113.02, 113.63, 116.56, 127.23, 127.60, 127.72, 128.16, 128.22, 128.43, 131.57, 132.17, 132.59, 149.23, 149.90, 150.23, 150.35, 150.46, 150.73, 150.94, 169.75.; IR ν: 1052, 1207, 1682, 3411, 3610 cm^{-1}; MS (m/z): (MALDI-TOF) Calcd. for [M+H$^+$] m/z = 1155.4, found: 1155.4; Elemental analysis. Found (%): C, 67.64; H, 8.19; N, 2.83; P, 2.93. $C_{65}H_{91}N_2O_{14}P$. Calculated (%): C, 67.57; H, 7.94; N, 2.42, P, 2.68.

Fig. S1. ^{1}H NMR spectrum of 4-[(*N*-{4'-aminobutyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2), $CDCl_3$, 298 K, 400 MHz.



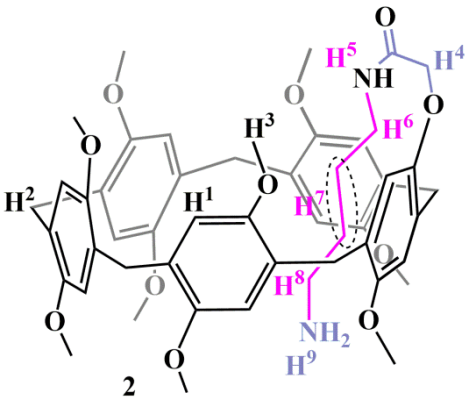
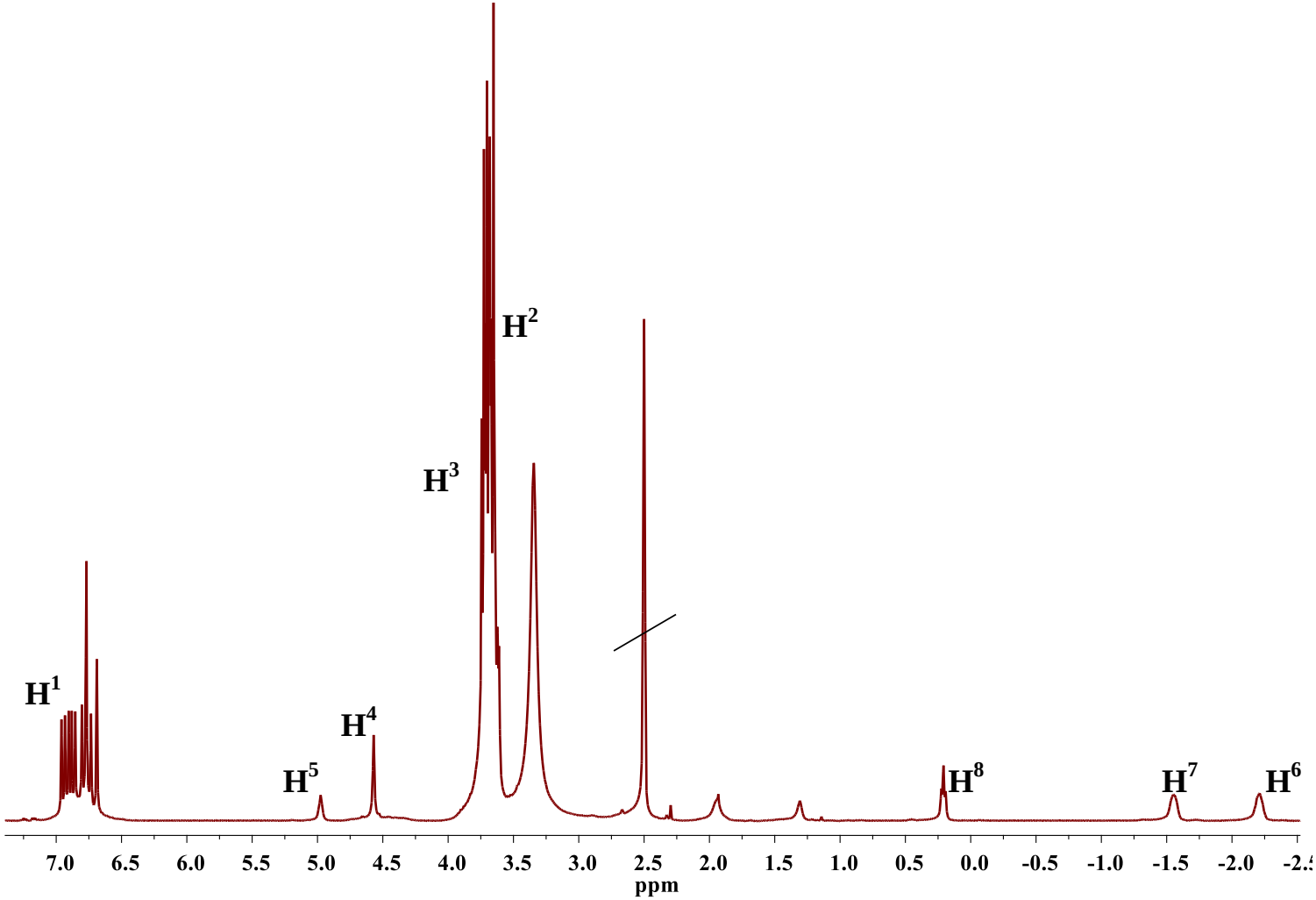


Fig. S2. ^{1}H NMR spectrum of 4-[(*N*-{4'-aminobutyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2), DMSO-d_6, 298 K, 400 MHz.



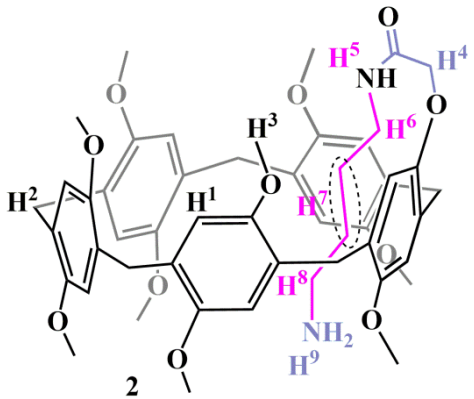
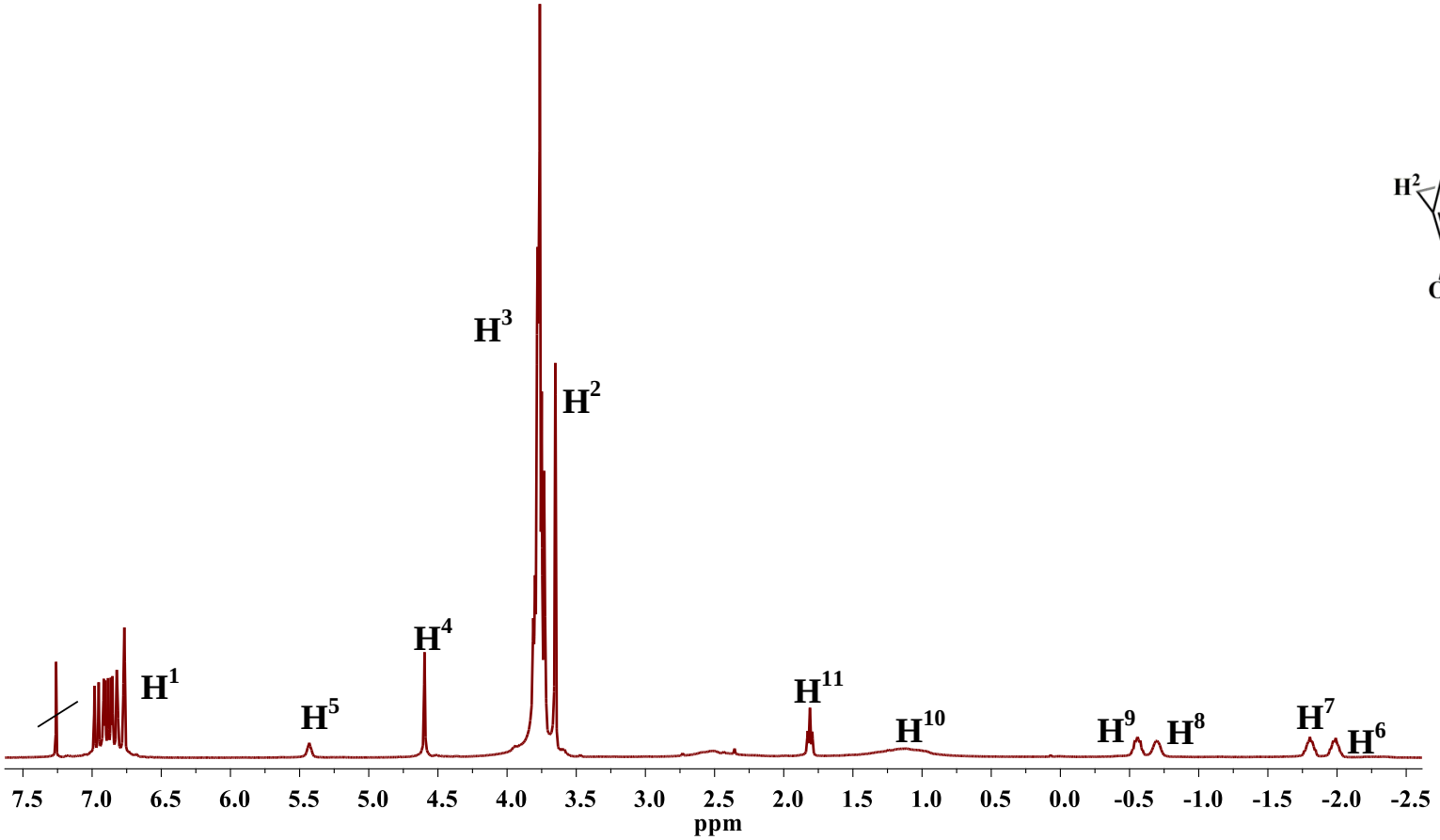


Fig. S3. ^{1}H NMR spectrum of 4-[(*N*-{6'-aminohexyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3), $CDCl_3$, 298 K, 400 MHz.



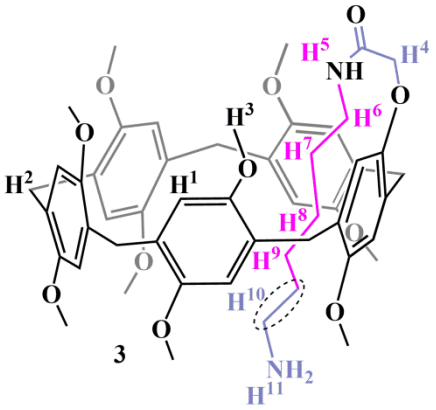
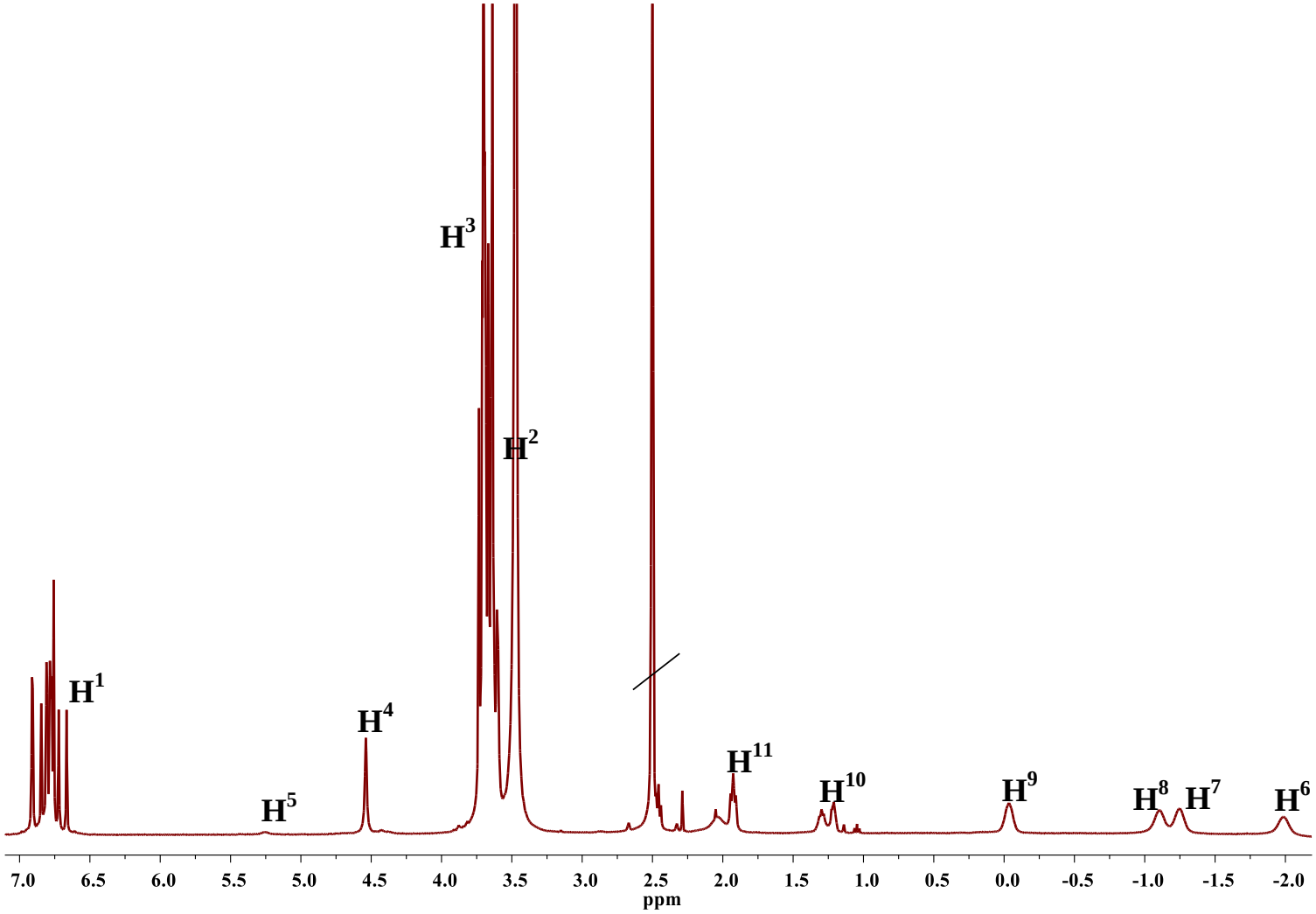


Fig. S4. ^{1}H NMR spectrum of 4-[(*N*-{6'-aminohexyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3), DMSO-d_6, 298 K, 400 MHz.



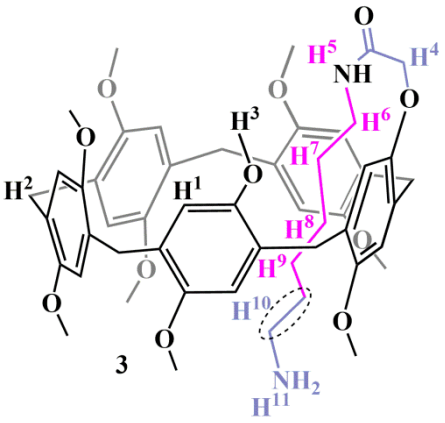


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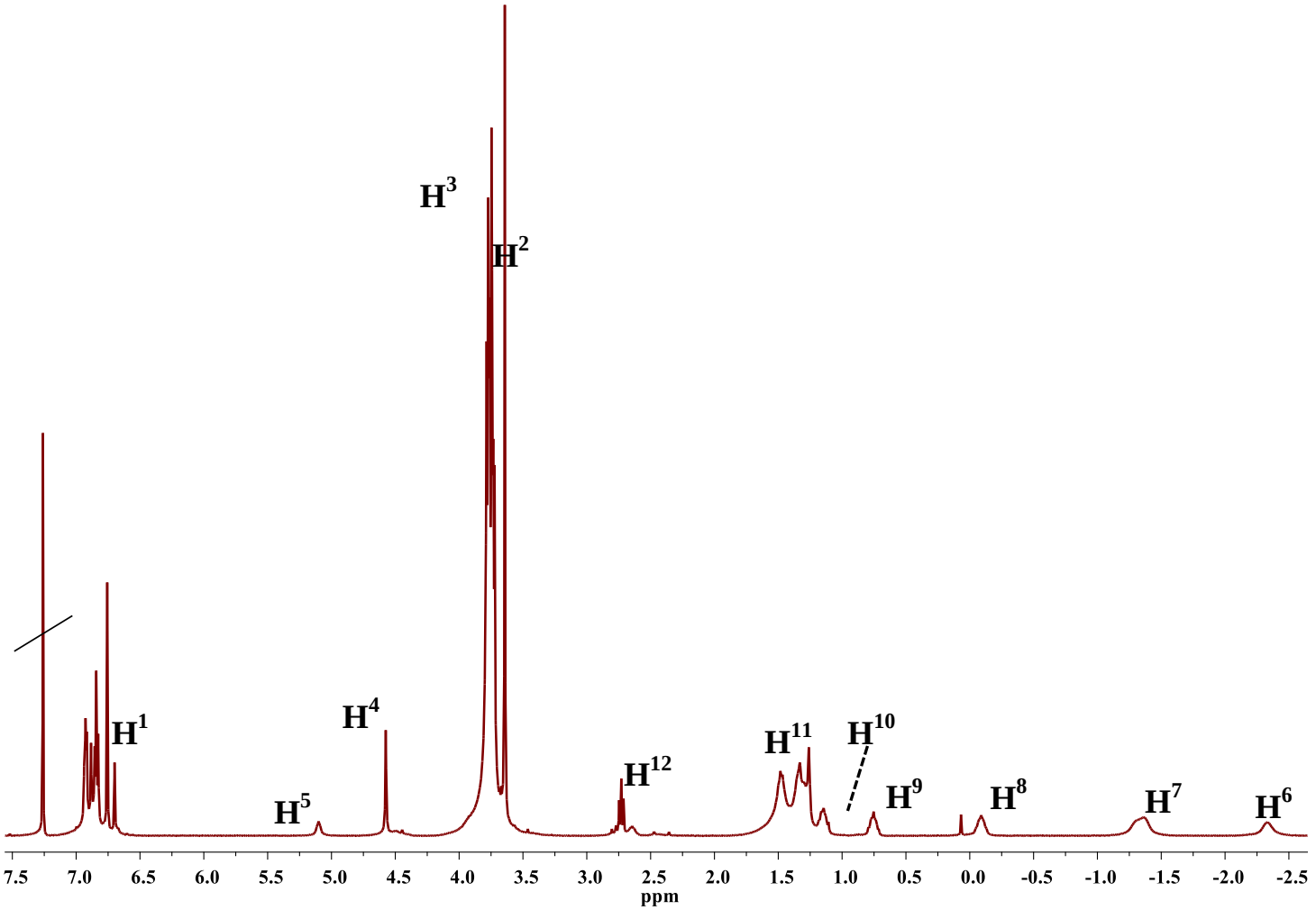
Fig. S5. ^{1}H NMR spectrum of 4-[(*N*-{12'-aminododecyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), $CDCl_3$, 298 K, 400 MHz.



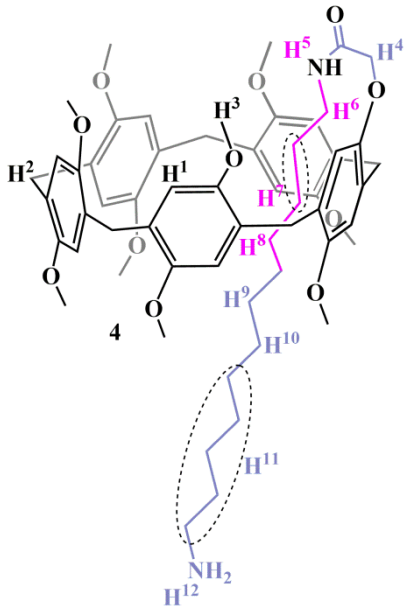
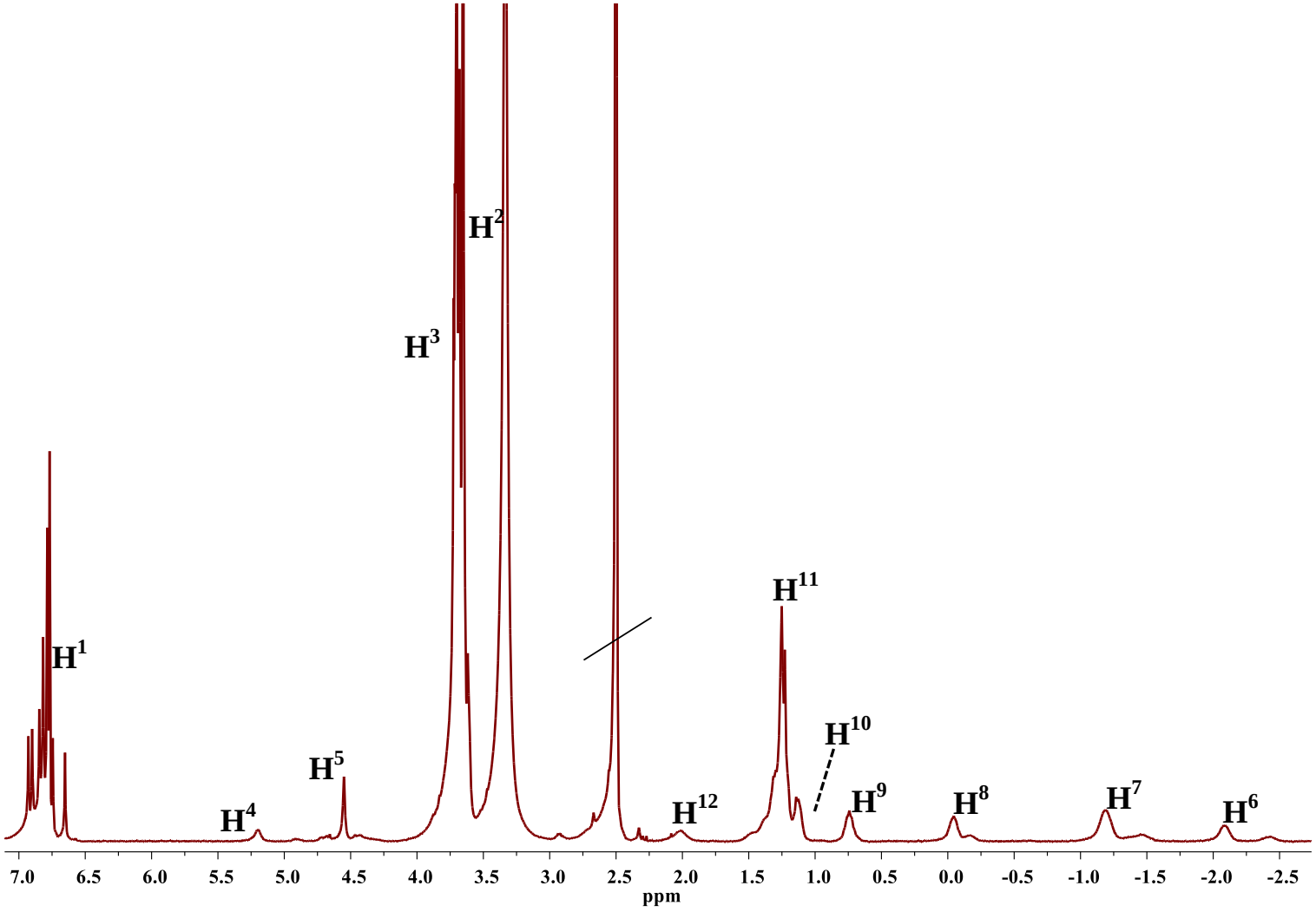


Fig. S6. ^{1}H NMR spectrum of 4-[(*N*-{12'-aminododecyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), DMSO-d_6, 298 K, 400 MHz.



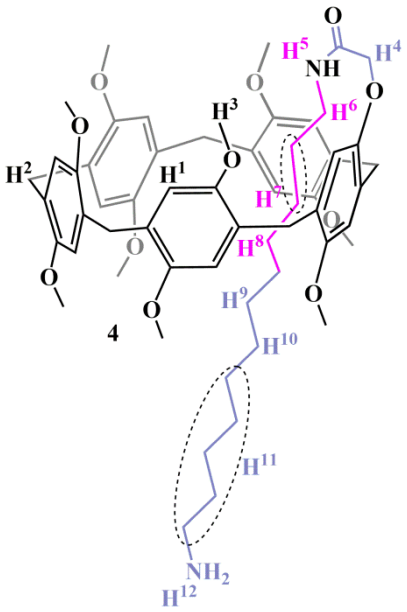
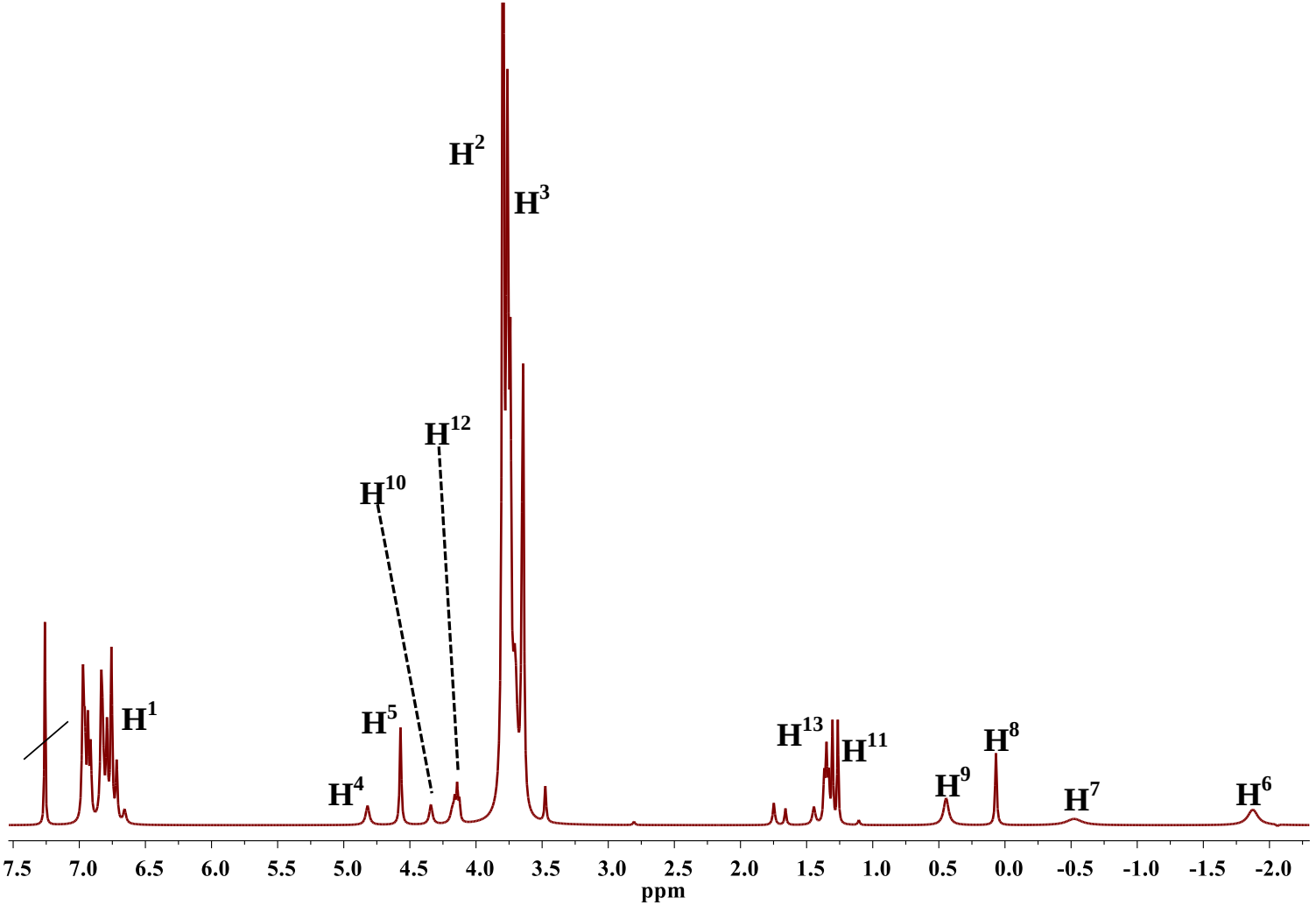


Fig. S7. ^{1}H NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{4'-aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), $CDCl_3$, 298 K, 400 MHz.



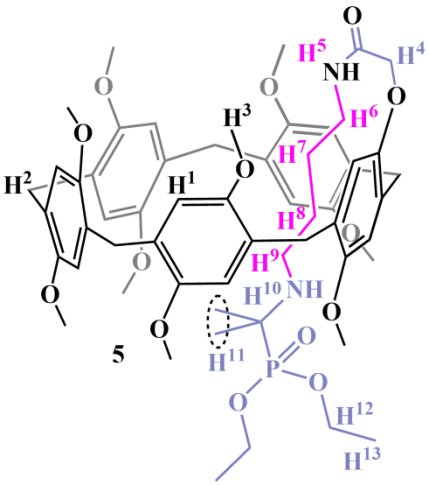


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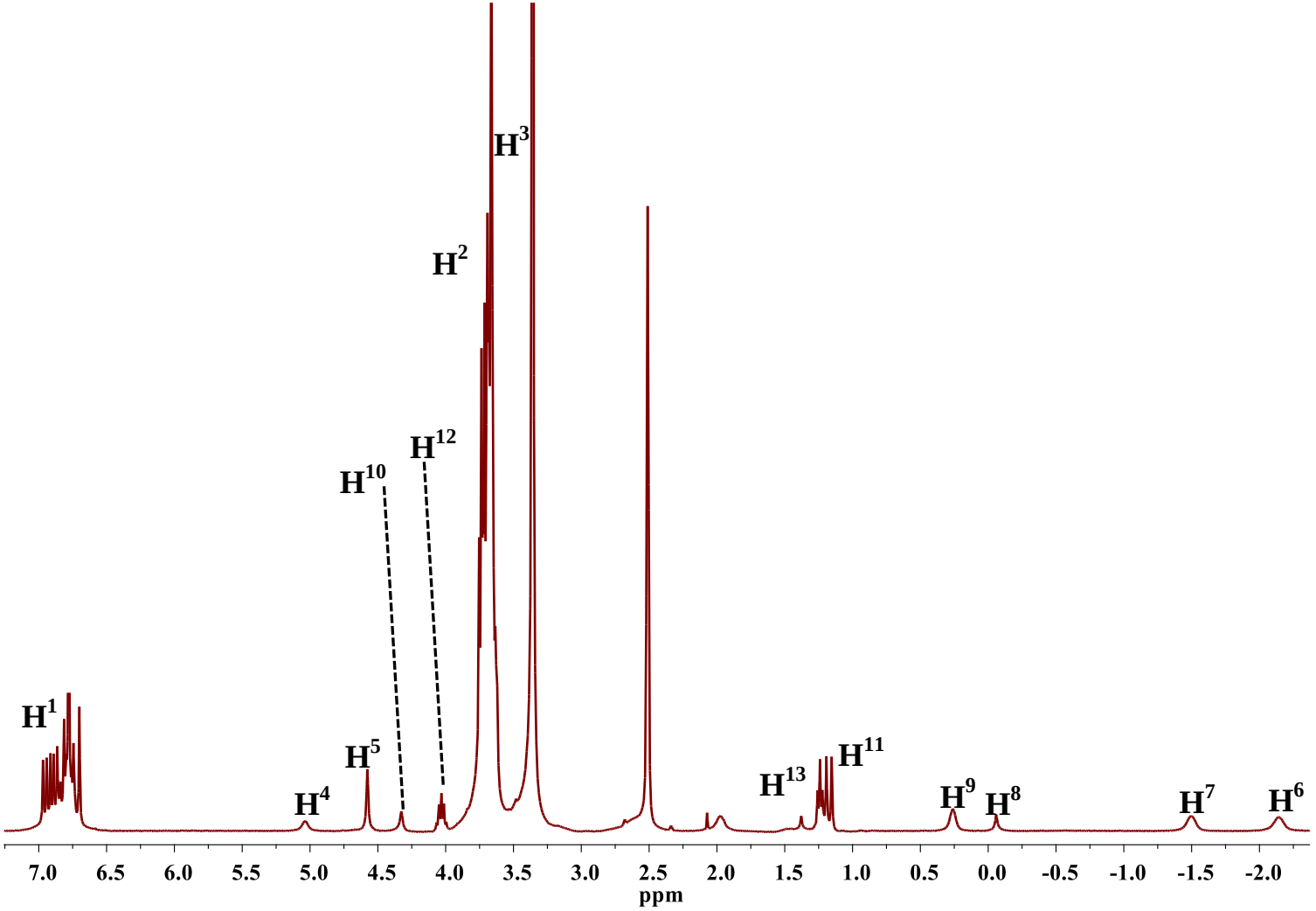
Fig. S8. ^{1}H NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{4'-aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), DMSO-d_6, 298 K, 400 MHz.



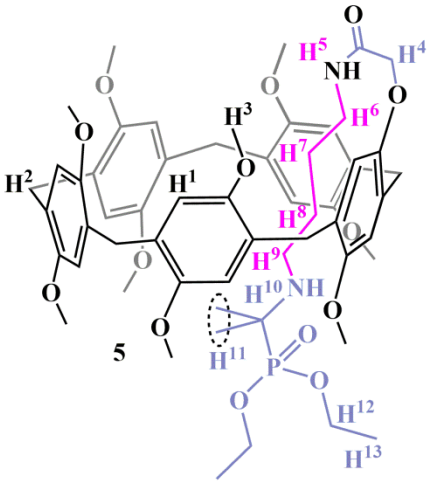
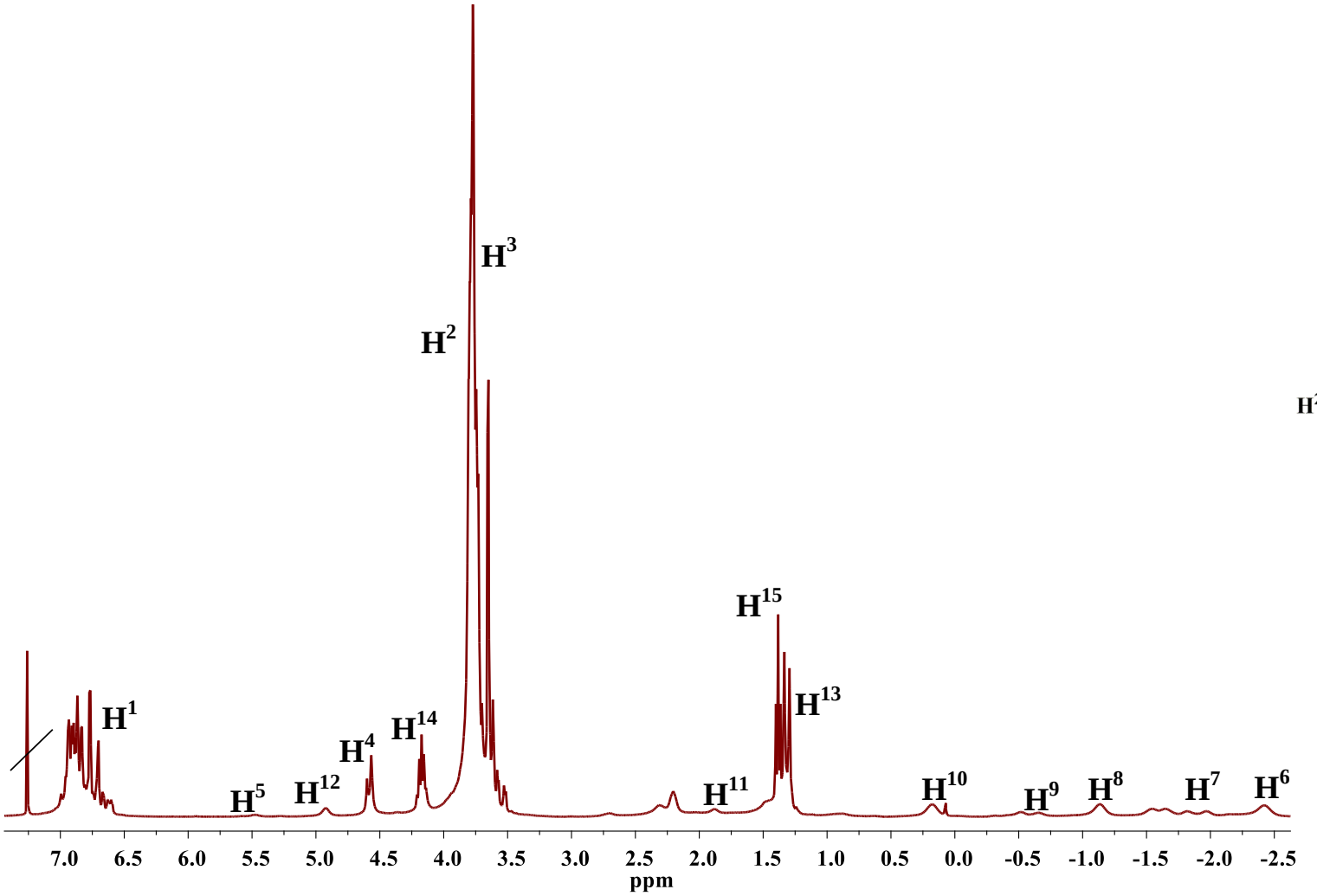


Fig. S9. ^{1}H NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{6'-aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), $CDCl_3$, 298 K, 400 MHz.



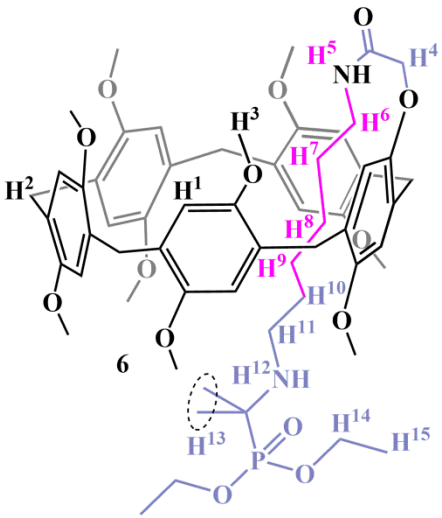
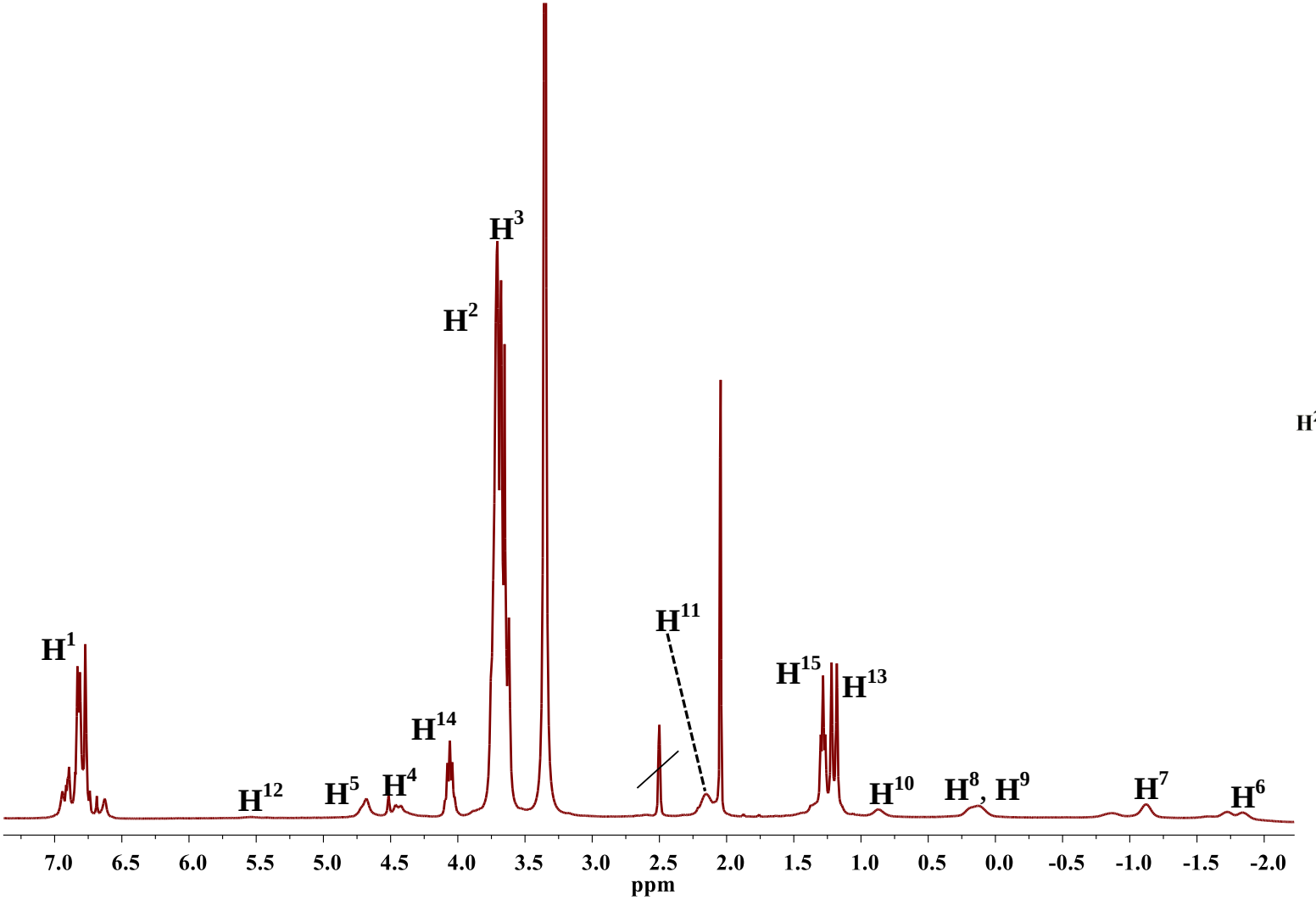


Fig. S10. ^{1}H NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{6'-aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), DMSO-d_6, 298 K, 400 MHz.



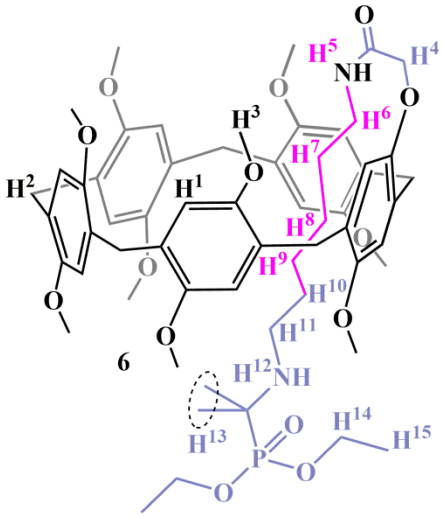
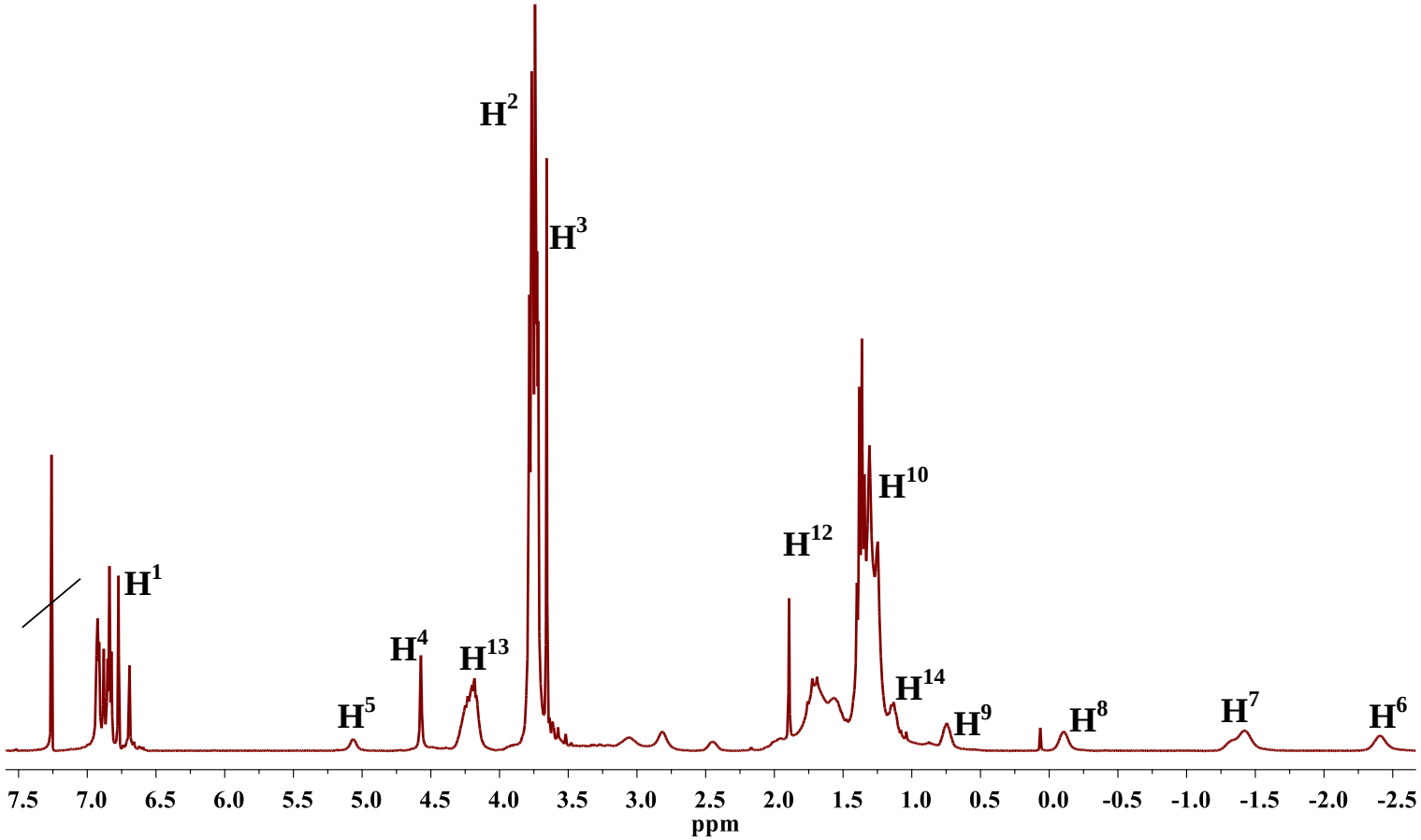


Fig. S11. ^{1}H NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{12'-aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (7), $CDCl_3$, 298 K, 400 MHz.



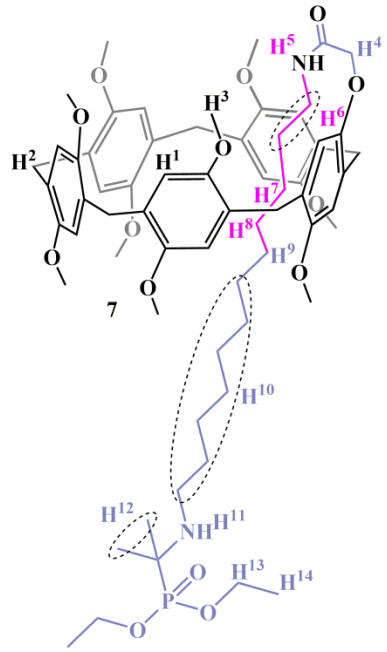
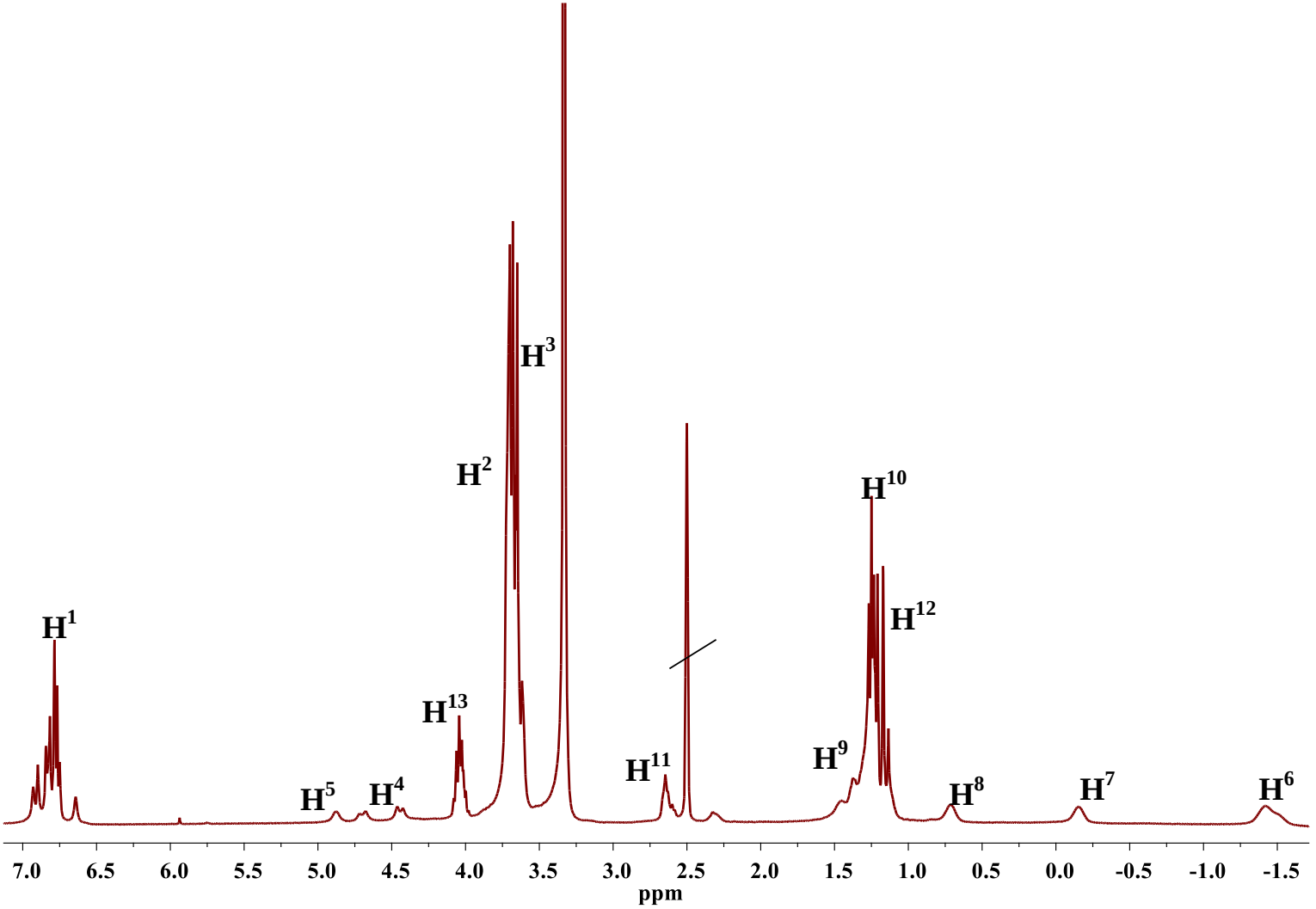


Fig. S12. ^{1}H NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{12'-aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (7), DMSO-d_6, 298 K, 400 MHz.



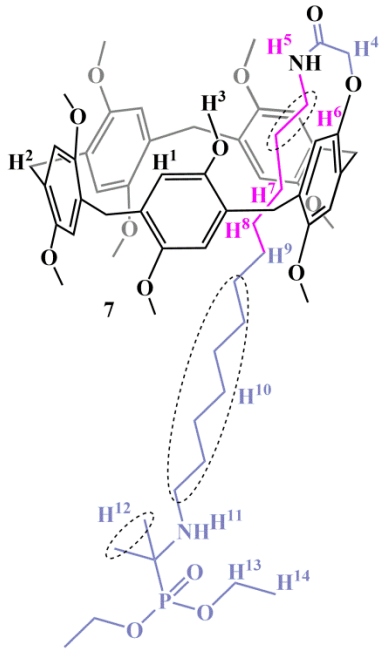


Fig. S13. $^{31}P\{^{1}H\}$ NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{4'-aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), $CDCl_3$, 298 K, 162 MHz.

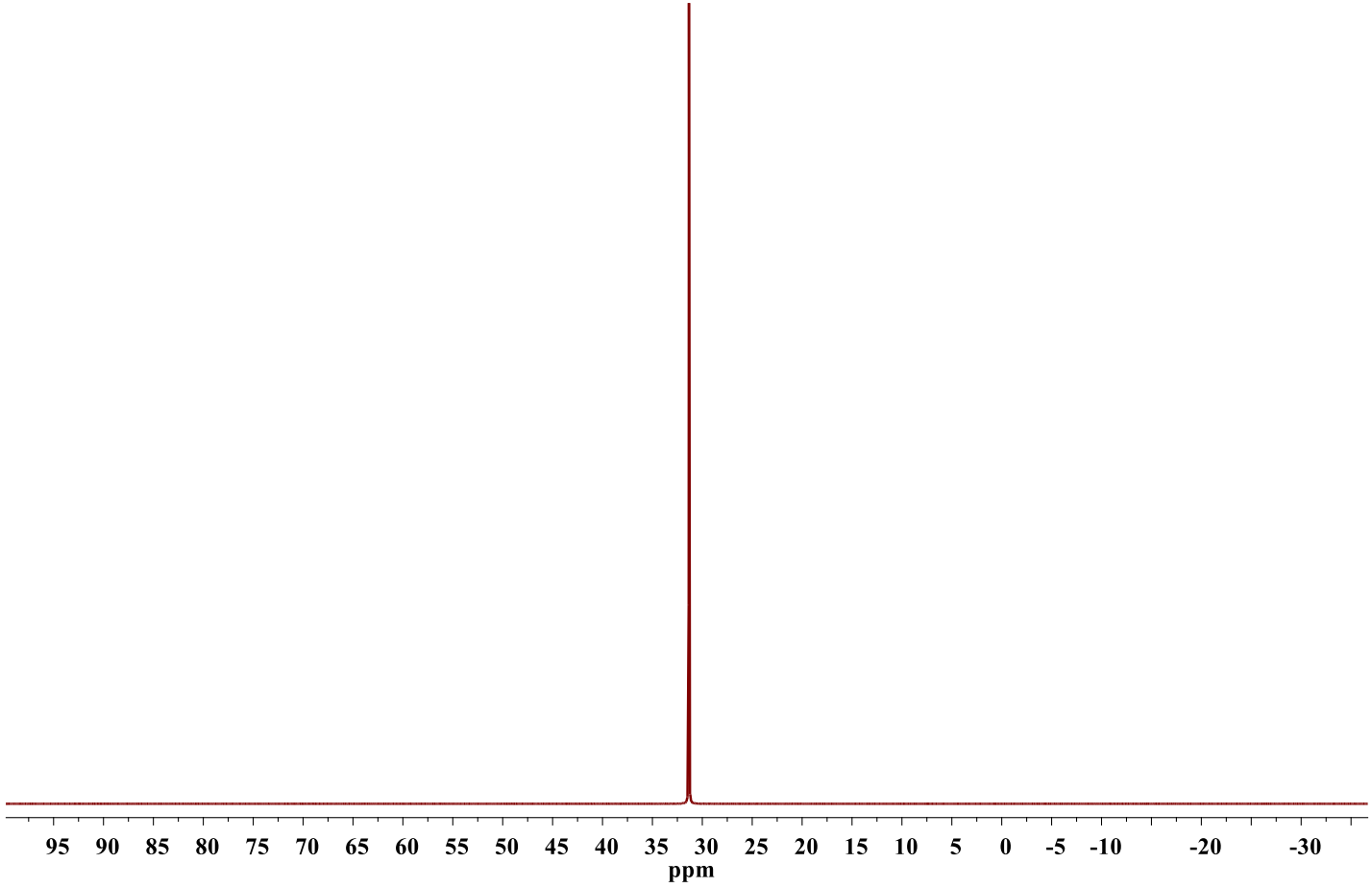


Fig. S14. $^{31}P\{^{1}H\}$ NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{6'-aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), $CDCl_3$, 298 K, 162 MHz.

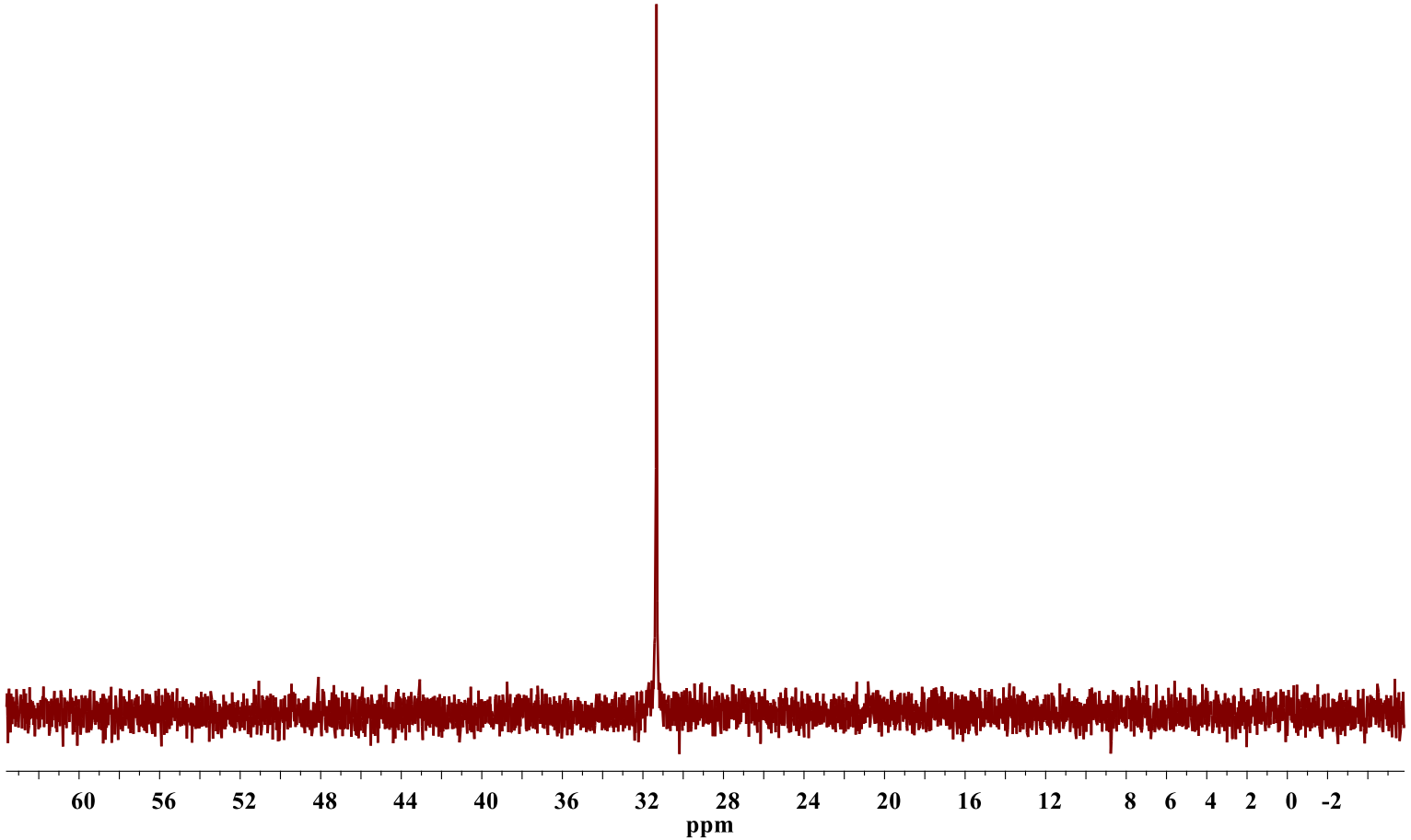


Fig. S15. $^{31}P\{^{1}H\}$ NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{12'-aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (7), $CDCl_3$, 298 K, 162 MHz.

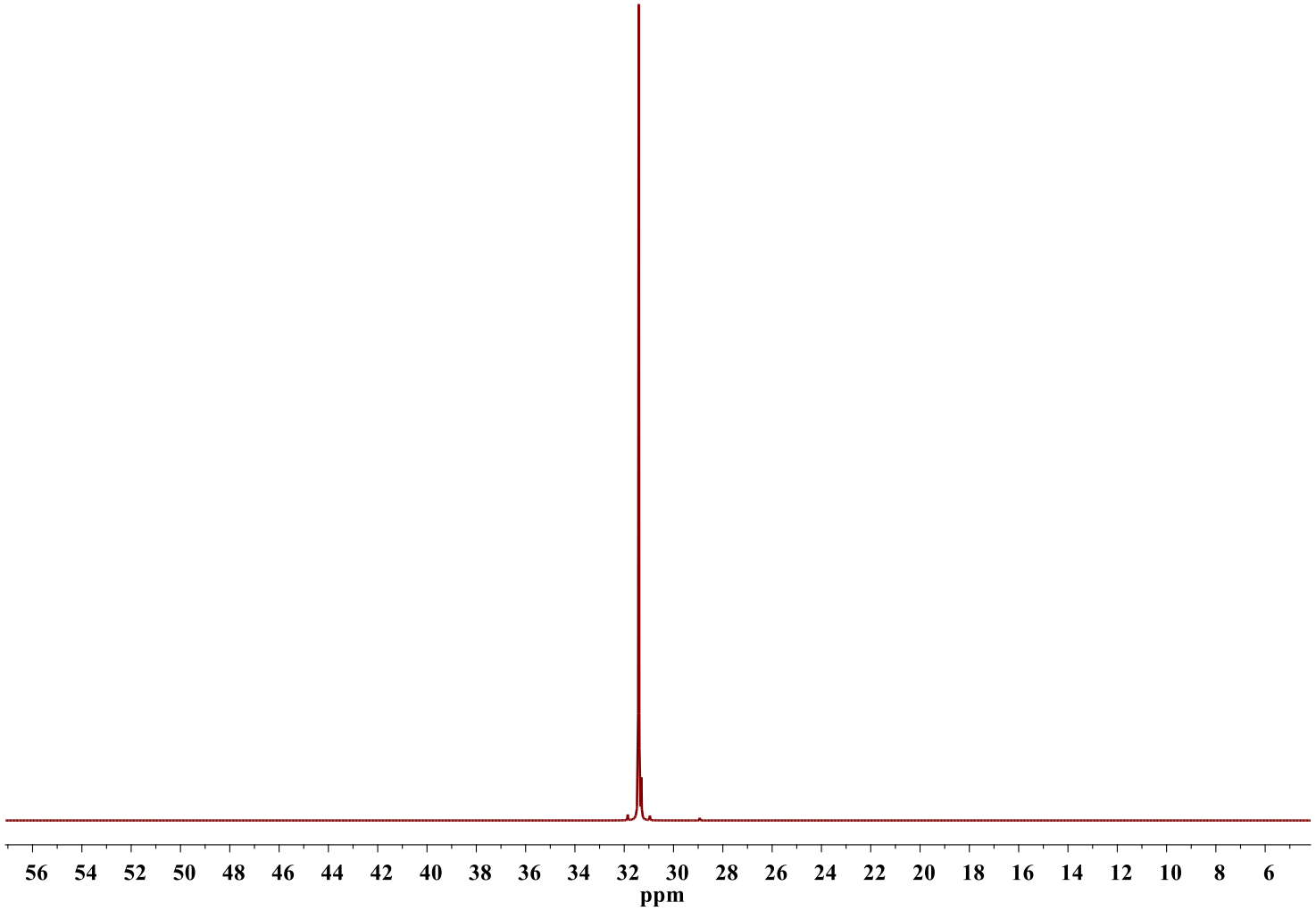


Fig. S16. ^{13}C NMR spectrum of 4-[(*N*-{4'-aminobutyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2), $CDCl_3$, 298 K, 100 MHz.

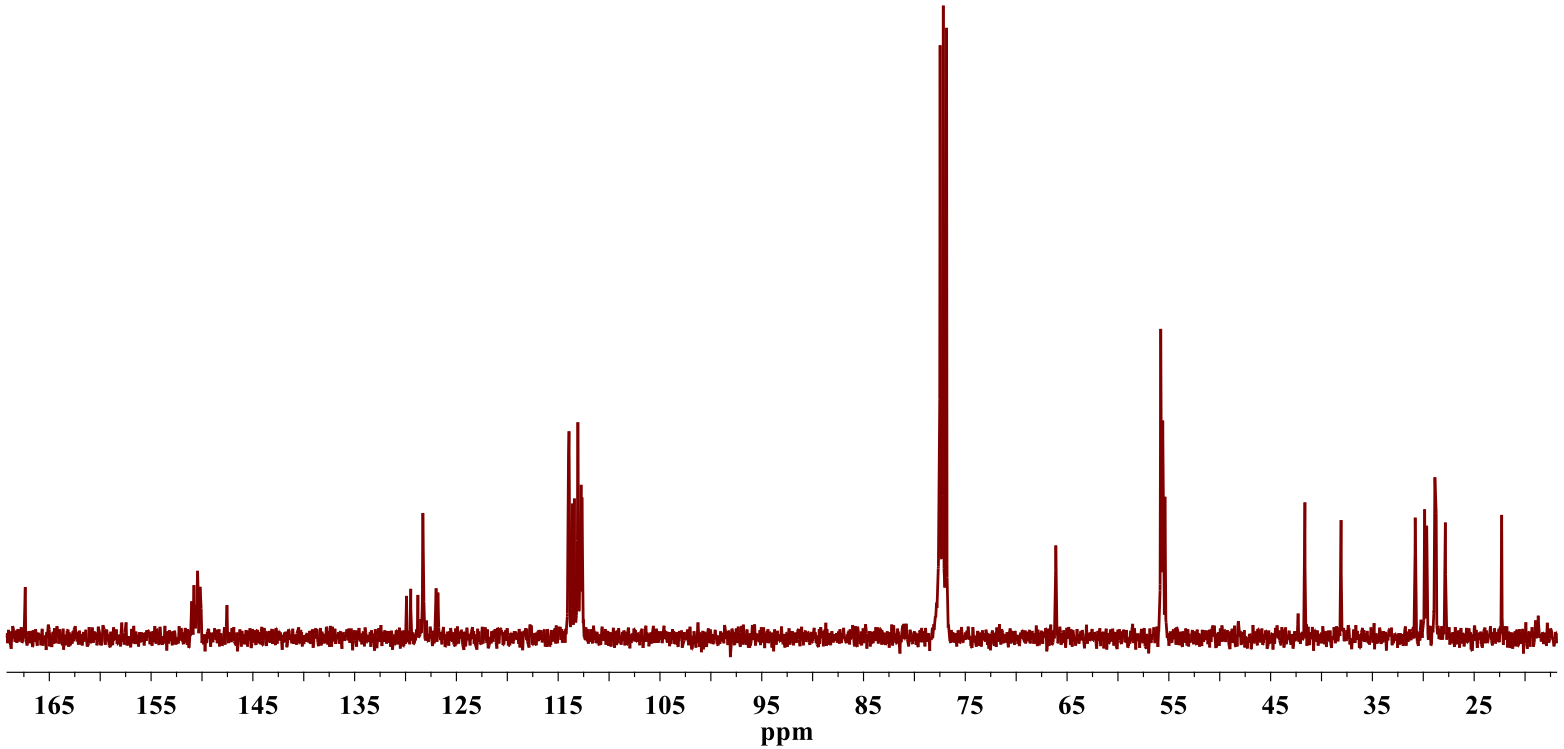


Fig. S17. ^{13}C NMR spectrum of 4-[(*N*-{6'-aminohexyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3), $CDCl_3$, 298 K, 100 MHz.

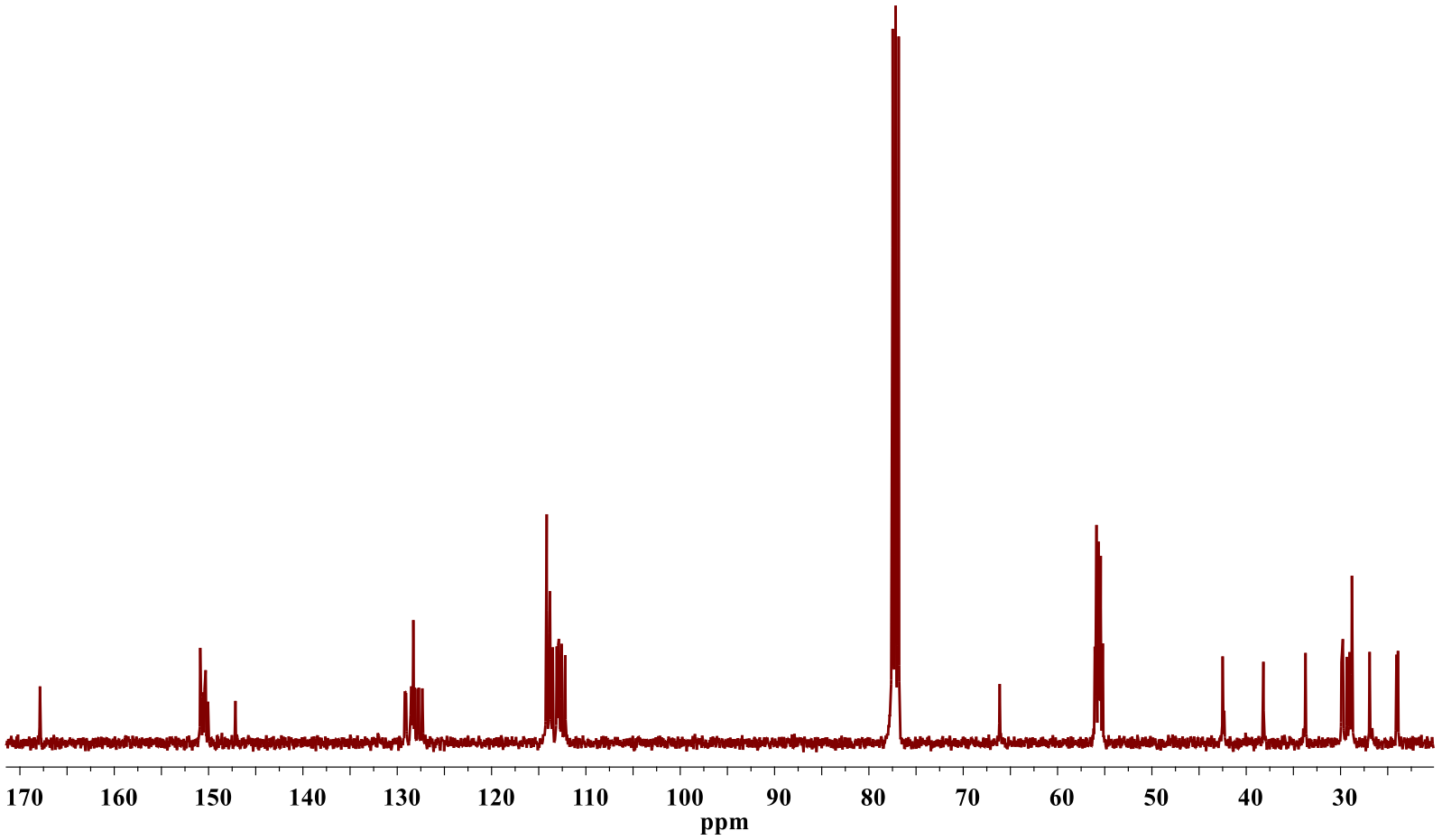


Fig. S18. ^{13}C NMR spectrum of 4-[(*N*-{12'-aminododecyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), $CDCl_3$, 298 K, 100 MHz.

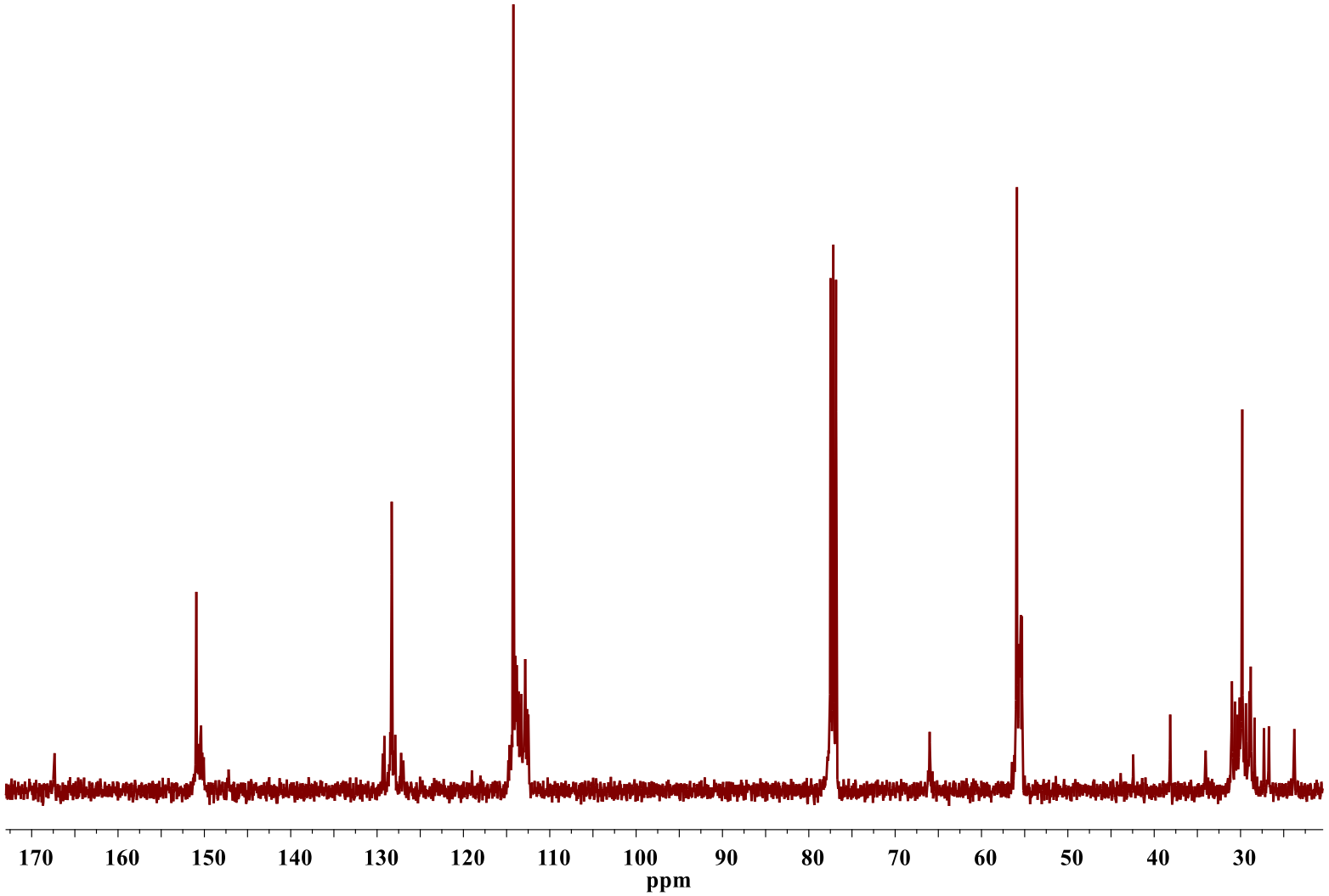


Fig. S19. ^{13}C NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{4'-aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), $CDCl_3$, 298 K, 100 MHz.

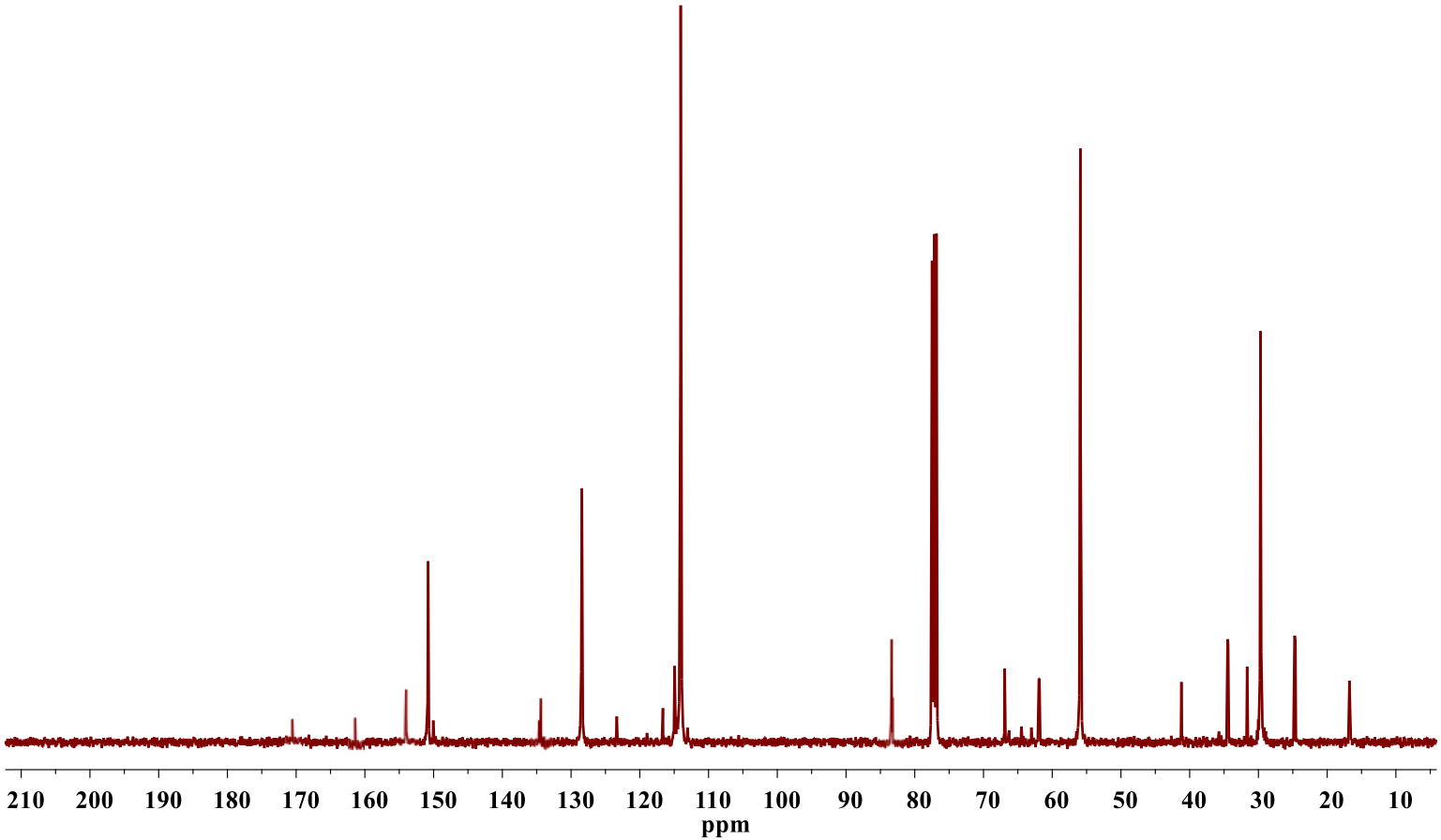


Fig. S20. ^{13}C NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{6'-aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), $CDCl_3$, 298 K, 100 MHz.

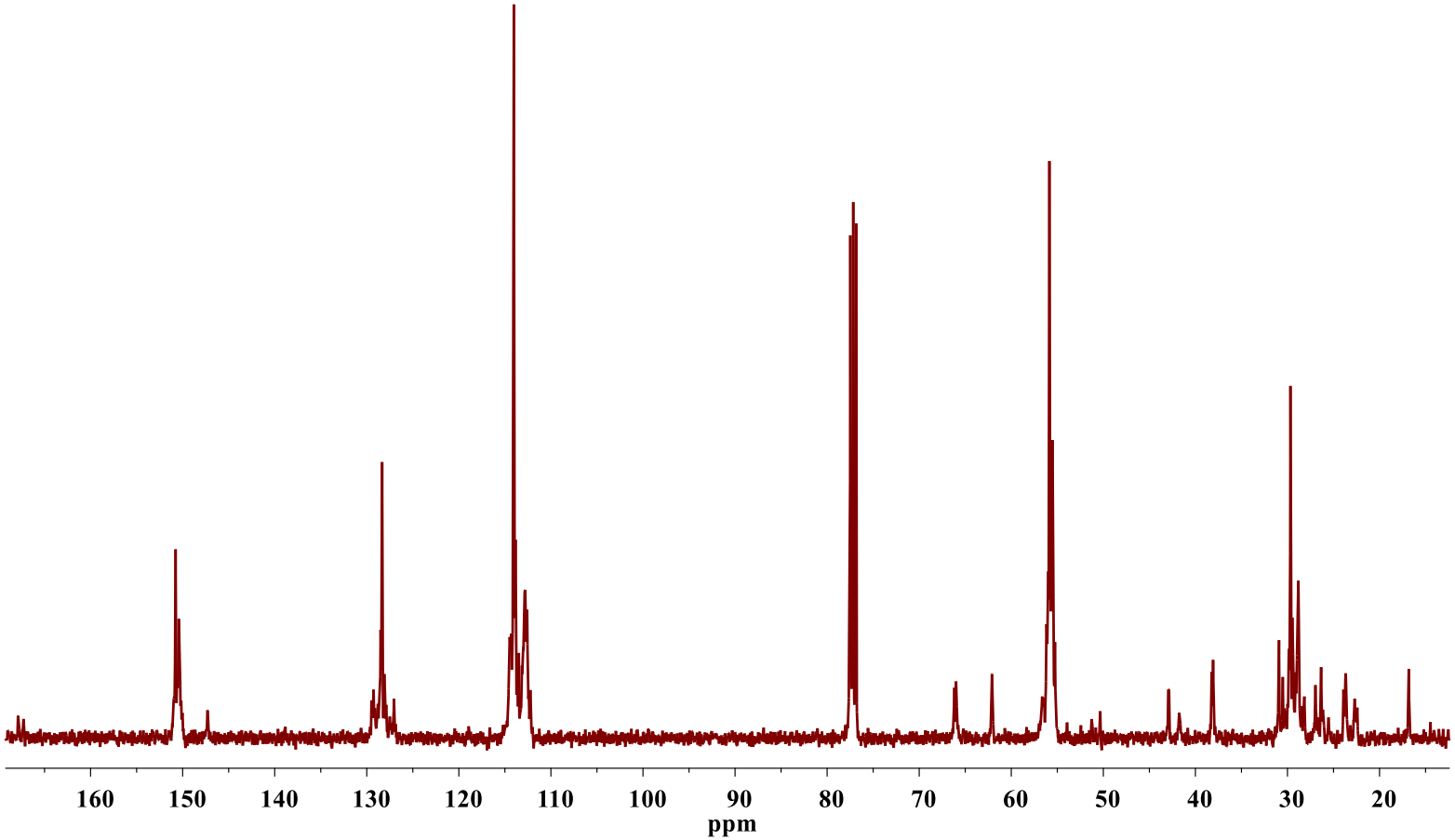


Fig. S21. ^{13}C NMR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{12'-aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (7), $CDCl_3$, 298 K, 100 MHz.

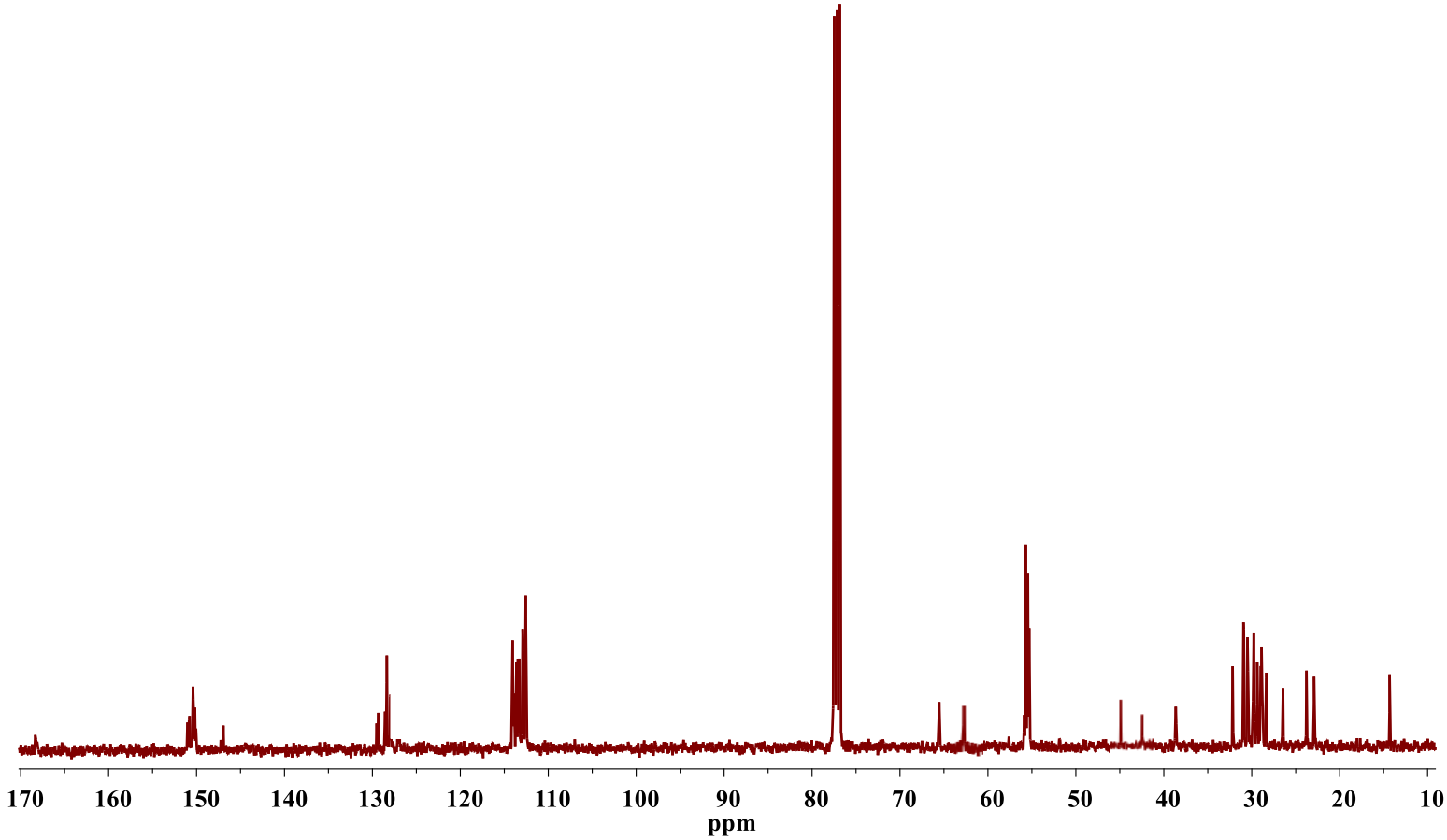


Fig. S22. Mass spectrum (MALDI) of 4-[(*N*-{4'-aminobutyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2).

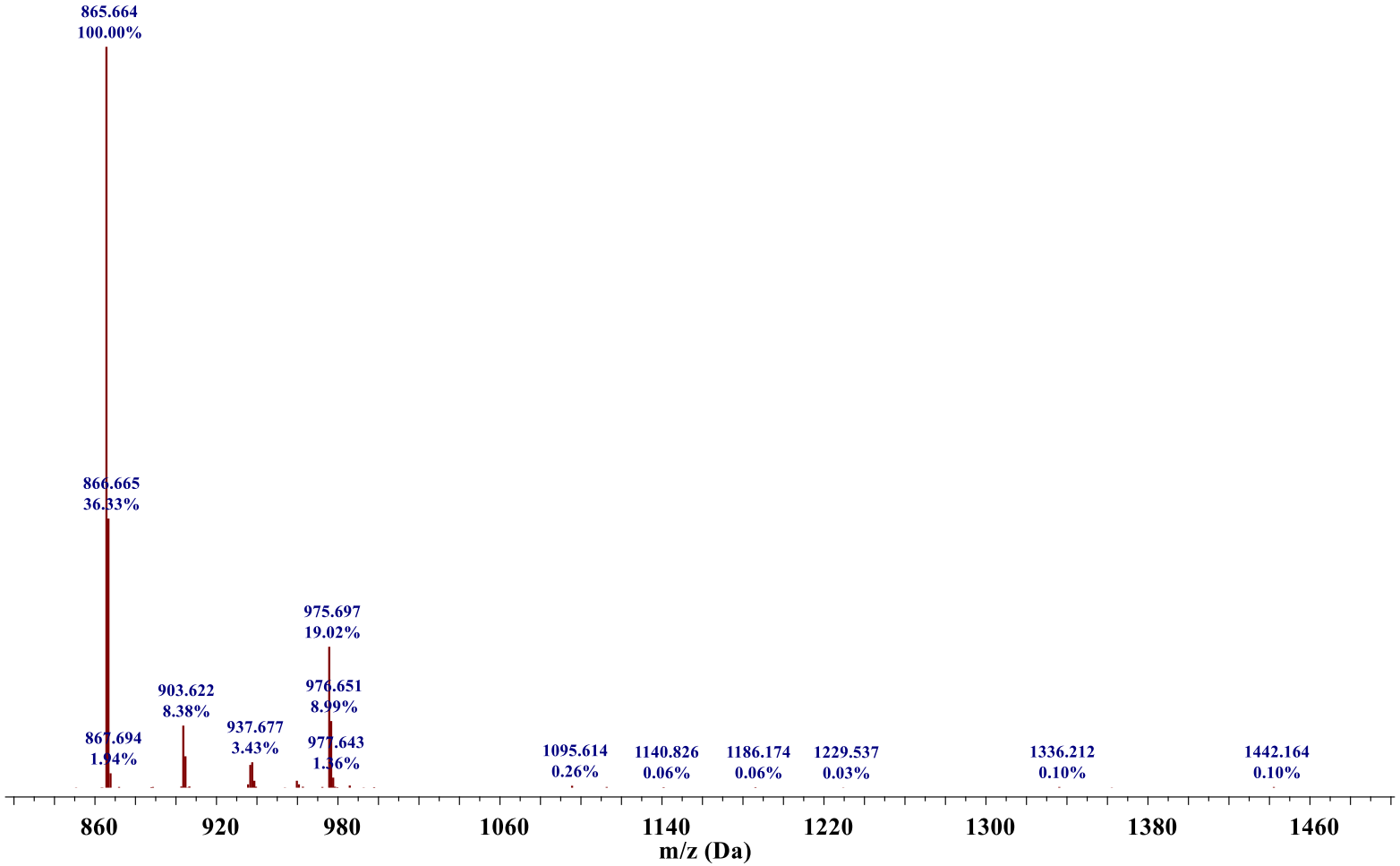


Fig. S23. Mass spectrum (MALDI) of 4-[(*N*-{6'-aminohexyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3).

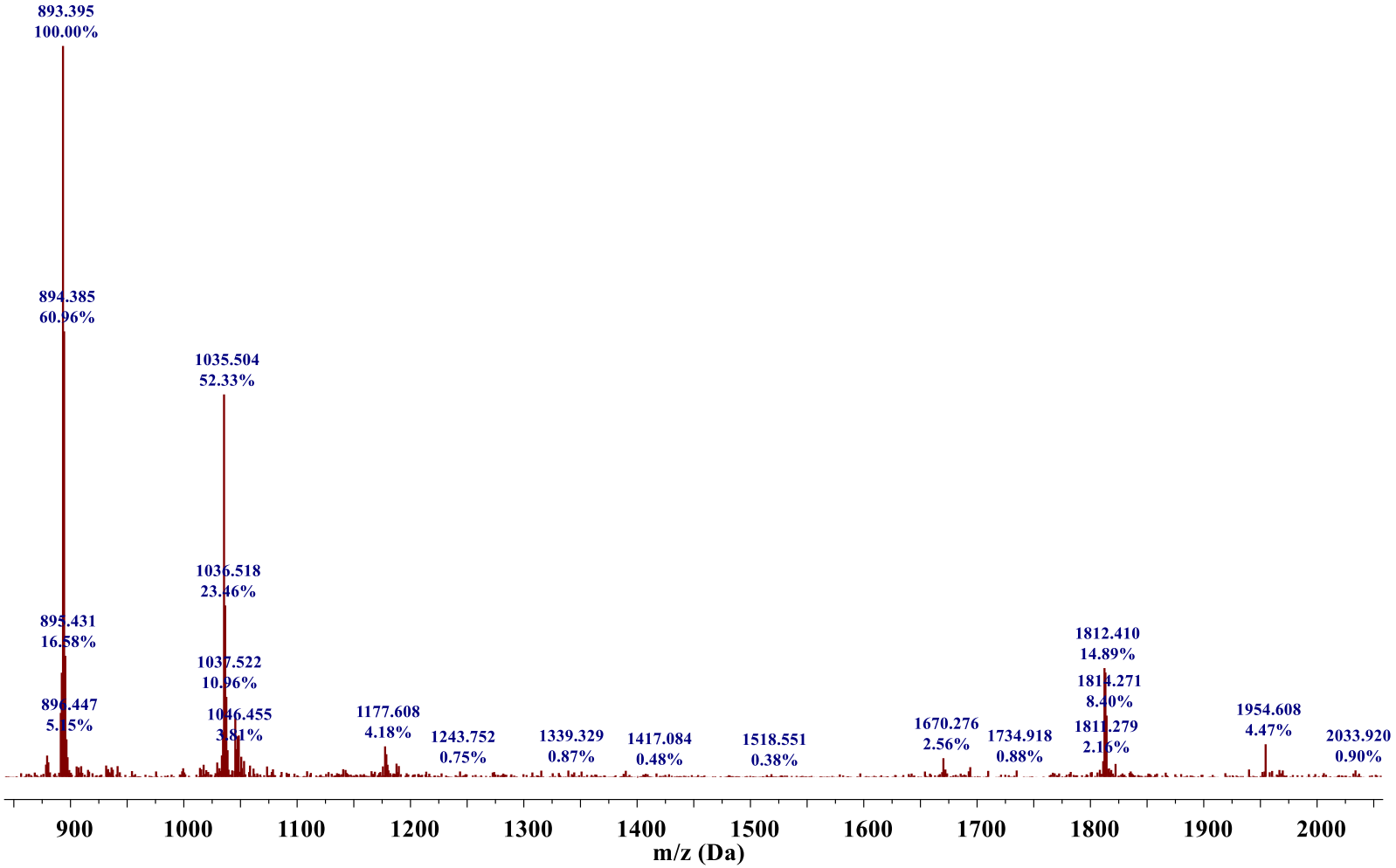


Fig. S24. Mass spectrum (MALDI) of 4-[(*N*-{12'-aminododecyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4).

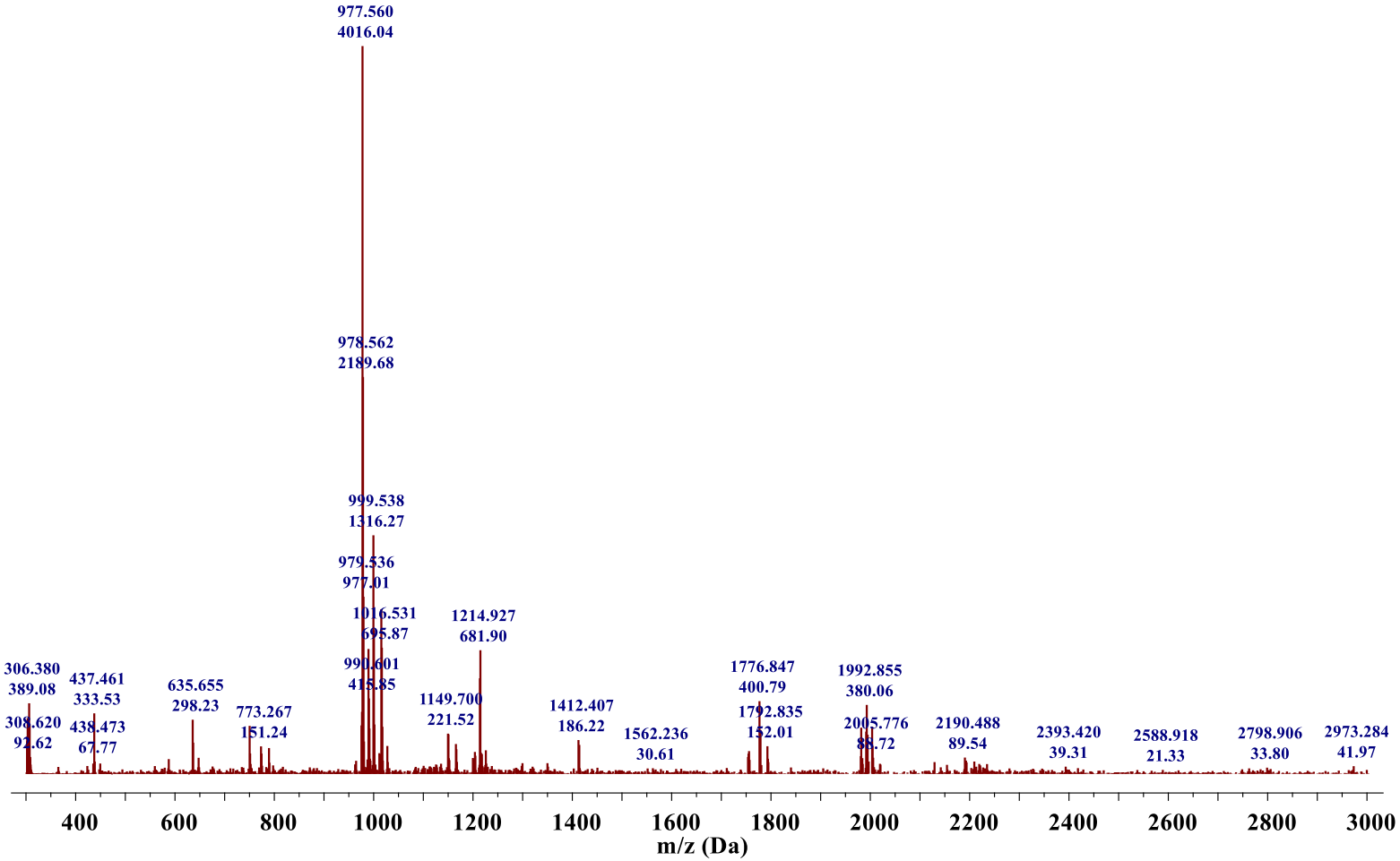


Fig. S25. Mass spectrum (MALDI) of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{4'-aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5).

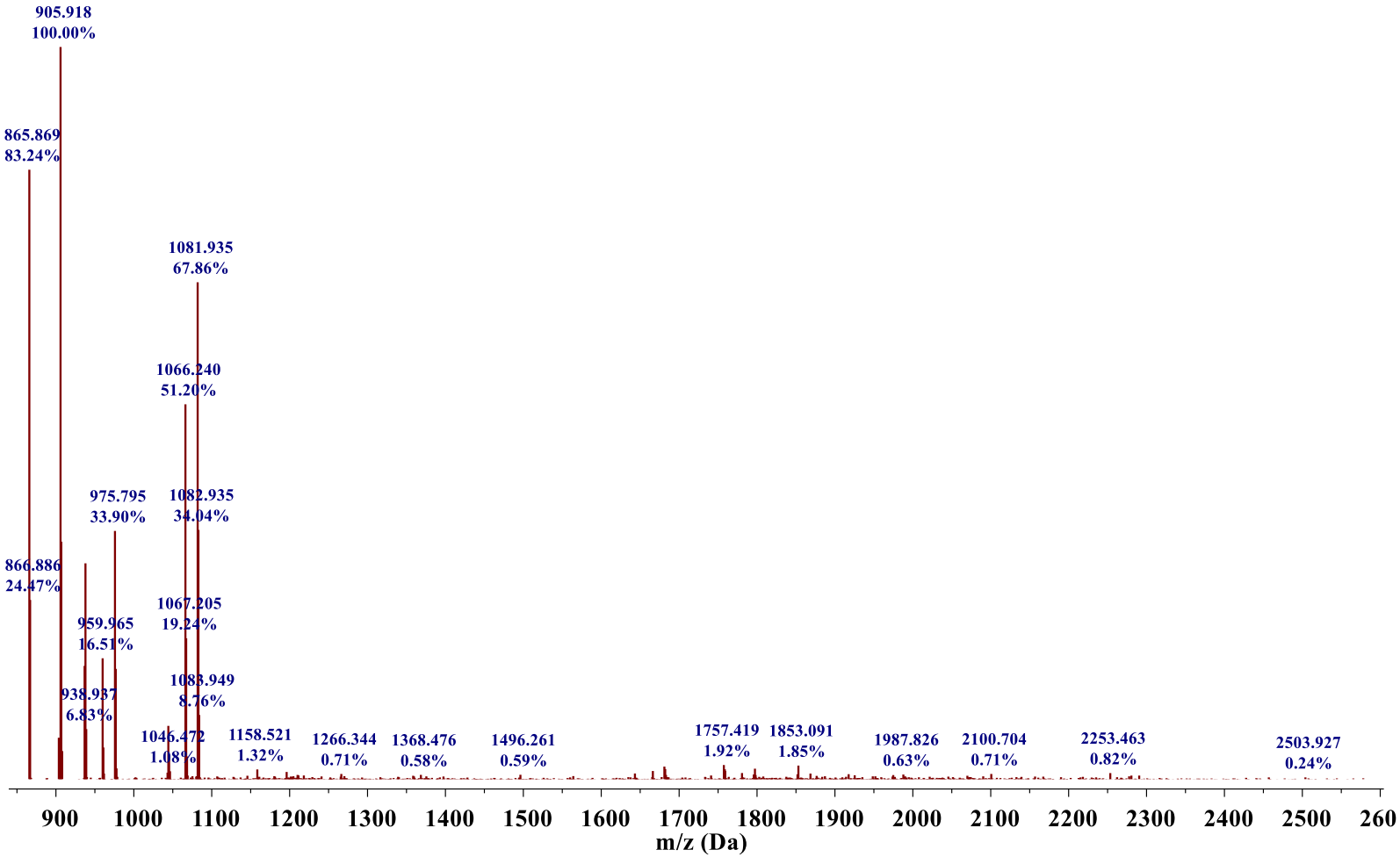


Fig. S26. Mass spectrum (MALDI) of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{6'-aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6).

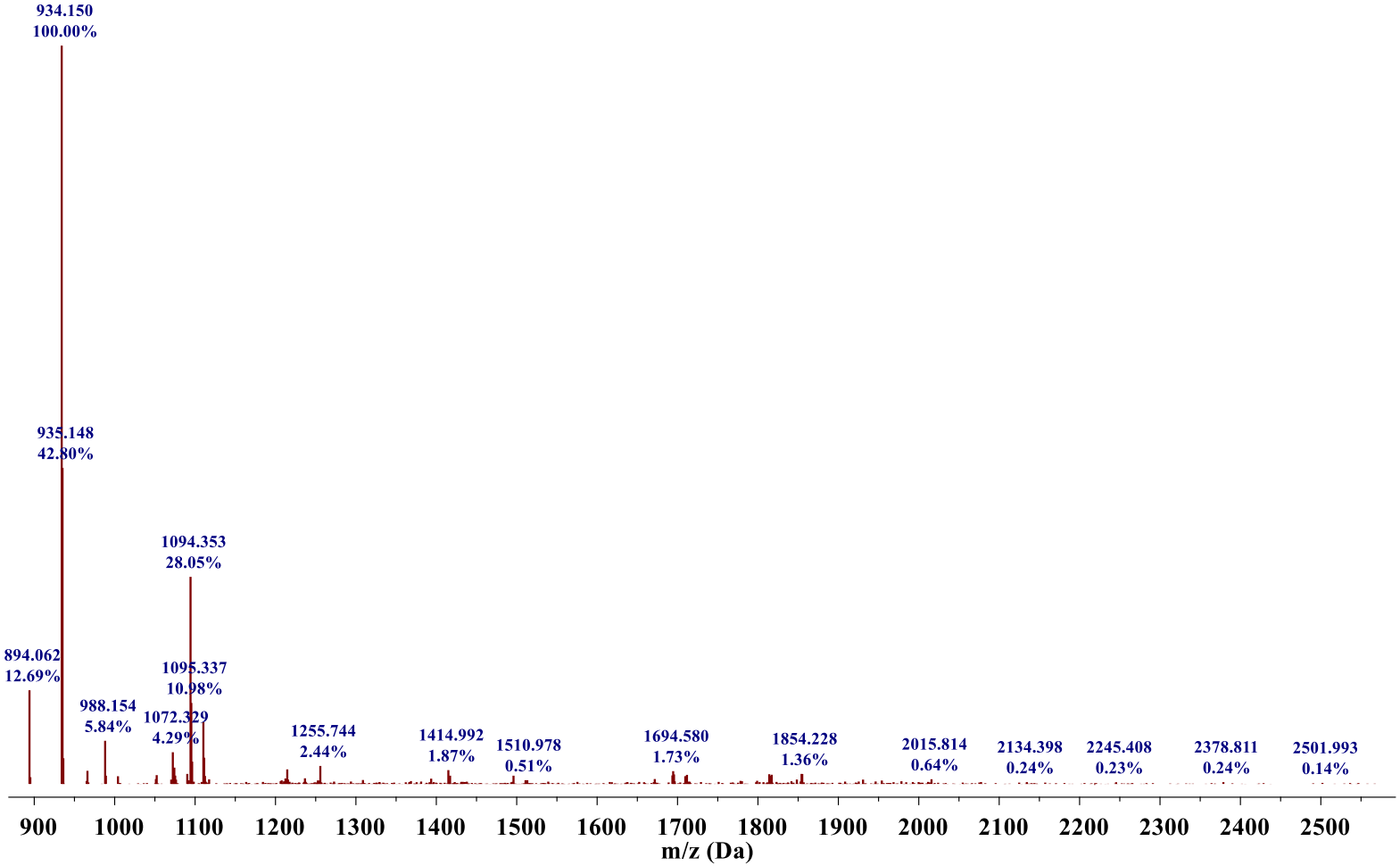


Fig. S27. Mass spectrum (MALDI) of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{12'-aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (7).

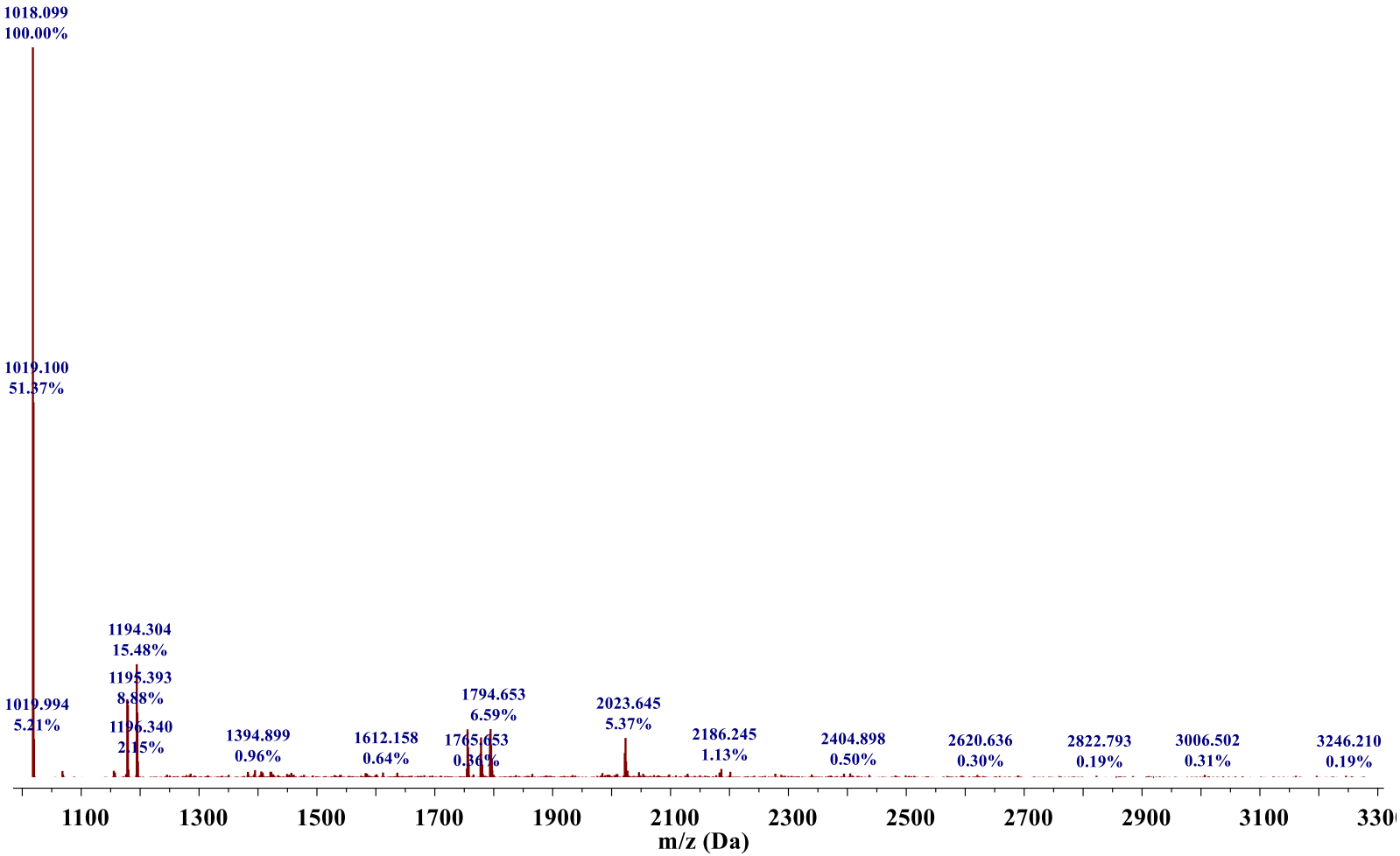


Fig. S28. IR spectrum of 4-[(*N*-{4'-aminobutyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2).

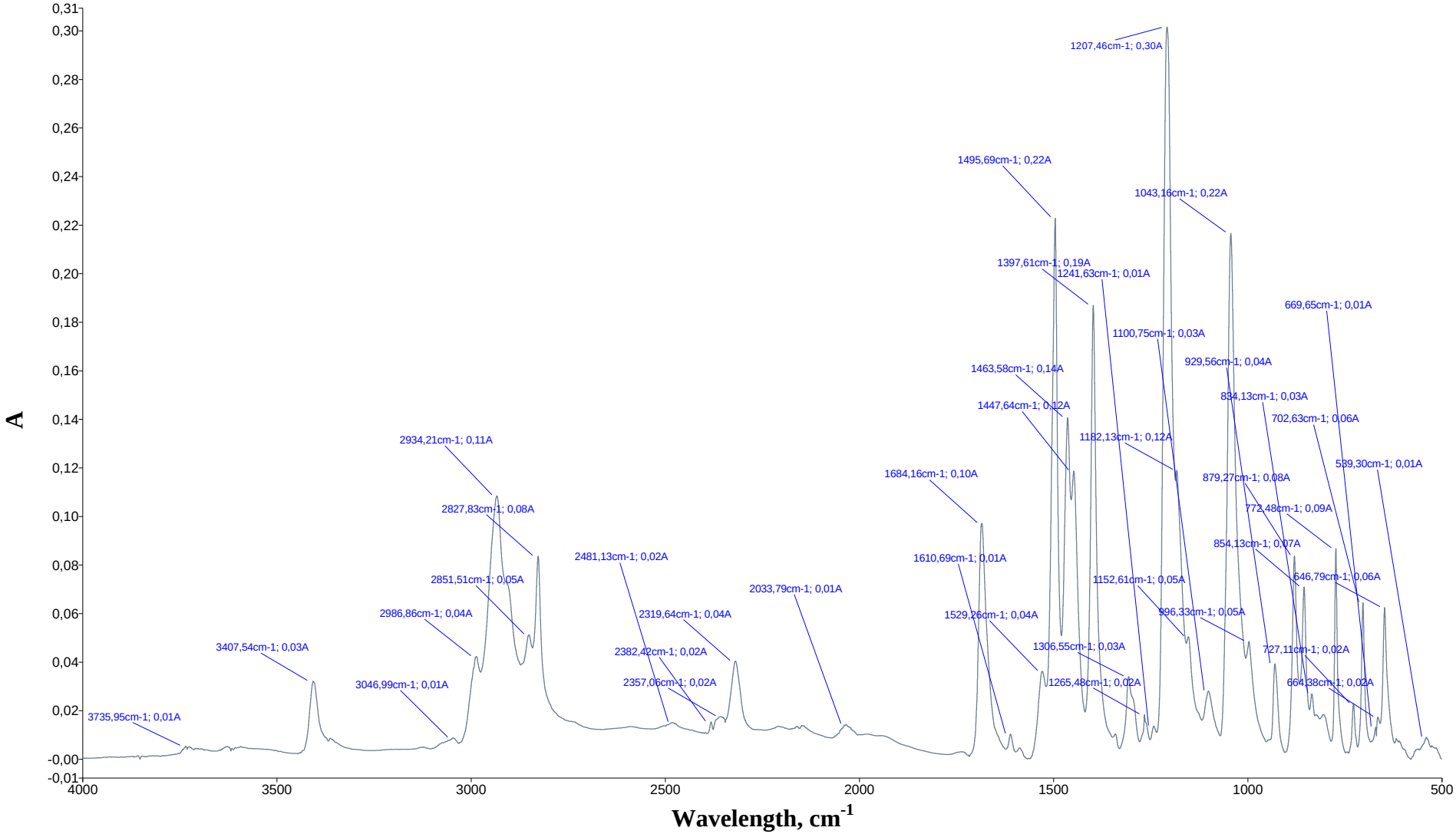


Fig. S29. IR spectrum of 4-[(*N*-{6'-aminohexyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3).

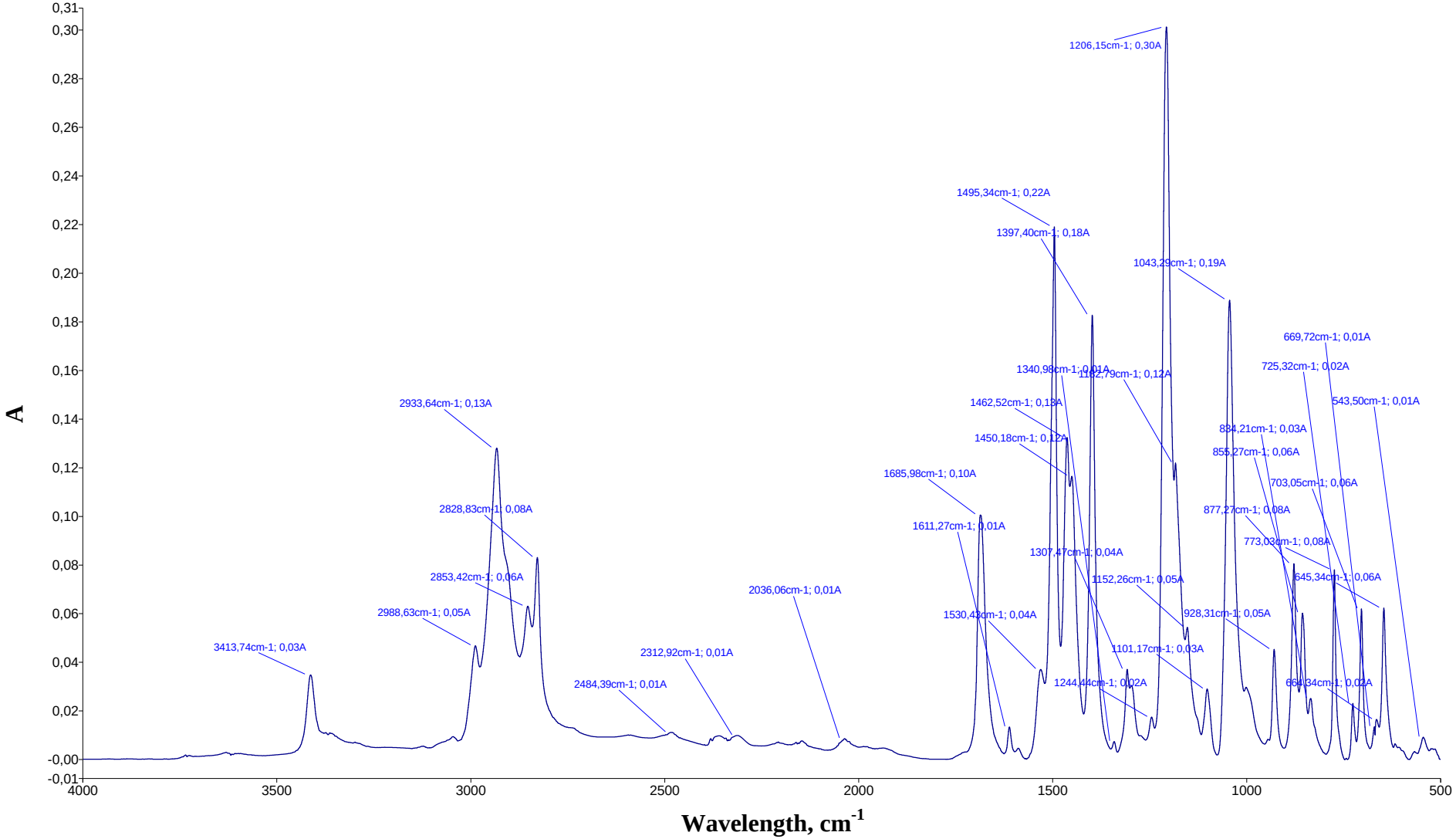


Fig. S30. IR spectrum of 4-[(*N*-{12'-aminododecyl}-amino)-carbomoylmthoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4).

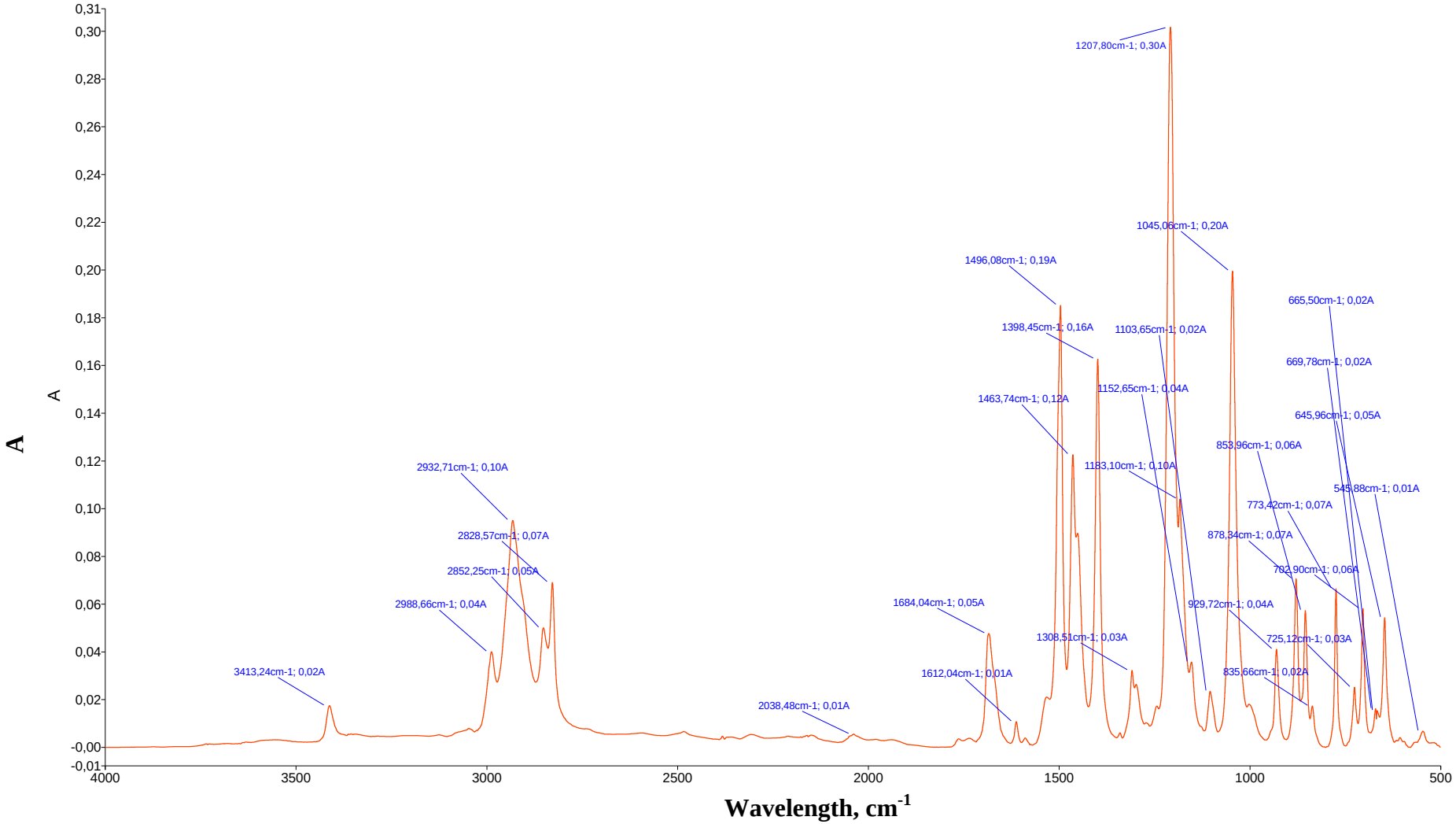


Fig. S31. IR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{4'-aminobutyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5).

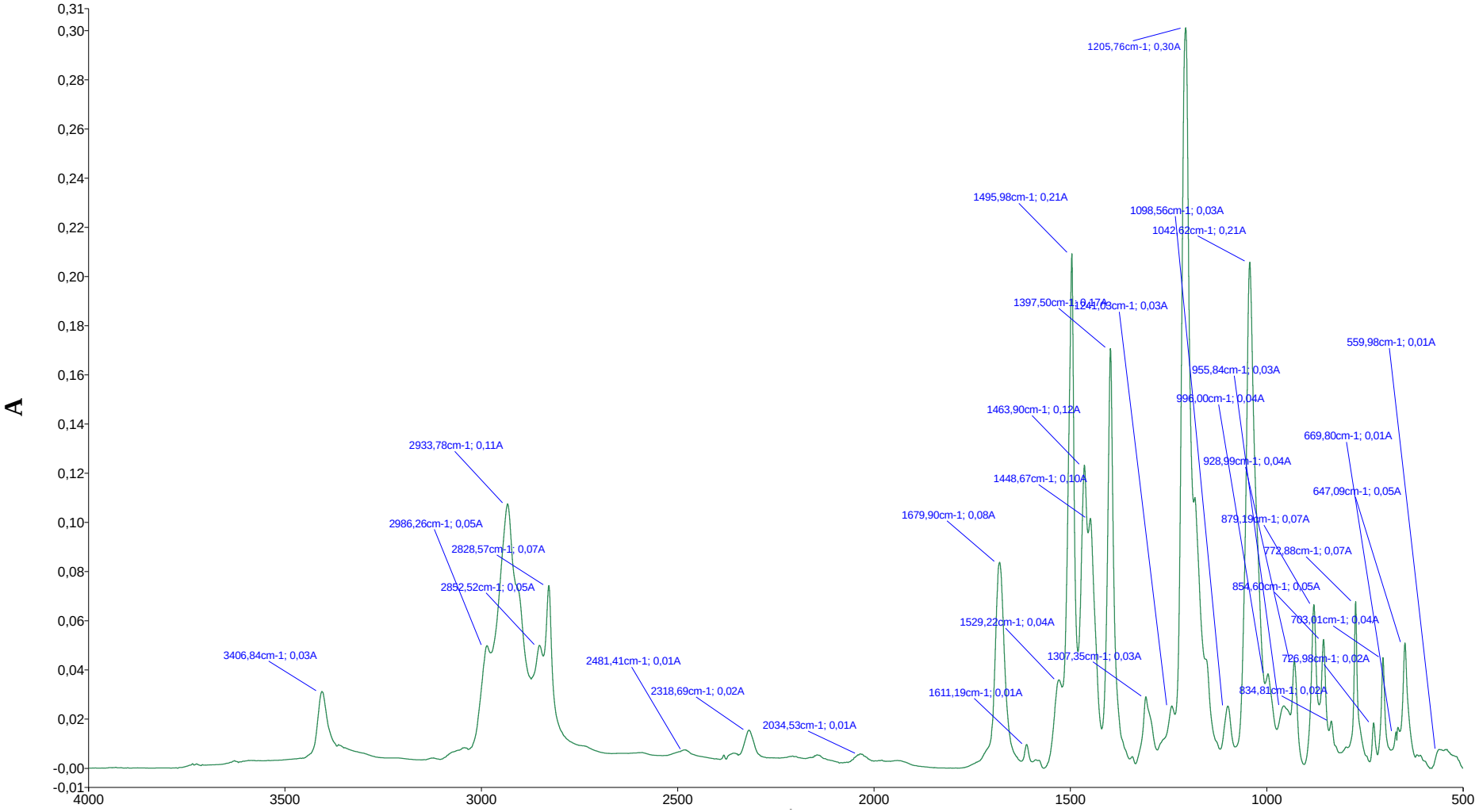


Fig. S32. IR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{6'-aminohexyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6).

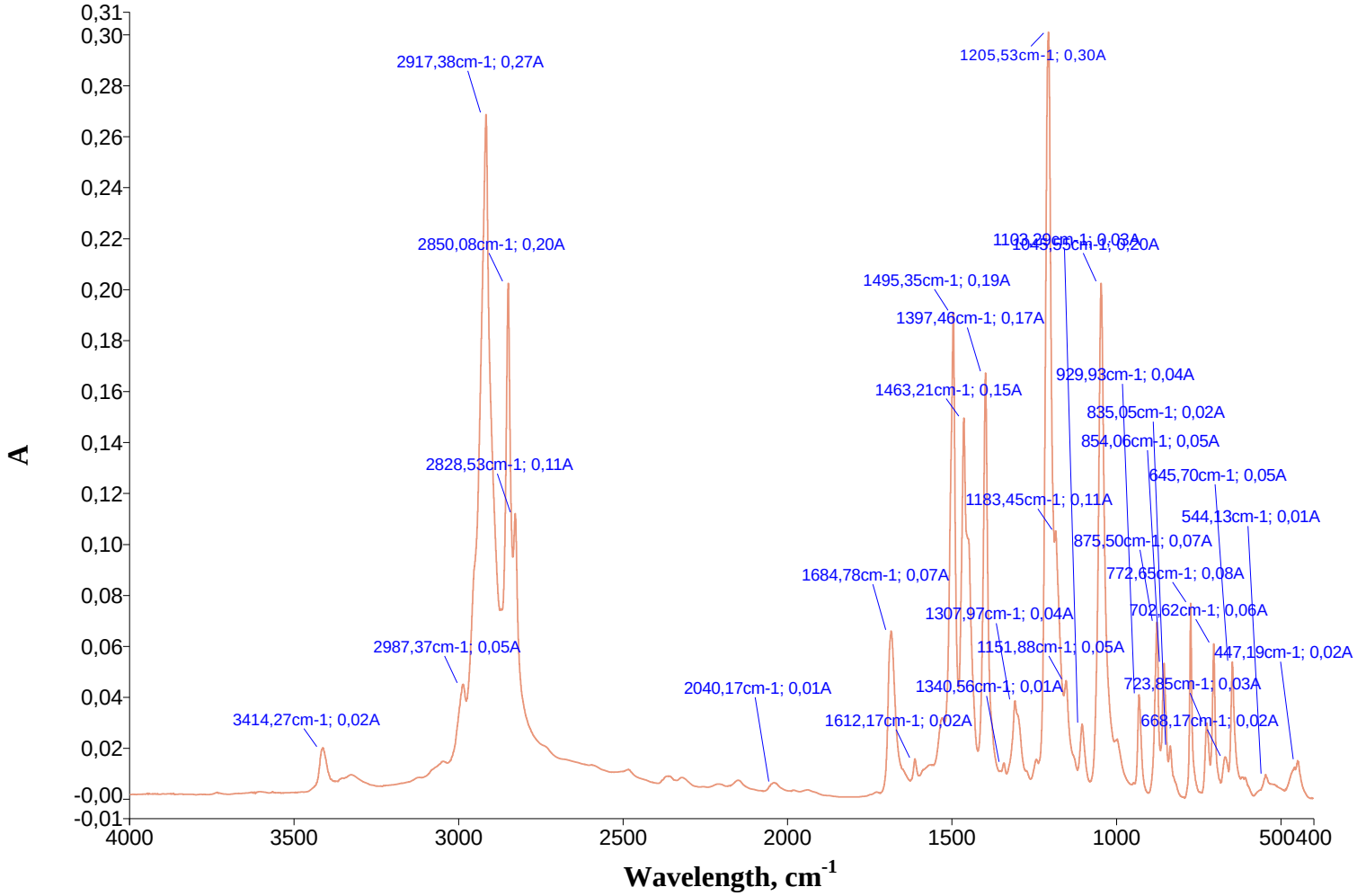


Fig. S33. IR spectrum of 4-[(*N*-[1-(O,O-diethylphosphoryl)-1-methylethyl]-{12'-aminododecyl}-amino)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (7).

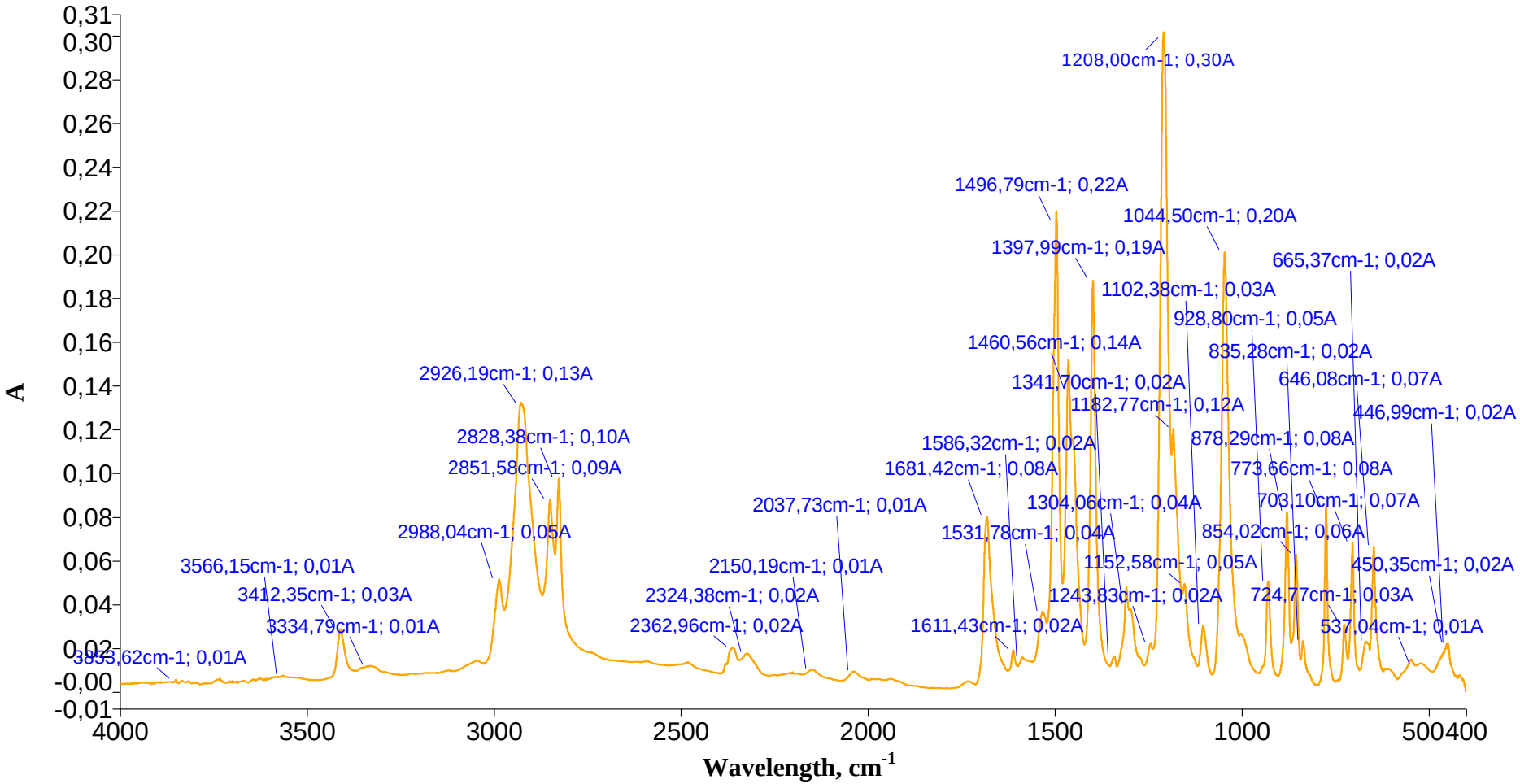


Fig. S34. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(*N*-{4'-aminobutyl}-amino)-carbomoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2), $CDCl_3$, 298 K, 400 MHz.

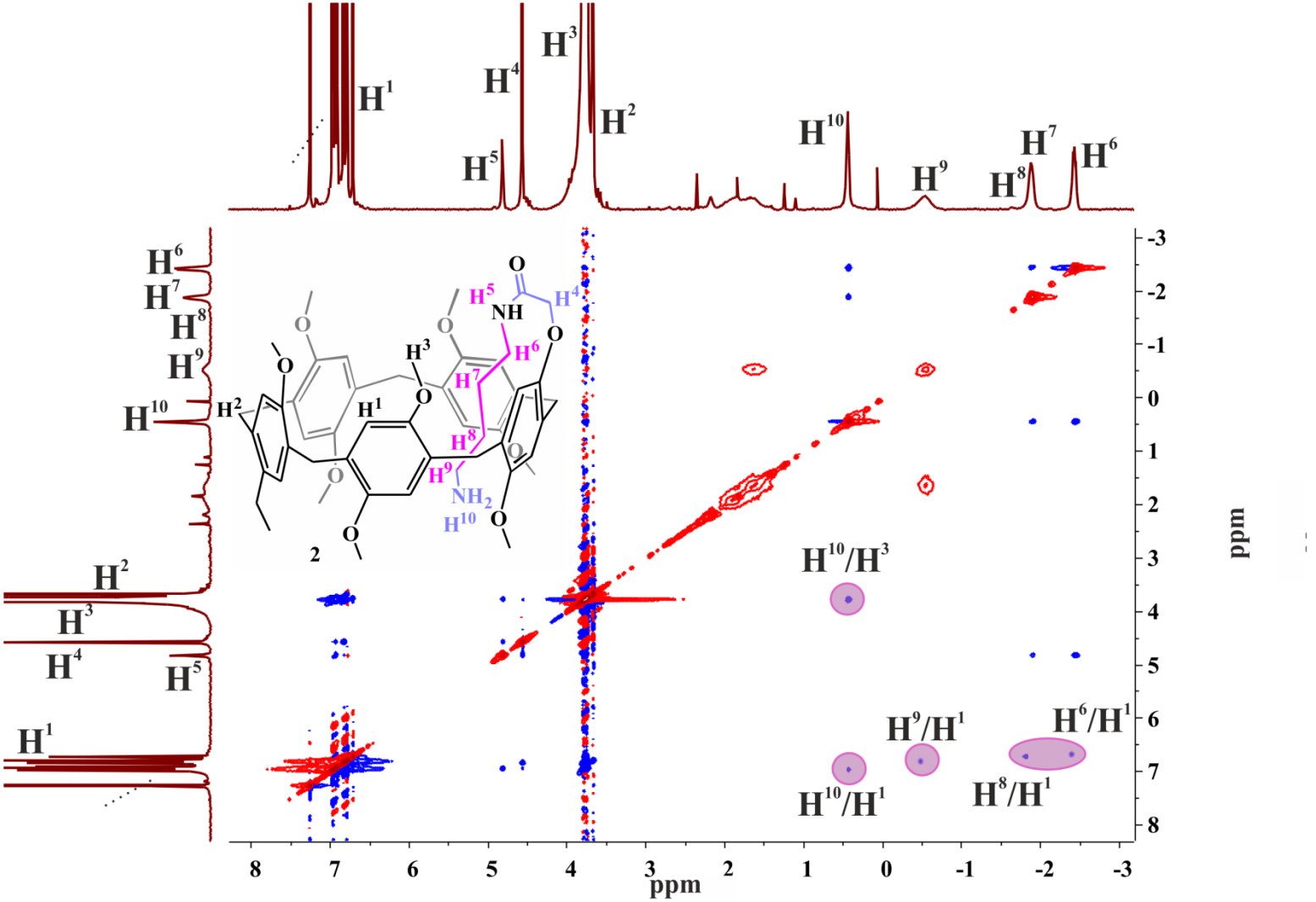


Fig. S35. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(*N*-{4'-aminobutyl}-amino)-carbomoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2), DMSO-d_6, 298 K, 400 MHz.

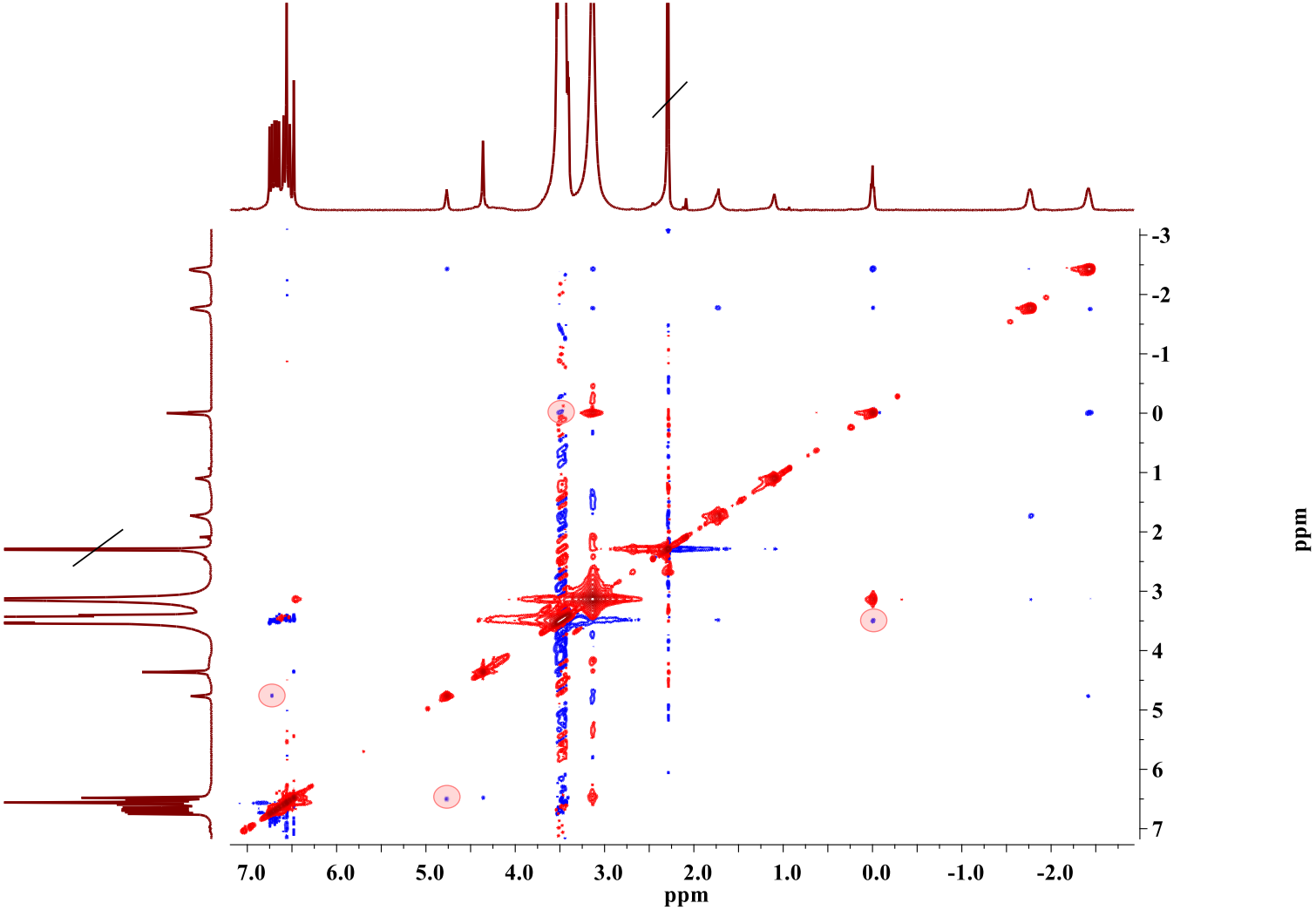


Fig. S36. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(*N*-{6'-aminohexyl}-amino)-carbomoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3), $CDCl_3$, 298 K, 400 MHz.

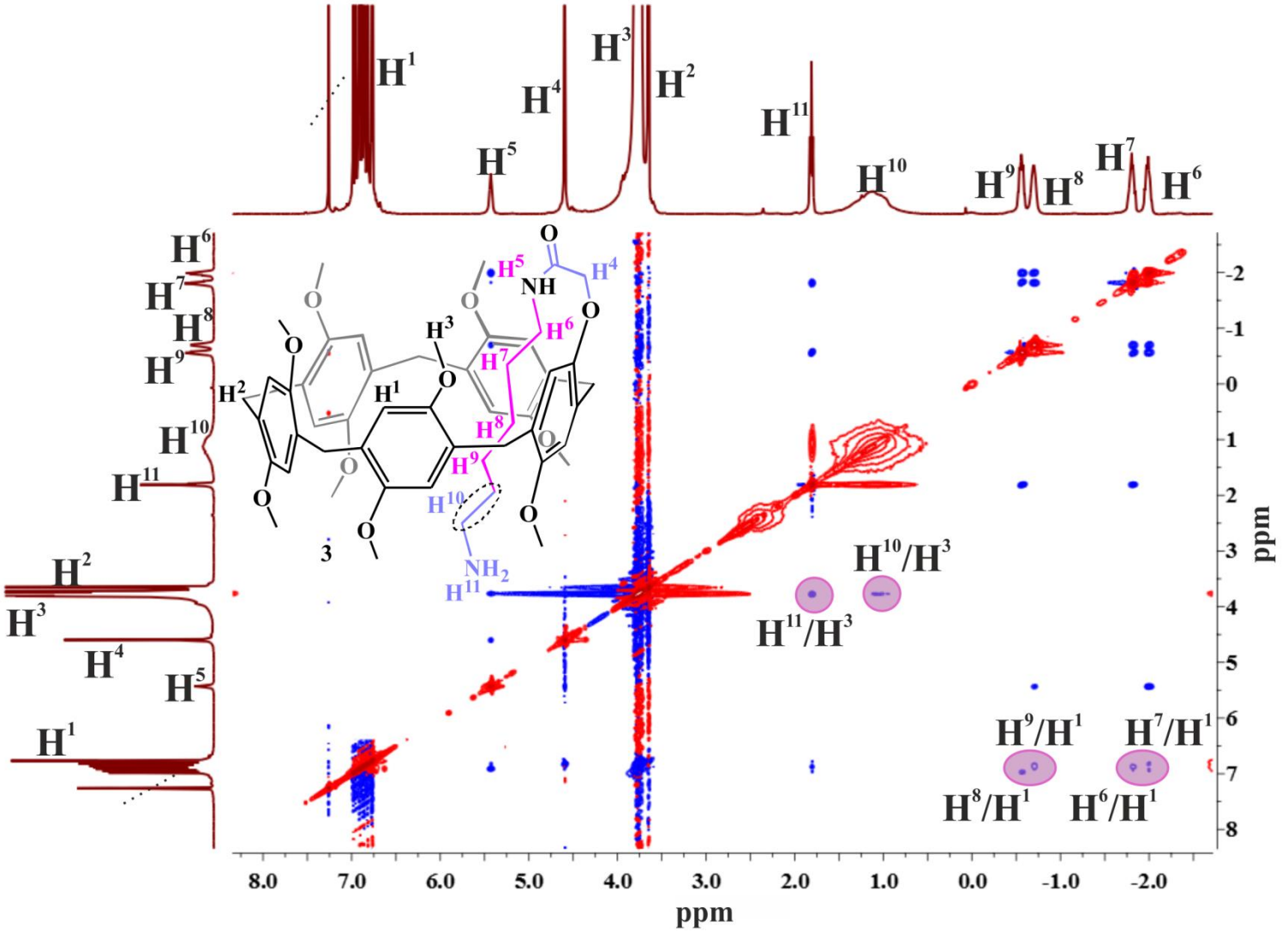


Fig. S37. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(*N*-{6'-aminohexyl}-amino)-carbomoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3), DMSO-d_6, 298 K, 400 MHz.

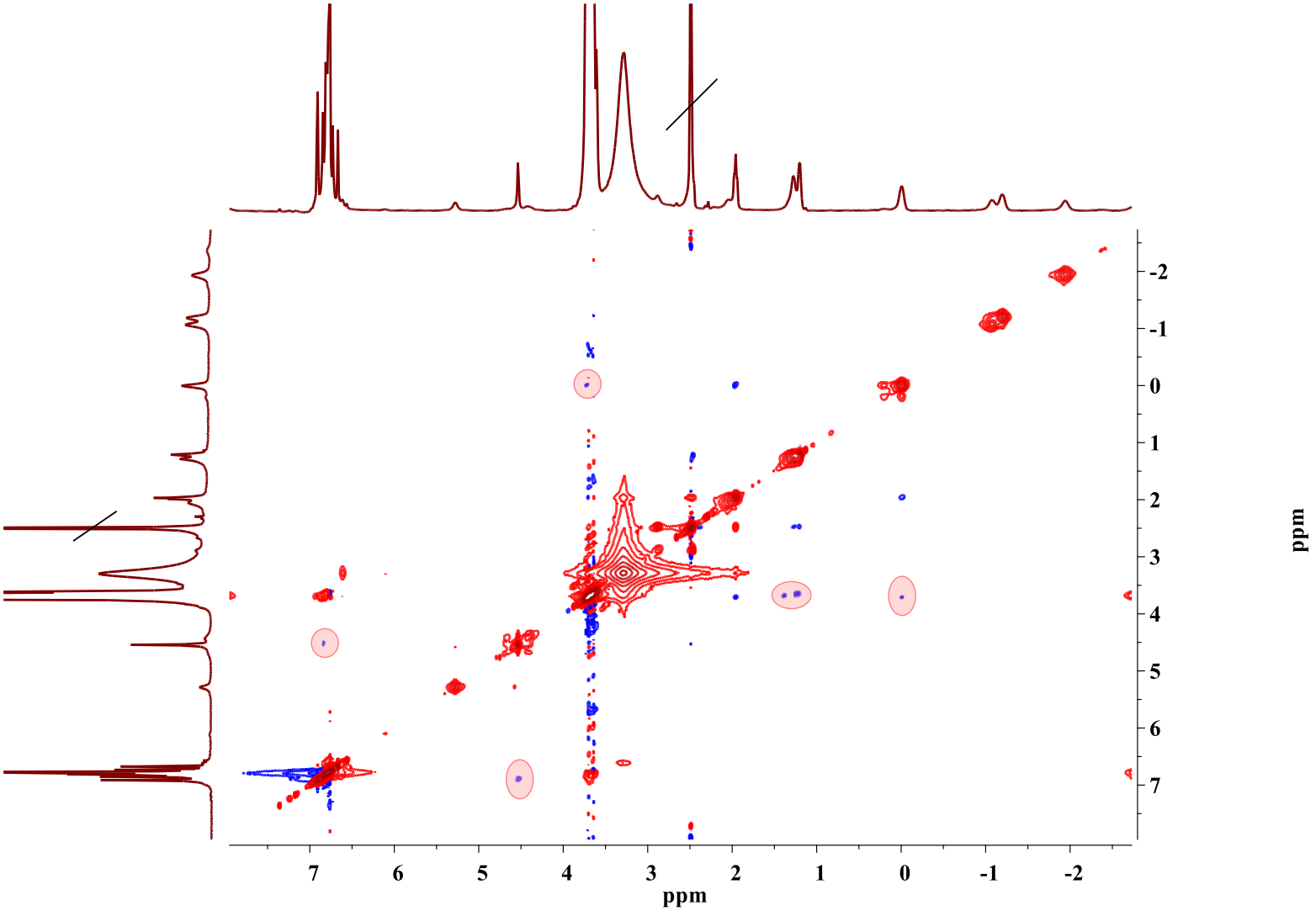


Fig. S38. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(*N*-{12'-aminododecyl}-amino)-carbomoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), $CDCl_3$, 298 K, 400 MHz.

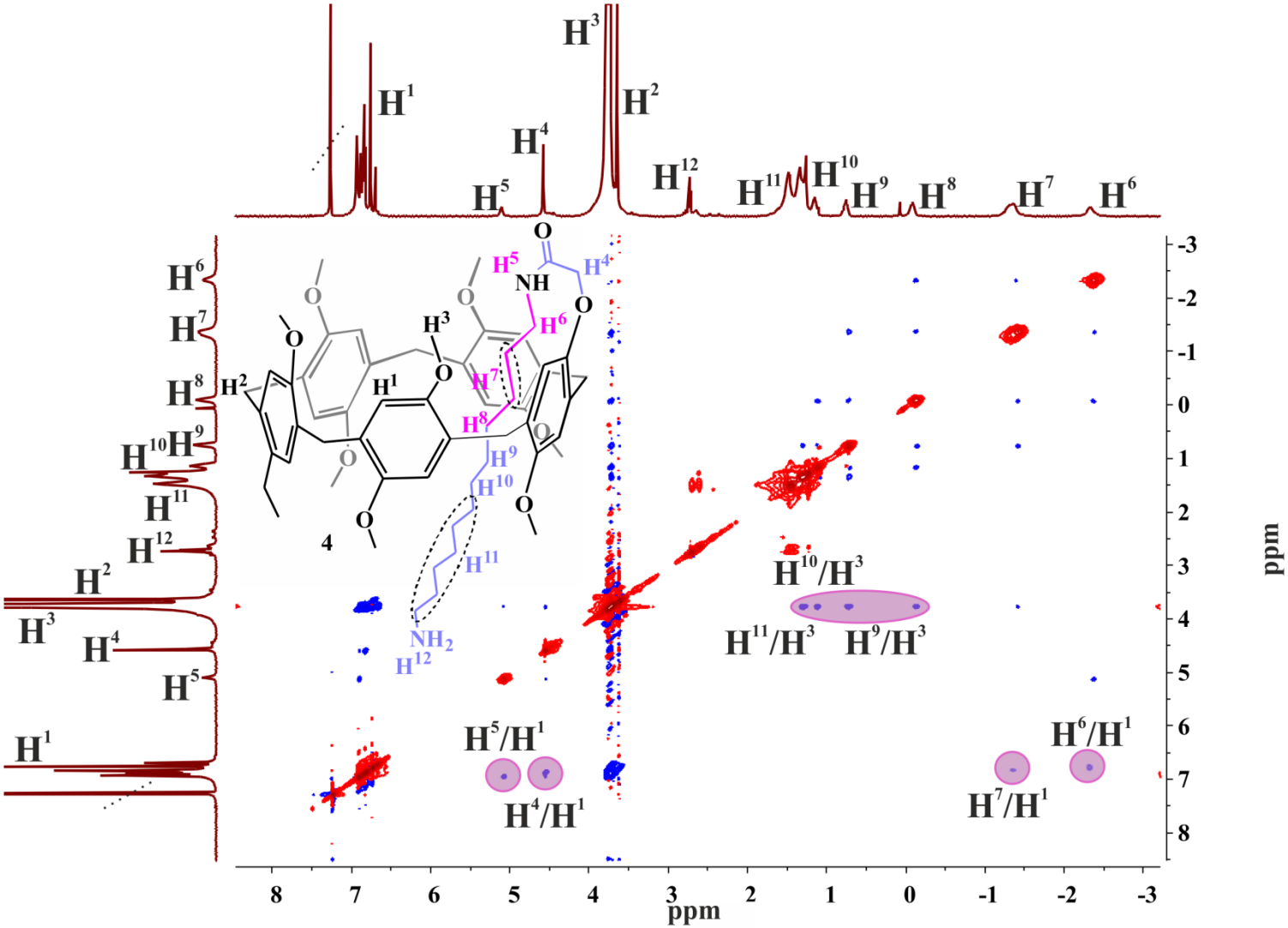


Fig. S39. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(*N*-{12'-aminododecyl}-amino)-carbomoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), DMSO-d_6, 298 K, 400 MHz.

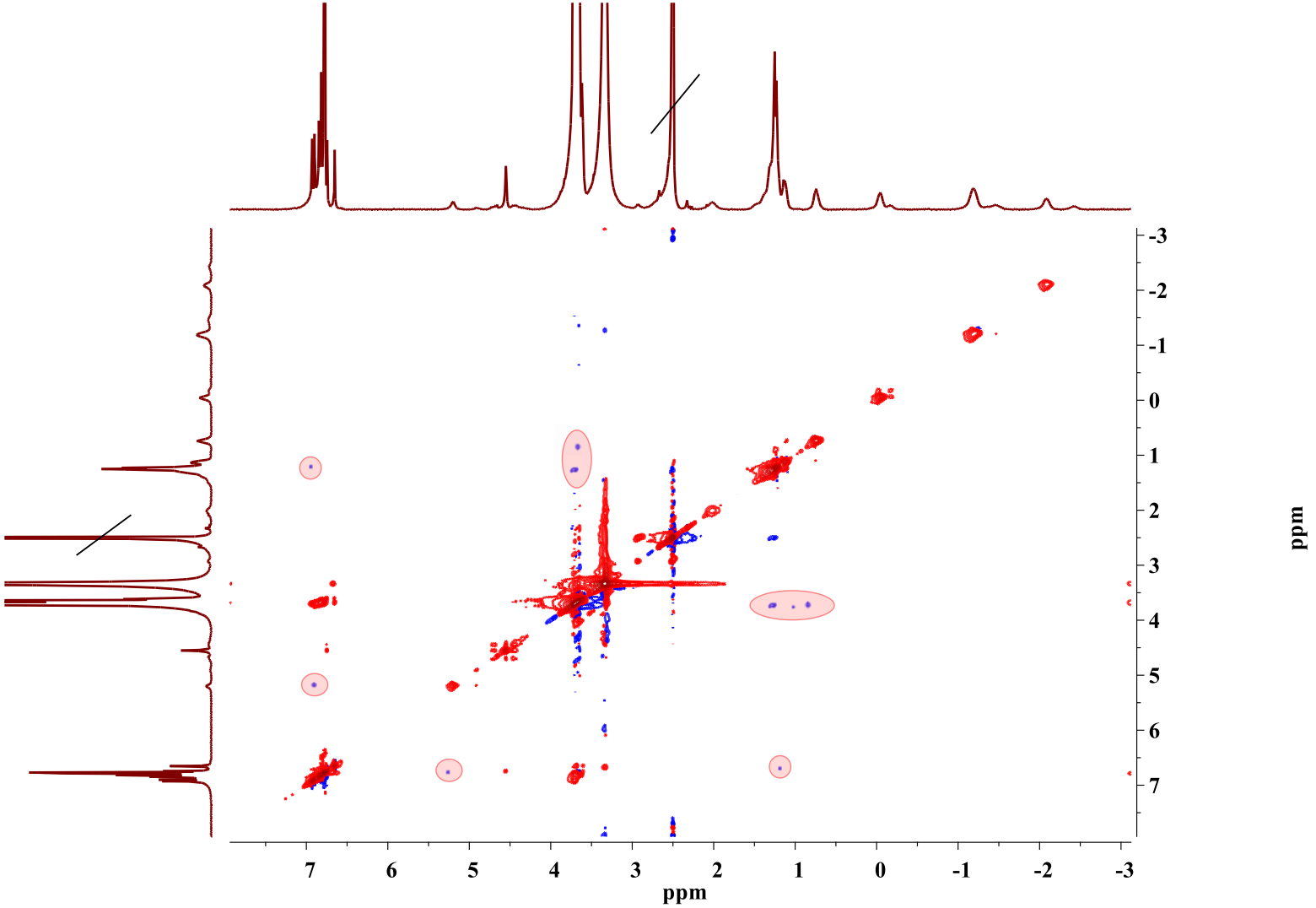


Fig. S40. Variable-temperature ^{1}H NMR spectra of pillar[5]arene (5) (DMSO-d_6, 400 MHz) at: a) 353 K; b) 298 K.

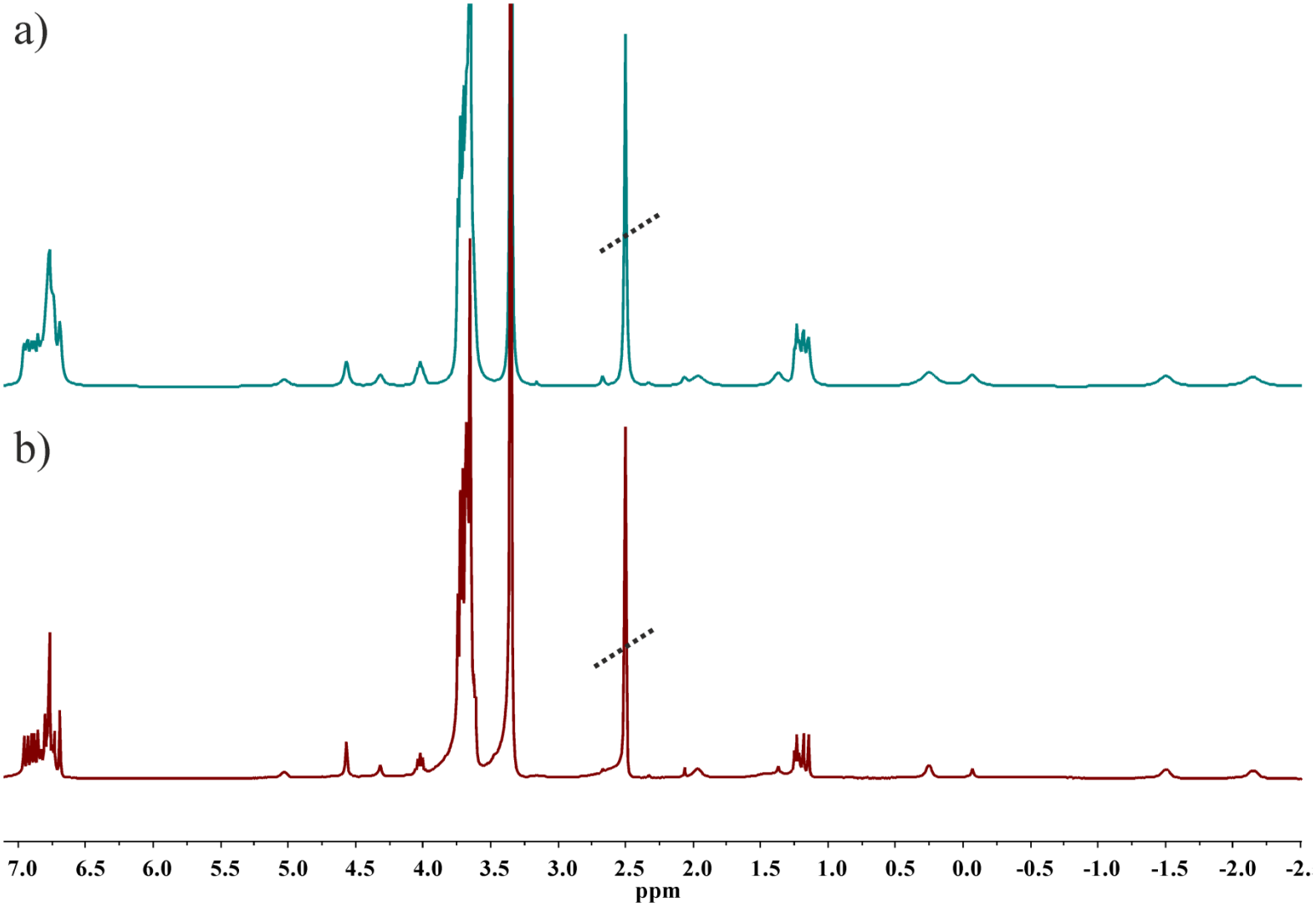


Fig. S41. Variable-temperature ^{1}H NMR spectra of pillar[5]arene (6) (DMSO-d_6, 400 MHz) at: a) 353 K; b) 298 K.

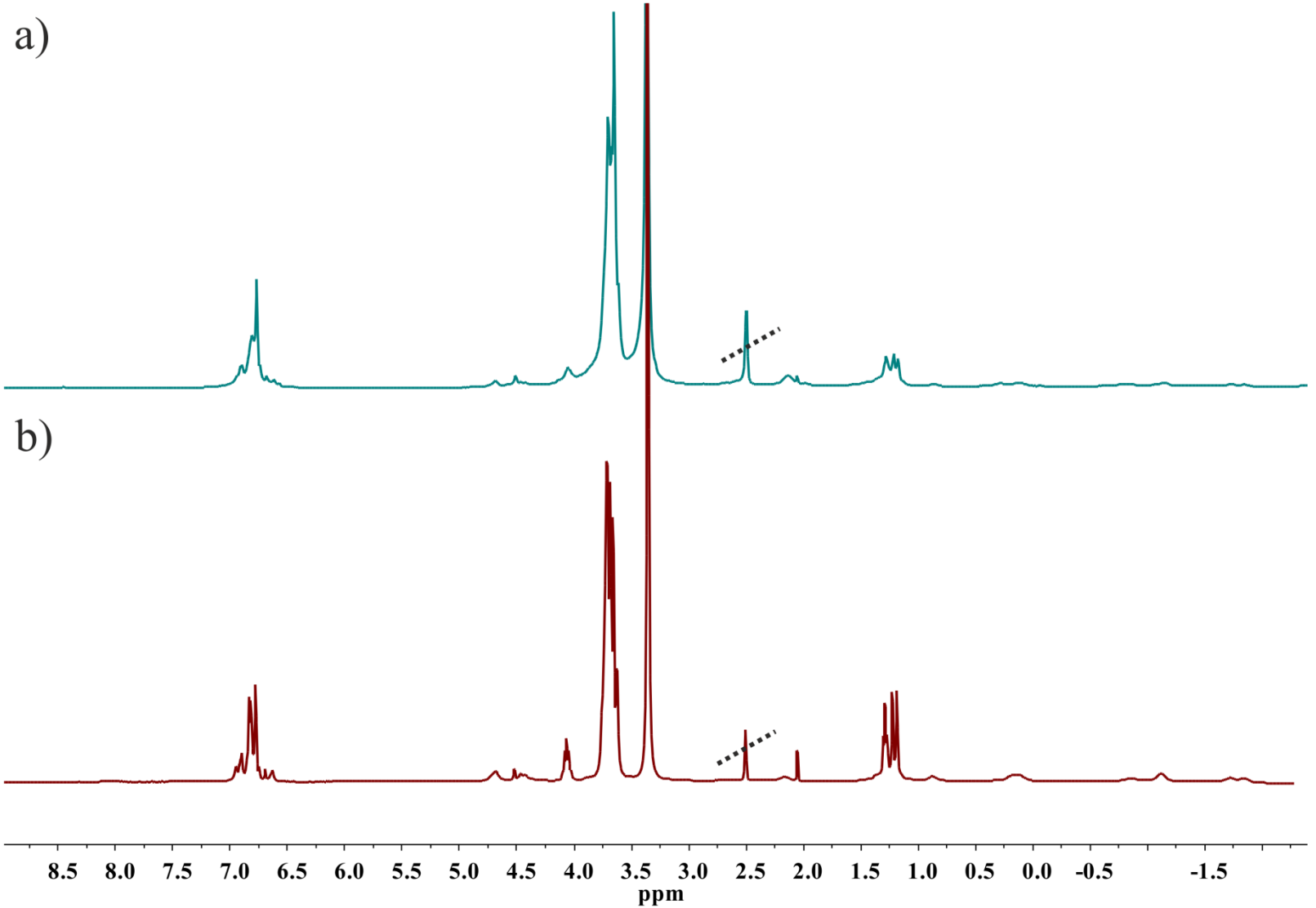
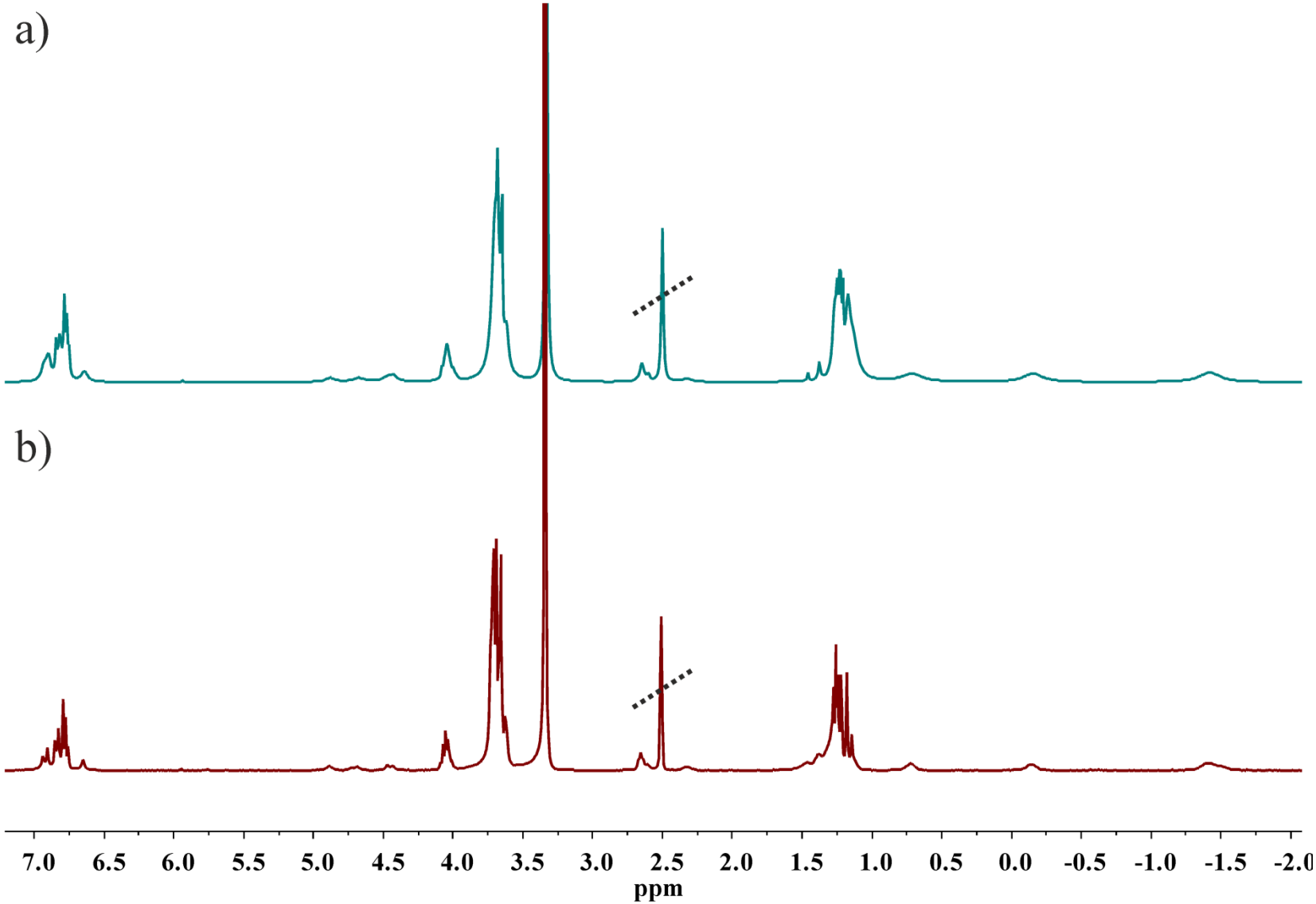


Fig. S42. Variable-temperature ^{1}H NMR spectra of pillar[5]arene (7) (DMSO-d_6, 400 MHz) at: a) 353 K; b) 298 K.



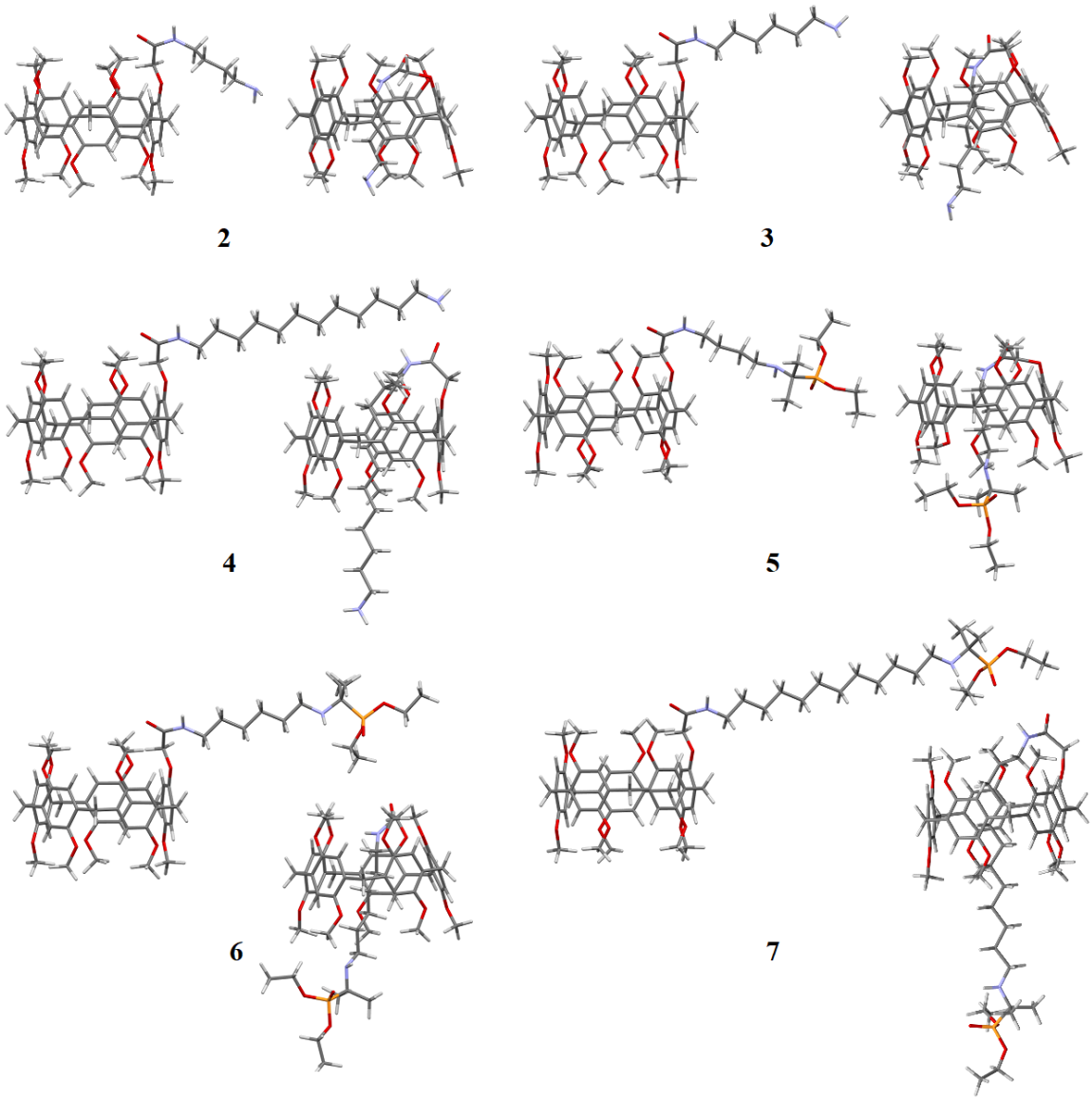
Computational method

Models of **2**-**7** were built using *Spartan 20* [S2] in two conformers. In the first series, the amide substituent was oriented outside the macrocyclic cavity; in the second a pseudo[1]rotaxane (**2**-**4**) or [1]rotaxane (**3**-**7**) structure was formed. Following geometry optimization by molecular mechanics (Merck Molecular Force Field) the structures were further refined by DFT/EDF2/6-31G* and their Gibbs free energies calculated. For **2**-**4**, the shorter substituents were more stable as the pseudo[1]rotaxane, however, in all cases the energy barrier to threading and de-threading was less than 12 kJ mol^{-1}. As these are gas phase calculations, no account has been made of the solvent used in the reaction and it is likely that both endo- and exo- forms exist in equilibrium. The isolated yields for [1]rotaxanes **5**-**7** are around 60% suggesting a slight thermodynamic preference for the formation of pseudo[1]rotaxanes which are subsequently stoppered.

Pillar[5]arene	ΔG (kJ mol^{-1})
2	-4.49
3	-10.86
4	10.78
5	4.41
6	-14.72
7	11.45

Table S1. Free energies for pseudo[1]rotaxane and [1]rotaxane formation

Fig. S43. Calculated structures for 2-7 (left: unthreaded, right: threaded).



References

S1 Y. Chen, D. Cao, L. Wang, M. He, L. Zhou, D . Shollmeyer, H. Meier, Chem. Eur. J. **2013**, 19, 7064-7070.
S2 *Spartan 20*, Wavefunction, Inc., Irvine, CA, USA (2020)