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Employing phosphorylated betaines as kinetic hydrate promoters for gas storage application

Yulia F. Chirkova, Rustam R. Davletshin, Aidar M. Gayneev, Ulukbek Zh. Mirzakimov, Matvei E. Semenov, Roman S. Pavelyev, Andrey S. Stoporev and Mikhail A. Varfolomeev

Contents

General information

Alkyl bromides were used without purification (99%). Commercially available solvents (C_6H_6, Pr^iOH, petroleum ether) were purified by standard procedures. *p*-Toluenesulfonic acid (97.5% chemical grade) was employed.

NMR Spectroscopy

NMR spectra were recorded on the Bruker Avance III instrument with an operating frequency of 162 MHz for ^{31}P spectra, an operating frequency of 400 MHz for ^{1}H spectra and an operating frequency of 100.6 MHz for ^{13}C spectra in a solution of $CDCl_3$. The following abbreviations are used to describe coupling: s = singlet, br s = broad singlet, br t = broad triplet, br q = broad quartet, br m = broad multiplet.

FT-IR Spectroscopy

The Fourier Transformed InfraRed (FT-IR) spectrum of the sample was recorded using Perkin Elmer UATR Two FT-IR Spectrometer (Spectrum Two) with an ATR (attenuated total reflectance) diamond crystal.

MS

MS and MS/MS mass spectra were obtained on an AB Sciex QTRAP 6500 quadrupole mass spectrometer with a linear ion trap (AB SCIEX PTE. Ltd., Singapore) using a Turbo V turbo ion sputtering source (atomizer nitrogen gas, positive ionization polarity, 5200 V needle voltage). Spectra were recorded in the modes "Q1" with the collision energy 10 eV and the declustering potential 90 eV and "Product Ion" with the collision energy 25 eV and the declustering potential 90 eV. Samples with a concentration of 5 μmol/l were prepared by dissolving the test compounds in methanol (LC-MS, Merck).

Melting points

Melting points were measured with an IA9000 SERIES Electrothermal digital melting point apparatus with ± 0.5 °C accuracy and 0.1 °C resolution.

Rocking cells data

The experimental *P*, *T*-curves for a hydrate formation stage in methane – propane – aqueous solution system obtained in this work on RC5 (30 ml 316L stainless steel rocking cells) were compared with the data on Sintanol ALM-7 obtained in [S3] on RCS6 (22 ml leucosapphire rocking cells). The volume of the test solution/the swing angle/rocking frequency were 10 ml/±20°/5 min^{-1} for SDS* (RC5), 15 ml/±45°/10 min^{-1} for betaine **B12** (RC5), and 10 ml/±45°/10 min^{-1} for 0.25 mass% Sintanol ALM-7 (RSC6). The initial pressure and temperature, temperature program, and hydrate-forming gas were the same in all cases.

The effect of the synthesised compounds on the formation of methane-propane hydrates was investigated by rocking cells (Rocking Cell 5 (RC5), PSL Systemtechnik GmbH, Germany). This work used 4.34 mol% C_3H_8 + 95.66 mol% CH_4 as a hydrate former. The 316L steel cells were equipped with steel balls for sample stirring, temperature and pressure transducers (accuracy ± 0.2 °C and 0.1 bar, respectively). The experiments were carried out according to the following test procedure. The volume of the test solution was 15 ml, the swing angle was ±45° and the frequency equaled 10 min^{-1}. Hydrate-forming gas was fed into the pre-purge cells. The experimental cycle was started by incubating the cells at 18.5 °C and 60 bar for 1 h followed by cooling at 1 °C/h from 18.5 °C to –0.5 °C under isochoric conditions. In the case of SDS, additional experiments were also carried out using a different technique (marked with an asterisk for the difference). The difference was the rocking mode and the volume of the solution: rocking angle ±20°, 5 min^{-1}, and 10 ml respectively (SDS*).

The synthesis of compounds **B8-B18** was described in [S1,S2].

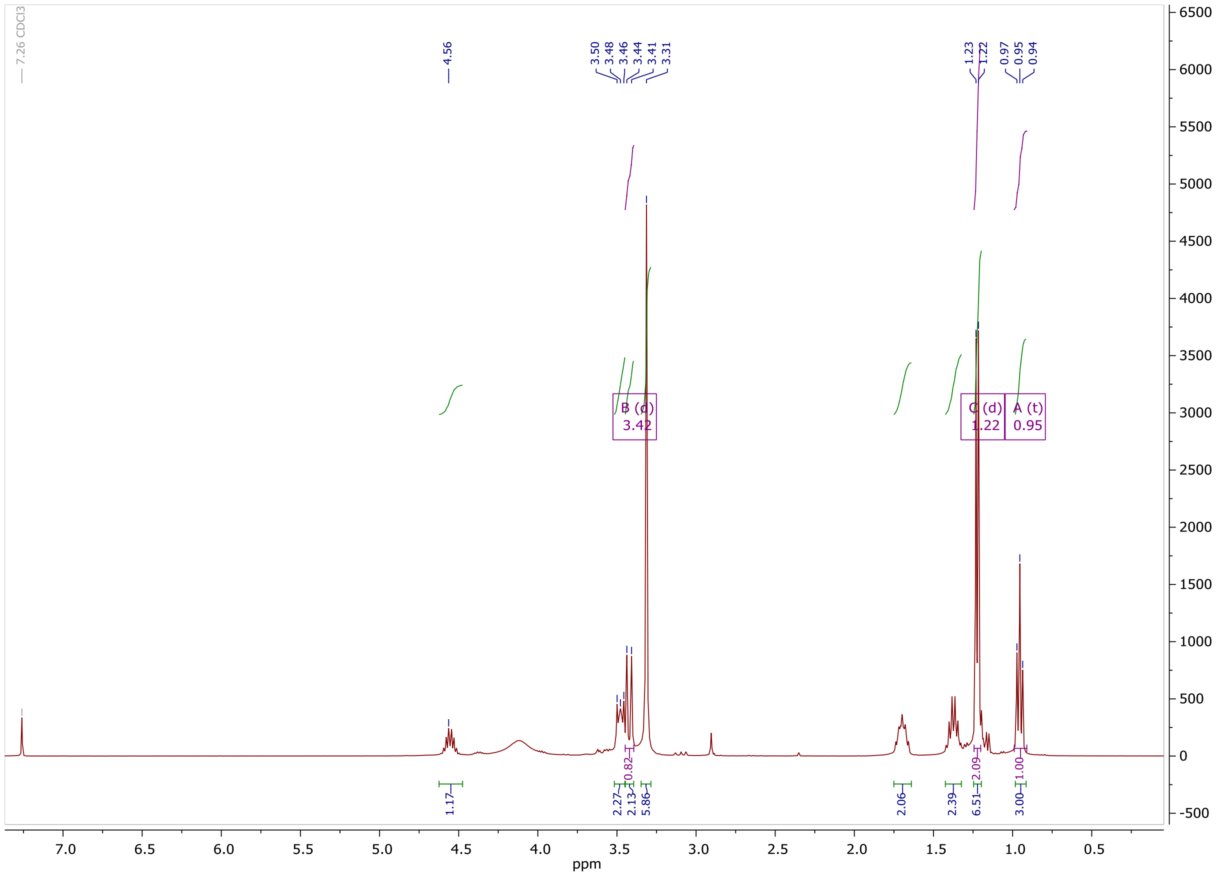
NMR, IR and HRMS Spectra

Isopropyl [(*N*-butyl-*N*,*N*-dimethylammonio)methyl]phosphonate (B4)

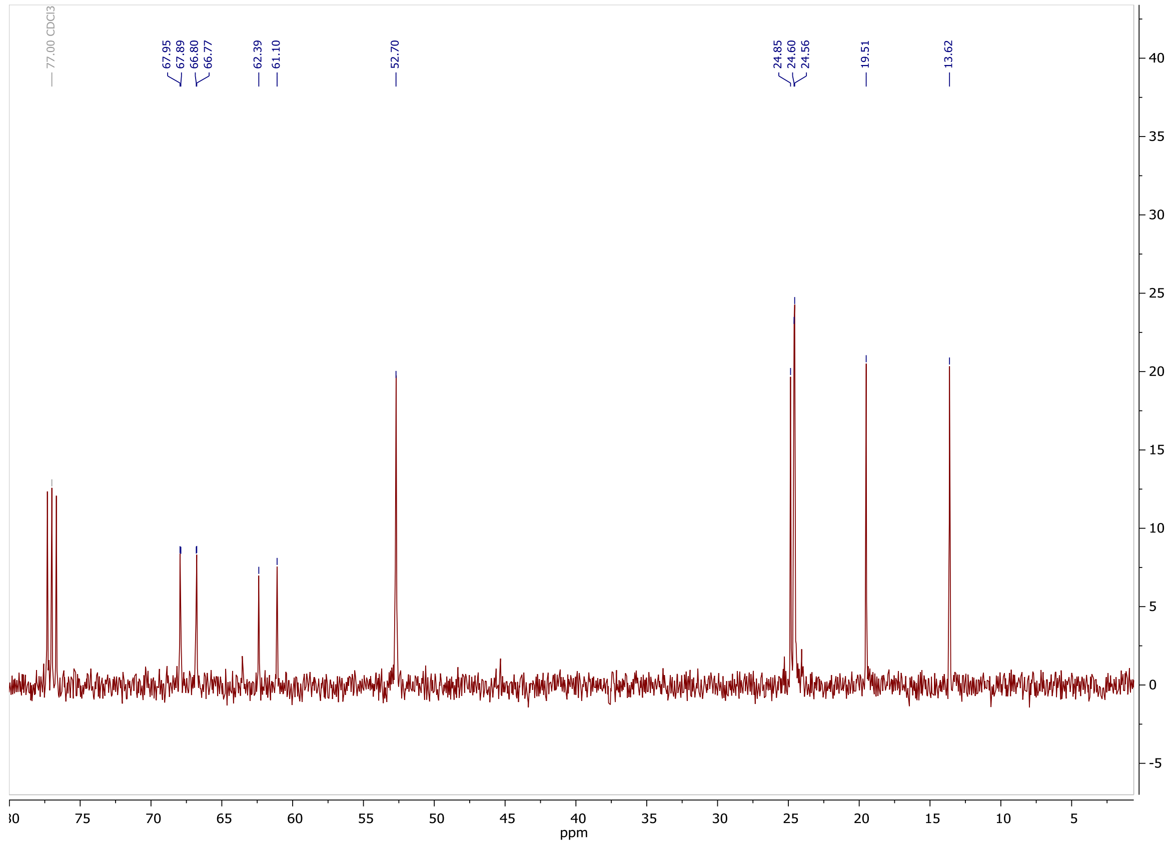
White powder. M.p. 68 °C. Yield 83 %. IR spectrum, cm^{-1}: 1068 (P-O-C), 1218 (P=O). ^{1}H NMR (CDCl$_3$), δ_H, m.d.: 0.95 t. (3H, $C\underline{H}_3CH_2$, $^3J_{HH}$ 7.34 Hz), 1.22 d. (6H, $(C\underline{H}_3)_2CH$, $^3J_{HH}$ 6.19 Hz), 1.36-1.69 m. (4H, $(C\underline{H}_2)_2CH_3$,), 3.31 s. (3H, $C\underline{H}_3N$), 3.42 d. (2H, $PC\underline{H}_2$, $^2J_{PH}$ 12.04 Hz), 3.45-3.51 m. (2H, $NC\underline{H}_2CH_2$), 4.50-4.60 m. (1H, $C\underline{H}O$). ^{13}C NMR (CDCl$_3$), δ_C, m.d.: 13.62 s. ($\underline{C}H_2CH_3$), 24.58 d. ($OCH(\underline{C}H_3)_2$ $^3J_{CP}$ 4.07 Hz), 19.51 s., 24.85 s. ($CH_2(\underline{C}H_2)_2CH_3$), 52.70 d. ($N\underline{C}H_3$, $^3J_{CP}$ 1.62 Hz), 61.75 d. ($N\underline{C}H_2P$, $^1J_{CP}$ 130.20 Hz), 66.77 d. ($N\underline{C}H_2CH_2$, $^3J_{CP}$ 3.47 Hz), 67.92 d. ($PO\underline{C}H$, $^2J_{CP}$ 5.87 Hz). ^{31}P NMR (CDCl$_3$): δ_P 3.1 m.d. MS-TIS [M+H]$^+$ 238.1 (calculated for $C_{10}H_{25}NO_3P$, 238.15).

Isopropyl [(*N*-hexyl-*N*,*N*-dimethylammonio)methyl]phosphonate (B6)

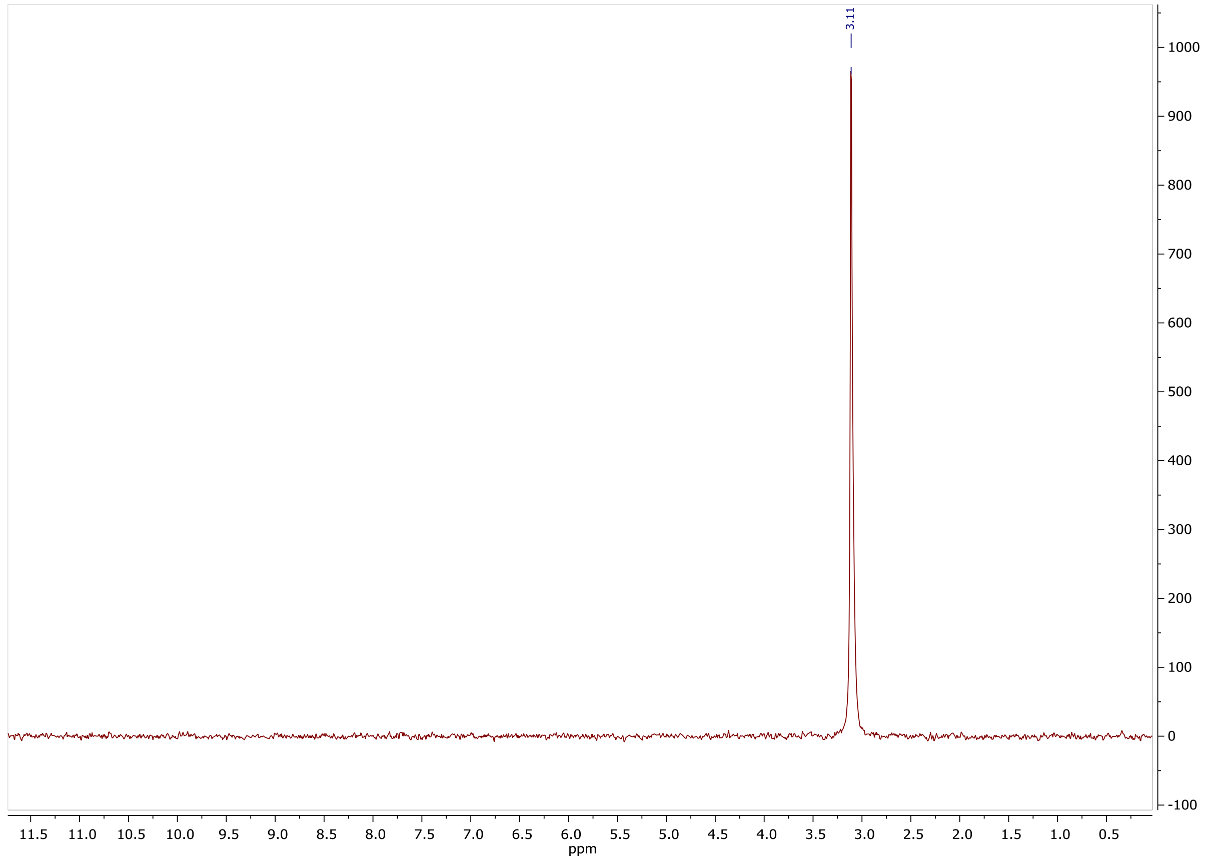
White powder. M.p. 70 °C. Yield 80 %. IR spectrum, cm^{-1}: 1063 (P-O-C), 1210 (P=O). ^{1}H NMR (CDCl$_3$), δ_H, m.d.: 0.87 t. (3H, $C\underline{H}_3CH_2$, $^3J_{HH}$ 6.51 Hz), 1.27 d. (6H, $(C\underline{H}_3)_2CH$, $^3J_{HH}$ 6.09 Hz), 1.28-1.81 m. (8H, $(C\underline{H}_2)_4CH_3$), 3.36 s. (3H, $C\underline{H}_3N$), 3.57 d. (2H, $PC\underline{H}_2$, $^2J_{PH}$ 12.34 Hz,), 3.48-3.55 m. (2H, $NC\underline{H}_2CH_2$), 4.58-4.69 m. (1H, $C\underline{H}O$). ^{13}C NMR (CDCl$_3$), δ_C, m.d.: 13.84 s. ($CH_2\underline{C}H_3$), 24.52 d. ($OCH(\underline{C}H_3)_2$ $^3J_{CP}$ 4.23 Hz), 22.36 s., 22.95 s., 25.84 s., 31.23 s. ($CH_2(\underline{C}H_2)_4CH_3$), 52.83 d. ($N\underline{C}H_3$, $^3J_{CP}$ 2.40 Hz), 61.43 d. ($N\underline{C}H_2P$, $^1J_{CP}$ 130.96 Hz), 67.12 d. ($N\underline{C}H_2CH_2$, $^3J_{CP}$ 2.40 Hz), 68.63 d. ($PO\underline{C}H$, $^2J_{CP}$ 6.65 Hz). ^{31}P NMR (CDCl$_3$): δ_P 3.2 m.d. MS-TIS [M+H]$^+$ 266.2 (calculated for $C_{12}H_{29}NO_3P$, 266.18).



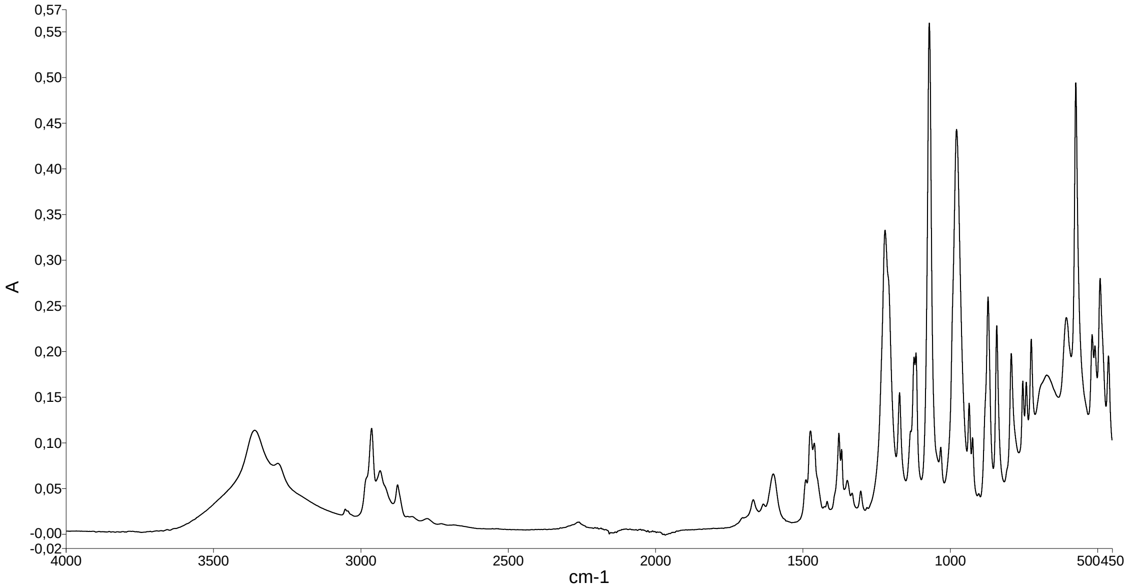
^{1}H NMR spectrum of **B4**



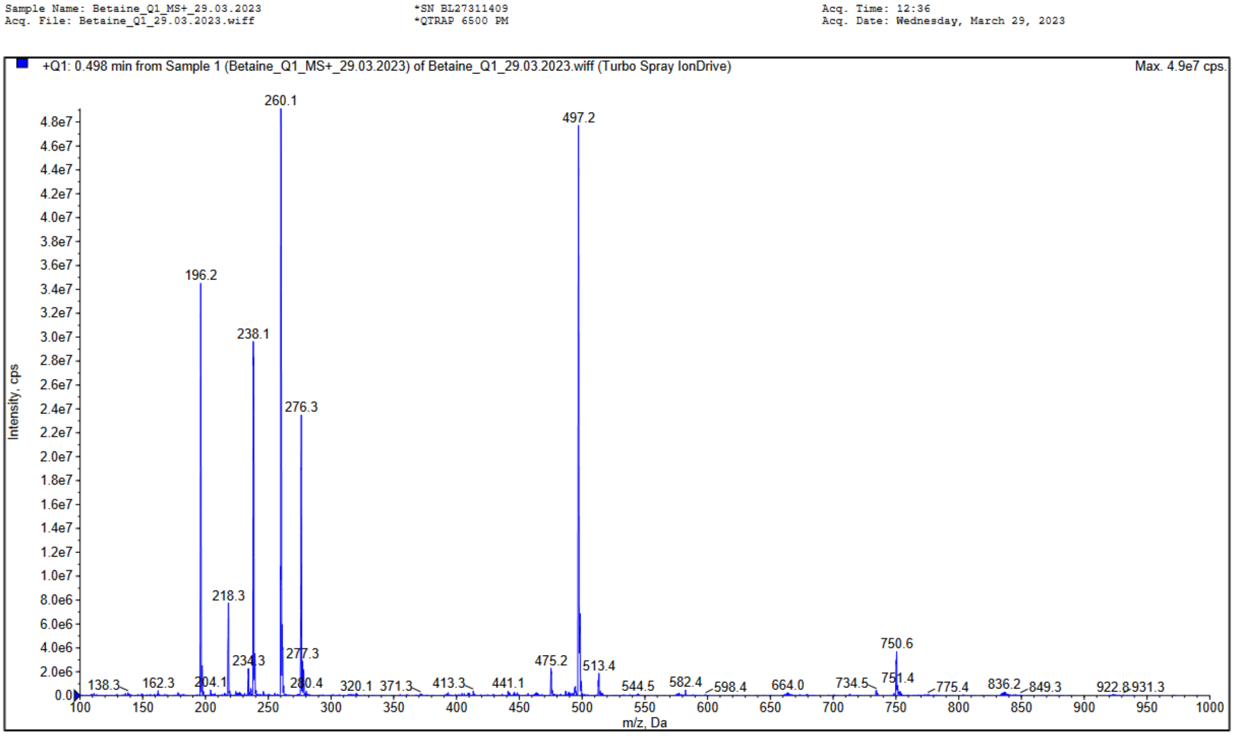
^{13}C NMR spectrum of **B4**



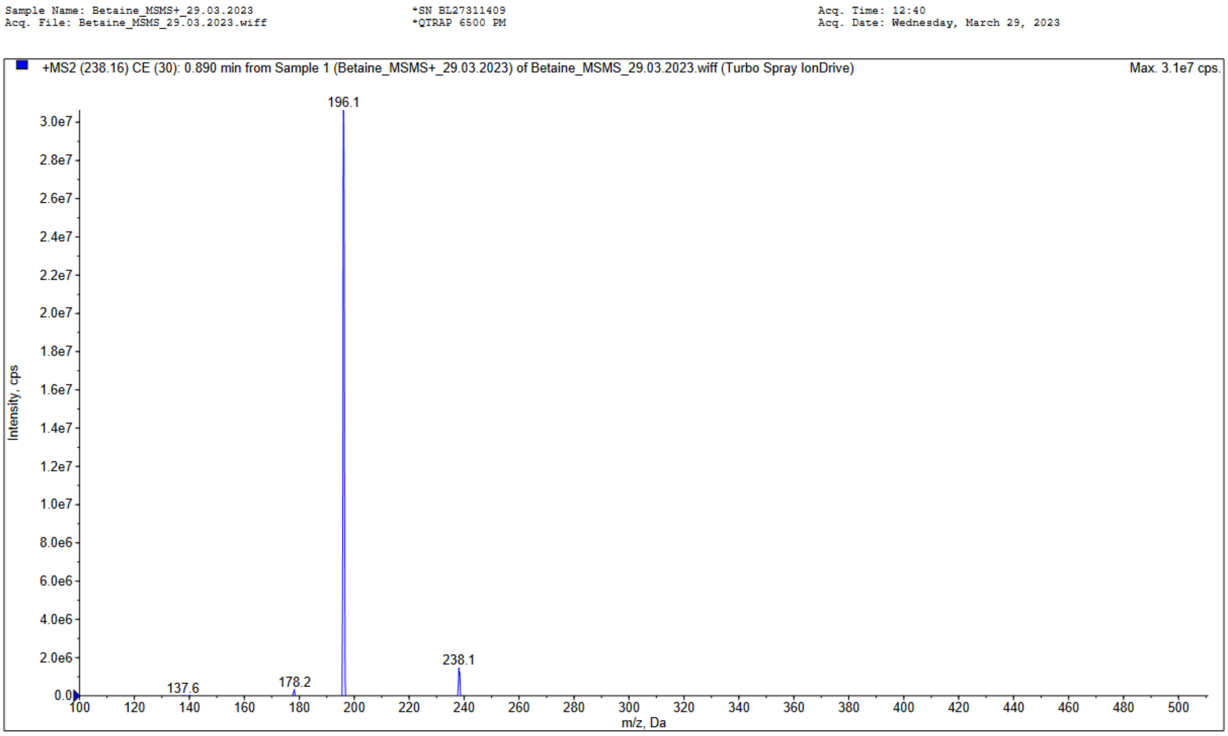
^{31}P NMR spectrum of **B4**



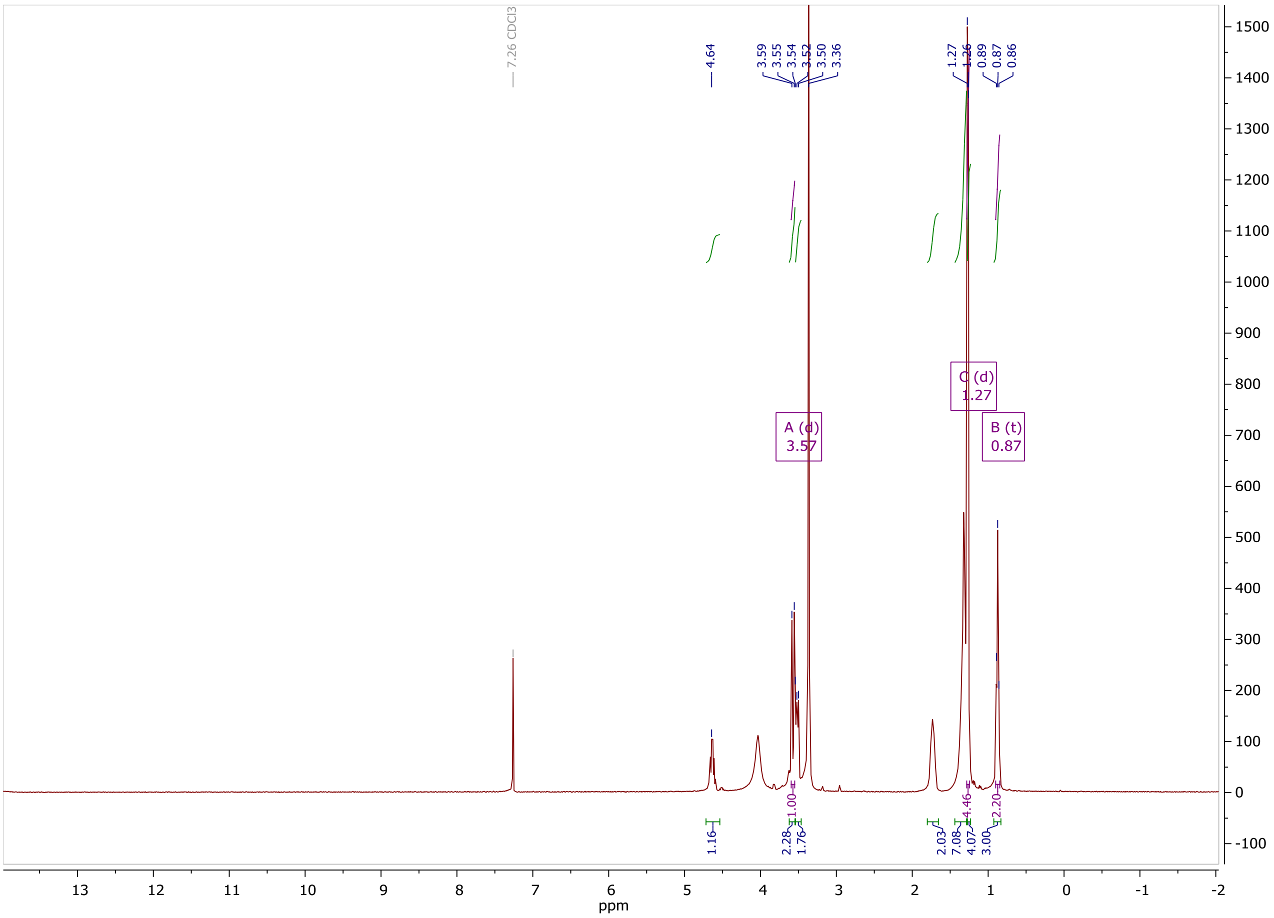
IR spectrum of **B4**



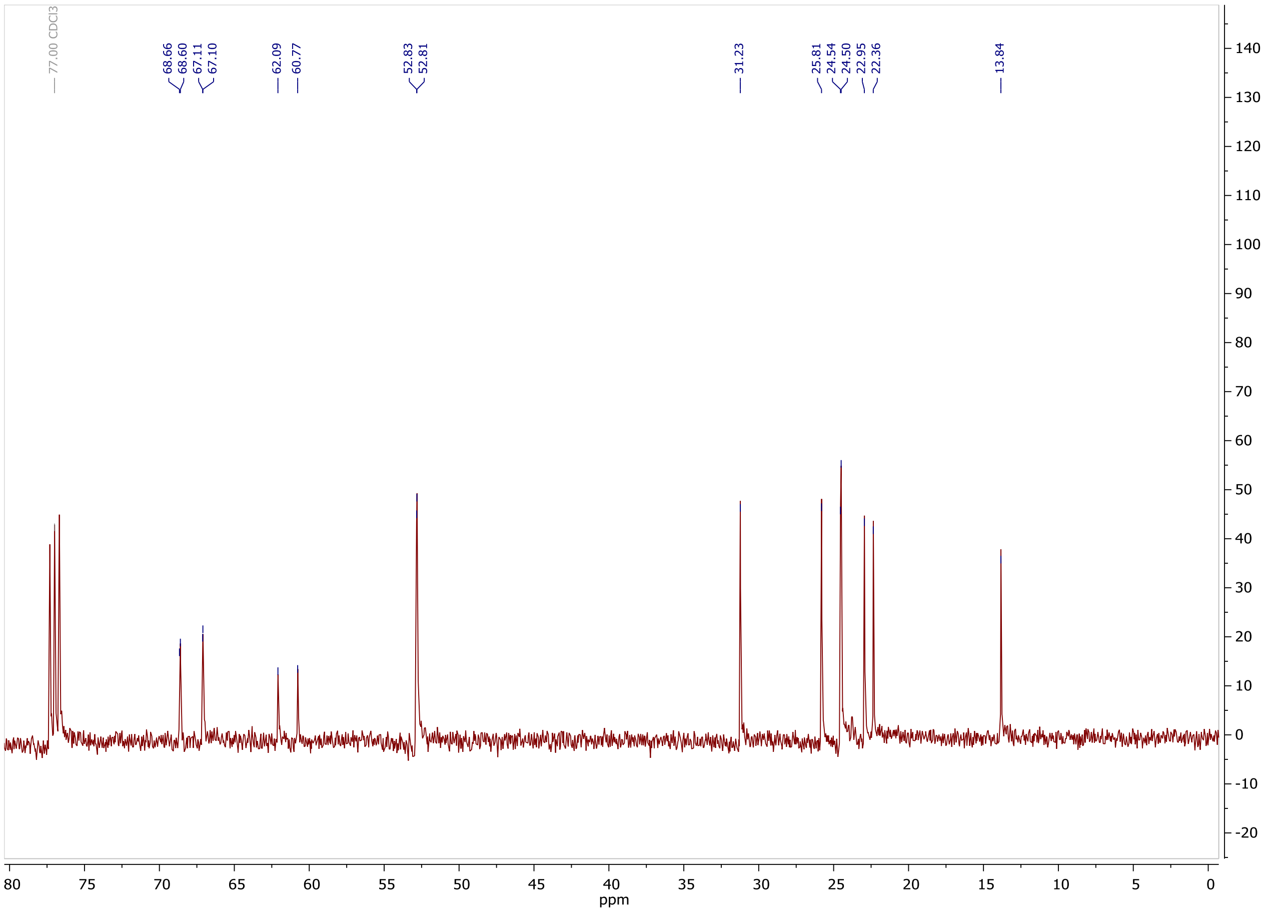
MS spectrum of **B4**



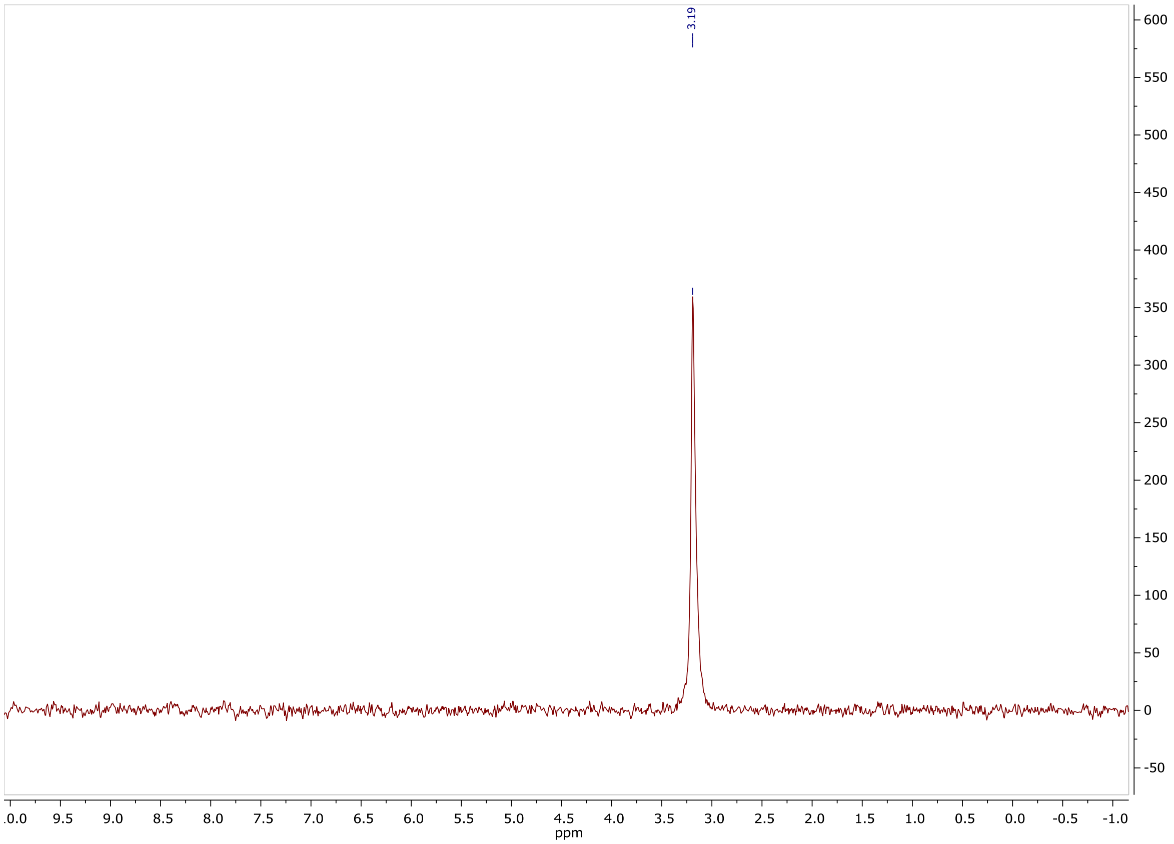
MS/MS spectrum of **B4**



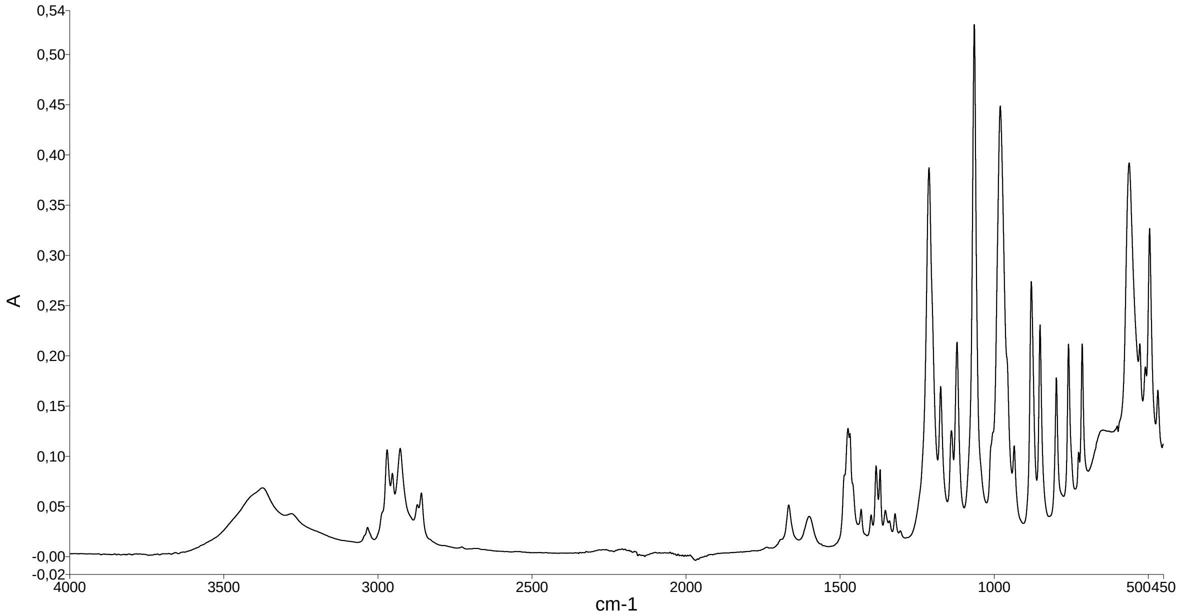
^{1}H NMR spectrum of **B6**



^{13}C NMR spectrum of **B6**



^{31}P NMR spectrum of **B6**



IR spectrum of **B6**

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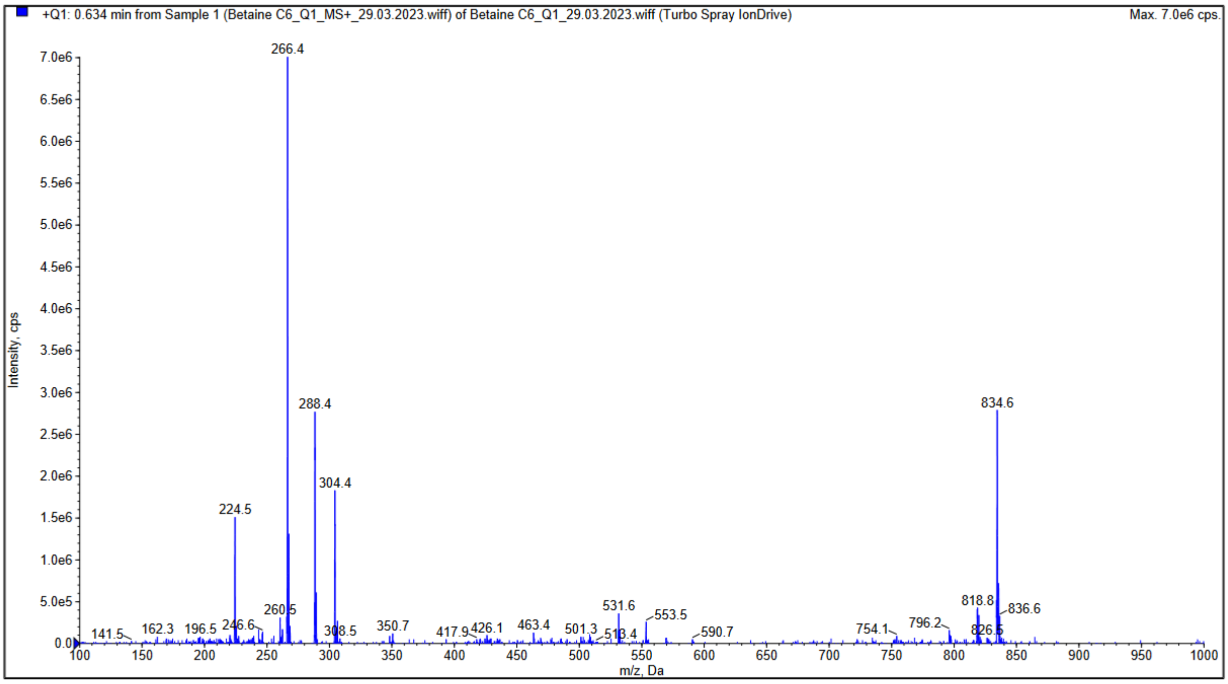

MS spectrum of **B6**

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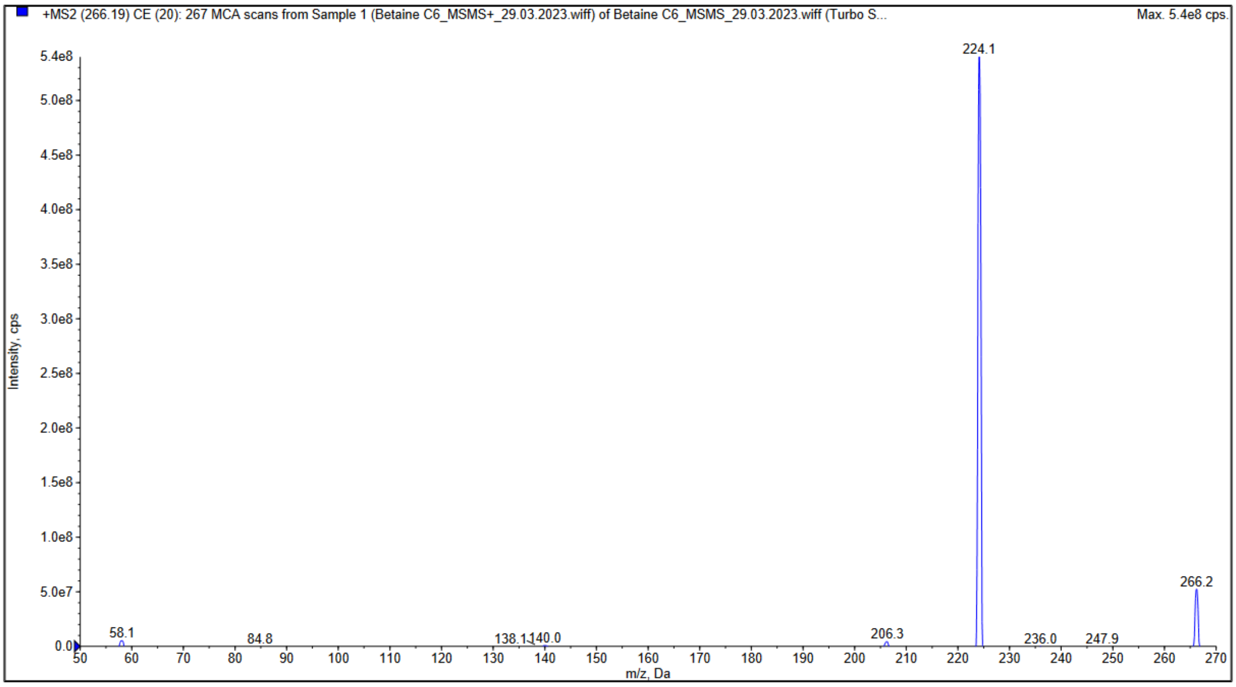
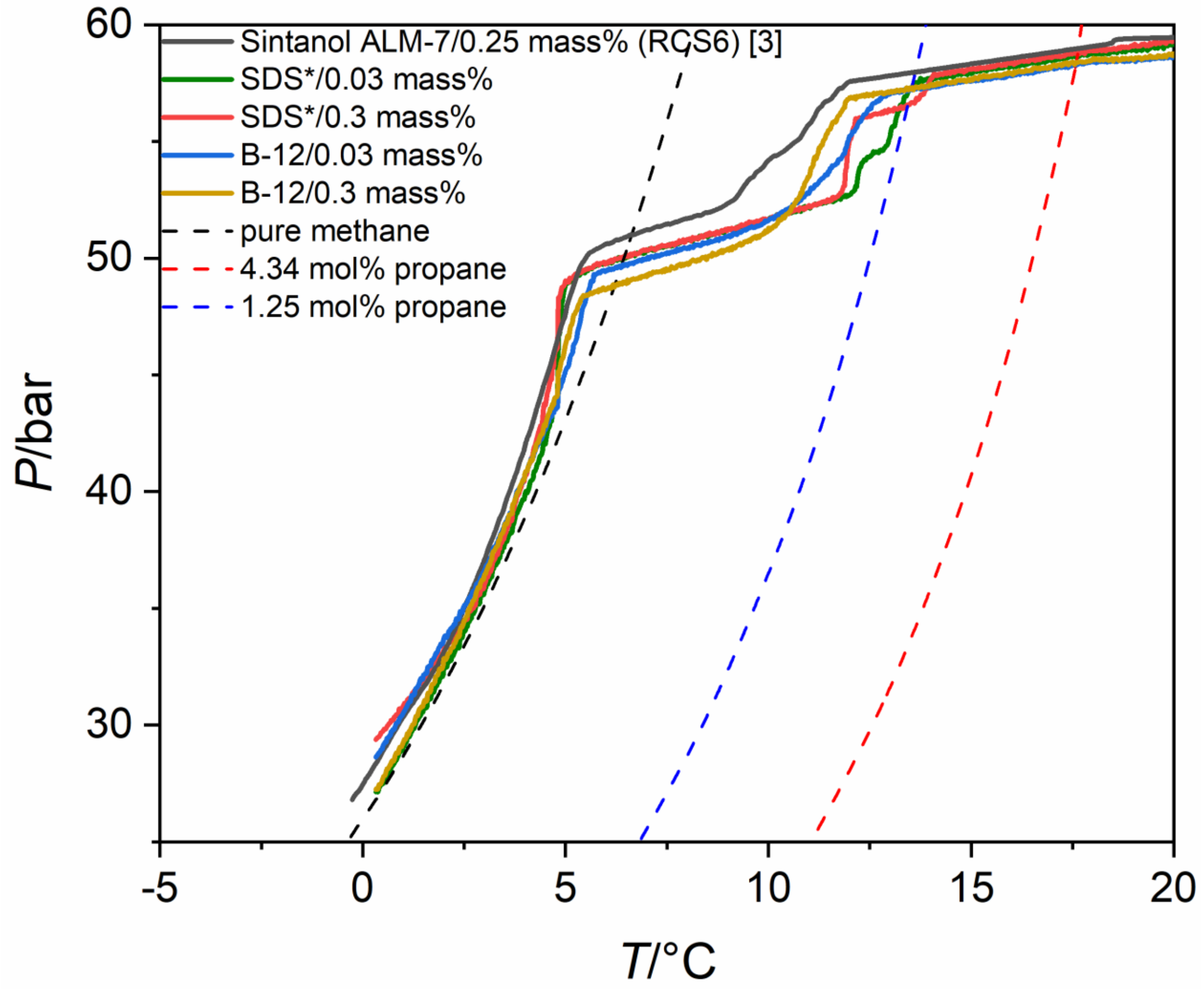


MS/MS spectrum of **B6**

Rocking cells data



The experimental *P*, *T*-curves (solid lines) for a hydrate formation stage in methane – propane – aqueous solution system; dashed curves correspond to equilibrium conditions of methane and methane-propane hydrates formation. The data obtained in this work on RC5 (SDS* and B-12) are compared with the data on Sintanol ALM-7 obtained in [S3] on RCS6.

References

S1. A. Gayneev, R. Davletshin, N. Davletshina, I. Galkina, M. Mirkhuzina, A. Sedov, E. Kuchaev and D. Islamov, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2022, **197**, 654.

S2. R. R. Davletshin, A. M. Gayneev, E. A. Ermakova, N. V. Davletshina, I. V. Galkina, K. A. Ivshin, M. P. Shulaeva and O. K. Pozdeev, *Mendeleev Commun.*, 2022, **32**, 180.

S3. A. P. Semenov, R. I. Mendgaziev, A. S. Stoporev, A. A. Kuchierskaya, A. A. Novikov and V. A. Vinokurov, *J. Nat. Gas Sci. Eng.*, 2020, **82**, 103491.