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Synthesis and structure of bis(*N*-methylaza-15-crown-5)-fused 2,5-dibenzylidenecyclopentanone and its novel bis-sandwich complex with Ba^{2+} ions

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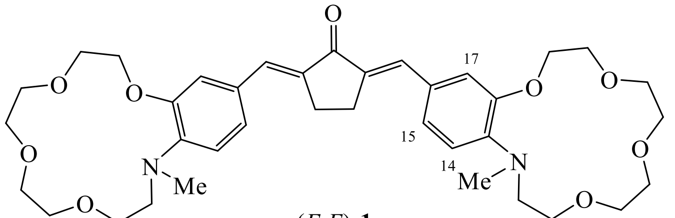
Experimental details

General methods. Melting point was measured on a MEL-Temp II apparatus in a capillary. The ^{1}H NMR spectrum was obtained on a Bruker DRX500 instrument (operating frequency 500.13 MHz) in MeCN-d_3 using the solvent as internal standard (δ 1.96 ppm). The IR spectrum was recorded on a Bruker IFS-113V spectrophotometer in a KBr pellet. High resolution ESI mass spectrum was measured on a MicrOTOF Instrument (Bruker Daltonics) in the range of m/z = 50–3000 for positive ions (MeCN solution inlet, nitrogen gas flow, 4500 V capillary voltage). Elemental analysis was carried out in the Microanalytical Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow, Russian Federation). The sample for elemental analysis was dried *in vacuo* at 80 °C.

Synthesis. *(2E,5E)-2,5-Bis[(13-methyl-2,3,5,6,8,9,12,13-octahydro-11H-1,4,7,10,13-benzotetraoxazacyclopentadecyn-16-yl)methylene]cyclopentanone* (*E*,*E*)-**1**.



(*E*,*E*)-**1**

An 1 M NaOH solution in a EtOH–water mixture (4 : 1, v/v, 40 μL) was slowly added with stirring to a solution containing 5'-formyl-*N*-methylbenzoaza-15-crown-5 ether (28 mg, 91 μmol) and cyclopentanone (3.6 mg, 43 μmol) in EtOH (0.5 mL). The reaction mixture was kept at room temperature for 5 h and evaporated *in vacuo*. The residue was purified by column chromatography on Al_2O_3 (Type T, Basisch, 63–200 μm, Merck) using a gradient mixture of benzene and EtOAc up to 100% of the latter. Compound (*E*,*E*)-**1** (22 mg, 76% yield) was obtained as a red-orange powder, mp 174–176 °C.

^{1}H NMR (500 MHz, MeCN-d_3, J/Hz, 27 °C) δ: 2.87 (s, 6H, 2 MeN), 3.12 (s, 4H, CH_2CH_2), 3.25 (t, ^3J 7.3, 4H, 2 CH_2N), 3.64 (s, 8H, 4 CH_2O), 3.67 (m, 8H, 4 CH_2O), 3.89 (m, 4H, 2 CH_2CH_2OAr), 3.91 (t, ^3J 7.3, 4H, 2 CH_2CH_2N), 4.18 (m, 4H, 2 CH_2OAr), 6.45 (d, ^3J 8.2, 2H, 2 H^{14}), 7.17 (d, ^4J 1.4, 2H, 2 H^{17}), 7.24 (dd, ^3J 8.2, ^4J 1.4, 2H, 2 H^{15}), 7.39 (s, 2H, 2 CHAr) (Fig. S3). IR (KBr) ν: 1678 cm^{-1} (C=O) (Fig. S4). ESI MS (m/z): 334.18 $[M + 2H]^{2+}$, 667.36 $[M + H]^+$, 689.34 $[M + Na]^+$, 705.32 $[M + K]^+$ (Fig. S5). Calcd for $C_{37}H_{50}N_2O_9$ (666.80): C, 66.65; H, 7.56; N, 4.20; found: C, 66.36; H, 7.63; N, 4.04%.

Spectrophotometric titrations were conducted on a Specord 250 Plus spectrophotometer (Agilent) at ambient temperature using 1-cm quartz cells. MeCN (spectral grade, Cryochrom), deionized water (HPLC grade, Sigma–Aldrich), and Bu_4NClO_4 (Fluka) were used to prepare solutions with ionic strength of 0.01 *M*. All manipulations were fulfilled in dark room at red light to prevent *E*–*Z* isomerization of compound **1**.

The stability constants of the 1 : 1 and 2 : 2 complexes of dienone (*E*,*E*)-**1** with barium perchlorate were measured as follows: the total concentration of (*E*,*E*)-**1** was maintained constant at 5×10^{-6} or 1×10^{-5} M level, whereas the total concentration of $Ba(ClO_4)_2$ was varied incrementally from 0 to (3–10) × 10^{-5} M. The analysis of concentration dependences of absorption spectra and the calculations of stability constants of the complexes were carried out using the HypSpec program included in the Hyperquad software package [S1].

[S1] P. Gans, A. Sabatini, A. Vacca, *Talanta*, 1996, **43**, 1739; https://doi.org/10.1016/0039-9140(96)01958-3.

X-ray diffraction. In structure (*E*,*E*)-**1**, a part of one of the two macrocycles is disordered over two positions with the site occupancy ratio of 0.56:0.44. In structure (*E*,*E*)-**1**·$Ba(ClO_4)_2\cdot 4.5C_6H_6$, six independent benzene solvate molecules were found, three of them being located at the centres of symmetry. Three benzene molecules are disordered each over two positions with the site occupancy ratios of 0.87:0.13, 0.68:0.32, and 0.69:0.31 (rotation or small displacement in the plane of the benzene ring). AFIX 66, SADI, and ISOR commands were applied in the refining processes.

In structure (*E*,*E*)-**1**·$Ba(ClO_4)_2\cdot 4.5C_6H_6$, the barium cations are located at approximately equal distances between the two coordinating 15-membered macroheterocycles. The Ba(1) deviations from the mean planes through all heteroatoms of two neighboring azacrown ether moieties are 1.71 and 1.66 Å. The barium cation is coordinated by all heteroatoms of these two macrocycles. The Ba(1)...O(1–4,5A–8A) distances vary in the 2.763(3)–2.882(3) Å range (see Table S3), while the Ba(1)...N(1,2A) coordination is characterized by distances of 3.123(3) and 3.016(3) Å. Since the covalent radii of the oxygen and nitrogen atoms are ~1.4 and 1.5 Å, respectively, all heteroatoms of the two macrocycles are approximately equally involved in the binding of the Ba^{2+} ion.

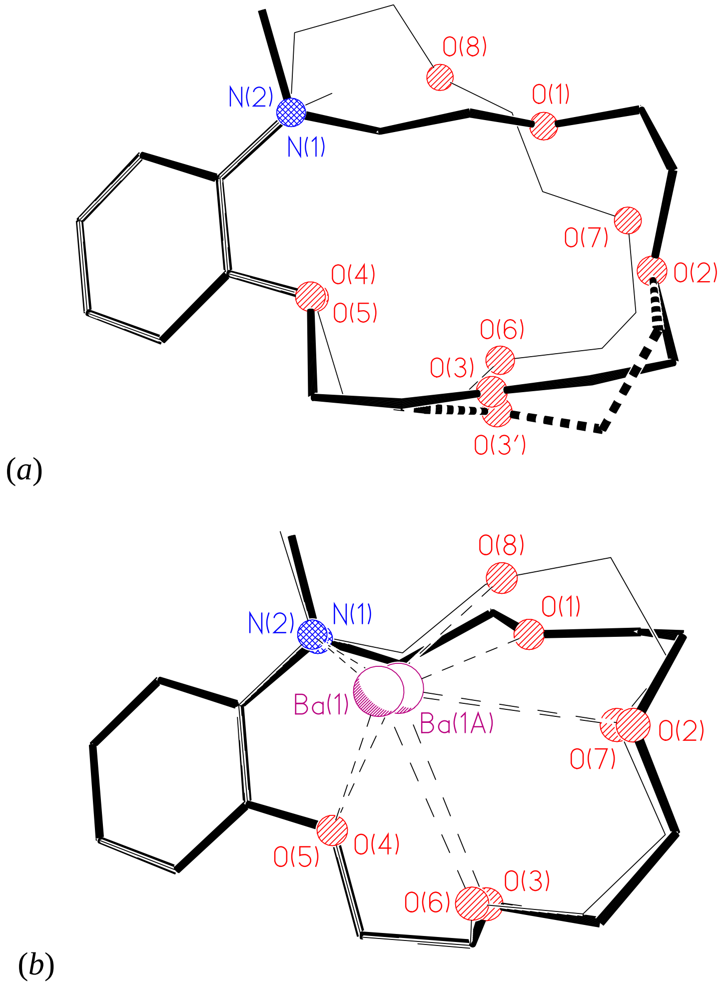


Figure S1. Superimposition of *N*-methylbenzoazacrown ether moieties of (*E*,*E*)-**1** (*a*) and (*E*,*E*)-**1**$\cdot Ba(ClO_4)_2\cdot 4.5C_6H_6$ (*b*) over the benzene rings. The H atoms are not shown.

In structure (*E*,*E*)-**1**, in the macrocycle with the N(1) atom, the methyl group is located nearly in the benzene ring plane, with the C_{Ar}–C_{Ar}–N(1)–Me torsion angle being 19.6°, whereas the CH_2N group substantially deviates from this plane, with the C_{Ar}–C_{Ar}–N(1)–CH_2 torsion angle being –112.4°. The second macrocycle with the N(2) atom has a different conformation in which, on the contrary, the CH_2N group lies approximately in the plane of the benzene ring, whereas the methyl group markedly deviates from this plane: the corresponding torsion angles are –18.1° and 131.9° (Fig. S1*a*). The identified differences demonstrate the conformational flexibility of the *N*-methylbenzoaza-15-crown-5 ether macrocycle.

In structure (*E*,*E*)-**1**$\cdot Ba(ClO_4)_2\cdot 4.5C_6H_6$, the conformations of the two macroheterocycles complexed with barium differ little from each other (Fig. S1*b*) and are similar to the conformation of the first macrocycle in (*E*,*E*)-**1**. The C_{Ar}–C_{Ar}–N(1,2)–Me and C_{Ar}–C_{Ar}–N(1,2)–CH_2 torsion angles amount to 14.0°, –108.9° and –13.9°, 111.8°.

In structure (*E*,*E*)-**1**, the hybridization of nitrogen atoms is intermediate between sp^2 and sp^3 hybridizations, in which the sums of the nitrogen bond angles in the ideal case are 360° and 328.4°, respectively. Indeed, in this structure, the sums of the N(1) and N(2) bond angles are 341.7(6)° and 353.4(7)°, respectively. In complex [(*E*,*E*)-**1**·Ba(ClO$_4$)$_2$]$_2$, the sums of the N(1) and N(2) bond angles substantially decrease down to 333.0(3)° and 335.6(3)°, respectively. In other words, the contribution of the sp^3-hybridization of these nitrogen atoms increases. Evidently, this promotes switching of the lone pairs of electrons (LPE) of nitrogens from the conjugation with the benzene rings to the Ba^{2+} coordination. Weakening of the conjugation of these LPEs is confirmed by some elongation of the N(1,2)–C$_{Ar}$ bonds in [(*E*,*E*)-**1**·Ba(ClO$_4$)$_2$]$_2$ compared to those in free dienone (*E*,*E*)-**1**: 1.431(5), 1.444(4) and 1.417(10), 1.373(11) Å, respectively. These data are well correlated with the results of spectral studies (see Fig. 1 in the article).

Table S1. Parameters of crystals (*E*,*E*)-**1**, (*E*,*E*)-**1**$\cdot$Ba(ClO$_4$)$_2\cdot$4.5C$_6$H$_6$ and X-ray experiments.

Parameter	(*E*,*E*)-**1**	(*E*,*E*)-**1**$\cdot$Ba(ClO$_4$)$_2\cdot$4.5C$_6$H$_6$
Empirical formula	$C_{37}H_{50}N_2O_9$	$C_{64}H_{77}BaCl_2N_2O_{17}$
Formula weight, g·mol^{-1}	666.79	1354.51
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P\bar{1}$
Unit cell dimensions:		
a, Å	14.951(2)	12.1915(5)
b, Å	7.6562(11)	14.4273(6)
c, Å	15.708(2)	20.1461(8)
α, °	90	96.864(1)
β, °	109.441(4)	101.241(1)
γ, °	90	113.400(1)
Volume, Å^3	1695.6(4)	3112.4(2)
Z	2	2
Density (calc.), g·cm^{-3}	1.306	1.445
F(000)	716	1402
Absorption coefficient μ(Mo-K$_\alpha$), mm^{-1}	0.093	0.796
Temperature, K	100(2)	150(2)
Crystal size, mm	0.30 × 0.04 × 0.03	0.16 × 0.04 × 0.02
θ range for data collection, °	2.65–27.00	1.89–27.18
Index ranges	$-19 \le h \le 19$, $-9 \le k \le 9$, $-20 \le l \le 20$	$-15 \le h \le 15$, $-18 \le k \le 18$, $-25 \le l \le 25$
Reflections collected	22242	41665
Independent reflections	7132 [*R*(int) = 0.1332]	13802 [*R*(int) = 0.0683]
with $I > 2\sigma(I)$	3728	10591
Data / restraints / parameters	7132 / 117 / 472	13802 / 276 / 864
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.1057$, $wR_2 = 0.1932$	$R_1 = 0.0506$, $wR_2 = 0.1093$
for all data	$R_1 = 0.1970$, $wR_2 = 0.2261$	$R_1 = 0.0761$, $wR_2 = 0.1197$
Goodness-of-fit on F^2	1.024	1.030
Absolute structure parameter	0.0(10)	none
Residual electron density (min/max), ē·Å^{-3}	–0.375 / 0.616	–1.397 / 1.142

Table S2. Selected bond lengths and dihedral angles in structures (*E*,*E*)-**1** and (*E*,*E*)-**1**·$Ba(ClO_4)_2$·$4.5C_6H_6$.

Structure	Bond length, Å						Dihedral angle phenyl/phenyl, °
	C(14)–C(16)	C(16)=C(17)	C(17)–C(18)	C(18)–C(19)	C(19)=C(22)	C(22)–C(23)	
(*E*,*E*)-**1**	1.460(11)	1.335(11)	1.487(11)	1.466(11)	1.335(11)	1.475(11)	28.4
(*E*,*E*)-**1**·$Ba(ClO_4)_2$·$4.5C_6H_6$	1.481(5)	1.350(5)	1.467(5)	1.489(6)	1.357(5)	1.447(5)	4.4

Table S3. Coordination bond distances Ba–heteroatom (*d*, Å) in structure (*E*,*E*)-**1**·$Ba(ClO_4)_2$·$4.5C_6H_6$.

Bond	*d*	Bond	*d*
Ba(1)–N(1)	3.123(3)	Ba(1)–N(2A)	3.016(3)
Ba(1)–O(1)	2.791(3)	Ba(1)–O(5A)	2.792(2)
Ba(1)–O(2)	2.803(3)	Ba(1)–O(6A)	2.782(2)
Ba(1)–O(3)	2.825(2)	Ba(1)–O(7A)	2.882(3)
Ba(1)–O(4)	2.854(2)	Ba(1)–O(8A)	2.763(3)

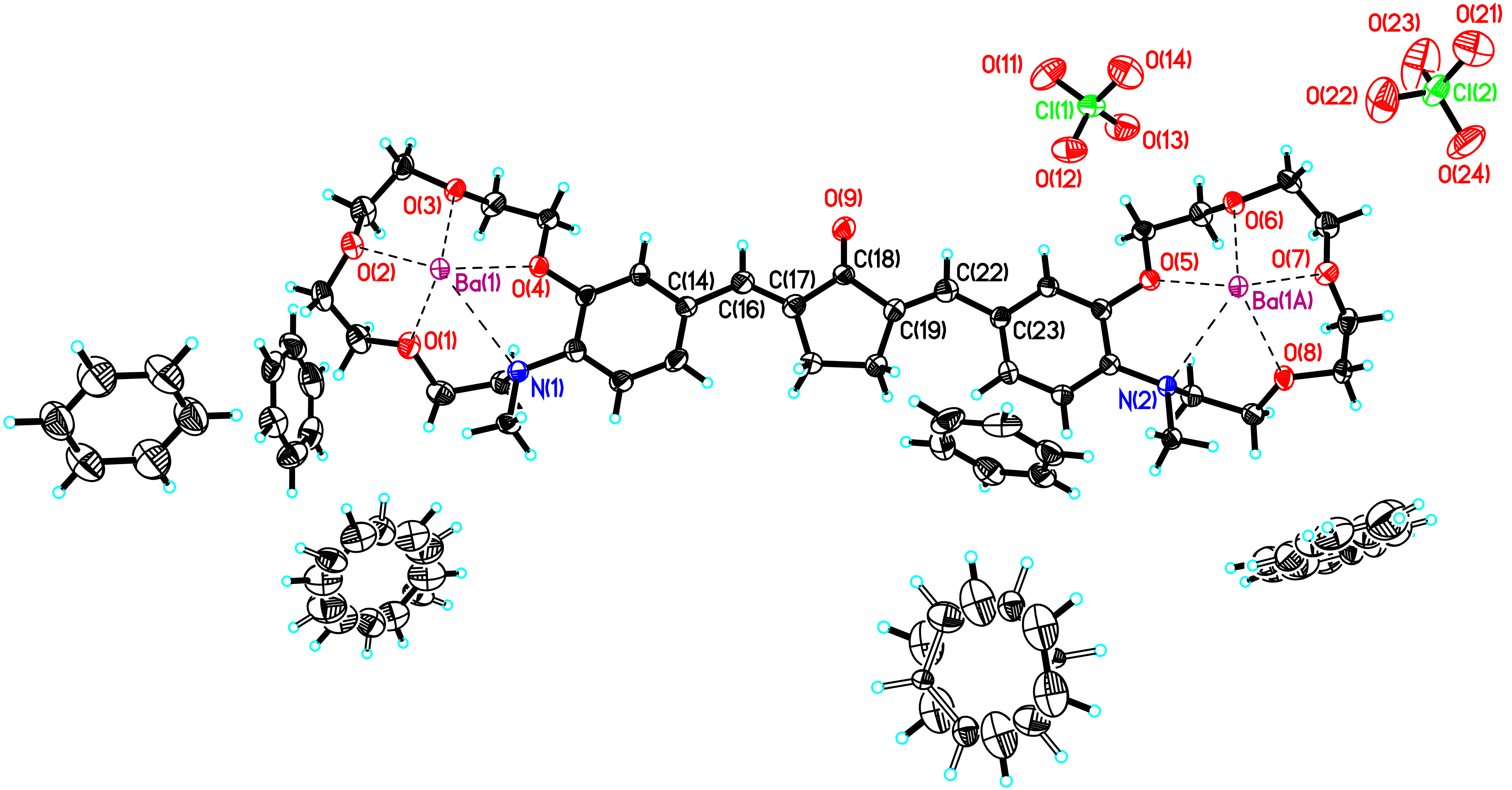


Figure S2. Structure (*E*,*E*)-**1**·$\mathrm{Ba(ClO_4)_2}$·$4.5\mathrm{C_6H_6}$. Thermal ellipsoids are drawn at the 50% probability level. Coordination bonds are drawn with dashed lines. Atom Ba(1A) is obtained through the $(2 - x, 1 - y, 2 - z)$ symmetry operation.

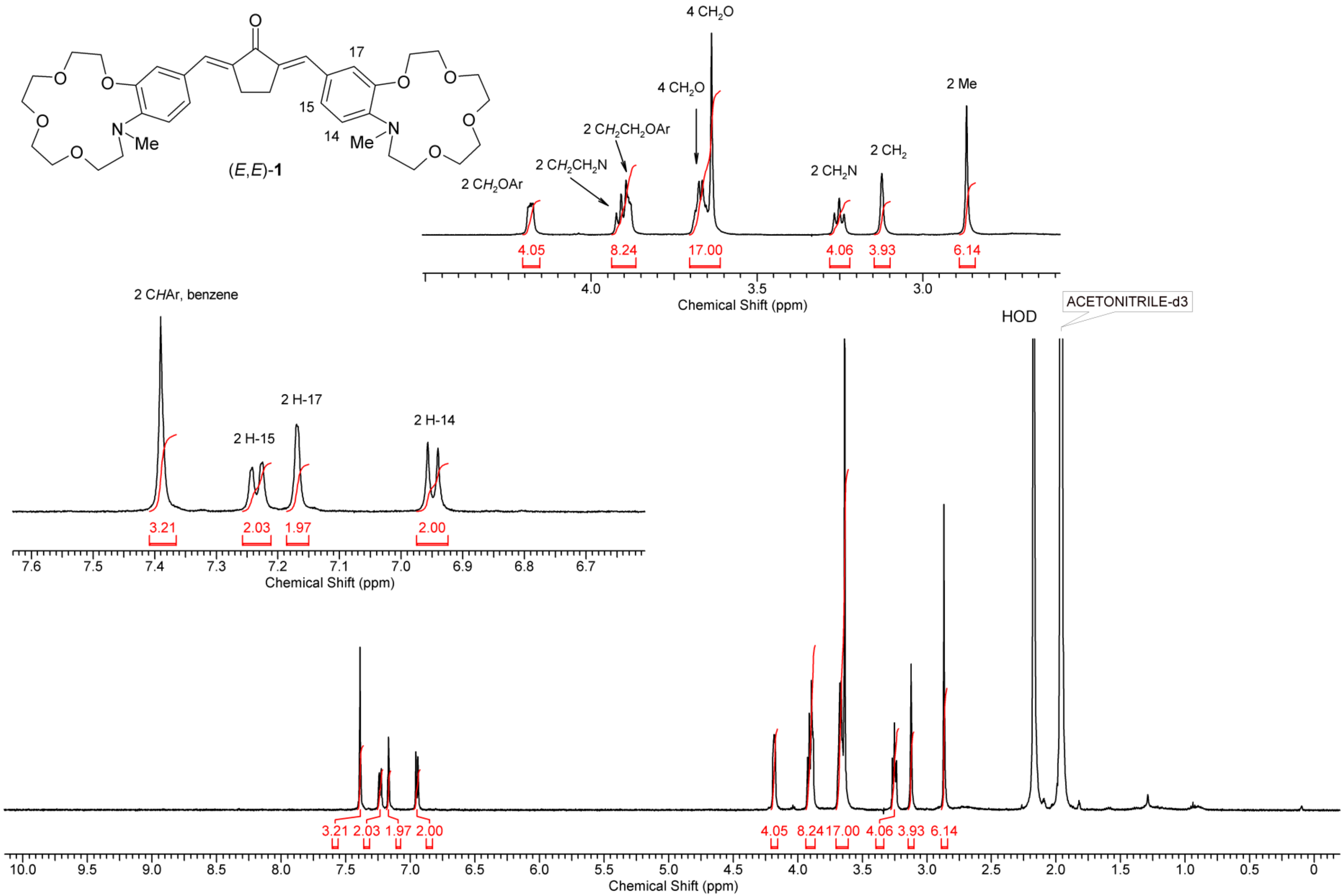


Figure S3. ^{1}H NMR spectrum of compound (*E*,*E*)-**1** (500.13 MHz, MeCN-d_3, 27 °C).

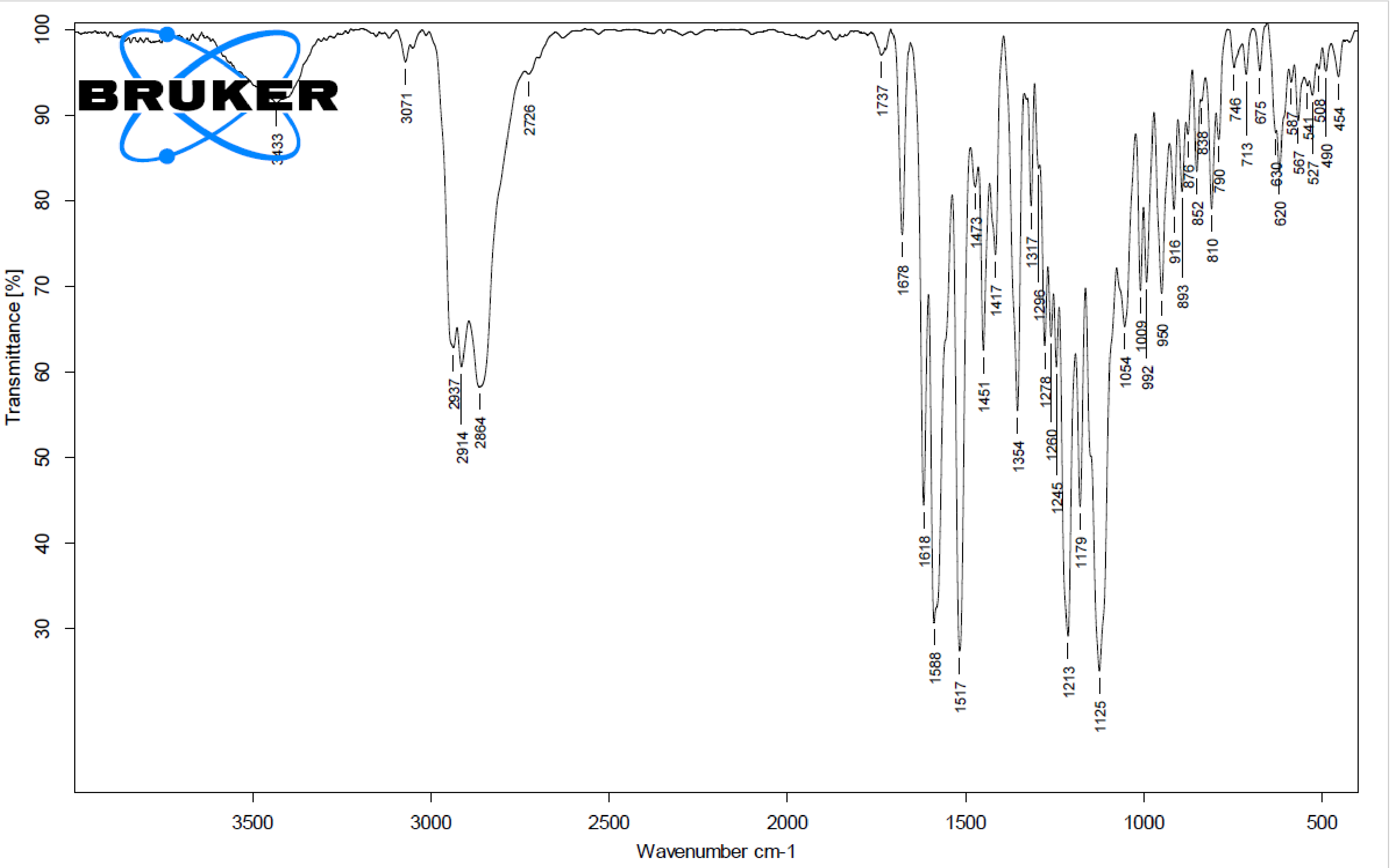
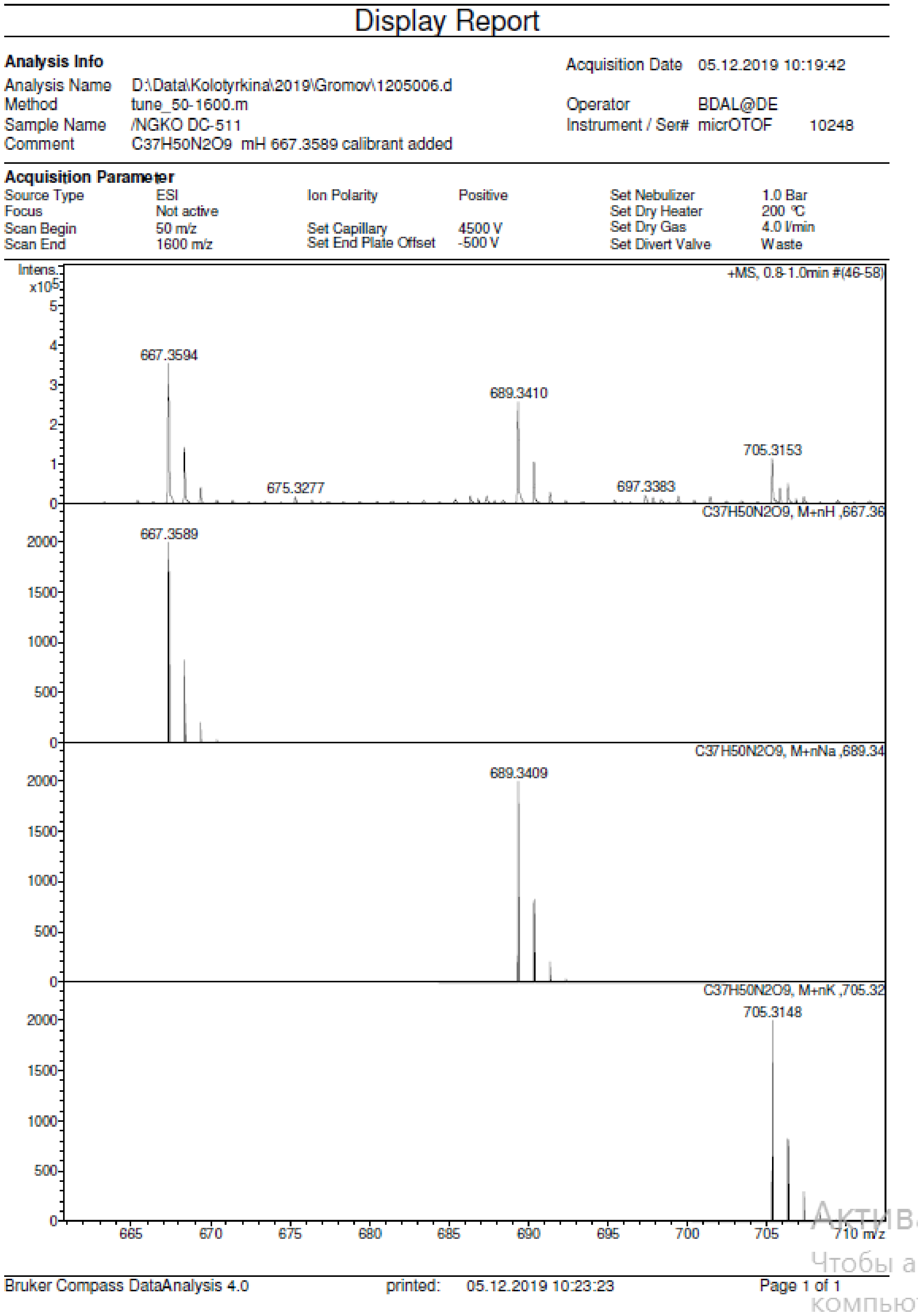


Figure S4. IR spectrum of compound (*E*,*E*)-**1** (in KBr pellet).



Display Report

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Instrument / Ser#	micrOTOF 10248

Acquisition Parameter

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Figure S5. ESI mass spectrum of compound (*E*,*E*)-**1**.

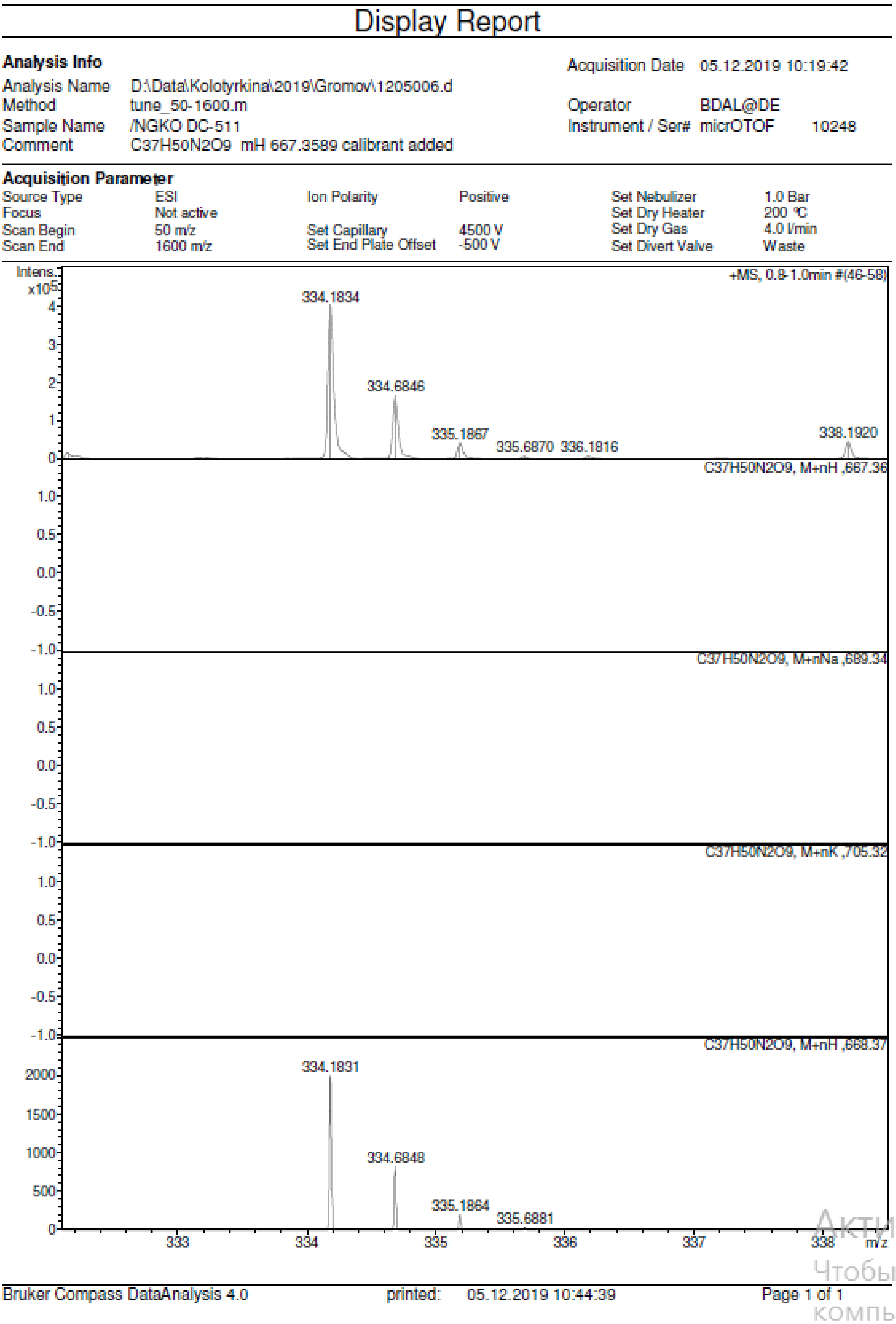

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Figure S5 (continued)**.**