Urea-cavitands: [1+1] *vs.* [2+2] Binding of Anionic Guest

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Molecular capsules are self-assemblies of more than two precursors capable of systematic multiple interactions each other by noncovalent forces such as hydrogen bonding, metal-ligand interactions, or electrostatic interactions.[1] Self-assembled molecular capsules have an internal cavity of characteristic size, shape, and charge, in which a complementary guest should be encapsulated and isolated from the bulk environment. Such molecular capsules are capable of the selective molecular recognitions,[2] stabilization of reactive species,[3] and stereoselective reactions.[4] Also the reversible guest encapsulation enhances the potential applicabilities of molecular capsules.[5]

Many precursors of self-assembled molecular capsules are based on calix[4]arene or resorcin[4]arene and the hydrogen bonding groups used for assembly of precursors are urea,[6] imide,[7] hydroxy,[8] urethane,[9] and hydrazide.[10] Due to the weak hydrogen bonding forces, much less than 10% of covalent bonds, the self-assembled molecular capsule should be well organized to optimize hydrogen bondings between precursors and they definitely necessitate a complementary guest to sustain its labile structure.

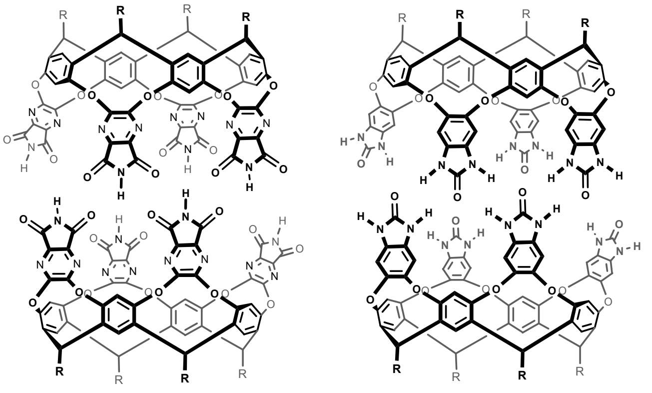
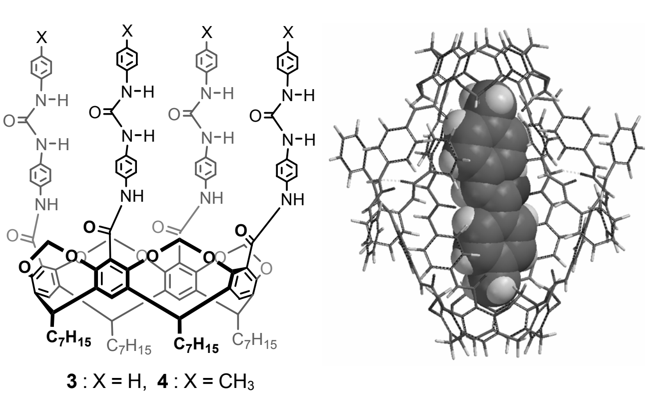


Figure 1. Typical imide molecular capsule **1·1** (left) and cyclic urea capsule **2·2** (right).



3 : X = H, **4** : X = CH_3

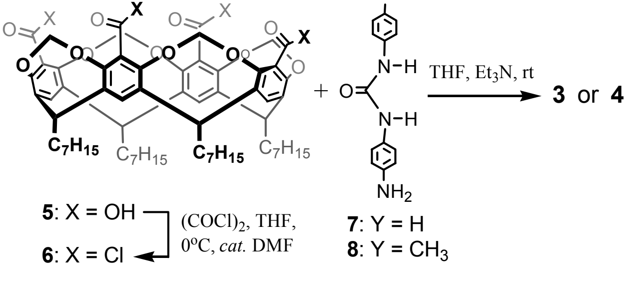
Figure 2. Ureacavitand **3** and **4**, and energy minimized structure of molecular capsule **3**·4-methyl-N-*p*-tolybenzamide·**3** by spartan'04 (MMFF Force-Field, The feet were substituted by methyl for clarity).

The typical molecular capsules **1·1** in Figure 1, dimer of two resorcin[4]arene bridged with pyrazinedicarboximide, have been reported by Rebek, Jr. *et al.*[7] and the analogous molecular capsule **2·2** with four phenyleneurea moieties was reported by Choi *et al.*[11] The capsule **1·1** binds reversibly various guests, from benzene to *N*-*p*-tolyl-4-methylbenzamide in mesitylene, but self-assembly **2·2** only exists as a complex of *N*-*p*-tolyl-4-methylbenzamide in mesitylene.

New ureacavitands **3** and **4** which could self-assemble to molecular capsules **3·3** and **4·4** having a larger cavity and better solubility than those **1·1** and **2·2** were synthesized and characterized. Even the urea arms are long, ureacavitands **3** and **4** may have a proper directional property to form a concave structure due to the enforced rigidity by the intramolecular hydrogen bonding between amido N-H and $-OCH_2O-$ bridge.[10] Molecular mechanics calculations show that these molecular capsules have a large cavity complementary to 4-methyl-N-*p*-tolybenzamide (Figure 2) or even C_{60}.

Results and Discussion

Treatment of tetracarboxy cavitand **5** with oxalyl chloride and catalytic amount of DMF at 0 °C followed by removal of the solvent gave chlorocarbonyl cavitand **6**,[10] which was taken directly to the reaction with urea derivatives **7** and **8** in the triethylamine/THF solution at room temperature to give ureacavitands **3** and **4** in 46% and 32% yields, respectively. Urea derivatives **7** and **8** were prepared from the reaction of phenyl isocyanate and *p*-tolyl isocyanate with an excess of 1,4-diaminobenzene in dry THF at room temperature in 85%



Scheme 1. Synthesis of ureacavitands **3** and **4**.

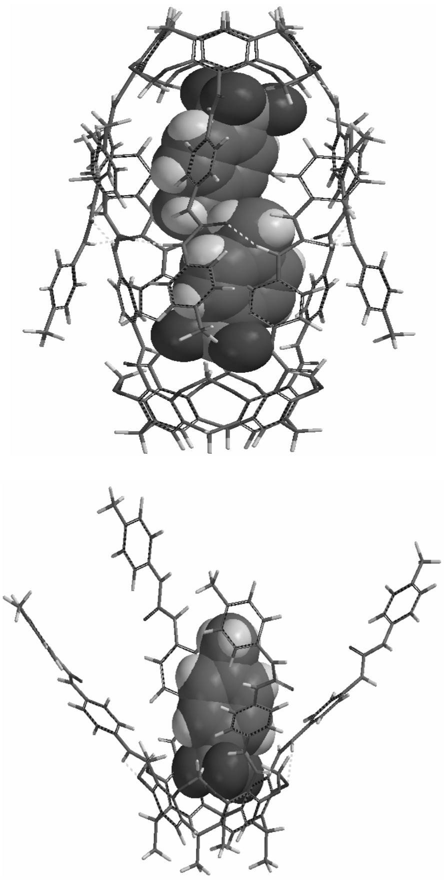


Figure 3. Energy minimized structures of molecular capsular complex [**3@**2 tosylate**@3**] and caviplex [**3@**tosylate] by spartan '04 (MMFF Force-Field, The feet were substituted by methyl for clarity).

and 75% yields, respectively.[12]

Tetraurea cavitands **3** and **4** are soluble in DMSO or THF, but insoluble in nonpolar solvents such as CH_2Cl_2, $CHCl_3$, $C_2H_2Cl_4$, or toluene due to the firm aggregation through the four polar urea groups. Even the addition of potential guests (*N-p*-tolyl-4-methylbenzamide, C_{60} etc.) doesn't improve the solubility in nonpolar solvents. But the addition of $Bu_4N^+X^-$ (X = Br, acetate, mesylate, or tosylate) to the suspension of tetraurea cavitand **3** or **4** in $CDCl_3$ or $C_2D_2Cl_4$ make it homogeneous solution. The first speculation was the formation of [2 + 2] molecular capsular complex such as **3@**2 tosylate**@3** shown in Figure 3 (upper).

Self-assembled molecular capsules for anionic guest are limited compared to those for cationic or neutral guests.[10] Binding phenomena of urea **4** for anions were studied by ^{1}H and ^{19}F NMR spectroscopies in $CDCl_3$ solution at room temperature. The addition of 4 equiv $NBu_4^+CH_3CO_2^-$ or $NBu_4^+CH_3SO_3^-$ to the solution of ureacavitand **4** gave new peaks corresponding to the methyl protons of the complexed guest at -1.64 ($\Delta\delta$ = 3.57 ppm) and -1.39 ppm ($\Delta\delta$ = 4.16 ppm), respectively. Addition of $NBu_4^+TsO^-$ to a solution of **4** in $CDCl_3$ also gave the resonance signals of encapsulated TsO^- ion at 6.32 and 6.88 ppm for Ar-H ($\Delta\delta$ = 0.93 and 0.84 ppm) and at δ = 2.16 ppm for methyl ($\Delta\delta$ = 0.07 ppm). The stoichiometries of ureacavitand **4**: guest were all 1:1 for those 3 cases, which implies the complex could be [1 + 1] or [2 + 2] of ureacavitand **4** and anionic guest.

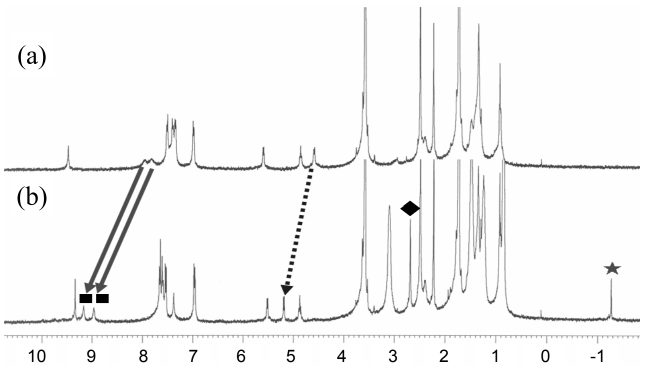


Figure 4. ^{1}H NMR spectra (400 MH$_Z$, THF-$_{d4}$, 298 K): (a) **4** (2 mM), (b) **4** + 4 equiv $CH_3SO_3NBu_4$, ■ = urea protons, ◆ = methyl of free $CH_3SO_3^-$, ★ = methyl of complexed $CH_3SO_3^-$, dash line = downfield shift of H$_i$.

From the large difference of chemical shift change of guests upon complexation their binding modes can be illustrated. In case of small anions such as acetate or mesylate, their methyls are nesting deeply in the cavity, but for a large tosylate, its nonpolar part is directing outward as shown in Figure 3 (lower), which implies the major hydrogen bonding for complexation is between amido N-H and anion instead of that between urea and anion.

In general the peaks of non-hydrogen bonding urea or amide appear around 6.0-7.0 ppm, while those of hydrogen-bonding appear around 8.0-10.0 ppm in ^{1}H NMR spectra.[13] The amide peaks of ureacavitand **3** or **4** appear at 9.2-9.8 ppm without significant chemical shift upon complexation due to their intrinsic intramolecular hydrogen bonding to -OCH_2O-bridge. ^{19}F NMR specrum showed two peaks at -80.1 ppm and -81.1 ppm in 1:5 ratio for free and complexed CF_3COO^- when 1.2 equiv guest was added to a solution of ureacavitand **4** in $CDCl_3$.

^{1}H NMR spectra of ureacavitand **4** and [**4** + 4 equiv CH_3SO_3-NBu_4] in THF-d_8 show typical chemical shift changes (Figure 4). Amide peak at 9.33 ppm doesn't change significantly, but the two urea peaks at 9.16 ($\Delta\delta$ = -1.15 ppm) and 8.96 ppm ($\Delta\delta$ = -1.23 ppm) and the peak of inner hydrogen (H$_i$) of -OCH_2O-bridge at 5.18 ppm ($\Delta\delta$ = 0.58 ppm) in Fiure 4(b) show large downfield shifts, which imply these hydrogens are involved more or less in the complexation mode.

The FT-IR spectrum of ureacavitand **4** in $CHCl_3$ shows a broad band of NH at 3360 cm^{-1} but that of a mixture of **4** and 4 equiv $CH_3SO_3NBu_4$ in $CHCl_3$ gave two kinds of NH bands at 3259 cm^{-1} of hydrogen bonding N-H and 3428 cm^{-1} of nonhydrogen bonding N-H.

The negative mode Maldi-TOF MS spectra of ureacavitand **3** or **4** and 4 equiv $CH_3SO_3NBu_4$ in $C_2H_2Cl_4/CH_3CN$ showed base peaks at m/z 2037.92 of [**3**@$CH_3SO_3^-$]$^-$ and 2093.77 of [**4**@$CH_3SO_3^-$@]$^-$ showing only the [1 + 1] complex of ureacavitand and anion. If molecular capsule [**4**@2 $CH_3SO_3^-$@**4**]$^{-2}$ were formed, the peak of [**4**@(CH_3SO_3H + $CH_3SO_3^-$)@**4**]$^{-1}$ at 4187.54 together with [**4**@2 $CH_3SO_3^-$@**4**]$^{-2}$ at 2093.77 should appear.[12] Finally to confirm the [1 + 1] complexation, a amidocavitand without urea unit, tetrakis(*p*-nitrophenyl-amido)cavitand, was synthesized from acid chloride **6** and *p*-nitroaniline and it complexed firmly all the anions tested above in 1:1

ratio, which supports that the combined hydrogen bonding interactions between amido N-H and anions and between inner hydrogen (H$_i$) of -OCH$_2$O- bridge[14] and anion are enough for [1 + 1] complexation as shown in Figure 3 (lower).

In conclusion, ureacavitands **3** and **4** were synthesized and their anion binding properties were studied. Even though the hydrogen bonding interaction between urea group of cavitands **3** or **4** and anionic guest is observable, the combined hydrogen bonding interactions between amido N-H and anions and between inner hydrogen (H$_i$) of -OCH$_2$O- bridge and anion are the major interactions for [1 + 1] complexation of ureacavitands **3** or **4** and anionic guest. The formation of molecular capsule **3·G·3** or **4·G·4** cannot be observed. The study on the anion binding of amidoresorcin[4]arene by the -CON-H···anion interaction is under investigation,

Experimental Section

All commercial solvents and reagents were used without further purification except as noted below. THF was distilled from sodium benzophenone ketyl. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F254 glass plate and column chromatography was performed on Merck silica gel 60 (70 - 230 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Bruker Avance Digital 400 (400 MHz for ^{1}H, and 100 MHz for ^{13}C) spectrometer. Chemical shifts are reported relative to tetramethylsilane peak or solvent peak. IR spectra were obtained using a JASCO FT/IR-4100 spectrometer. ESI MS spectra were obtained using Waters-Micromass LC/MS System ZQ-4000 at CBMH (Yonsei University) and the negative mode MALDI-TOF spectra were obtained using an Applied Biosytems Voyager-DE STR biospectrometer at NCIRF (Seoul National University). Elemental analyses were performed using a CE Instrument EA 1110 elemental analyzer at NCIRF.

Tetrakis(phenylurea)cavitand 3. To a stirred solution of phenylurea **7** (1.0 g, 4.4 mmol) and triethylamine (0.5 mL, 3.6 mmol) in dry THF (10 mL) was added dropwise a solution of chlorocarbonyl cavitand **6** (420 mg, 0.35 mmol) in dry THF (10 mL) over night at room temperature. The solvent was removed and the excess phenylurea **7** was dissolved in MeOH (50 mL). The precipitate was filtered and washed with MeOH (50 mL). The brown solid was dried under high vacuum to give 320 mg (46%) of product. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.30 (s, 4H, -CONH), 8.67 (s, 4H, urea NH), 8.61 (s, 4H, urea NH), 7.84 (s, 4H, Ar-H), 7.63 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.51 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.35 (d, *J* = 12.0 Hz, 8H, Ar-H), 7.26 (t, *J* = 8.0 Hz, 8H, Ar-H), 6.95 (t, *J* = 8.0 Hz, 4H, Ar-H), 5.66 (d, 4H, -OCH$_2$O-), 4.68 (t, *J* = 7.6 Hz, 4H, -CH-), 4.52 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 2.44 (m, 8H, -CH$_2$-), 1.47 - 1.28 (m, 76H, -(CH$_2$)$_5$- and -C(CH$_3$)$_3$), 0.89 (t, *J* = 6.8 Hz, 12H, -CH$_3$); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 153.4, 151.2, 140.6, 139.0, 136.4, 133.9, 129.6, 128.3, 122.5, 121.1, 120.8, 119.3, 118.9, 118.8, 32.2, 30.2, 29.8, 28.7, 23.0, 14.8, 0.97; ESI-MASS m/z 1964.76 [M+Na$^+$]; Anal. Calcd. for $C_{116}H_{124}N_{12}O_{16}$+H$_2$O+2MeOH: C, 70.22; H, 6.78; N, 8.19. Found: C, 70.20 H, 6.71 N, 8.04.

Tetrakis(*p*-tolylurea)cavitand 4. The procedure for ureacavitand **3** was followed except using *p*-tolylurea **8** (1.0 g, 4.1 mmol) and a 230 mg (32%) of product was obtained. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.28 (s, 4H, -CONH), 8.57 (s, 4H, urea NH), 8.47 (s, 4H, urea NH), 7.72 (s, 4H, Ar-H), 7.49 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.34 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.30 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.05 (d, *J* = 8.0 Hz, 8H, Ar-H), 5.65 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 4.67 (t, *J* = 7.6 Hz, 4H, -CH-), 4.53 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 2.44 (m, 8H, -CH$_2$-), 2.23 (s, 12H, CH$_3$, tolyl), 1.47-1.28 (m, 76H, -(CH$_2$)$_5$- and -C(CH$_3$)$_3$), 0.89 (t, *J* = 6.8 Hz, 12H, -CH$_3$); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 187.4, 165.2, 153.4, 151.3, 139.0, 138.0, 137.2, 134.6, 131.3, 129.9, 128.3, 121.2, 119.2, 119.0, 46.5, 32.2, 30.1, 29.8, 28.7, 22.9, 21.1, 14.8, 9.7, 0.96; ESI-MASS m/z 2020.28 [M+Na$^+$]; Anal. Calcd for $C_{120}H_{132}N_{12}O_{16}$+4H$_2$O+CH$_2Cl_2$: C, 67.46; H, 6.64; N, 7.80. Found: C, 67.62 H, 6.46 N, 7.80.

Preparation of Caviplexes. The ^{1}H NMR solution was prepared by sonicating for 1 h a 1:4 mixture of ureacavitand **3** or **4** [2 mM] and a tetrabuthylammonium X (X = guest anion) in 1 mL of CDCl$_3$ or THF-d$_8$.

Caviplex [3@CH$_3$SO$_3^-$]. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.50 (s, 4H, -CONH), 9.03 (s, 4H, urea NH), 8.83 (s, 4H, urea NH), 7.65 (s, 4H, Ar-H), 7.63 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.58 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.55 (d, *J* = 12.0 Hz, 8H, Ar-H), 7.20 (t, *J* = 8.0 Hz, 8H, Ar-H), 6.95 (t, *J* = 8.0 Hz, 4H, Ar-H), 5.57 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 5.16 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 4.87 (t, *J* = 7.6 Hz, 4H, -CH-), 2.85 (s, free CH$_3$SO$_3^-$), 2.21 (m, 8H, -CH$_2$-), 1.47-1.28 (m, 76H, -(CH$_2$)$_5$- and -C(CH$_3$)$_3$), 0.89 (t, J = 6.8 Hz, 12H, -CH$_3$), -1.30(s, 3H, encapsulated CH$_3$SO$_3^-$); Negative mode Maldi-TOF MASS m/z 2037.9 [M +CH$_3$SO$_3^-$]

Caviplex [4@CH$_3$SO$_3^-$]. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.41 (s, 4H, -CONH), 8.83 (s, 4H, urea NH), 8.72 (s, 4H, urea NH), 7.56 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.46 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.37 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.12 (s, 4H, Ar-H), 6.93 (d, *J* = 8.0 Hz, 8H, Ar-H), 5.49 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 5.08 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 4.79 (t, *J* = 7.6 Hz, 4H, -CH-), 2.77 (s, free CH$_3$SO$_3^-$), 2.44 (m, 8H, -CH$_2$-), 1.68 (s, 12H, CH$_3$ tolyl), 1.47 - 1.28 (m, 76H, -(CH$_2$)$_5$- and -C(CH$_3$)$_3$), 0.89 (t, *J* = 6.8 Hz, 12H, -CH$_3$), -1.39 (s, 3H, encapsulated CH$_3$SO$_3^-$); ^{1}H NMR (400 MHz, THF-d$_8$) δ 9.33 (s, 4H, -CONH), 9.16 (s, 4H, urea NH), 8.96 (s, 4H, urea NH), 7.64 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.59 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.52 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.38 (s, 4H, Ar-H), 6.95 (d, *J* = 8.0 Hz, 8H, Ar-H), 5.50 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 5.18 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 4.85 (t, *J* = 7.6 Hz, 4H, -CH-), 2.68 (s, 3H, free CH$_3$SO$_3^-$), 2.19 (m, 8H, -CH$_2$-), 1.47-1.28 (m, 76H, -(CH$_2$)$_5$- and -C(CH$_3$)$_3$), 0.89 (t, *J* = 6.8 Hz, 12H, -CH$_3$), -1.27 (s, 3H, encapsulated CH$_3$SO$_3^-$); Negative mode Maldi-TOF MASS m/z 2093.77 [M + CH$_3$SO$_3^-$].

Caviplex [4@TsO$^-$]. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.13 (s, 4H, -CONH), 8.70 (s, 4H, urea NH), 8.64 (s, 4H, urea NH), 7.72 (d, *J* = 8.0 Hz, free TsO$^-$), 7.26 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.25 (d, *J* = 8.0 Hz, free TsO$^-$), 7.15 (s, 4H, Ar-H), 7.03 (d, *J* = 8.0 Hz, 8H, Ar-H), 6.98 (d, *J* = 8.0 Hz, 8H, Ar-H), 6.88 (d, *J* = 8.0 Hz, 2H, encapsulated TsO$^-$), 6.32 (d, *J* = 8.0 Hz, 2H, encapsulated TsO$^-$), 5.51 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 5.13 (d, *J* = 8.0 Hz, 4H, -OCH$_2$O-), 4.73 (t, *J* = 7.6 Hz, 4H, -CH-), 2.23 (s, free TsO$^-$), 2.16 (s, 12H, CH$_3$ tolyl), 2.12 (m, 8H, -CH$_2$-), 1.47-1.28 (m, 76H, -$(CH_2)_5$- and -$C(CH_3)_3$), 0.89 (t, $J = 6.8$ Hz, 12H, -CH_3); Negative mode Maldi-TOF MASS m/z 2170.06 [$M^+ + CH_3SO_3^-$].

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