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Cyclodextrin dimers connected with linkers through the secondary hydroxy groups

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Experimental

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX-400 spectrometer at the frequencies 399.78 and 100.53 MHz, respectively. The ^{1}H and ^{13}C chemical shifts are presented relative to tetramethylsilane in a solution of [D6]DMSO. Elemental analyses were performed on a FlashEA 1112 HT instrument. Thin layer chromatography was performed on aluminium plates with fixed layer of SiO_2 (Silufol UV-254), eluent: chloroform - methanol (1:7).

*General procedure obtaining of CD dimers **3a-d**.* Sodium hydride (0.0248 g, 1.032 mmol, 60% dispersion in mineral oil) was added at stirring to a solution of CD silyl derivative **1** (0.5 g, 0.258 mmol) in DMF (5 ml). The reaction mixture was stirred for 30 min at 20 ^{o}C, and a solution of difunctional derivative **2a-d** (0.129 mmol) in DMF (2 ml) was added at stirring for 10 min at 0 ^{o}C. The resulting solution was stirred for 24 h at 20 ^{o}C, diluted with MeOH (5 ml), stirred for 10 min and filtered. The filtrate was concentrated in a vacuum to 2 ml, poured into H_2O (15 ml). The separated precipitate was filtered off, dried in a vacuum, dissolved in acetone (10 ml) and poured into H_2O (10 ml), stirred, the separated precipitate was filtered off and dried in a vacuum (1 Torr) for 5 h at 60 ^{o}C.

1,3-Bis[per(6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin-2-O-yl]propane 3a. Yield: 0.36 g (71%); m.p. 232 – 235 ^{o}C (decomp.); R_f 0.88. Found, %: C 52.10; H 8.89. $C_{171}H_{340}O_{70}Si_{14}$. Calcul., %: C 52.53; H 8.77. ^{1}H NMR δ_H ppm: –0.06 (s, 84H, $Si(CH_3)_2$), 0.84 (s, 126H, $C(CH_3,)_3$), 1.22 (br. s, 2H, $OCH_2C\mathit{H}_2CH_2O$), 3.19-3.95 (m, 88H, C(2)H-C(5)H, OCH_2), 4.79 (br. s, 14H, C(1)H), 5.46 (br. s, 26H, C(2)OH, C(3)OH). ^{13}C NMR δ_C ppm: –4.8 and –4.9 ($Si(CH_3)_2$), 18.5 ($\mathit{C}(CH_3)_3$), 26.2 ($C(\mathit{C}H_3)_3$), 31.3 ($OCH_2\mathit{C}H_2CH_2O$), 60.1 (C^6), 62.3 ($O\mathit{C}H_2CH_2\mathit{C}H_2O$), 72.-72.9 (C(5), C(2), C(3)), 81.6 (C(4)), 102.7 (C(1)).

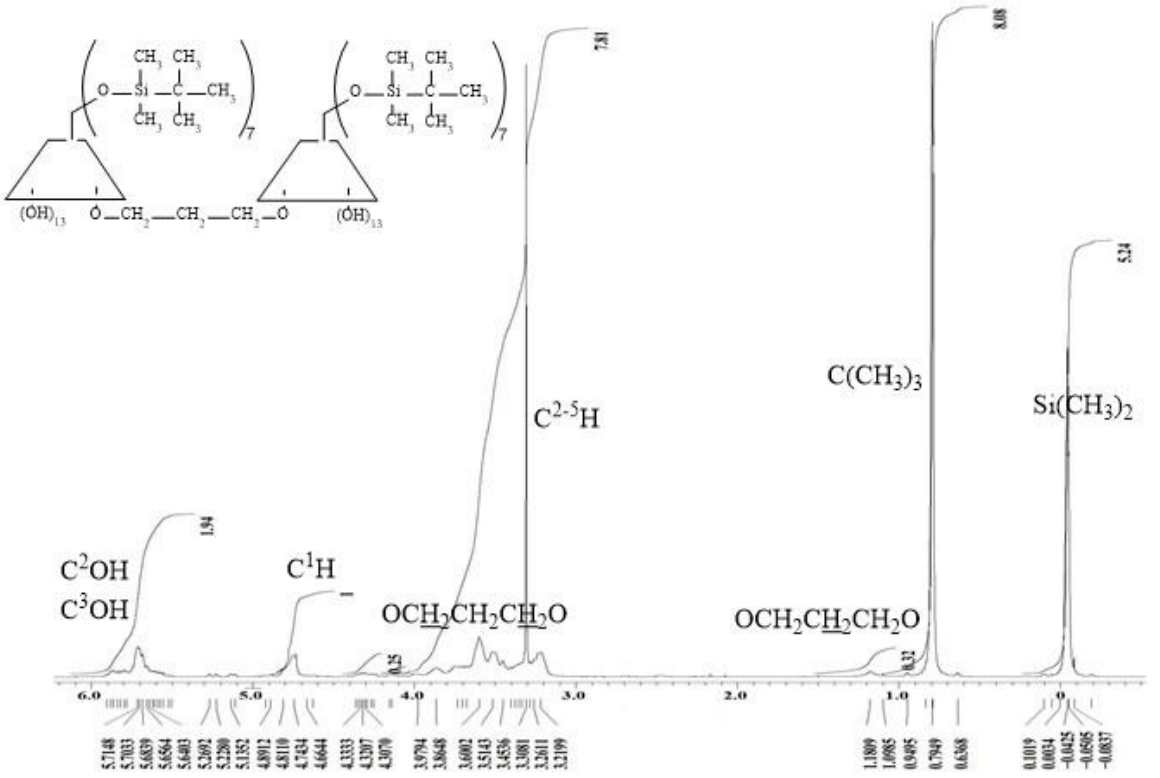
1,4-Bis[per(6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin-2-O-yl]butane 3b. Yield: 0.38 g (75%); m.p. 220 – 224 ^{o}C (decomp.); R_f 0.85. Found, %: C 52.32; H 8.85. $C_{172}H_{342}O_{70}Si_{14}$. Calcd., %: C 52.65; H 8.79. ^{1}H NMR δ_H ppm: –0.03 (s, 84H, $Si(CH_3)_2$), 0.84 (s, 126H, $C(CH_3,)_3$), 1.60 and 1.89 (br. s, 4H, ($OCH_2C\mathit{H}_2C\mathit{H}_2CH_2O$), 3.21-3.92 (m, 88H, C(2)H-C(5)H, OCH_2), 4.79 (br. s, 14H, C(1)H), 5.45 (br. s, 26H, C(2)OH, C(3)OH). ^{13}C NMR δ_C ppm: –4.8 and –4.9 ($Si(CH_3)_2$), 18.5 ($\mathit{C}(CH_3)_3$), 26.2 ($C(\mathit{C}H_3)_3$), 30.1 ($OCH_2\mathit{C}H_2\mathit{C}H_2CH_2O$), 60.1 (C(6)), 62.4 ($O\mathit{C}H_2CH_2CH_2\mathit{C}H_2O$), 72.4-73.2 (C(5), C(2), C(3)), 81.5 (C(4)), 102.4 (C(1)).

1,3-Bis[per(6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin-2-O-yl]propan-2-ol 3c. Yield: 0.30 g (59%); m.p. 248 – 252 ºC (decomp.); R_f 0.64. Found, %: C 52.02; H 8.94. $C_{171}H_{340}O_{71}Si_{14}$. Calcul., %: C 52.32; H 8.73. ^{1}H NMR δ_H ppm: –0.04 (s, 84H, $Si(CH_3)_2$), 0.88 (s, 126H, $C(CH_3,)_3$), 3.29-4.05 (m, 89H, C(2)H-C(5)H, $CH_2CH(OH)CH_2$), 4.88 (br. s, 14H, C(1)H), 5.27-6.74 (br. s, 26H, C(2)OH, C(3)OH, $CH_2CH(OH)CH_2$). ^{13}C NMR δ_C ppm: –5.0 and –5.1 ($Si(CH_3)_2$), 18.2 ($C(CH_3)_3$), 25.7 ($C(CH_3)_3$), 72.2 ($CH_2CH(OH)CH_2$), 61.6 (C(6)), 72.6-73.7 (C(5), C(2), C(3)), 81.8 (C(4)), 102.1 (C(1)).

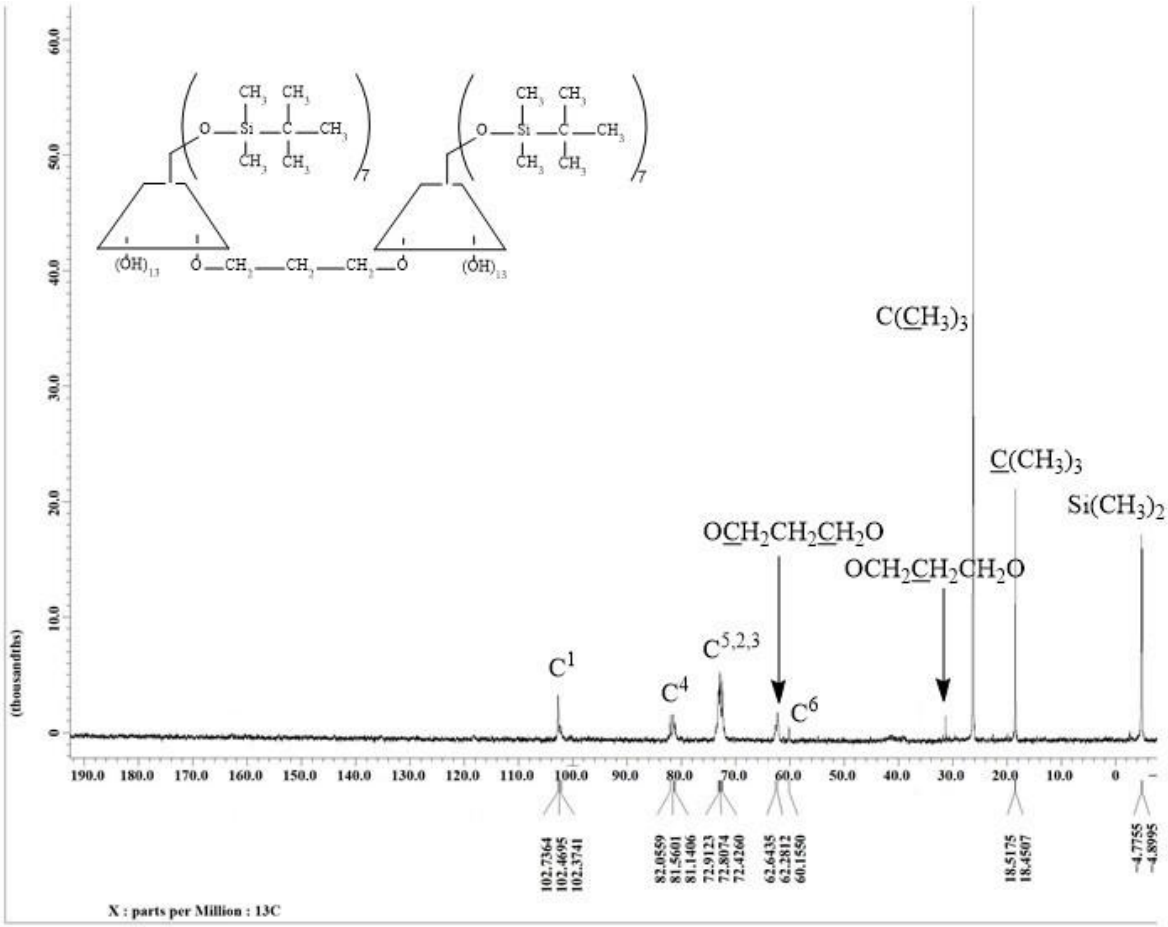
Bis[per(6-O-*tert*-butyldimethylsilyl)-β-cyclodextrin-2-O-yl] adipate 3d. Yield: 0.32 g (62%); m.p. 246 – 248 ºC (decomp.); R_f 0.84. Found, %: C 52.92; H 8.59. $C_{174}H_{342}O_{72}Si_{14}$. Calcd., %: C 52.51; H 8.66. ^{1}H NMR δ_H ppm: –0.11 (s, 84H, $Si(CH_3)_2$), 0.72 (s, 126H, $C(CH_3,)_3$), 1.14 (br. s, 4H, (CH_2CH_2)), 3.22-3.70 (m, 88H, C(2)H-C(5)H, $O(O)CCH_2CH_2CH_2CH_2C(O)O$), 4.77 (br. s, 14H, C(1)H), 5.61-6.80 (br. s, 26H, C(2)OH, C(3)OH). ^{13}C NMR δ_C ppm: –5.0 and –5.1 ($Si(CH_3)_2$), 17.7 ($C(CH_3)_3$), 24.4 ($(CH_2)_2$), 27.5 ($C(CH_3)_3$), 33.9 ($O(O)CCH_2CH_2CH_2CH_2C(O)O$), 61.9 (C(6)), 72.8-73.9 (C(5), C(2), C(3)), 82.1 (C(4)), 102.2 (C(1)), 173.1 (C(O)O).

Inclusion compound of dimer 3b with benzoic acid. Benzoic acid (0.0147 g, 0.12 mmol) was added to a solution of dimer **3b** (0.157 g, 0.04 mmol) in H_2O (5 ml) at 70 ºC. The resulting solution was stirred for 4 hrs at 70 ºC and cooled to 20 ºC. The precipitate formed was filtered off, washed with water (2x5 ml), acetone (2x5 ml) and dried in a vacuum (1 Torr). Yield: 0.05 g (30%); m.p. 248 - 252 ºC (decomp.); R_f 0.75. Found, %: C 52.90; H 8.89. $C_{186}H_{354}O_{74}Si_{14}$. Calcd., %: C 53.60; H 8.56. ^{1}H NMR δ_H ppm: –0.05 (s, 84H, $Si(CH_3)_2$), 0.81 (s, 126H, $C(CH_3,)_3$), 1.20 and 1.36 (br. s, 4H, $OCH_2CH_2CH_2CH_2O$), 3.23-3.89 (m, 84H, C(2)H-C(5)H), 4.34 (m, 4 H, $(OCH_2)_2$), 4.78 (br. s, 14H, C(1)H), 5.74 (br. s, 26H, C(2)OH, C(3)OH), 7.47 (d, 4H, $C_{meta}H$, $^3J_{HCCH}$ 7.8 Hz), 7.59 (m, 2H, $C_{para}H$), 7.91 (d, 4H, $C_{orto}H$, $^3J_{HCCH}$ 7.36 Hz), 12.90 (s, 2H, COOH).

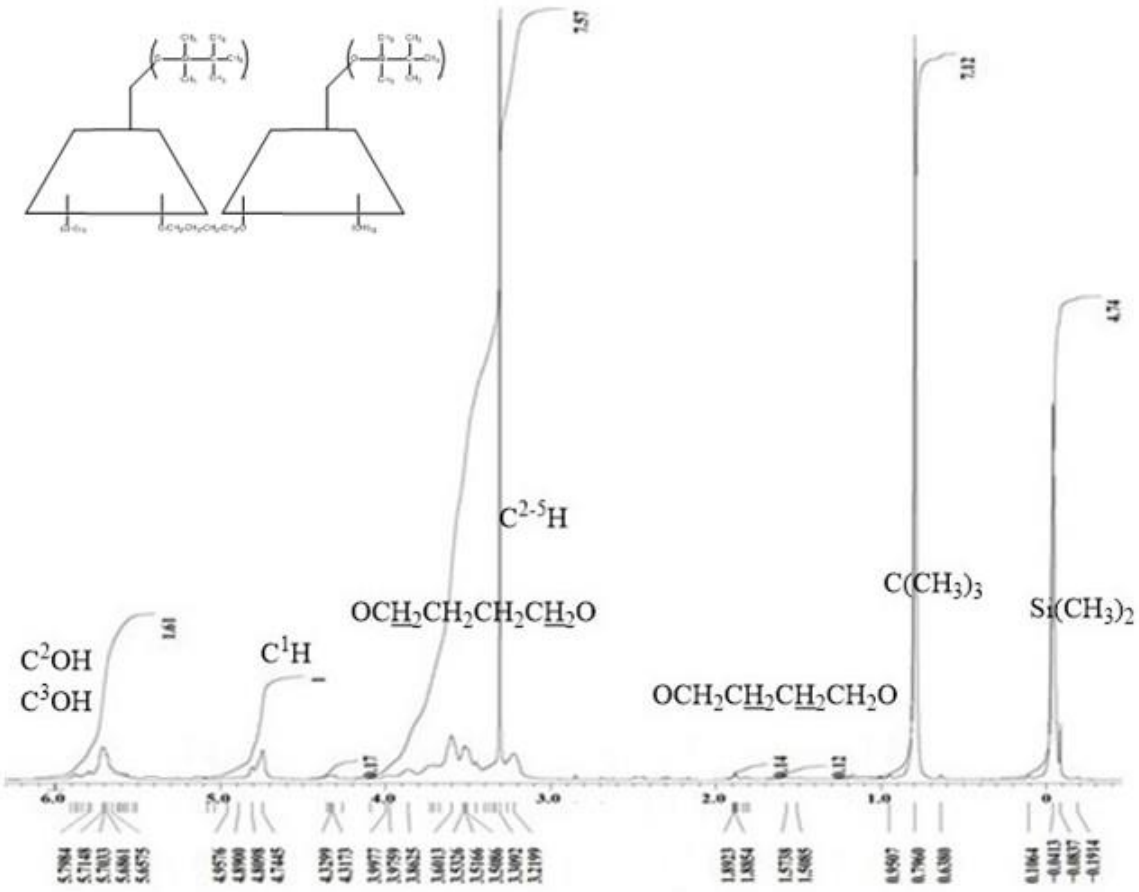
Inclusion compound of dimer 3d with benzoic acid was obtained analogously as above from benzoic acid (0.011 g, 0.09 mmol) and dimer **3d** (0.119 g, 0.03 mmol). Yield: 0.089 g (70%); m.p. 258 - 261 ºC (decomp.); *Rf* 0.81. Found, %: C 53.10; H 8.89. $C_{188}H_{354}O_{76}Si_{14}$. Calcul., %: C 53.46; H 8.45. ^{1}H NMR δ_H ppm: –0.09 (s, 84H, $Si(CH_3)_2$), 0.80 (s, 126H, $C(CH_3,)_3$), 1.28 (br. s, 4H, (CH_2CH_2)), 3.23-3.68 (m, 88H, C(2)H-C(5)H, $O(O)CCH_2CH_2CH_2CH_2C(O)O$), 4.78 (br. s, 14H, C(1)H), 5.57-5.80 (br. s, 26H, C(2)OH, C(3)OH), 7.46 (d, 4H, $C_{meta}H$, $^3J_{HCCH}$ 7.8 Hz), 7.48 (m, 2H, $C_{para}H$), 7.91 (d, 4H, $C_{orto}H$, $^3J_{HCCH}$ 7.36 Hz), 12.85 (s, 2H, COOH).



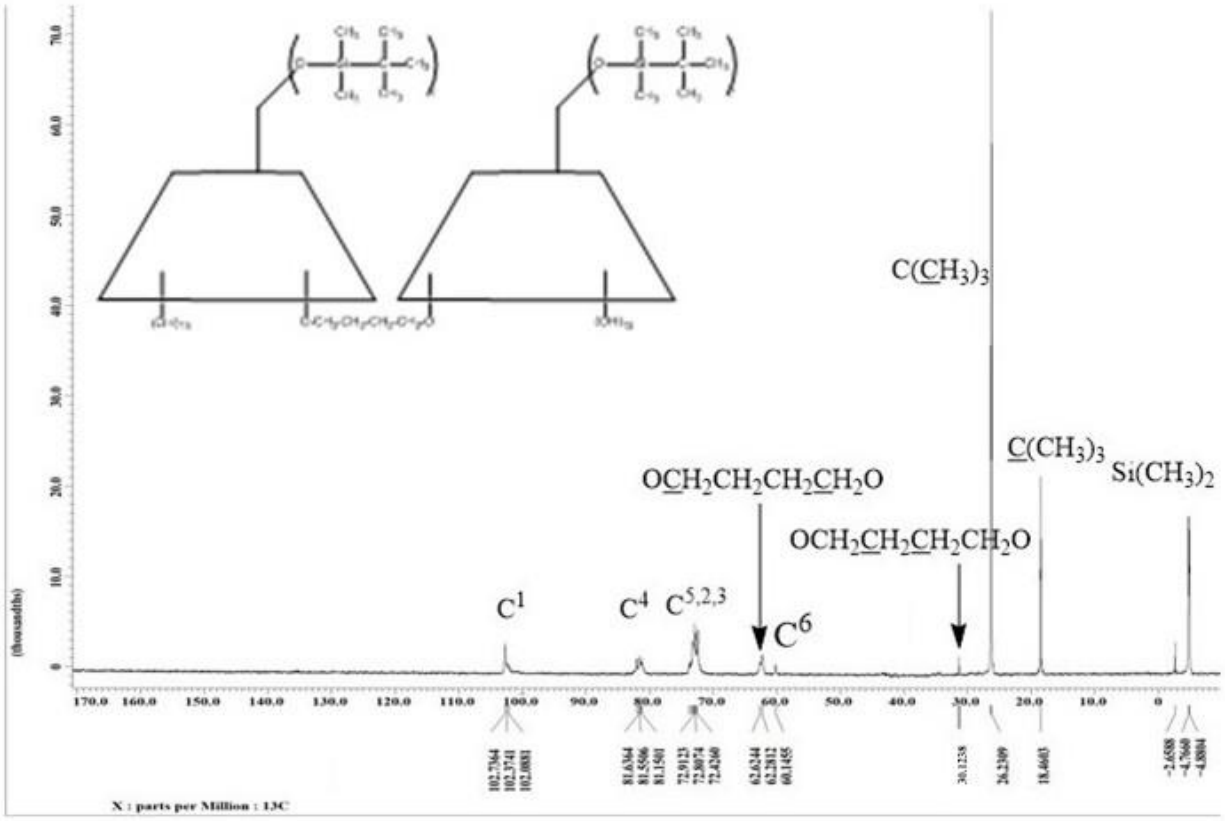
^{1}H NMR spectrum of compound **3a**.



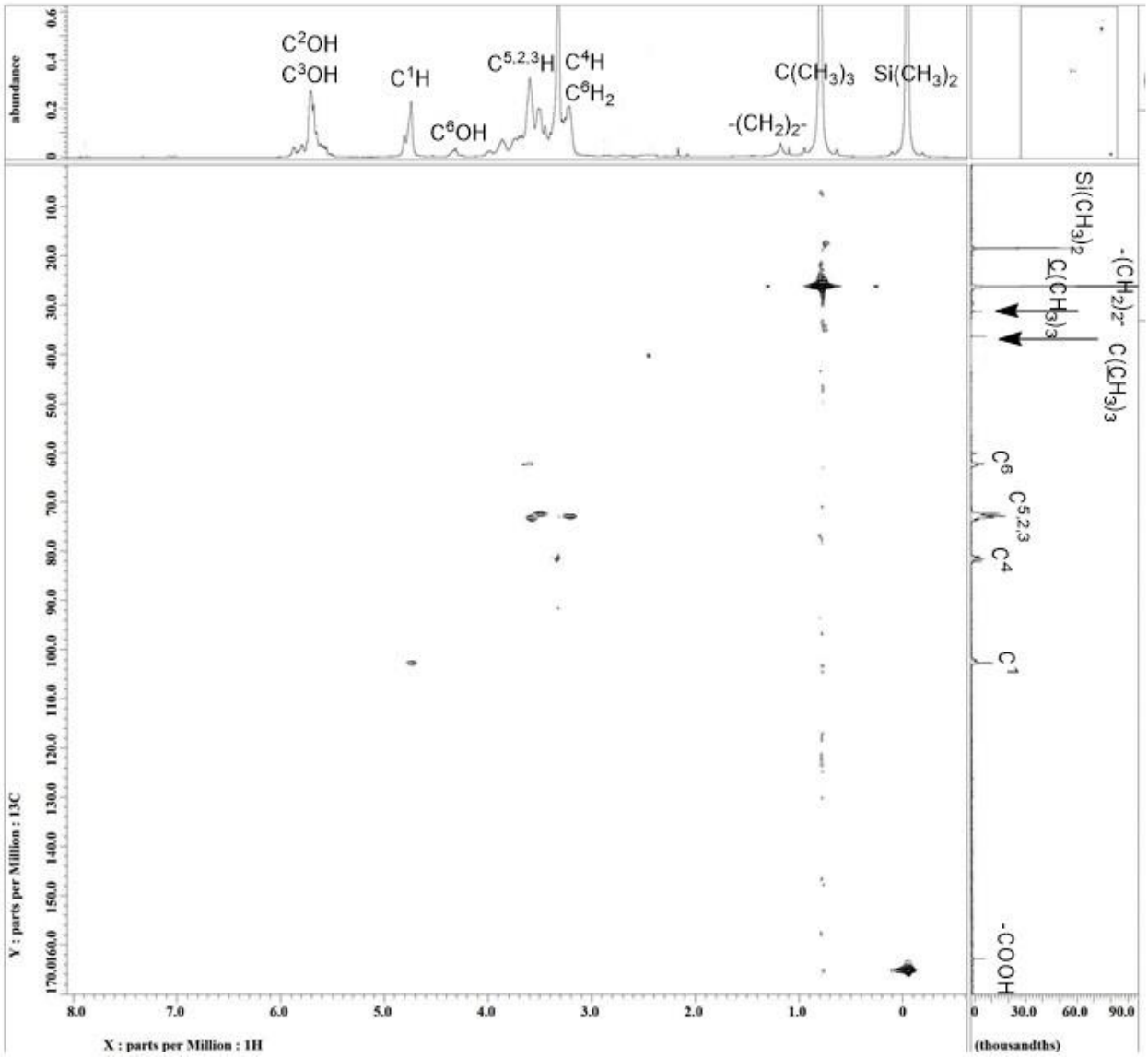
^{13}C NMR spectrum of compound **3a**.



^{1}H NMR spectrum of compound **3b**.



^{13}C NMR spectrum of compound **3b**.



2D HETCOR {^{1}H – ^{13}C} spectrum of compound **3d**