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Nitration of benzyl derivatives of acetylated hexaazaisowurtzitane

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4,10-Bis(*p*-nitrobenzyl)-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (2)

a) Nitration of 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **1** in nitric acid

In a flask equipped with a magnetic stirrer and a thermometer, fuming nitric acid (10 ml) is placed. The reduced temperature is maintained with the help of an ice-salt mixture at the level of -10 °C. 4,10-Dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **1** (1.87 g, 4 mmol) is loaded avoiding temperature increase. The reaction mixture is kept under stirring until complete conversion of the starting compound **1**. At the end of the reaction, the mixture is poured into a 25-fold excess of ice and left under stirring for 4-5 hours. The resulting precipitate is filtered off and recrystallized from acetone.

b) Nitration of 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **1** in a mixture of ammonium nitrate with trifluoroacetic acid

In a flask equipped with a magnetic stirrer and a thermometer, trifluoroacetic acid (7 ml) and ammonium nitrate (0.65 g, 0.008 mol) of are placed. The temperature is reduced with the help of an ice-salt mixture at the level of -10 °C. 4,10-Dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **1** (1.87 g, 0.004 mol) is loaded avoiding the temperature increase. The reaction mixture is kept under stirring until complete conversion of the starting compound **1**. At the end of the reaction, the mixture is poured into a 25-fold excess of ice and left under stirring for 4-5 hours. The resulting precipitate is filtered off and recrystallized from acetone.

c) General procedure for the nitration of 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **1** in a mixture of ammonium nitrate and sulfuric acid

In a flask equipped with a magnetic stirrer and a thermometer, sulfuric acid (10 ml) and ammonium nitrate (0.65 g, 0.008 mol) are placed. The temperature is regulated using an ice-salt mixture. 4,10-Dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **1** (1.87 g, 0.004 mol) is loaded not allowing the temperature to rise. The reaction mixture is kept under stirring until complete conversion of the starting compound **1**. At the end of the reaction, the mixture is poured into a 25-fold excess of ice and left under stirring for 4-5 hours. The resulting precipitate is filtered off and recrystallized from acetone.

mp 268-272 °C. IR (ν/cm^{-1}): 3077, 3044, 3017, 2917, 2863, 1661, 1605, 1517, 1395, 1347, 1290, 1259, 1131, 1038, 995, 853, 813, 773, 699, 629, 547. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ: 1.89-2.17 (m, CH_3, 12H), 4.01-4.27 (m, CH_2, 4H), 5.31-5.54 (m, CH, 4H), 6.40-6.74 (m, CH, 2H), 7.74-7.79 (m, CH_{ar}, 4H), 8.26-8.31 (m, CH_{ar}, 4H). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ: 21.10 (CH_3), 21.16 (CH_3), 22.27 (CH_3), 22.44 (CH_3), 54.58 (CH_2), 55.21 (CH_2), 68.59 (CH), 69.52 (CH), 70.21 (CH), 71.17 (CH), 71.93 (CH), 73.13 (CH), 123.85 (CH_{ar}), 124.10 (CH_{ar}), 129.81 (CH_{ar}), 130.34 (CH_{ar}), 146.44 (C_{ar}), 147.22(C_{ar}), 147.38(C_{ar}), 148.36(C_{ar}), 167.47(CO), 168.23(CO), 168.43(CO).

4-(*p*-Nitrobenzyl)-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (4)

a) Nitration of 4-benzyl-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **3** in nitric acid

In a flask equipped with a stirring bar and a thermometer, fuming nitric acid (10 ml) is placed. The temperature is maintained with the help of an ice-salt mixture at the level of -10 °C. 4-Benzyl-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **3** (1.92 g, 0.004 mol) is loaded avoiding temperature increase. The reaction mixture is kept under stirring until complete conversion of the starting compound **3**. At the end of the reaction, the mass is poured into a 25-fold excess of ice and left under stirring for 4-5 hours. The resulting precipitate is filtered off and recrystallized from acetone.

b) Nitration of 4-benzyl-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane in a mixture of ammonium nitrate with trifluoroacetic acid

In a flask equipped with a magnetic stirrer and a thermometer, trifluoroacetic acid (7 ml) and ammonium nitrate (0.32 g, 0.004 mol) of are placed. The reduced temperature is maintained with the help of an ice-salt mixture at the level of -10 °C. 4-Benzyl-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **3** (1.92 g, 0.004 mol) is loaded avoiding temperature increase. The reaction mixture is kept under stirring until complete conversion of the starting compound **3**. At the end of the reaction, the mass is poured into a 25-fold excess of ice and left under stirring for 4-5 hours. The resulting precipitate is filtered off and recrystallized from acetone.

c) General procedure for the nitration of 4-benzyl-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane in a mixture of ammonium nitrate and sulfuric acid

In a flask equipped with a magnetic stirrer and a thermometer, sulfuric acid (10 ml) and ammonium nitrate (0.32 g, 0.004 mol) of are placed. The required temperature is maintained with an ice-salt mixture. 4-Benzyl-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **3** (1.92 g, 0.004 mol) is loaded avoiding temperature increase. The reaction mixture is kept under stirring until complete conversion of the starting compound **3**. At the end of the reaction, the mass is poured into a 25-fold excess of ice and left under stirring for 4-5 hours. The resulting precipitate is filtered off and recrystallized from acetone.

mp 300-301°C. IR (ν/cm^{-1}): 2995, 2987, 2875, 1663, 1612, 1536, 1389, 1351, 1293, 1260, 1134, 1041, 998, 854, 811, 776, 683, 631, 548. ^{1}H NMR (400.13 MHz, DMSO-d$_6$) δ: 1.91-2.38 (m, CH_3, 15H), 4.07-4.22 (m, CH_2, 2H), 5.50-5.69 (m, CH, 2H), 6.29-6.87 (m, CH, 4H), 7.54-7.61 (m, CH_{ar}, 2H), 8.20-8.25 (m, CH_{ar}, 2H). ^{13}C NMR (100.61 MHz, DMSO-d$_6$) δ: 21.21 (CH_3), 21.32 (CH_3), 22.31 (CH_3), 22.39 (CH_3), 22.45 (CH_3), 55.10 (CH_2), 67.84 (CH), 69.03 (CH), 70.25 (CH), 71.59 (CH), 73.06 (CH), 73.87 (CH), 123.80 (CH_{ar}), 123.94 (CH_{ar}), 129.79 (CH_{ar}), 129.93 (CH_{ar}), 146.57 (C_{ar}), 146.96 (C_{ar}), 147.23 (C_{ar}), 147.31(C_{ar}), 167.43 (CO), 167.85 (CO), 168.37 (CO), 168.82 (CO), 169.93 (CO).

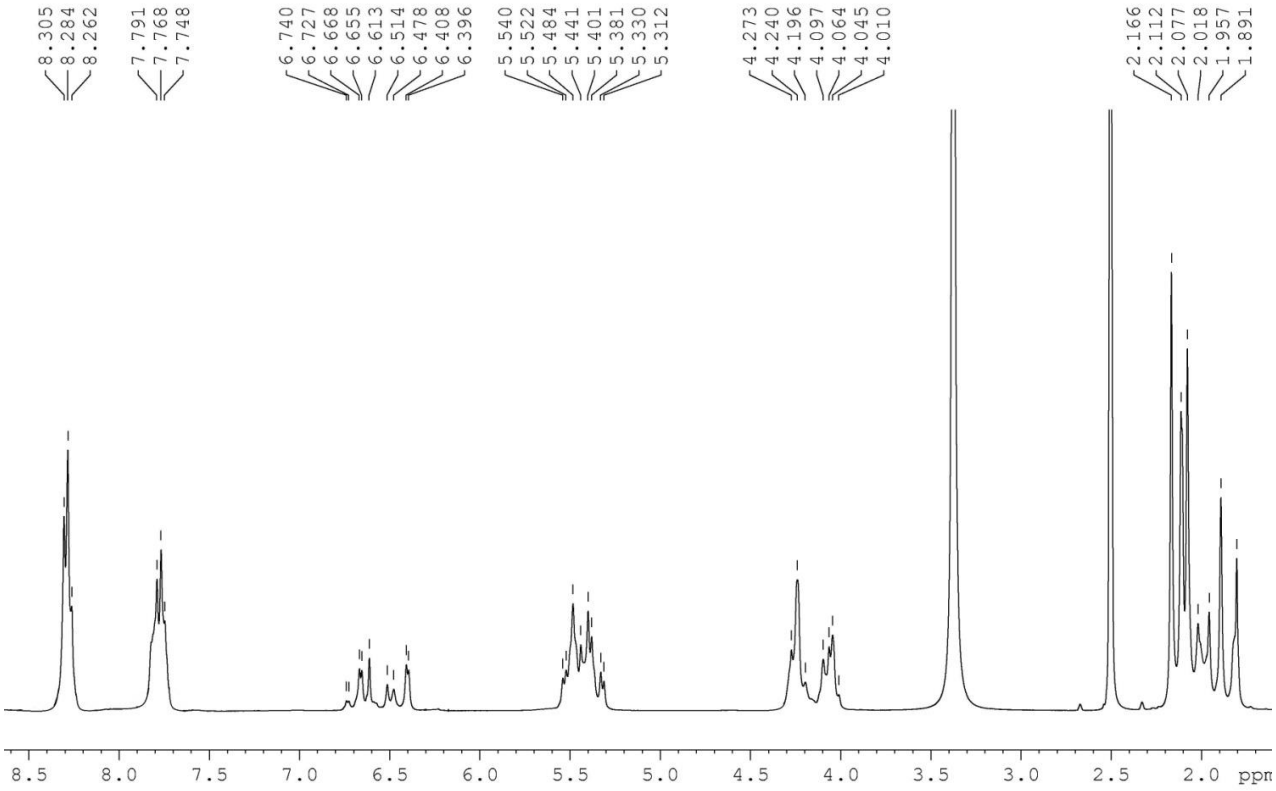

Figure S1 ^{1}H NMR 4,10-bis(*p*-nitrobenzyl)-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **2**

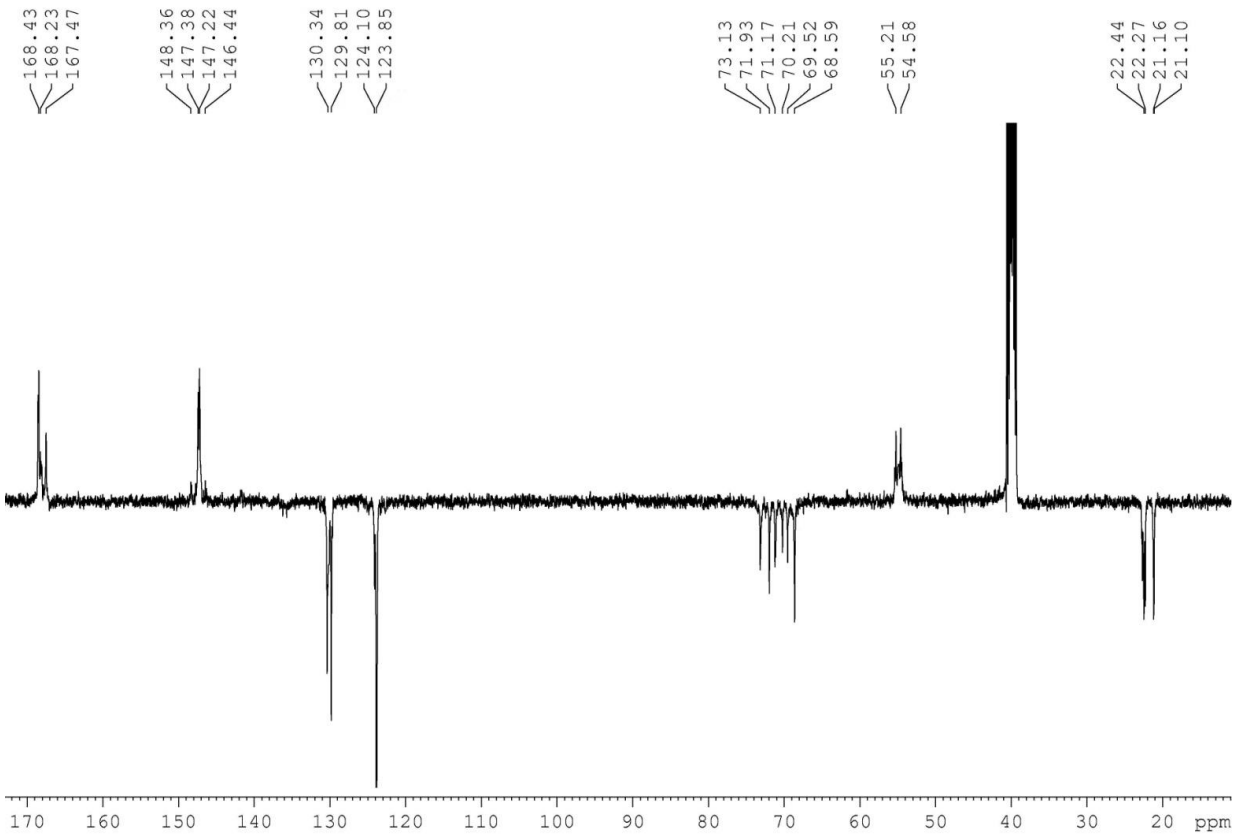

Figure S2 ^{13}C NMR 4,10-bis(*p*-nitrobenzyl)-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **2**

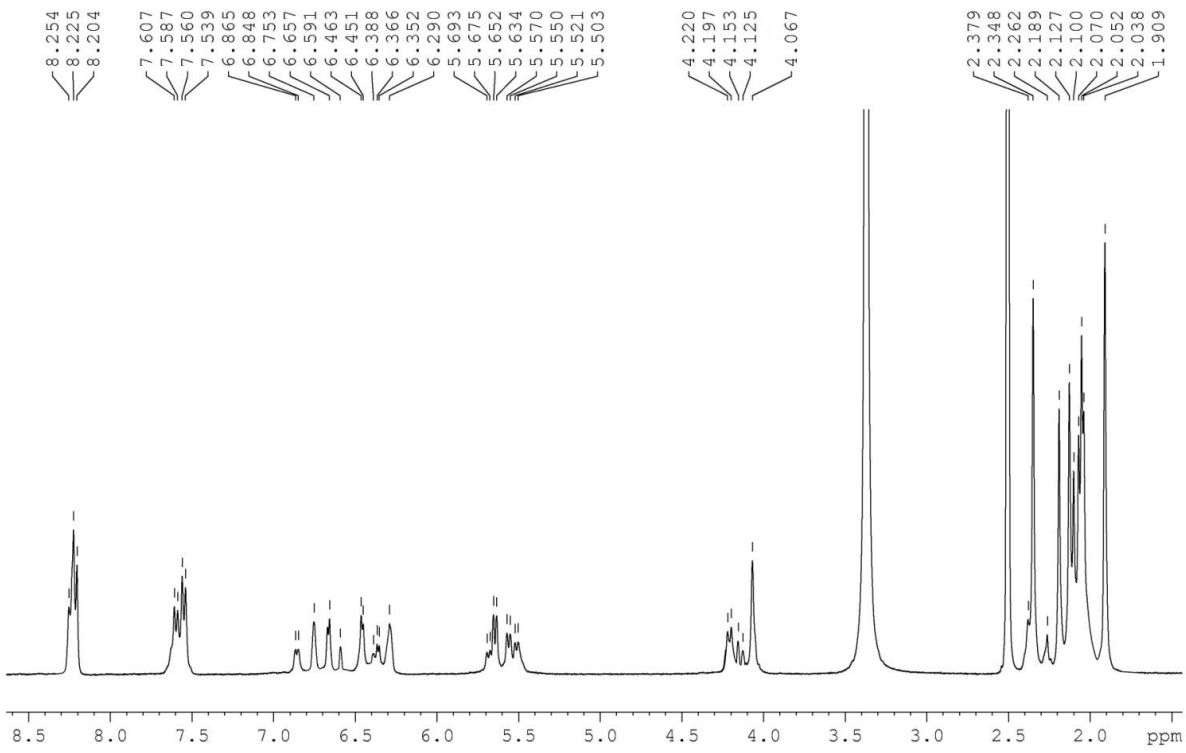

Figure S3 ^{1}H NMR 4-(*p*-nitrobenzyl)-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **4**

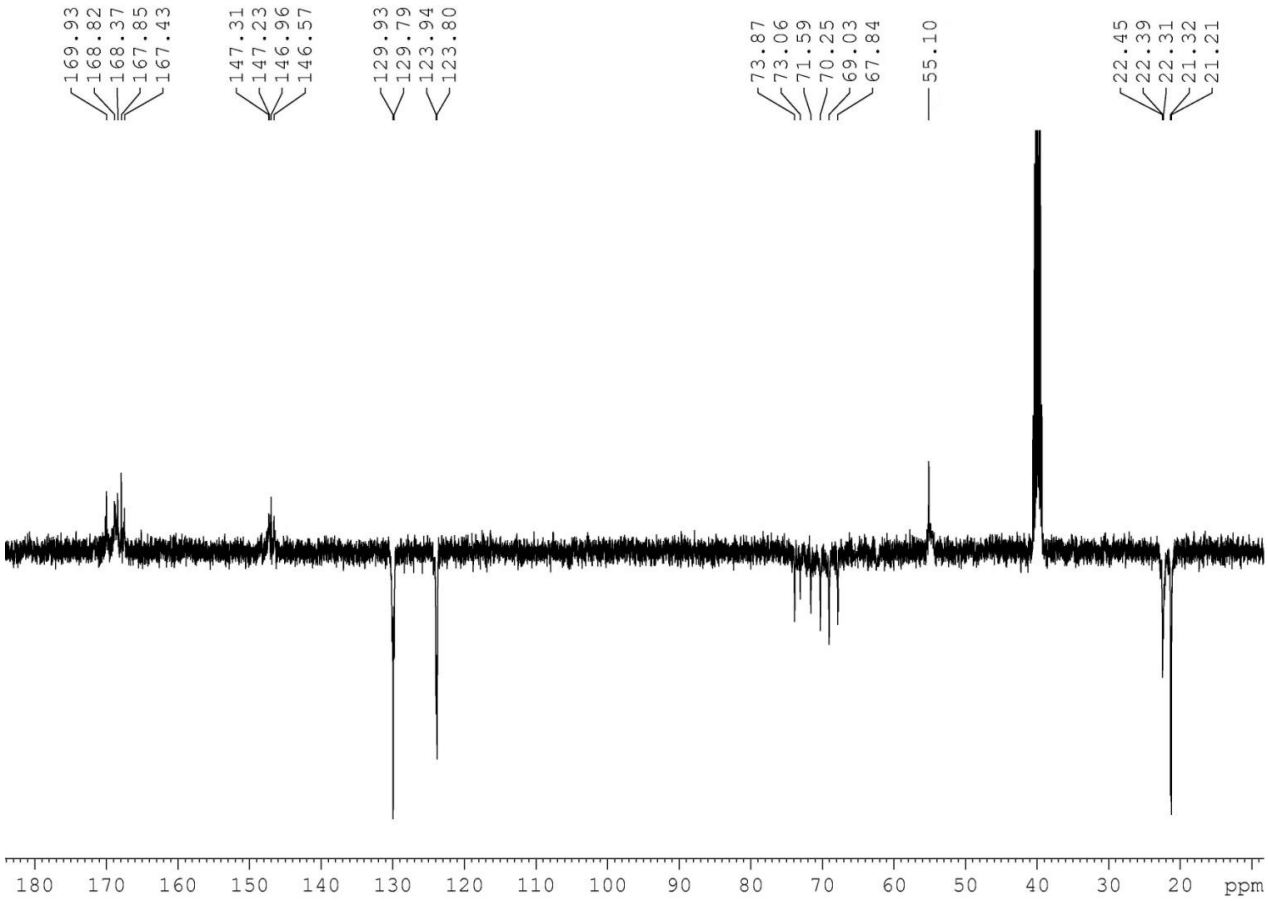

Figure S4 ^{13}C NMR 4-(*p*-nitrobenzyl)-2,6,8,10,12-pentaacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **4**