

Simple and Cost-Effective Polycondensation Routes to Antimicrobial Consumer Products

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Supporting Information

Synthesis

Base Polymer 2

3,3-Diamino-*N*-methyldipropylamine (0.98 g, 6.6 mmol), dimethyl methylmalonate (1.14 g, 6.6 mmol) and TBD (0.05 g, 0.35 mmol) were charged in a Schlenk tube. The reactants were vortexed until miscible (1-2 min) and heated in a sand bath (80 °C) under N₂. After 4 h, vacuum was applied for an additional 20 h to pull off the condensate and push the equilibrium towards product. The polymerization was self-limiting as the polymer crystallizes and becomes diffusion controlled.

M_n (GPC, DMF) = 21 600 g/mol, PDI = 1.43)

Quaternization of 2

Polymer **2** was dissolved in hot DMF (100 °C) and separated into 4 vials, (~0.5 g in 8-10 ml DMF per a vial). The polymer was quaternized at 90 °C for 24 h with 1.2 molar equivalence of a) methyl iodide (**2-MeI**), b) dimethyl sulfate (**2-Me₂SO₄**), c) benzyl bromide (**2-BnBr**), or d) hexyl bromide (**2-HexBr**). The polymers were isolated by precipitation in diethyl ether. The polymers were rinsed three times with ether and further purified via dialysis (MWCO 3,000 g/mol).

Base Polymer 3

Diethyl succinate (1.15g, 6.3 mmol), 3,3'-diamino-*N*-methyldipropylamine (0.92 g, 6.3 mmol) and TBD (0.05 g, 3.5 mmol) were charged in a Schlenk tube. The reactants were vortexed until miscible (1-2 min) and heated in a sand bath (80 °C) under N₂. After 4 h, vacuum was applied for an additional 20 h to pull

off the condensate and push the equilibrium towards product. The polymerization was self-limiting as the polymer crystallizes and becomes diffusion controlled.

Quaternization of 3

Polymer **3** was marginally soluble in DMF after heating to 120 °C, and once dissolved/homogenous, it was quaternized (85 °C, 24 h) with 1.2 molar equivalence of benzyl bromide. The polymer was isolated by precipitation in THF. The polymer was rinsed 3x with ether and further purified via dialysis.

Base Polymer 4

Polymer **4** was synthesized by reaction of 1,3-bis(tert-butoxycarbonyl)guanidine (1.00 g, 3.8 mmol), 3,3'-diamino-*N*-methyldipropylamine (0.92 g, 3.8 mmol) and TBD (0.05 g, 0.35 mmol) in a Schlenk tube. The reactants were mixed by simple vortex until miscible (1-2 min). The reaction was allowed to react at room temperature for 4 h and then the Schlenk tube was placed in a heated sand bath (150 °C, 10 h). Vacuum was pulled to drive off the byproduct and shift the equilibrium towards product. The polymerization was self-limiting as the polymer solidified as a rigid, solvent swollen gel, where the polymerization becomes diffusion controlled that limits molecular weight attained.

Quaternization of 4

Polymer **4** was soluble in DMF at room temperature and once dissolved/homogenous it was quaternized (25 °C, 24 h) with benzyl bromide. The polymers were isolated by precipitation in ether. The polymer was rinsed 3x with ether and further purified via dialysis.

Base Polymer 5

1,4-Bis(3-aminopropyl)piperazine (1.57 g, 7.8 mmol), dimethyl methylmalonate (1.36 g, 7.8 mmol) and TBD (0.05 g, 3.5 mmol) were charged in a Schlenk tube. The reactants were vortexed until miscible (1-2 min) and heated in a sand bath (80 °C) under N₂. After 10 h, vacuum was applied for an additional 20 h to pull off the condensate and push the equilibrium towards product. The polymerization was self-limiting as the polymer crystallizes and becomes diffusion controlled. M_n (GPC, DMF = 20 900 g/mol, PDI = 1.55)

Quaternization of 5

Polymer **5** was dissolved in hot DMF (100 °C) and separated into 3 vials, (~0.5 g in 8-10 ml DMF per a vial). The polymer was quaternized at 80 °C for 24 h with 1.2 molar equivalence of a) methyl iodide (**5-MeI**), b) dimethyl sulfate (**5-Me₂SO₄**), and c) benzyl bromide (**5-BnBr**). The polymers were isolated by precipitation in diethyl ether. The polymers were rinsed three times with ether and further purified via dialysis (MWCO 3,000 g/mol).

Base Polymer 6

Diethyl succinate (1.40 g, 8.0 mmol), 1,4-bis(3-aminopropyl)piperazine (1.61 g, 8.0 mmol), and TBD (0.05 g, 0.35 mol) were charged in a Schlenk tube. The reactants were mixed by simple vortex until miscible (1-2 min). The reaction was allowed to react at room temperature for 4 h and then the Schlenk tube was placed in a heated sand bath (100 °C, 1.5 h) followed by heating to 150 °C, 24 h. Vacuum was pulled to drive off the byproduct and shift the equilibrium towards product. The polymerization was self-limiting. M_n (GPC, DMF = 5 500 g/mol, PDI = 1.20)

Quaternization of 6

Polymer **6** was marginally soluble in DMF after heating to 120 °C and once dissolved/homogenous it was quaternized (85 °C, 24 h) with 1.2 molar equivalence of a) methyl iodide (**5-MeI**) or b) benzyl bromide (**5-BnBr**). The polymers were isolated by precipitation in THF. The polymer was rinsed 3X with ether and further purified via dialysis.

Base Polymer 7

Polymer **7** series contain 2.5 (**7a**), 5.0 (**7b**), or 10.0 (**7c**) mol% Jeffamine (ED2003), which has telechelic amine groups. High molecular weights were targeted, and the stoichiometry was calculated such that the diester : diamine molar ratio was 1:1. The following procedure is an example of polymer **7a**, which contains 2.5 mol% Jeffamine. Diethyl succinate (1.02 g, 5.8 mmol), 3,3'-diamino-*N*-methyldipropylamine (0.83 g, 5.65 mmol), ED2003 (0.3 g, 0.15 mmol), and TBD (0.05 g, 0.35 mmol) were charged in a Schlenk tube.

The reactants were vortexed until miscible (1-2 min) and heated in a sand bath (80 °C) under N₂. After 10 h, vacuum was applied for an additional 20 h to pull off the condensate and push the equilibrium towards product. The polymerization was self-limiting as the polymer crystallizes and becomes diffusion controlled.

Quaternization of 7

Polymer **7** was marginally soluble in DMF after heating to 120 °C (2-3 h) and once dissolved/homogenous it was quaternized (85 °C, 24 h) with 1.2 molar equivalence of benzyl bromide. The polymers were isolated by precipitation in THF. The polymer was rinsed 3x with ether and further purified via dialysis.

Base Polymer 8

Polymer **8** series contain 2.5 (**8a**), 5.0 (**8b**), or 10.0 (**8c**) mol% Jeffamine (ED2003), which has telechelic amine groups. High molecular weights were targeted, and the stoichiometry was calculated such that the diester : diamine molar ratio was 1:1. The following procedure is an example of polymer **8a**, which contains 2.5 mol% Jeffamine. 1,3-Bis(*tert*-butoxycarbonyl)guanidine (1.00 g, 3.8 mmol), 3,3'-diamino-*N*-methylpropylamine (0.547 g, 3.76 mmol), ED2003 (0.193 g, 0.096 mmol) and TBD (0.05 g, 0.35 mmol) were charged in a Schlenk tube. The reactants were vortexed until miscible (1-2 min) and heated in a sand bath (80 °C) under N₂. After 4 h, vacuum was applied for an additional 20 h to pull off the condensate and push the equilibrium towards product. The polymerization was self-limiting as the polymer solidified as a rigid gel, where the polymerization becomes diffusion controlled that limits molecular weight attainment.

Quaternization of 8

Polymer **8** was marginally soluble in DMF after heating to 100 °C (30 min) and once dissolved/homogenous it was quaternized (25 °C, 24 h) with 1.2 molar equivalence of benzyl bromide. As the reaction proceeded it progressively became more homogeneous until solvated. The polymers were isolated by precipitation in THF. The polymer was rinsed 3X with ether and further purified via dialysis.

Base Polymer 9

Polymer **9** series contain 2.5 (**9a**) or 5.0 (**9b**) mol% Jeffamine (ED2003), which has telechelic amine groups. High molecular weights were targeted, and the stoichiometry was calculated such that the diester : diamine molar ratio was 1:1. The following procedure is an example for polymer **9a**, which contains 2.5 mol% Jeffamine. Diethyl succinate (1.29 g, 7.4 mmol), ED2003 (0.37 g, 0.18 mmol) and TBD (0.05 g, 0.35 mmol) were charged in a Schlenk tube. The reactants were mixed by simple vortex until miscible (1-2 min). The reaction was allowed to react under nitrogen for 1 h (100 °C). 3,3'- Bis(3-aminopropyl)-piperazine (1.45 g, 8.2 mmol) was charged in the Schlenk tube was placed in a heated sand bath (150 °C, 20 h). After 10 h, vacuum was applied for an additional 20 h to pull off the condensate and push the equilibrium towards product. The polymerization was self-limiting as the polymer crystallizes and becomes diffusion controlled. M_n (GPC, DMF = 7 500 g/mol, PDI = 1.20)

Quaternization of 9

Polymer **9a** was marginally soluble in DMF after heating to 120 °C (2-3 h) and once dissolved/homogenous it was quaternized (85 °C, 24 h) with 1.2 molar equivalence of a) methyl iodide (**9a-MeI**) or b) benzyl bromide (**9a-BnBr**). The polymers were isolated by precipitation in THF. The polymer was rinsed 3X with ether and further purified via dialysis. A similar quaternization procedure with methyl iodide and benzyl bromide was used for the polymer **9b** series, which contained 5.0 mol% Jeffamine.

Base Polymer 10

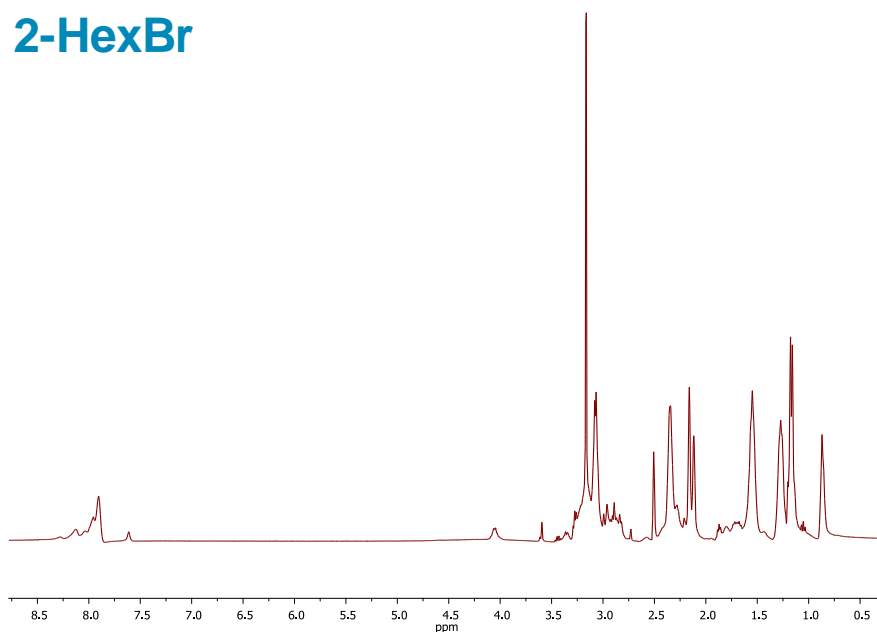
Diethyl carbonate (1.29 g, 7.4 mmol), ED2003 (0.37 g, 0.18 mmol) and TBD (0.05 g, 0.35 mmol) were charged in a Schlenk tube. The reactants were mixed by simple vortex until miscible (1-2 min). The reaction was allowed to react under nitrogen for 1 h (100 °C). 3,3'- Bis(3-aminopropyl)-piperazine (1.45 g, 8.2 mmol) was charged in the Schlenk tube was placed in a heated sand bath (150 °C, 20 h). After 10 h, vacuum was applied for an additional 20 h to pull off the condensate and push the equilibrium towards product. The polymerization was self-limiting as the polymer crystallizes and becomes diffusion controlled.

Quaternization of 10

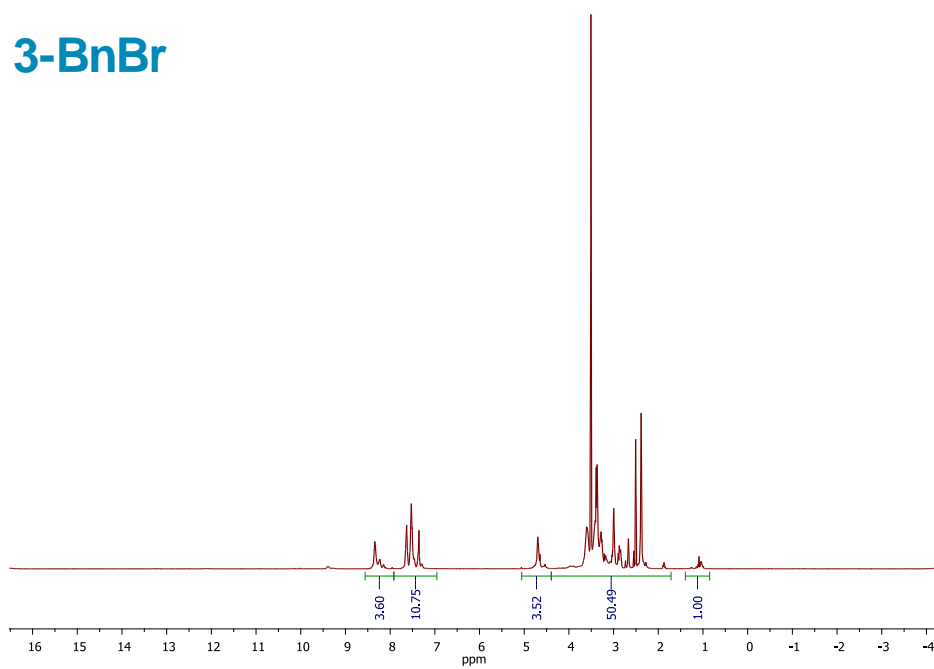
Polymer **10** was marginally soluble in DMF after heating to 120 °C (2-3 h) and once dissolved/homogenous it was quaternized (85 °C, 24 h) with 1.2 molar equivalence of a) methyl iodide (**10a-MeI**) or b) benzyl bromide (**10a-BnBr**). The polymers were isolated by precipitation in THF. The polymer was rinsed 3X with ether and further purified via dialysis. A similar quaternization procedure with methyl iodide and benzyl bromide was used for the polymer **9b** series, which contained 5.0 mol% Jeffamine.

¹H NMR Spectroscopy

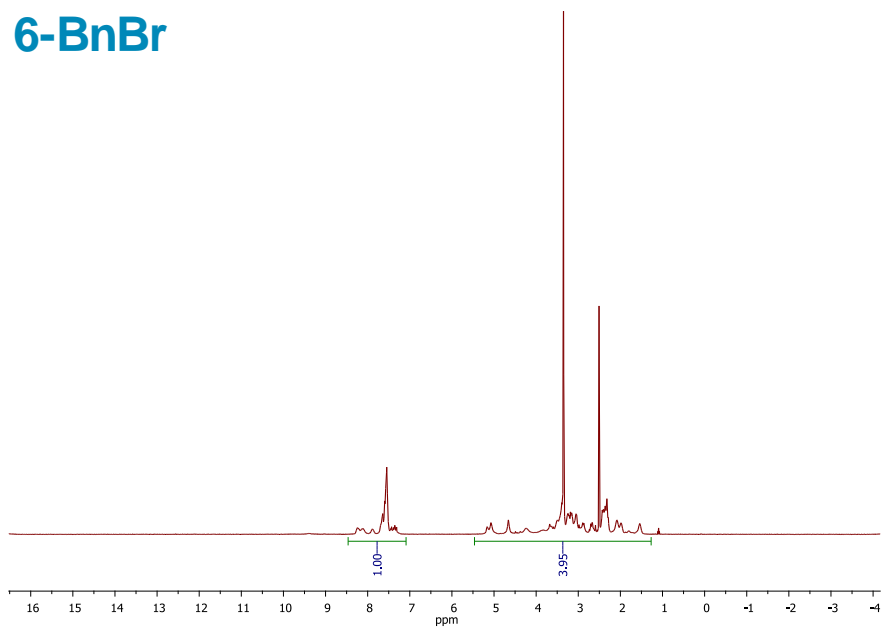
2-HexBr



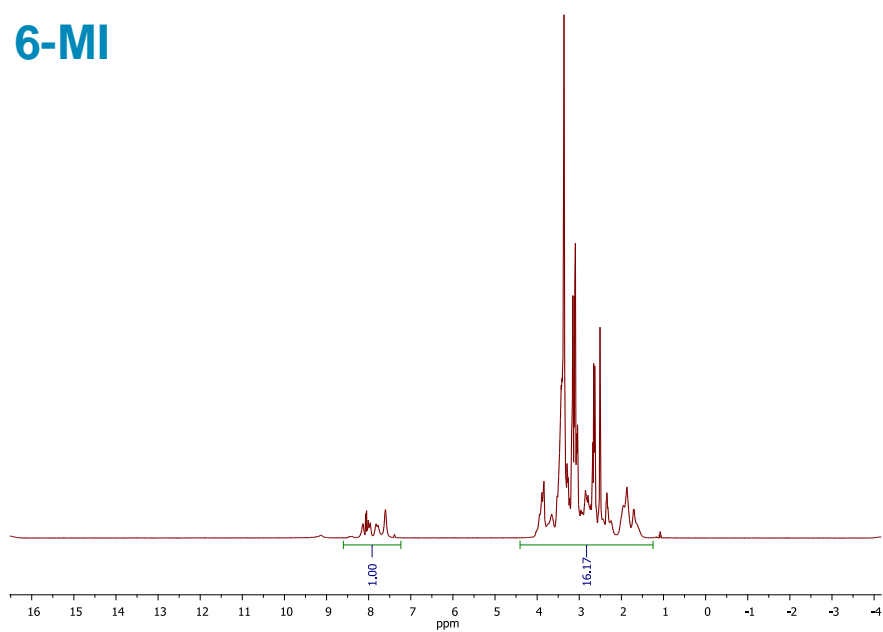
3-BnBr



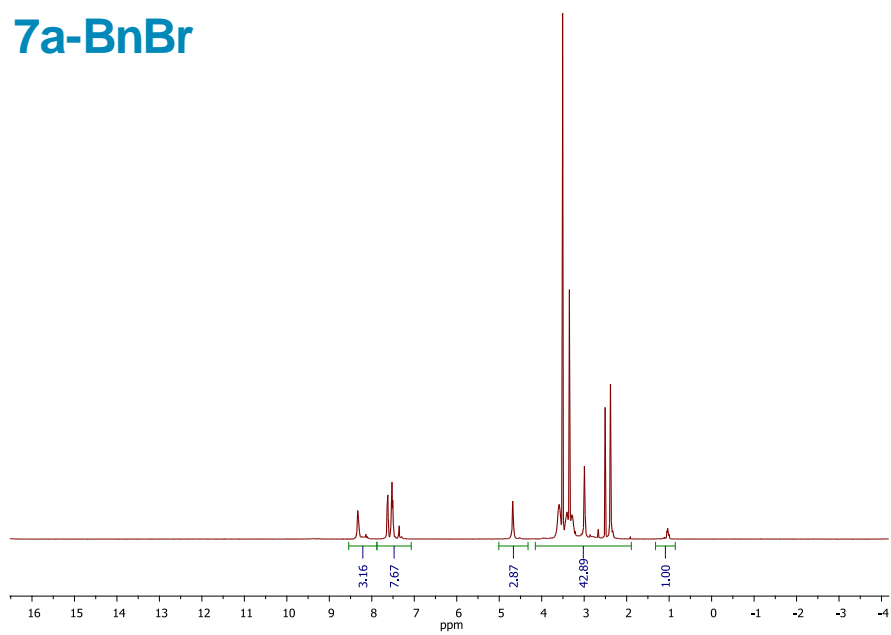
6-BnBr



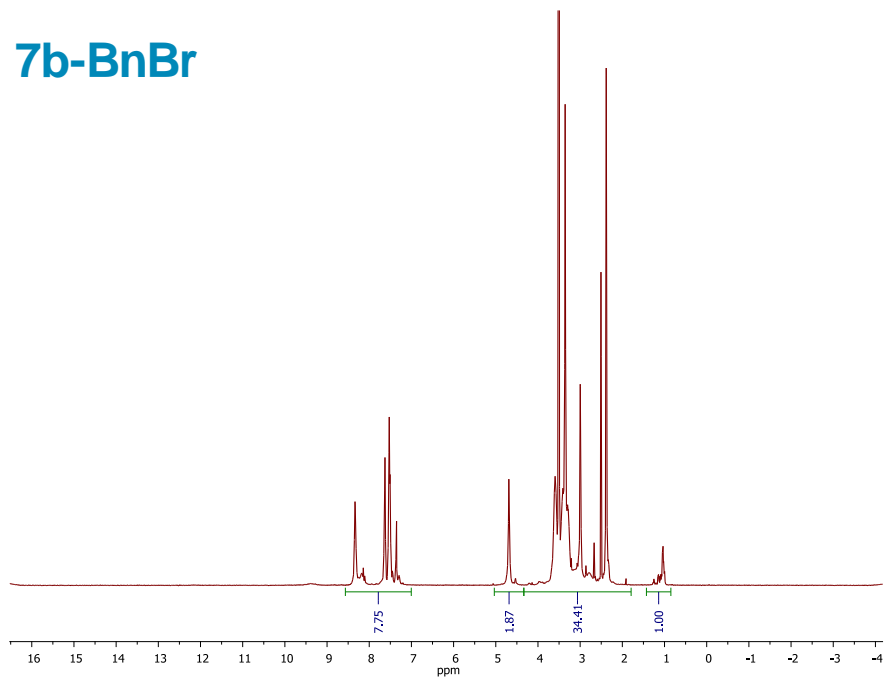
6-MI



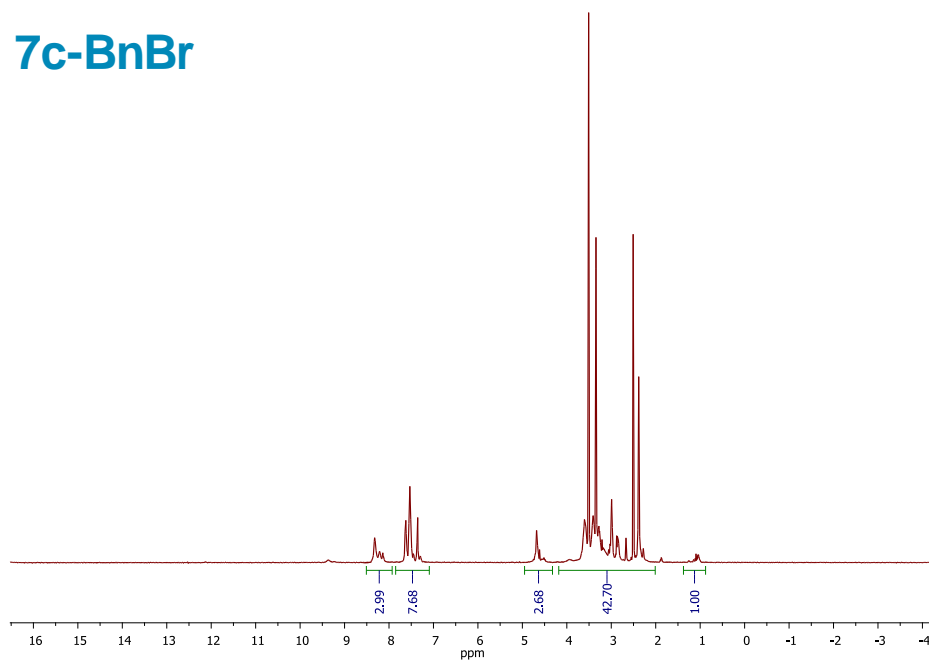
7a-BnBr



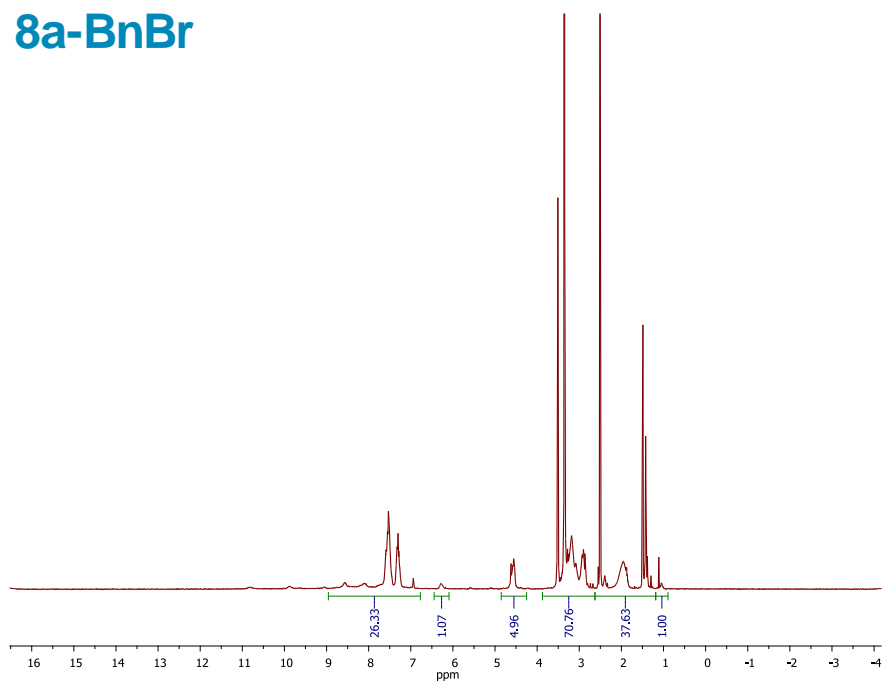
7b-BnBr



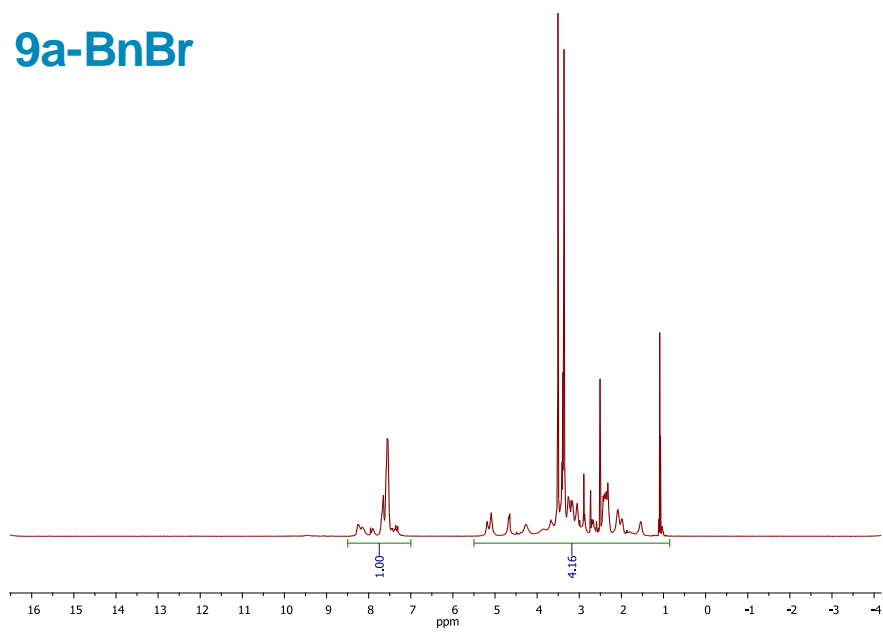
7c-BnBr



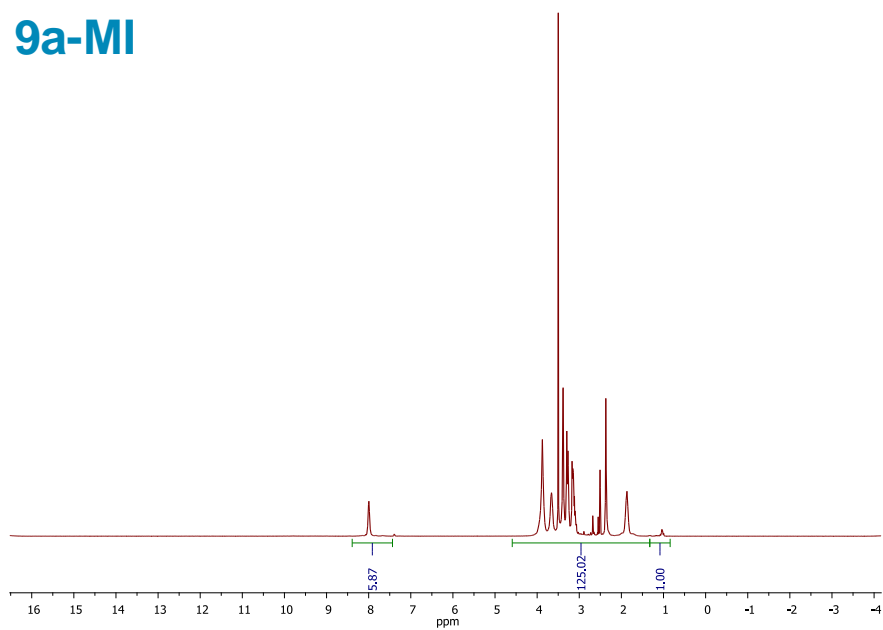
8a-BnBr



9a-BnBr



9a-MI



9b-BnBr

