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Synthesis of Cinchona Alkaloid Sulfonaminde Polymers as Sustainable Catalysts for the Enantioselective Desymmetrization of Cyclic Anhydrides

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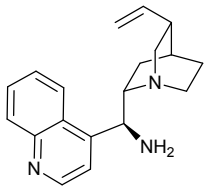
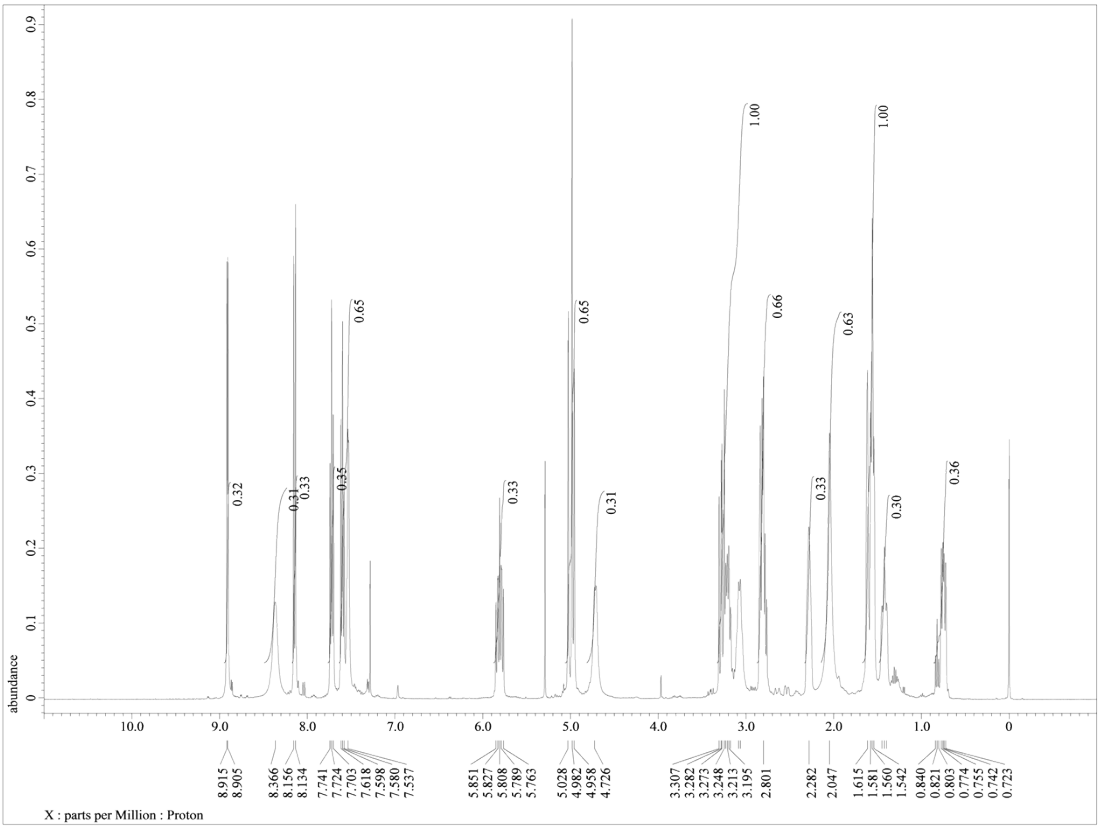
Materials and general considerations. All solvents and reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry (TCI) Co., Ltd. at the highest available purity and were used as received, unless otherwise noted. Reactions were monitored by thin-layer chromatography using precoated silica gel plates (Merck 5554, 60F254). Column chromatography was performed using a silica gel column (Wakogel C-200, 100–200 mesh). Melting points were recorded using a Yanaco micro melting apparatus and were uncorrected. NMR spectra were recorded on JEOL JNM-ECS400 spectrometers in $CDCl_3$ or DMSO-d_6 at room temperature operating at 400 MHz (^{1}H) and 100 MHz (^{13}C{^{1}H}). TMS was used as an internal standard for ^{1}H-NMR and $CDCl_3$ for ^{13}C-NMR. Chemical shifts were reported in ppm using TMS as a reference, and the *J* values were recorded in Hertz. IR spectra were recorded on a JEOL JIR-7000 FTIR spectrometer and are reported in cm^{-1}. Elemental analyses (carbon, hydrogen, nitrogen) were performed on a Yanaco-CHN coder MT-6 analyzer. HRMS (ESI) spectra

were recorded on a microTOF-Q II HRMS/MS instrument (BRUKER). HPLC analyses were performed with a JASCO HPLC system composed of a 3-line degasser DG-980, HPLC pump PV-980, column oven CO-965, equipped with a chiral column (CHIRALCEL AD-H, Daicel) using hexane/2-propanol as eluent. A UV detector (JASCO UV-975 for the JASCO HPLC system) was used for peak detection. Size exclusion chromatography (SEC) was performed using a Tosoh instrument with HLC 8020 UV (254 nm) or refractive index detection. DMF was used as the carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Two polystyrene gel columns of bead size 10 μm were used. A calibration curve was made to determine the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) values with polystyrene standards. Optical rotation was recorded using a JASCO DIP-149 digital polarimeter using a 10-cm thermostated microcell.

^{1}H NMR spectrum of **1C**



1C



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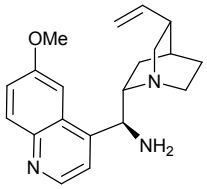
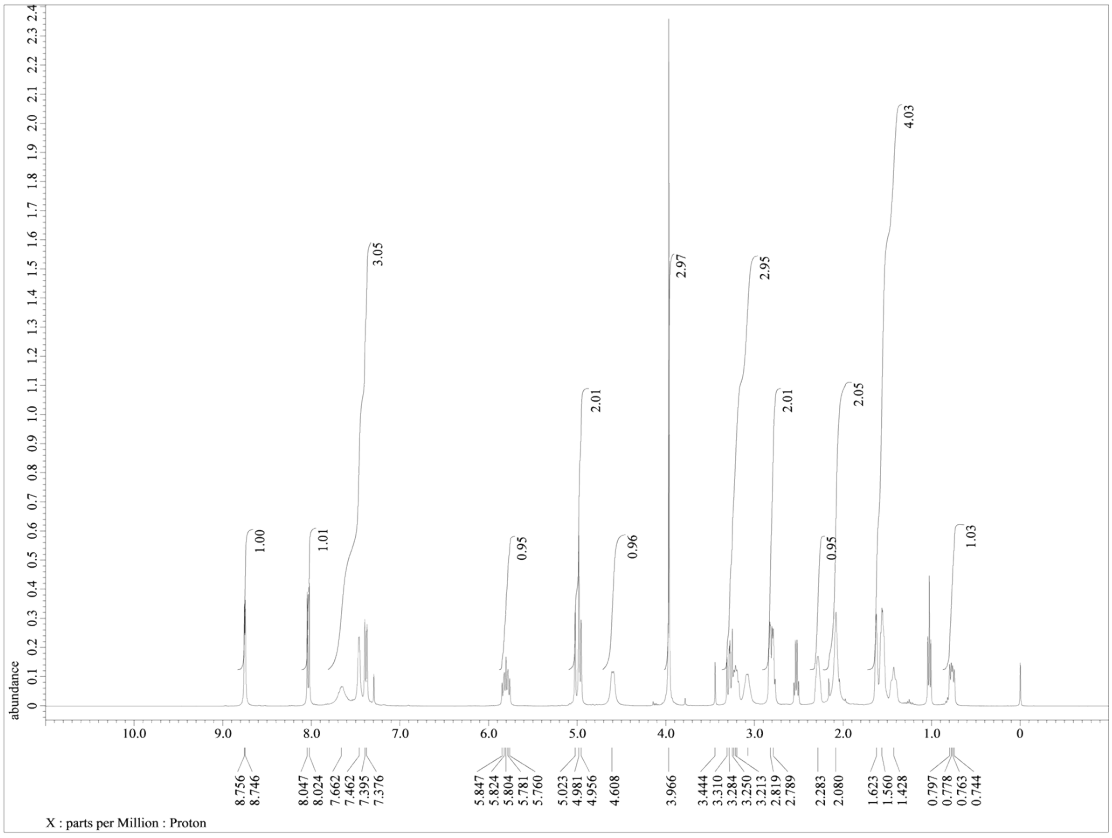


1Q



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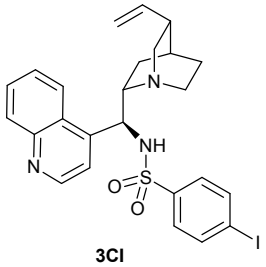

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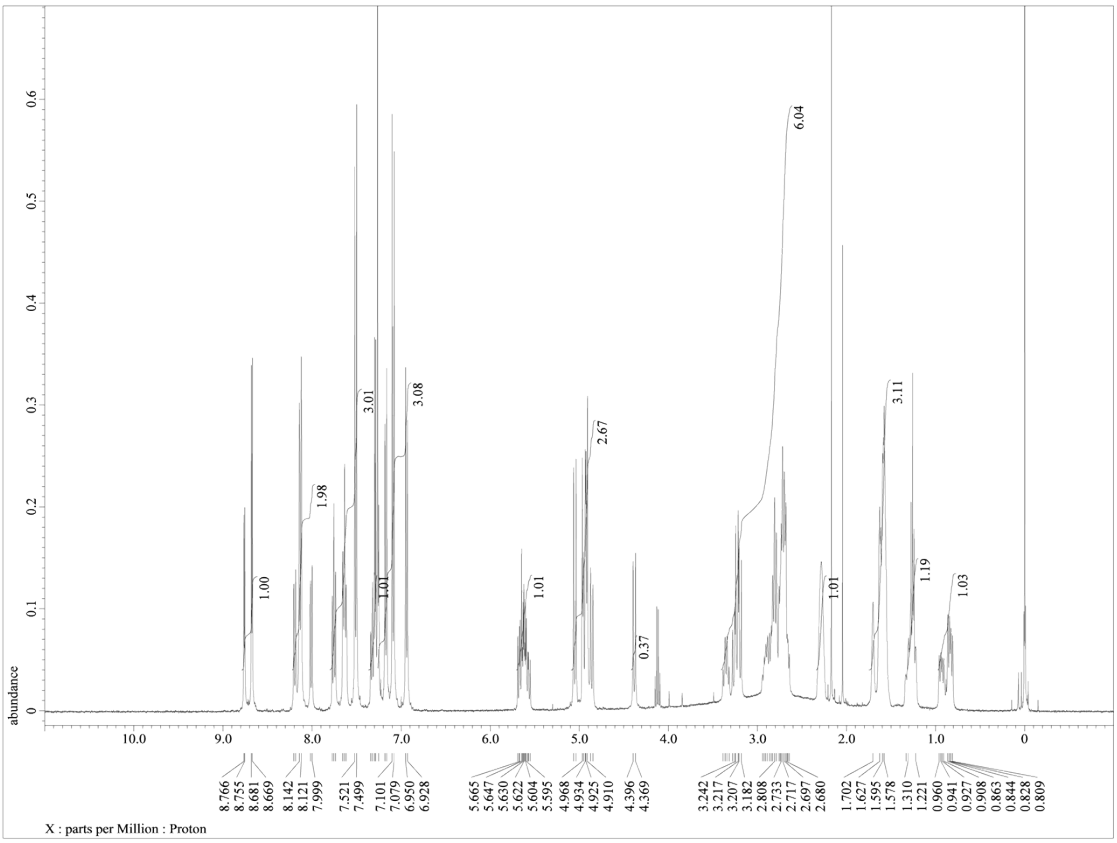

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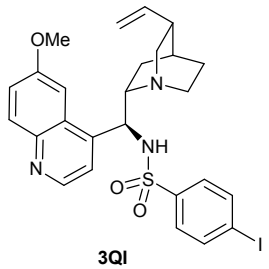

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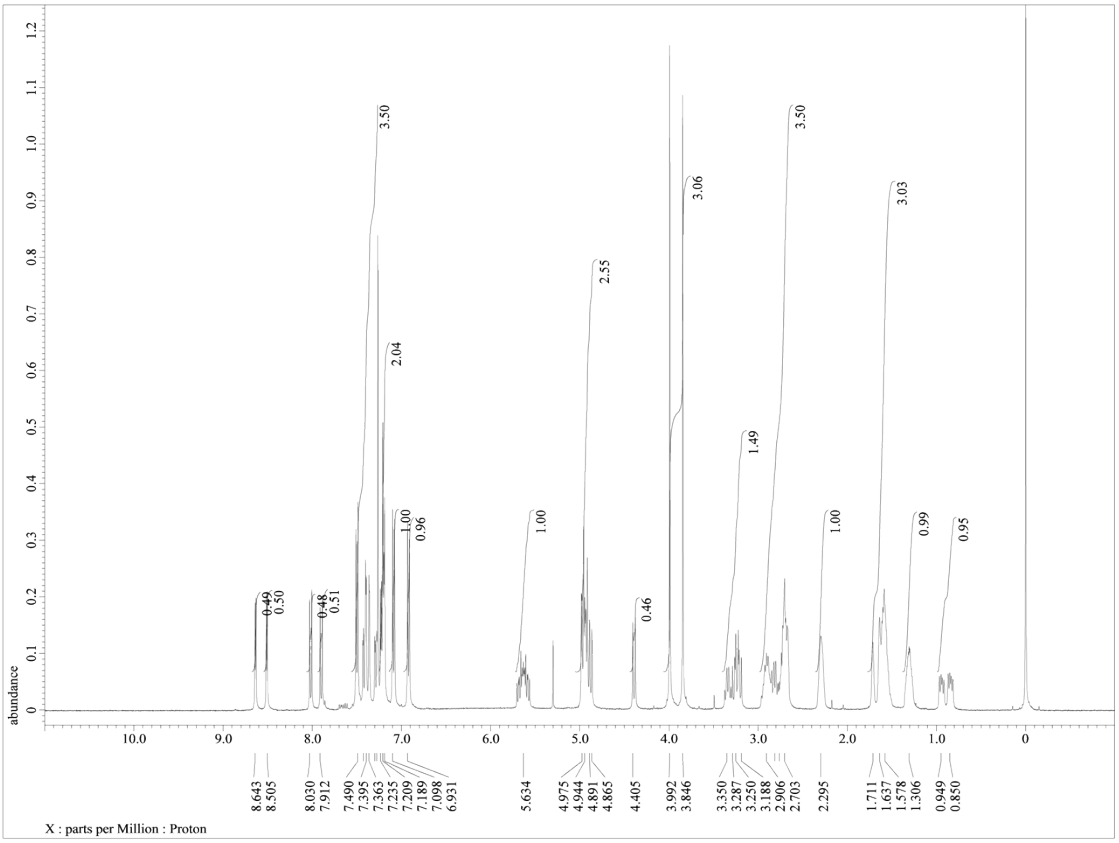

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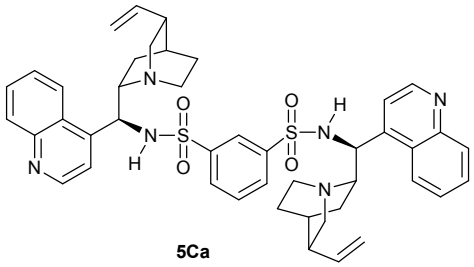

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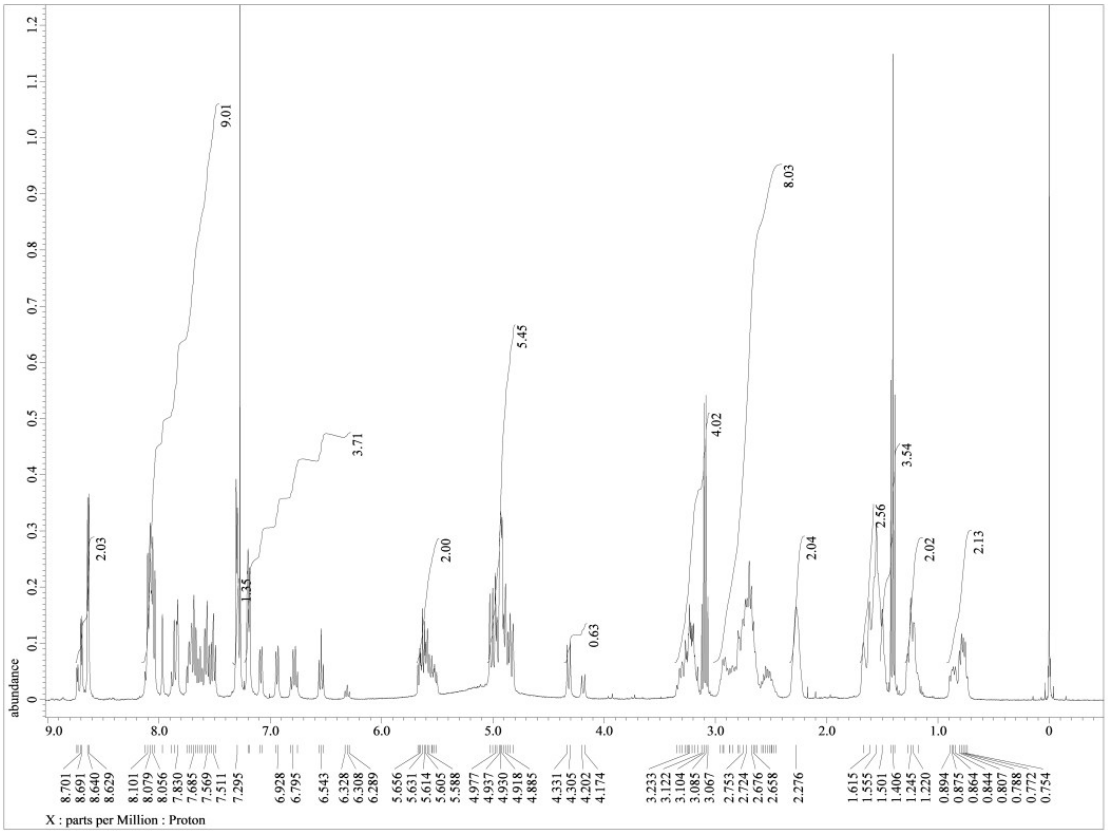

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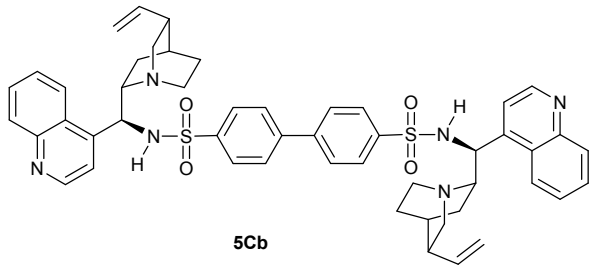
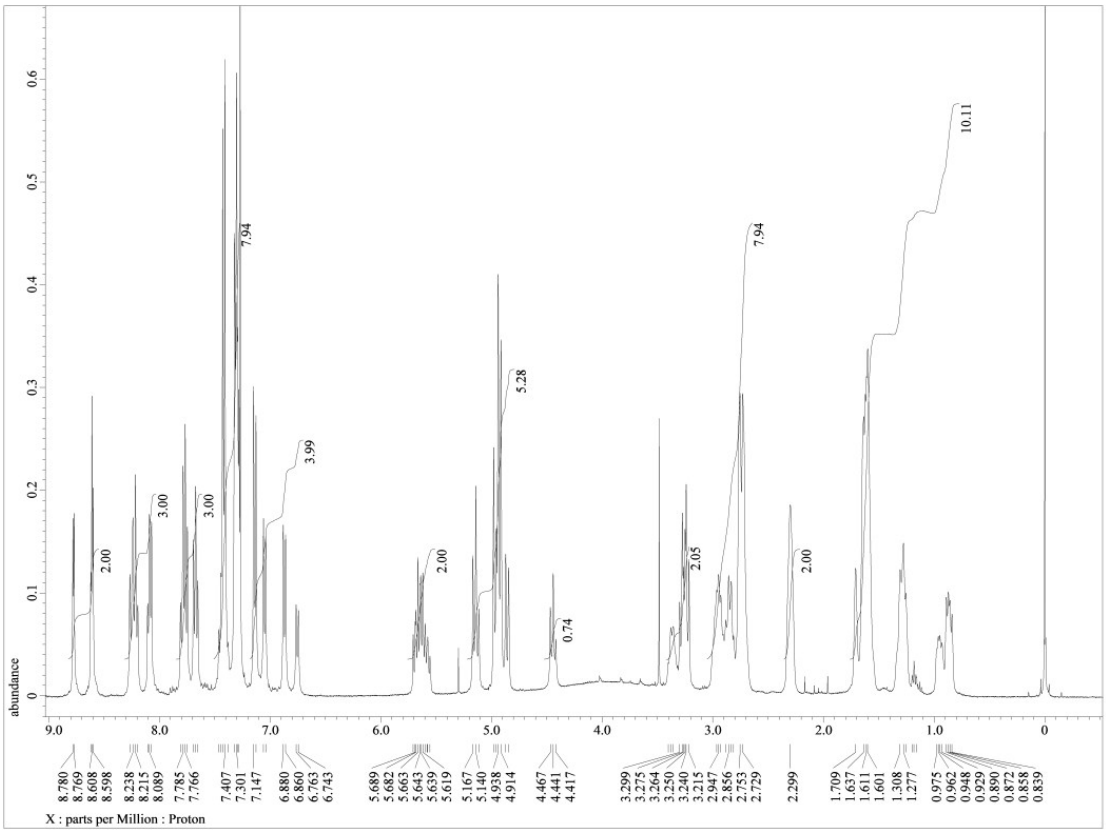


5Cb



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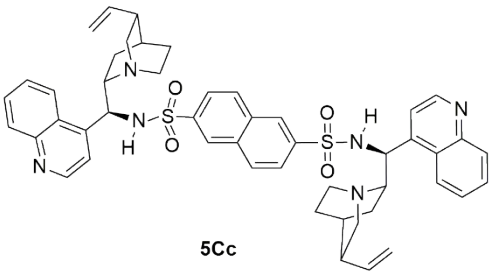

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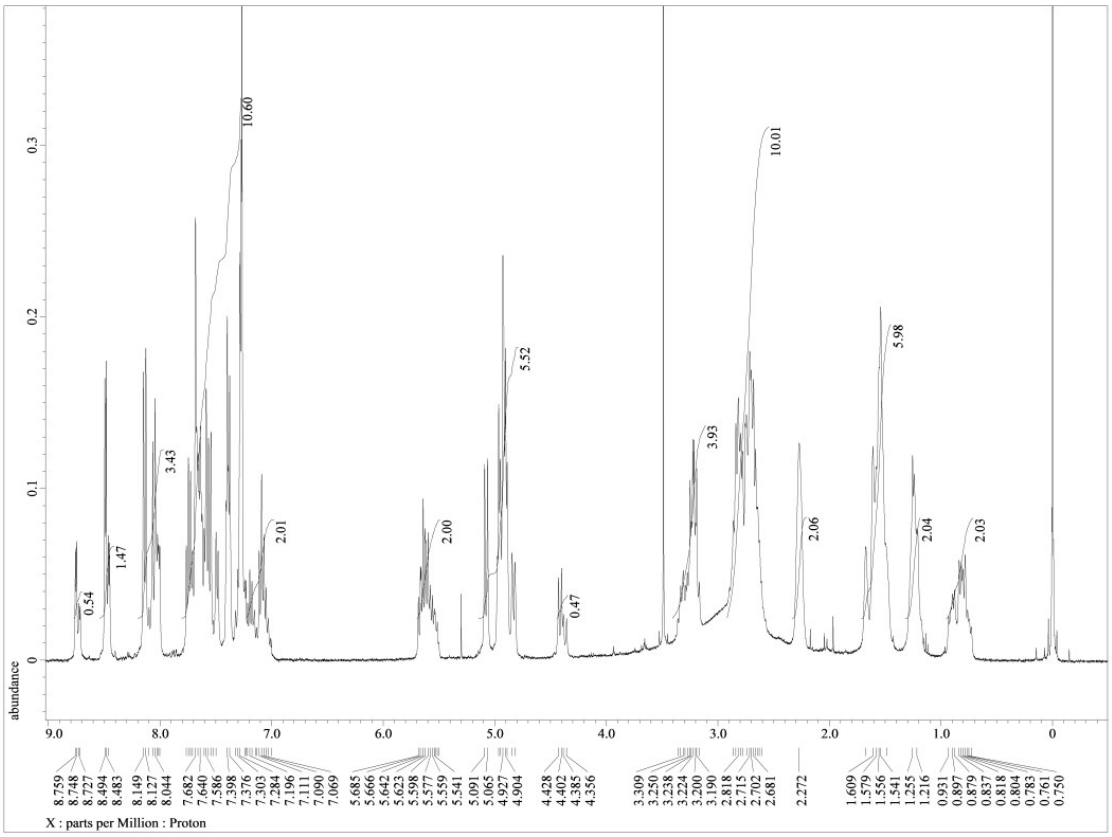

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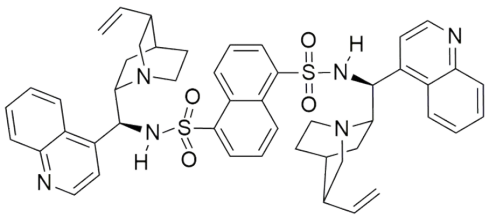

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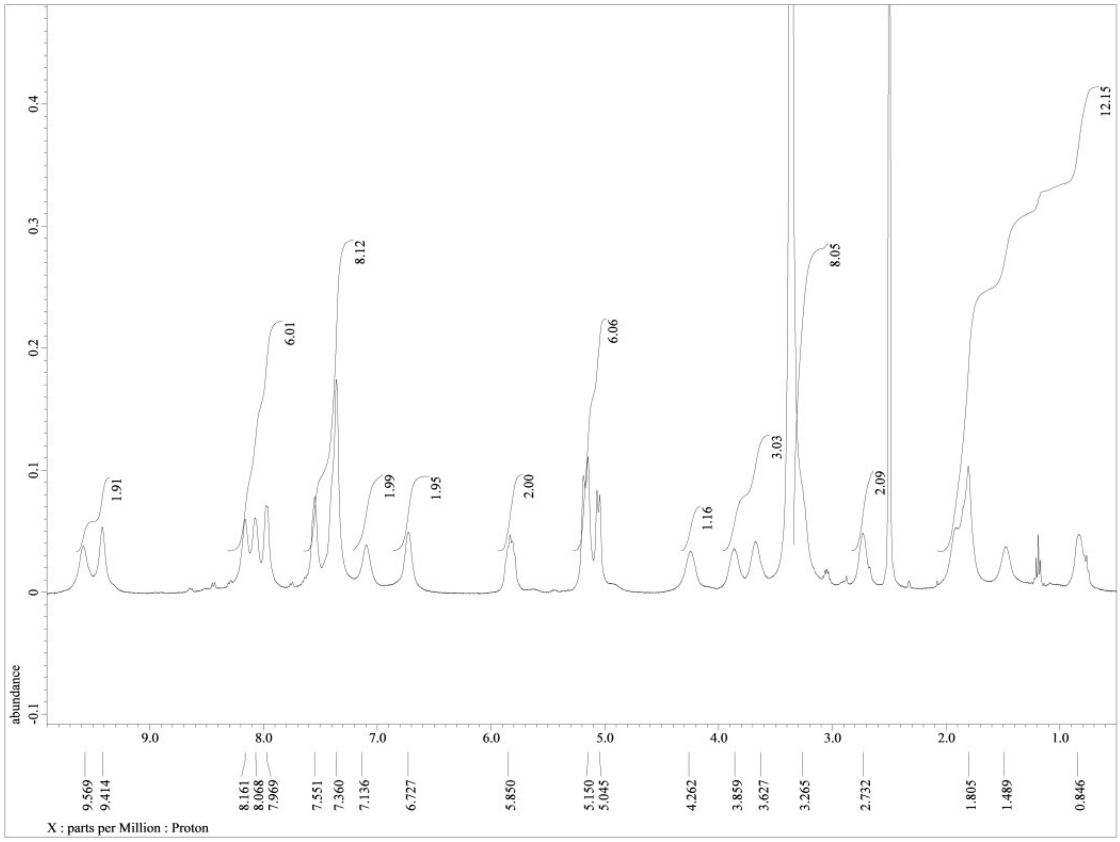

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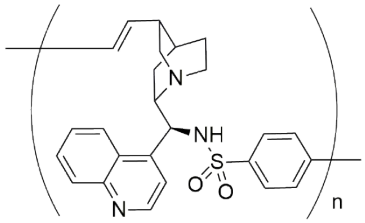
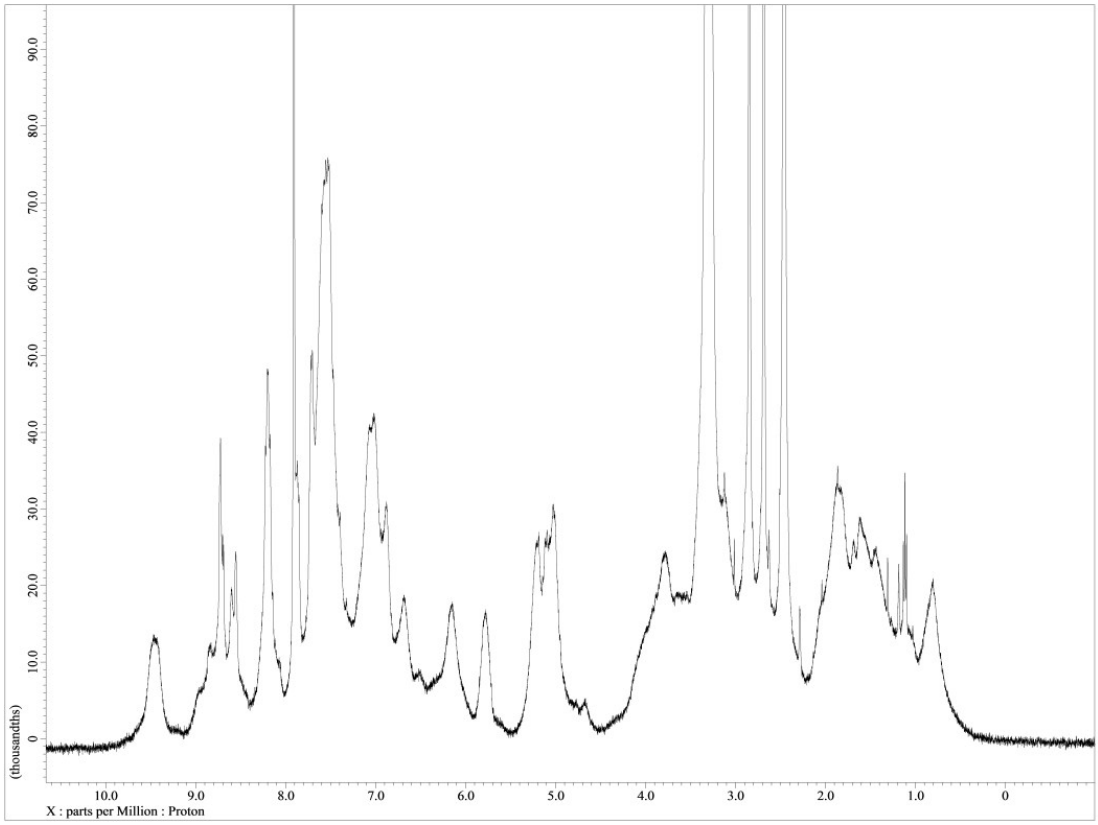


P1C



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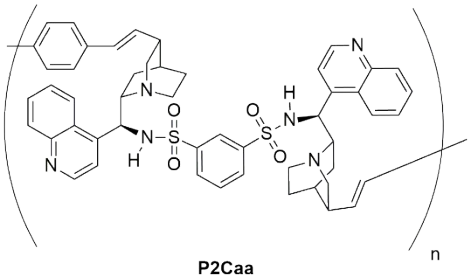

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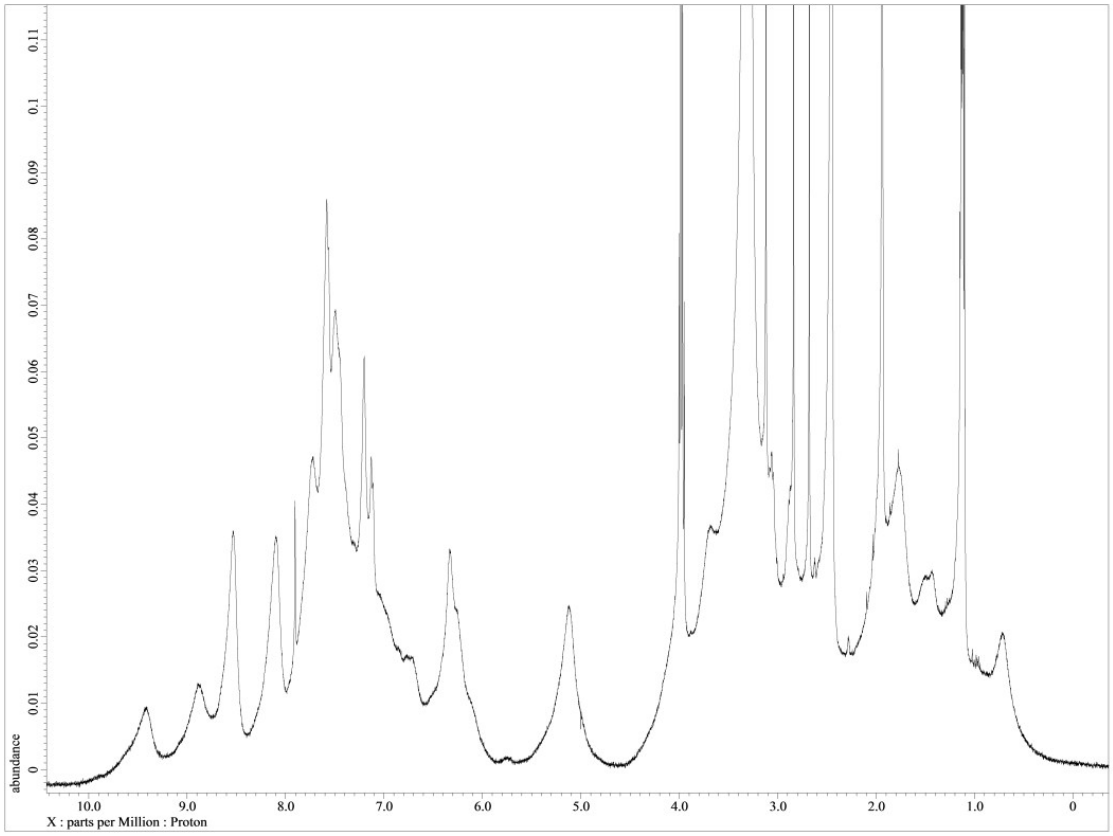

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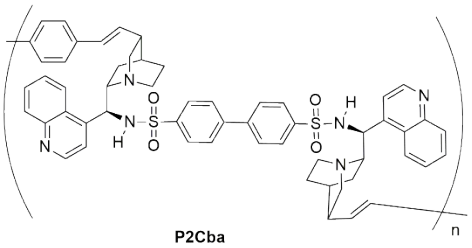

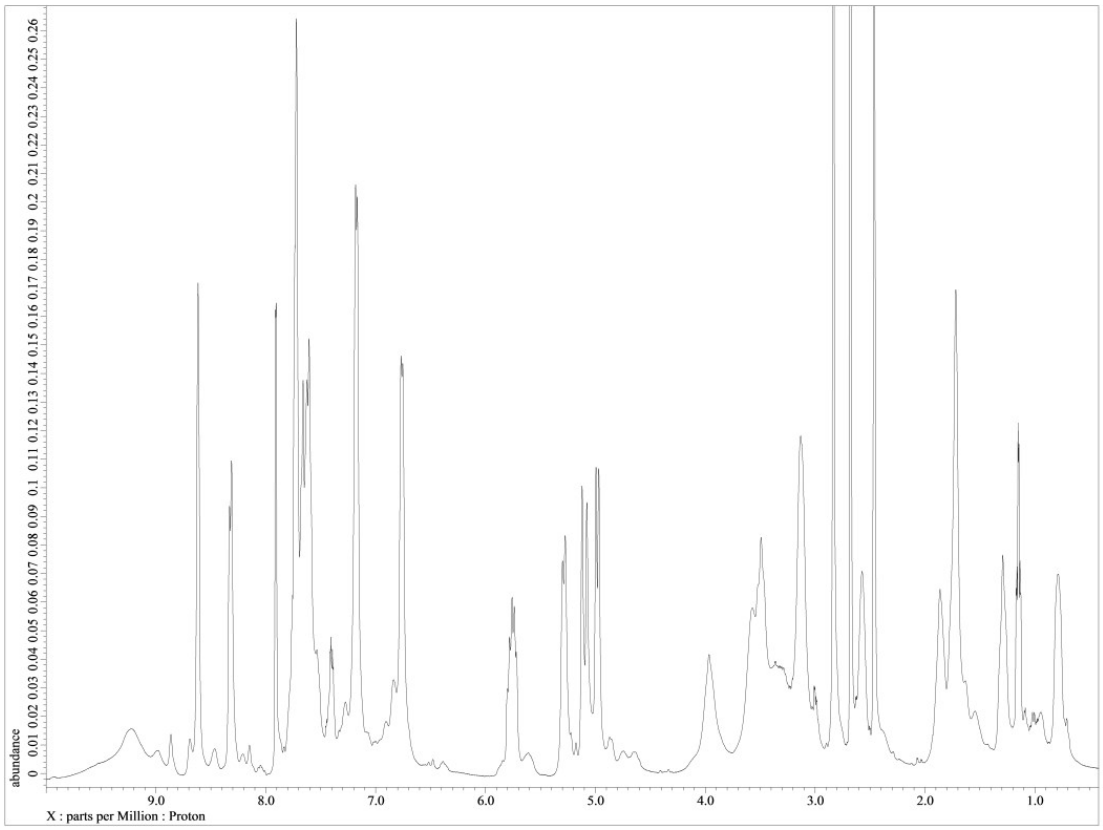

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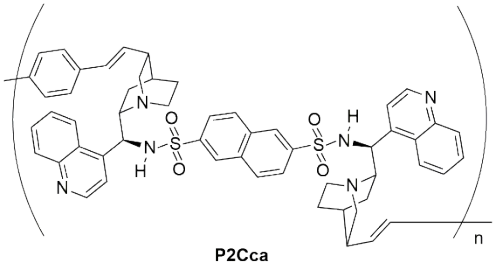

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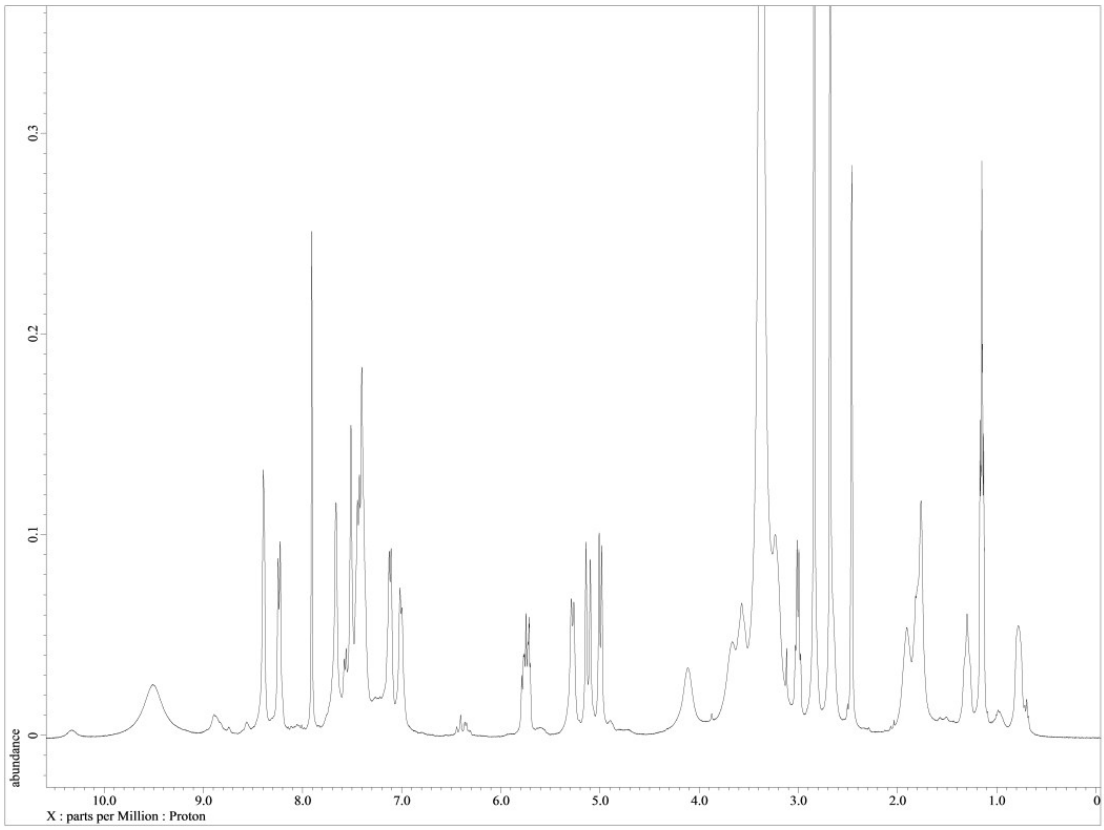

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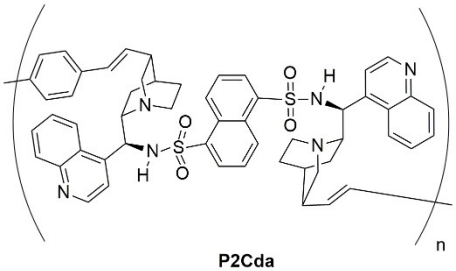

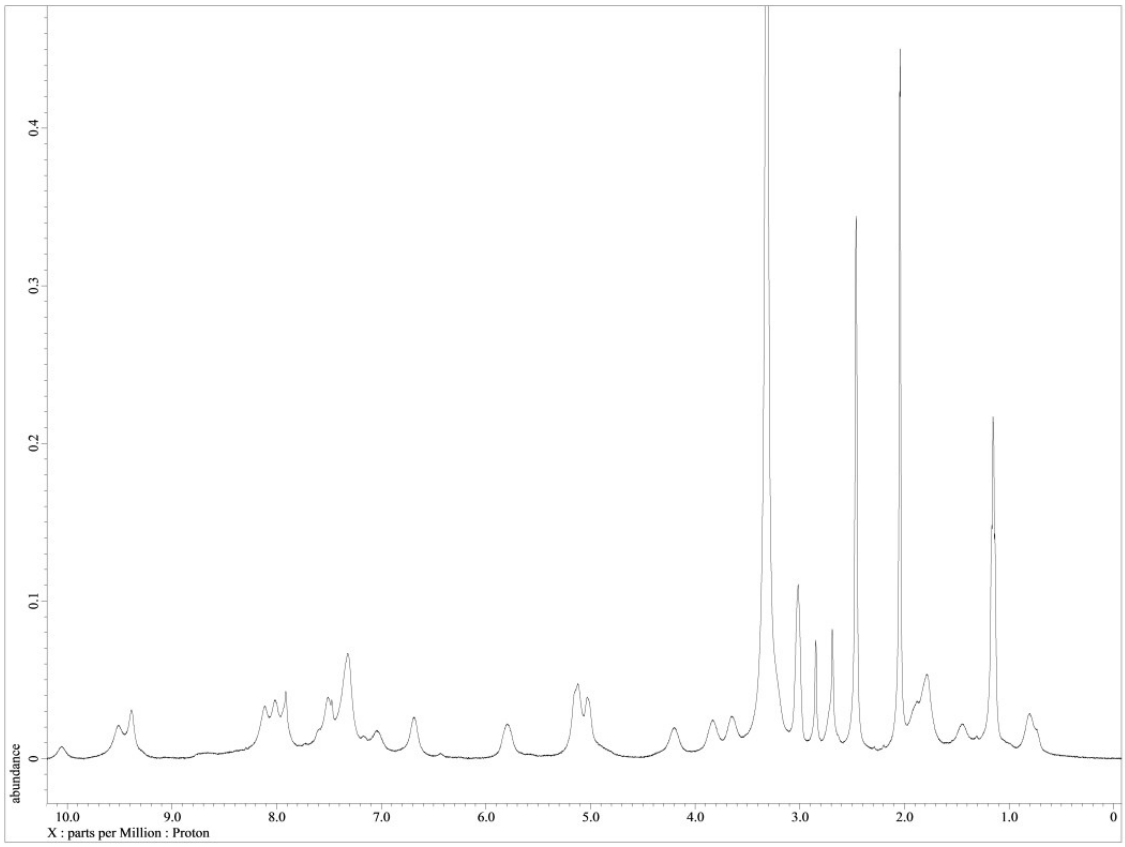

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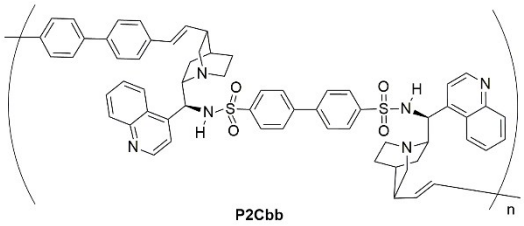

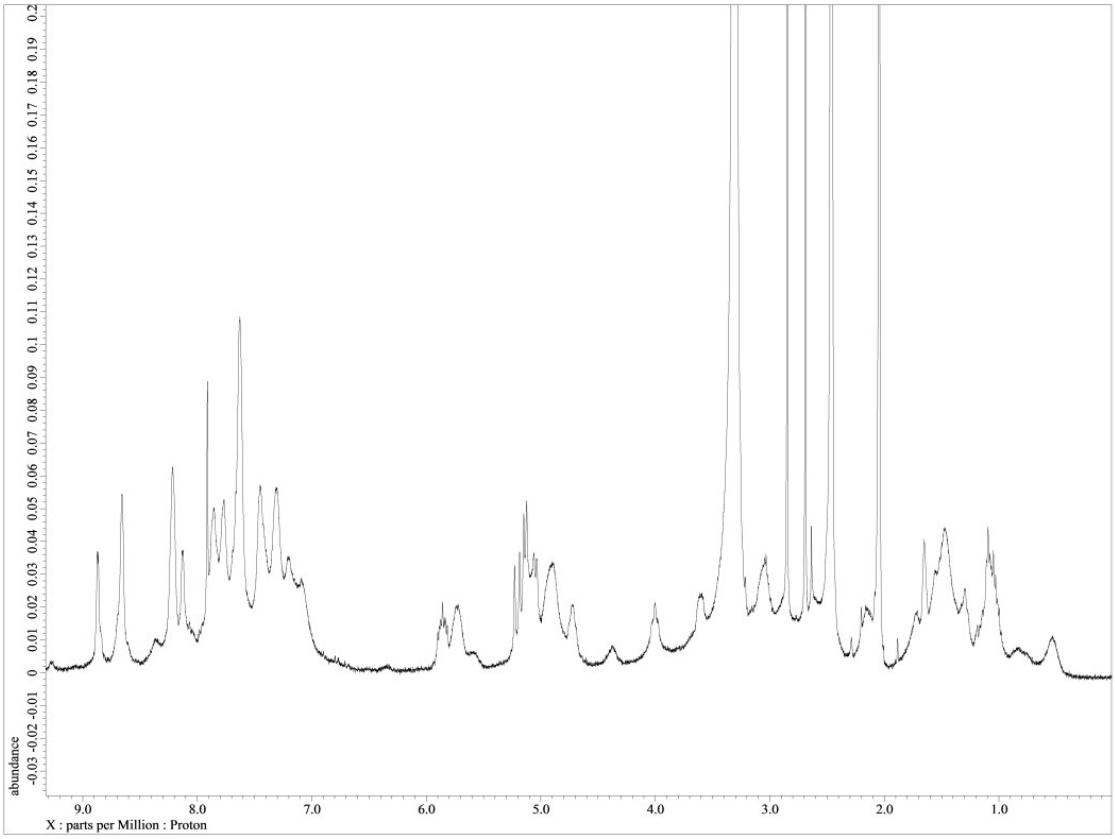

HPLC traces of the product obtained from asymmetric desymmetrization reaction

Table 2, entry 1

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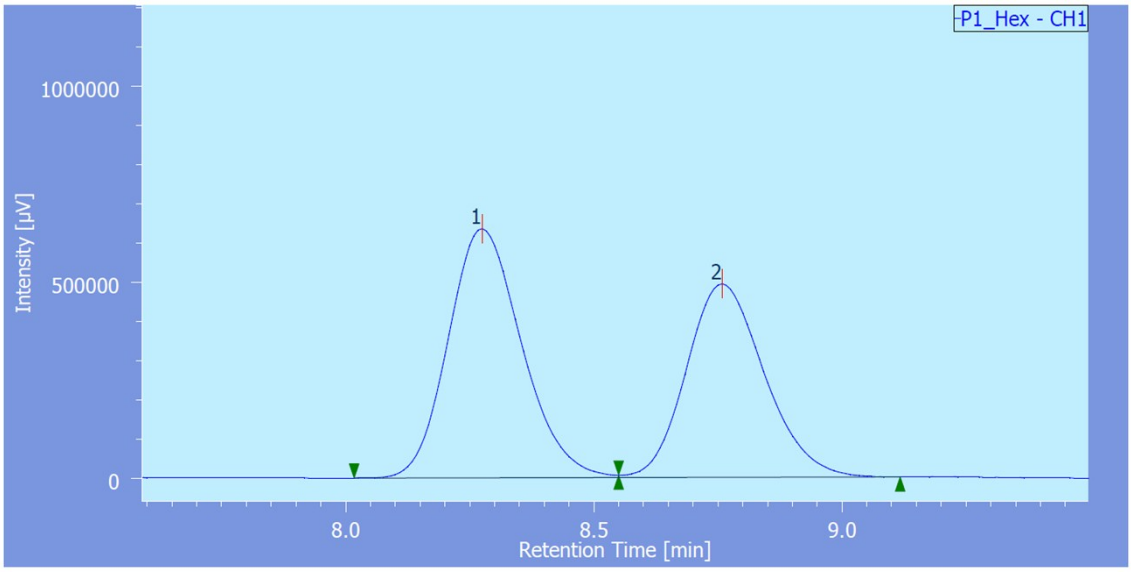

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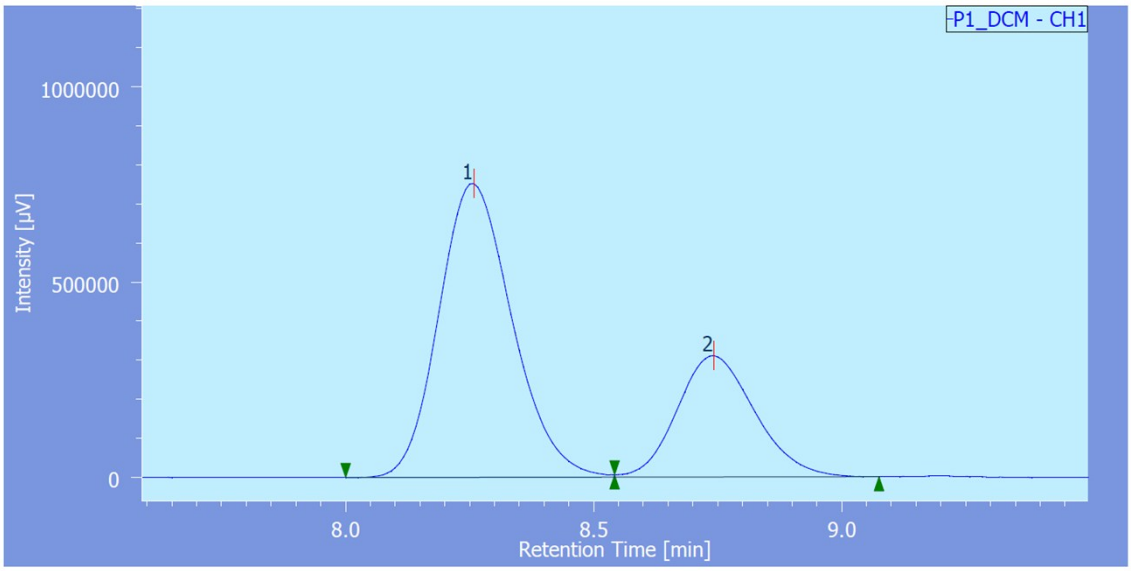

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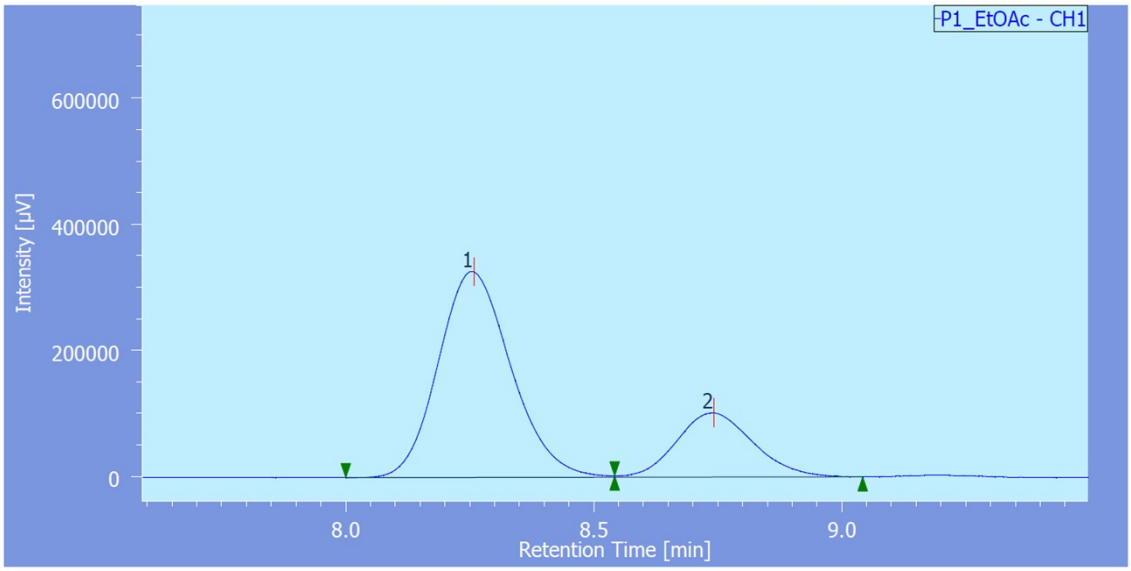

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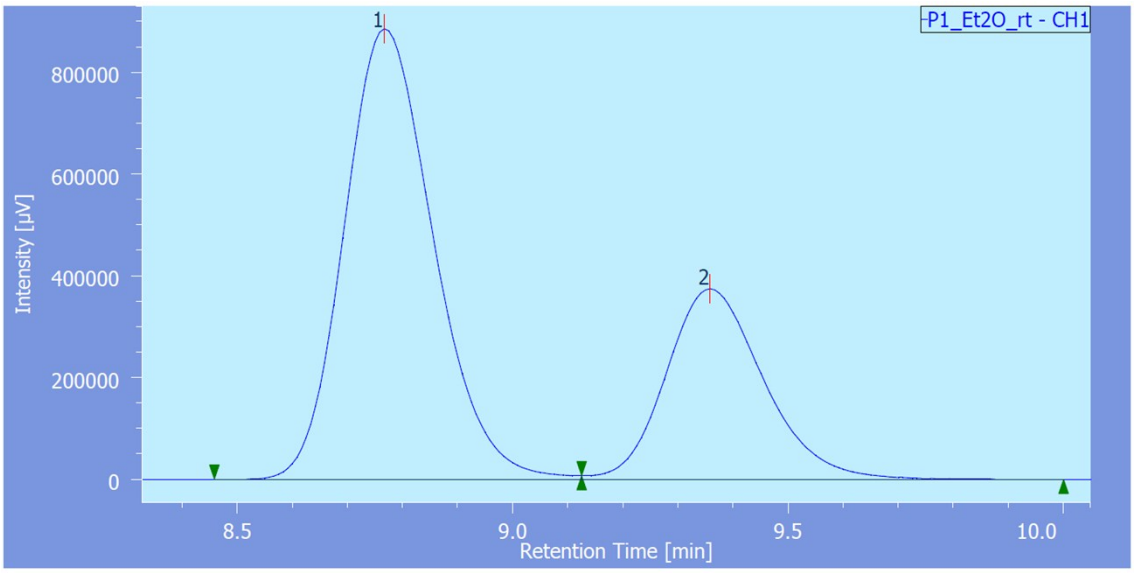

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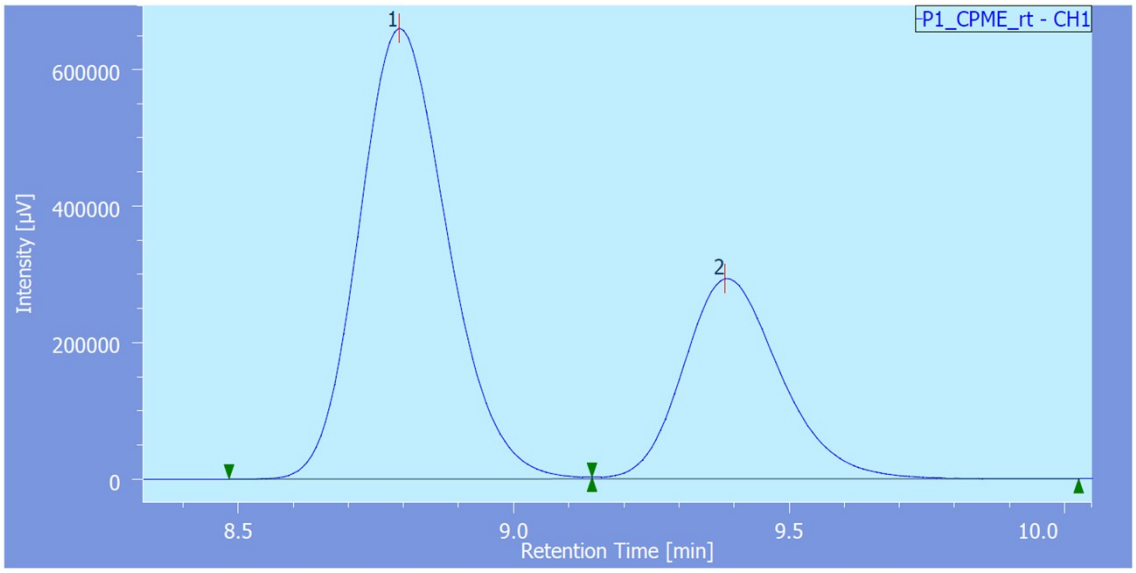

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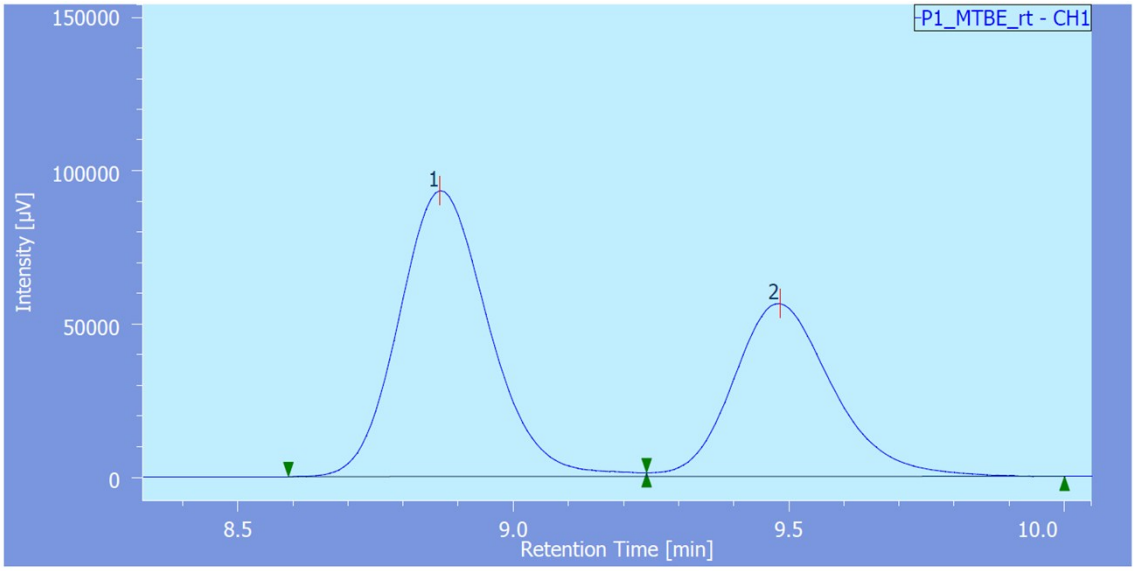

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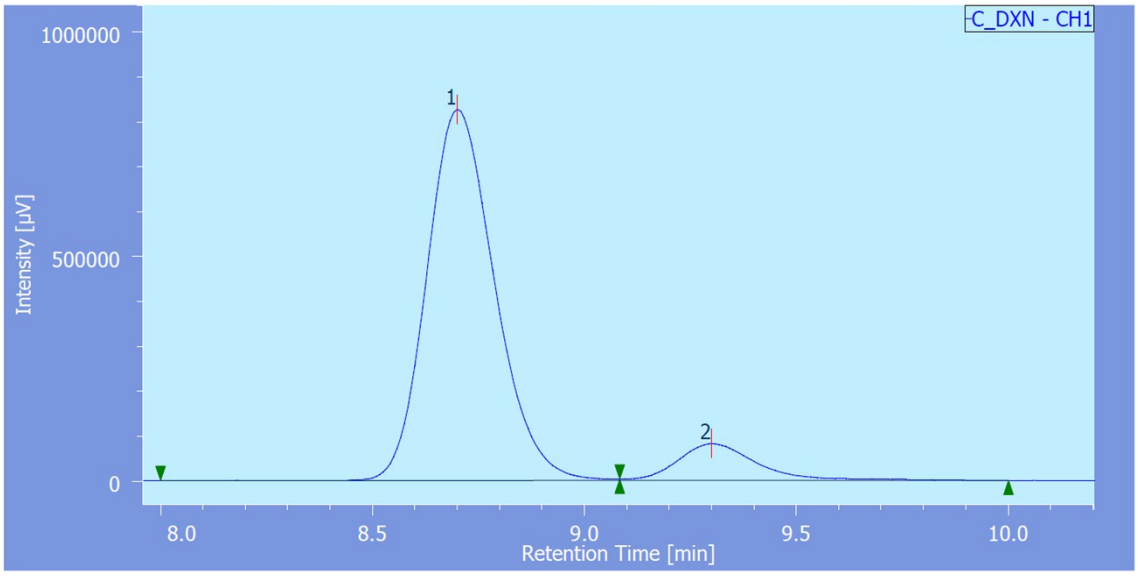

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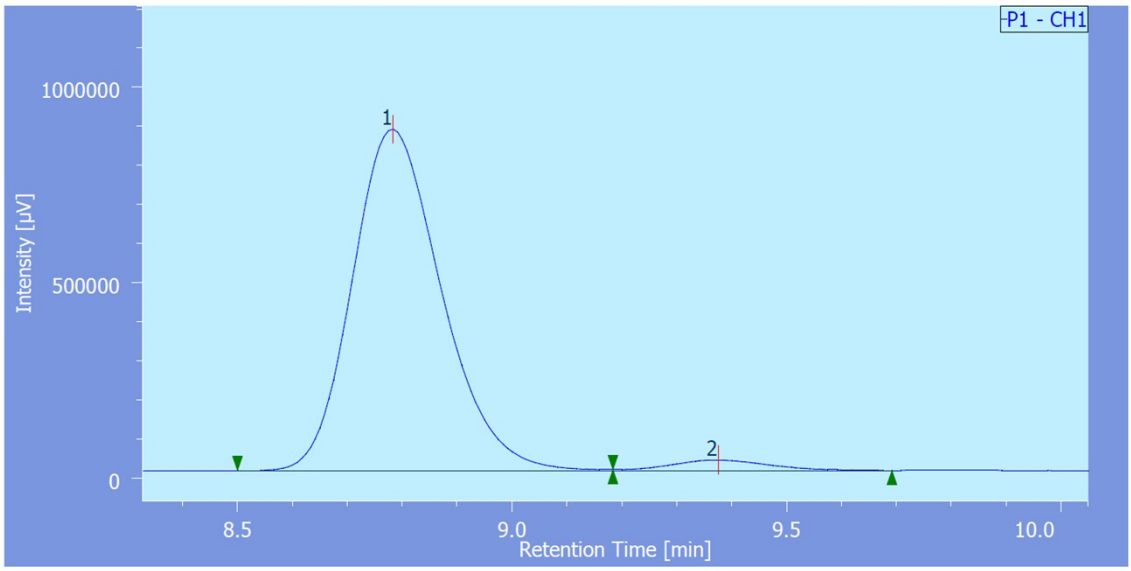

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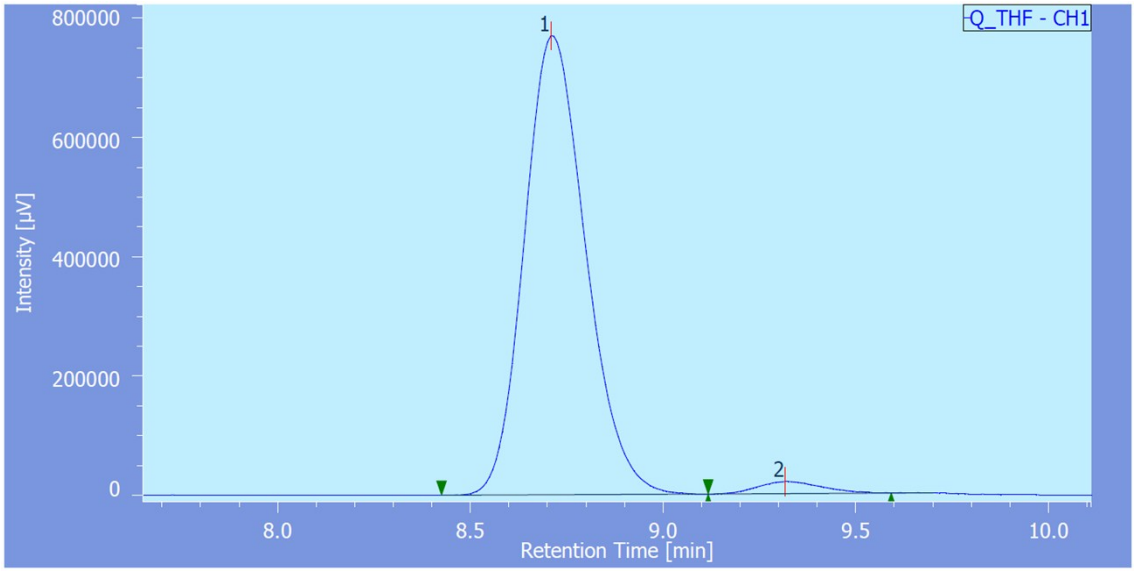

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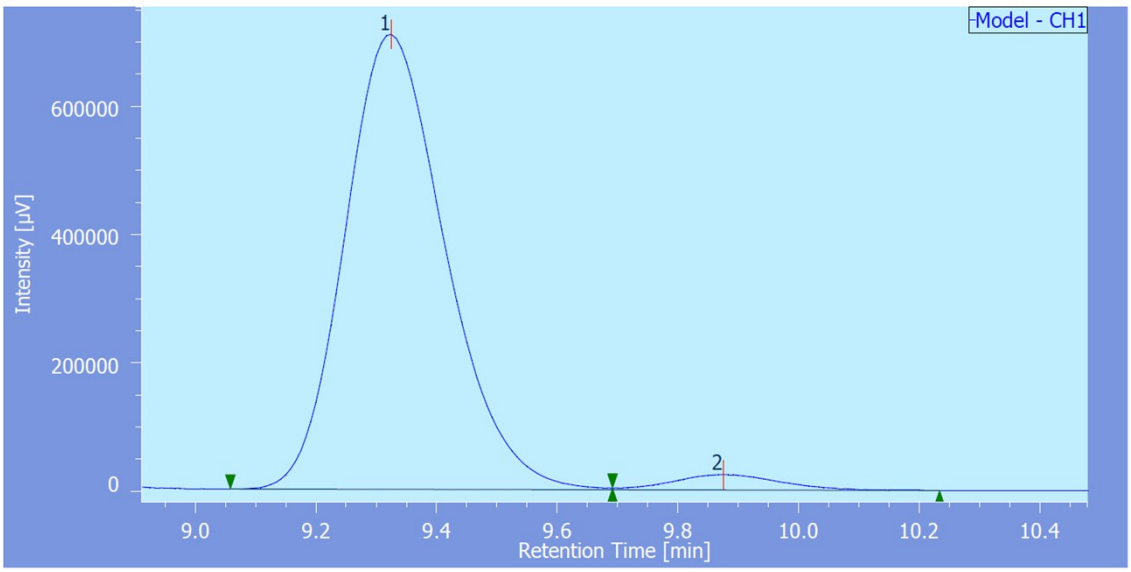

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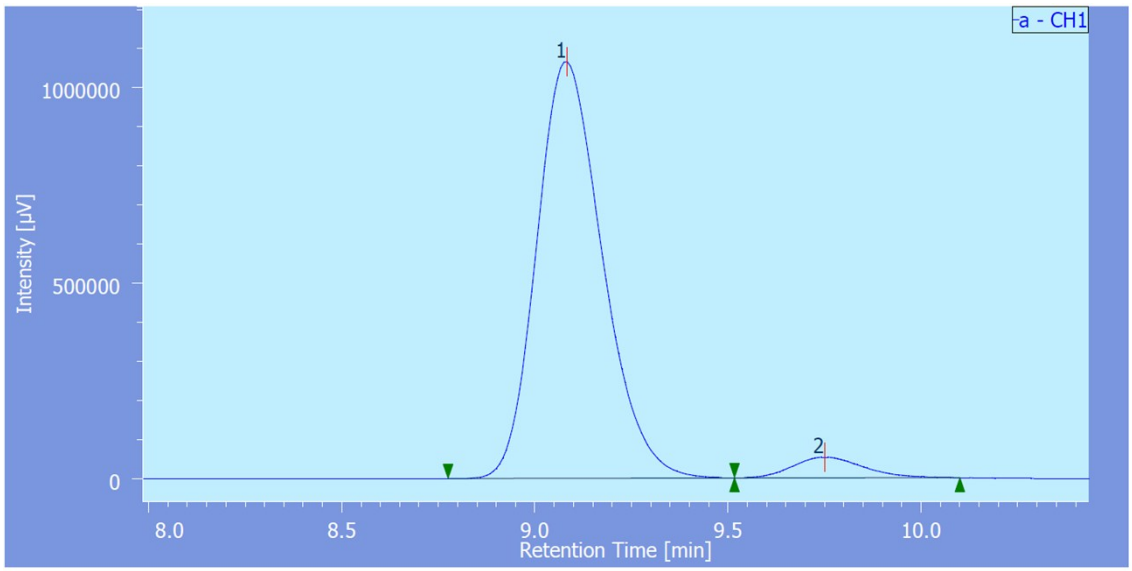

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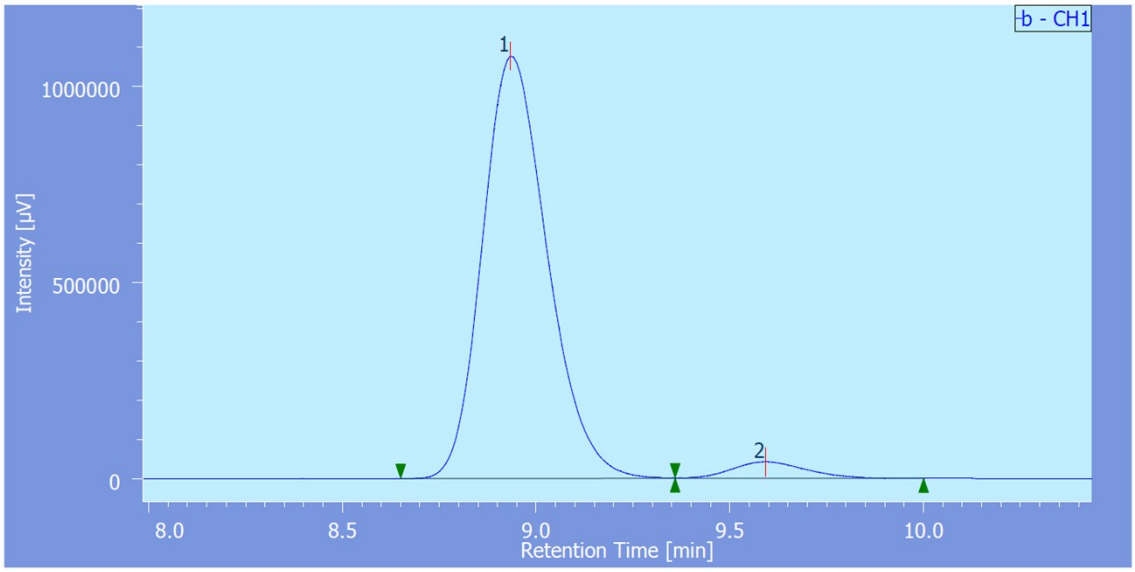

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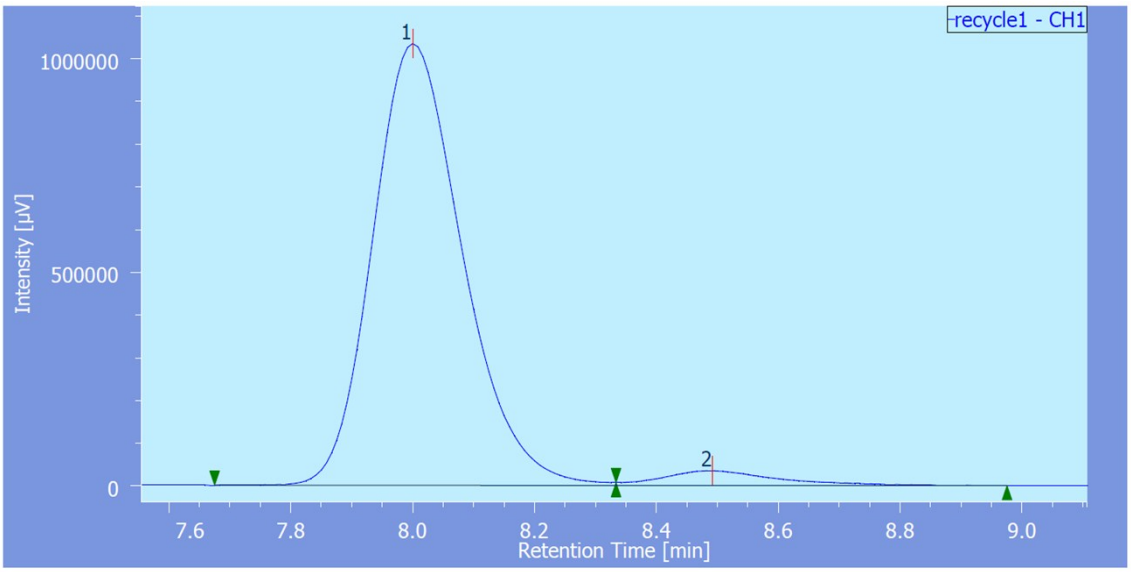

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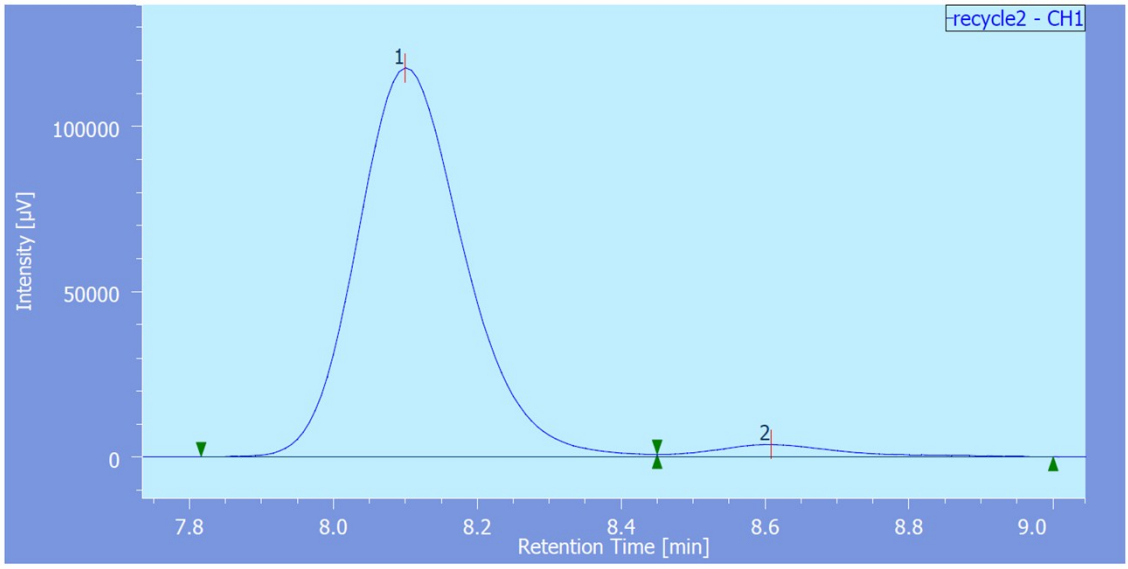

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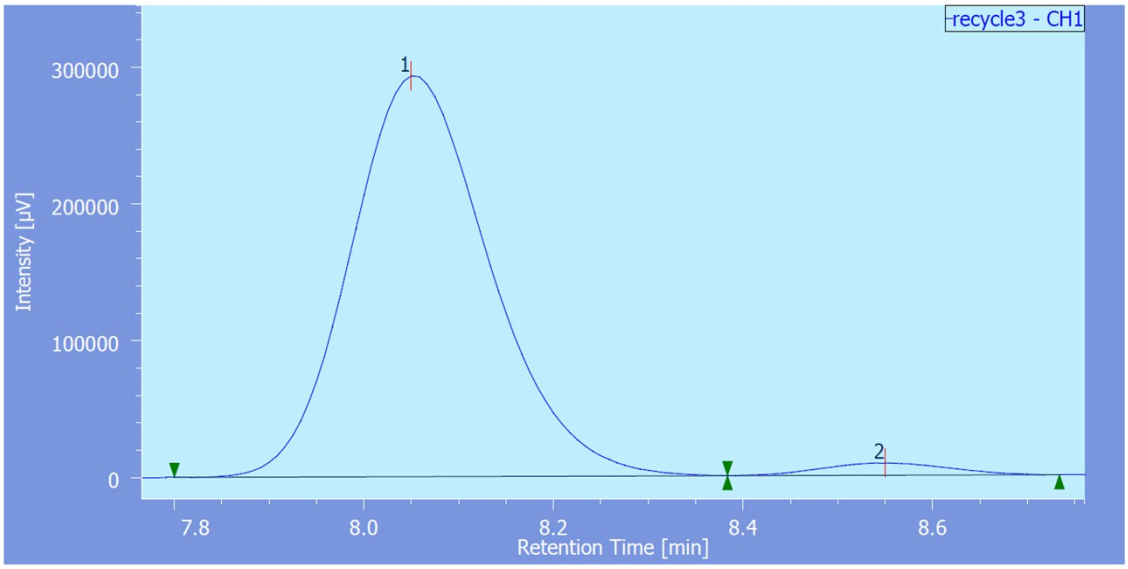

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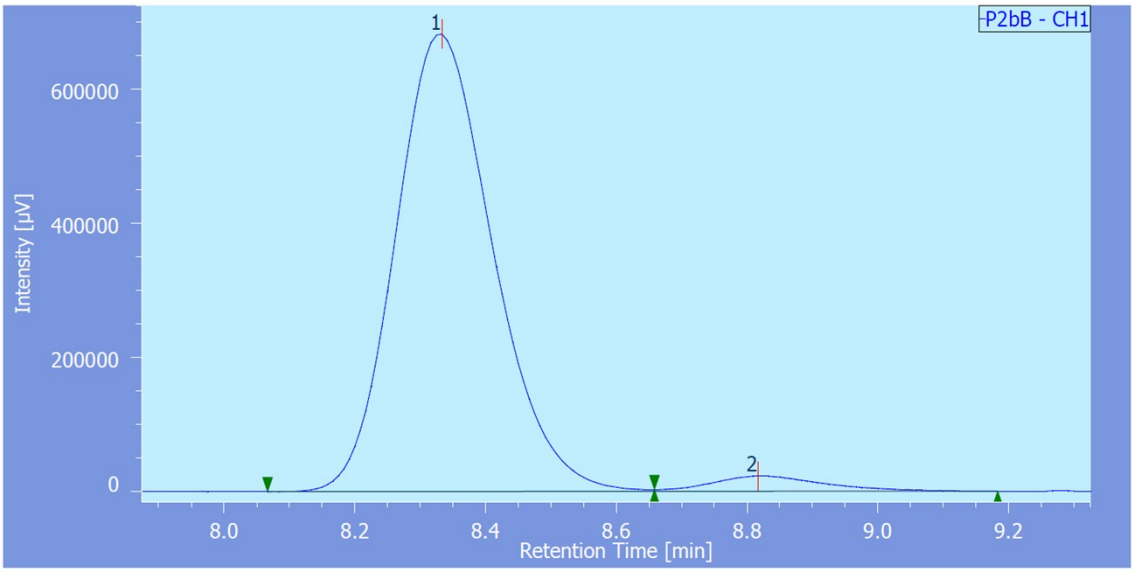

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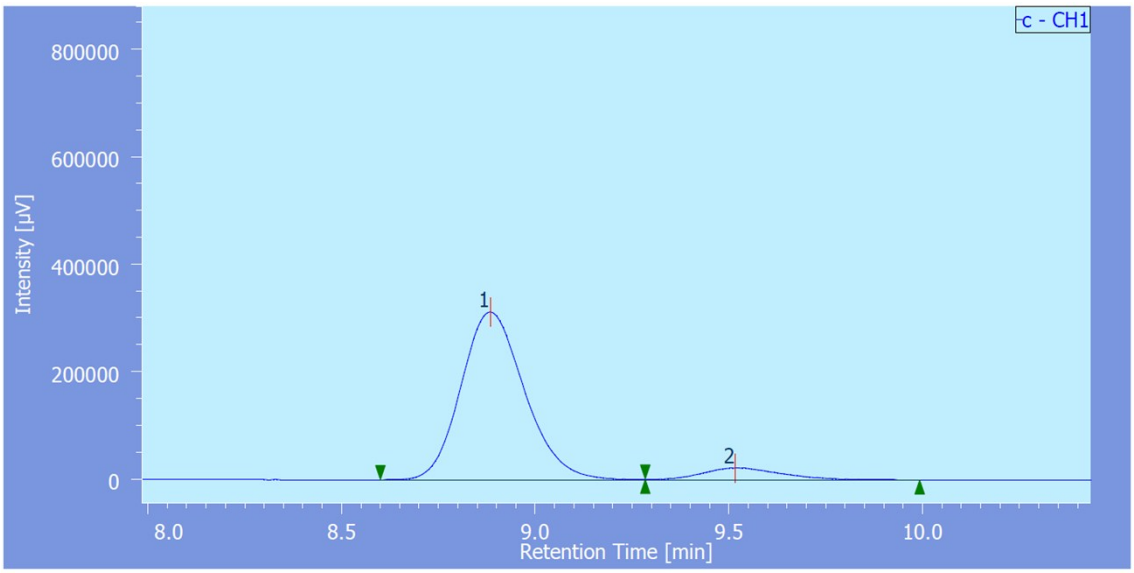

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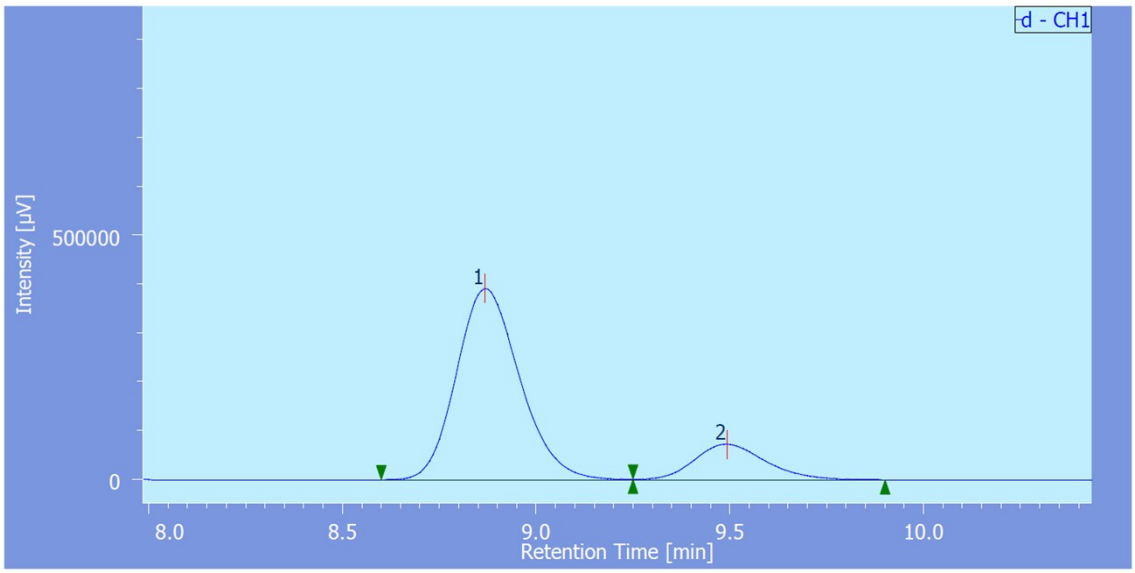

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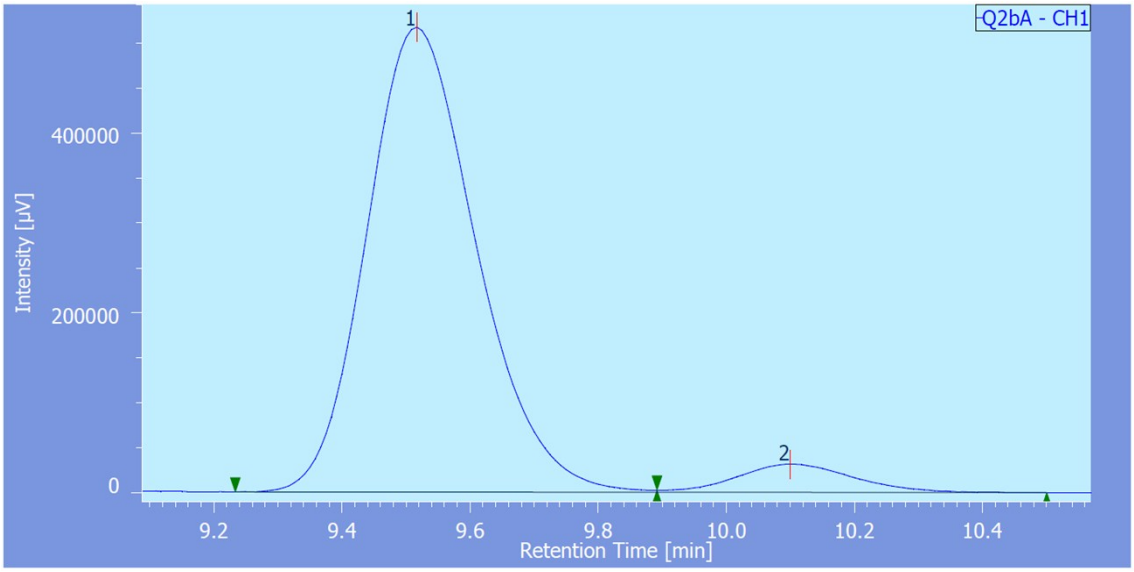

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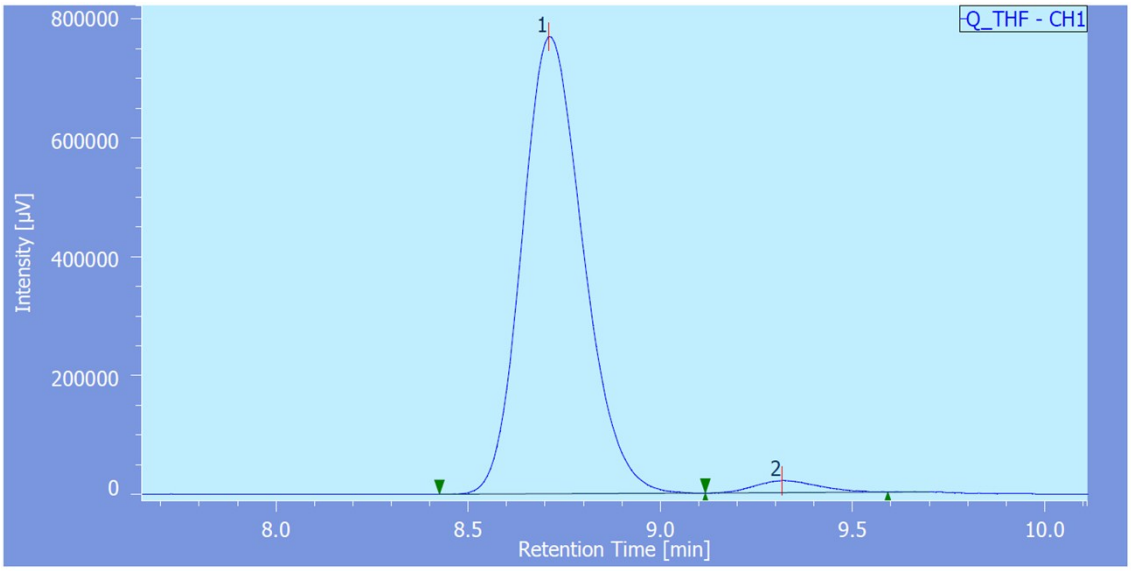

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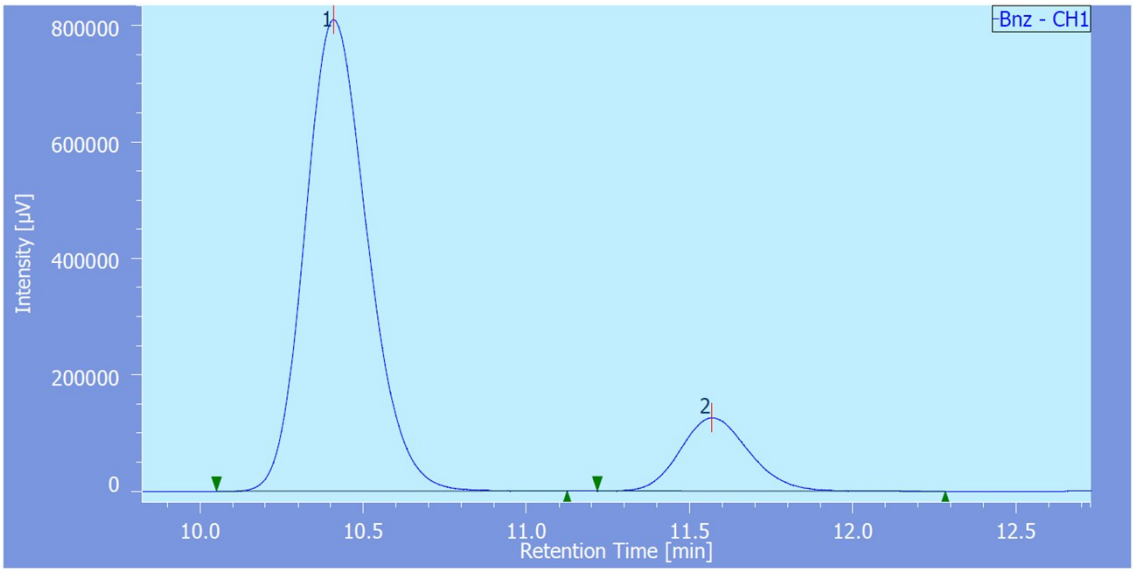
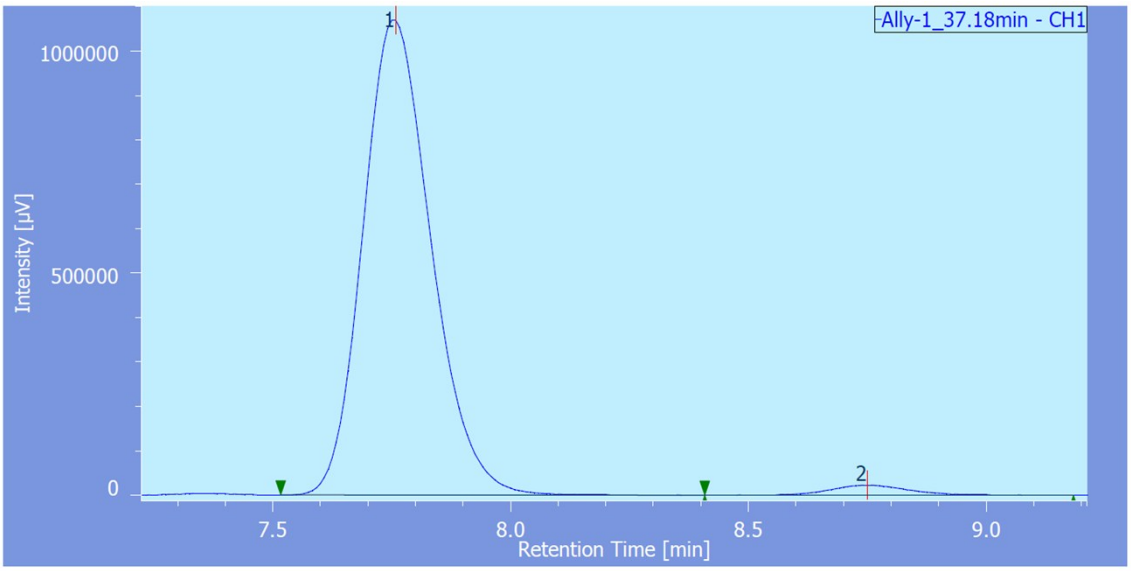


Table 4, entry 4

95% ee