Poly(quinoxaline-2,3-diyl) as a Traceless Nonbonding-Interaction-Based Chiral Shift Reagent

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Chiral shift reagents in NMR analysis have attracted wide attention as a method for the facile determination of an enantiomeric ratio of chiral organic compounds.[1] The method has potential advantages of availability of a wide array of chiral shift reagents suitable for various different chiral analytes. However, the analysis is mostly limited to the analytes that have specific bonding interaction such as coordination, hydrogen bonding, and acid-base interaction. Moreover, because of the need for high loading of chiral shift reagents, overlapping of their signals with those of analytes has been general problem in the quantification of enantiomeric ratios. We show here the use of helically chiral poly(quinoxaline-2,3-diyl) (PQX) bearing chiral ether side chains as a "traceless" NMR chiral shift reagent for various racemic compounds including styrene oxide (**SO**) (Figure 1a). The differentiation of the signals of two enantiomers was based on nonbonding interaction containing dispersion and electrostatic forces between the analytes and PQX, leading to differentiable up-field shifts of the ^{1}H NMR signals without broadening (Figure 1b and c). Selective suppression of polymer NMR signals using the T_2 filter (CPMG-PROJECT[2] pulse sequence) enabled the PQX to serve as a traceless chiral shift reagent, with which only ^{1}H-NMR signals of the analytes were observable (Figure 1d). This nonbonding interaction based enantiodifferentiation method could be applied to various chiral compounds such as haloalkanes, ethers, and carbonyl compounds.

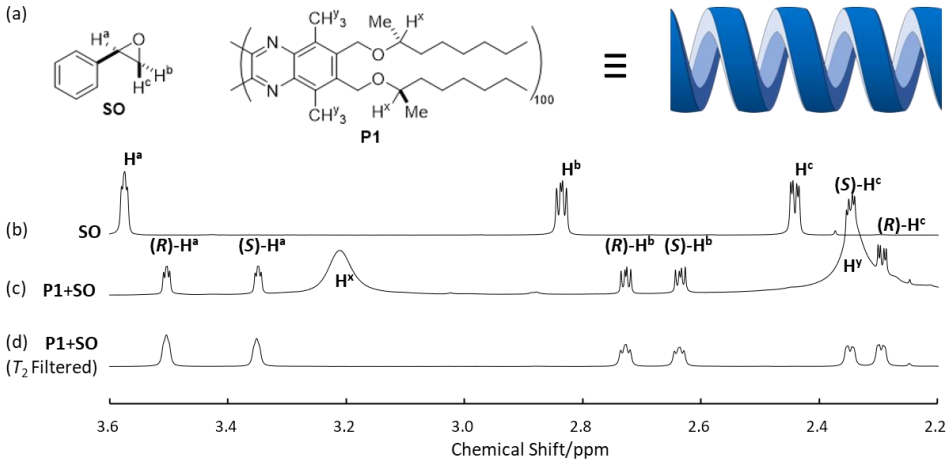

Figure 1. (a) Structure of helically chiral (*R*)-**P1** and (*R*)-styrene oxide (**SO**) (b) ^{1}H-NMR of *rac*-**SO** in cyclohexane-d_{12}. (c) ^{1}H-NMR spectrum of *rac*-**SO** and **P1** in cyclohexane-d_{12}. (d) T_2-filtered spectrum of (c).

1) T. Wenzel *Differentiation of Chiral Compounds Using NMR Spectroscopy*. Wiley, **2018**.
2) A. Aguilar, M. Nilsson, G. Bodenhausen, G. Morris *Chem. Commun.* **2011**, *48*, 811.