The use of a lanthanide complex [Eu(DPM)₃] in obtaining first-order, or more readily analyisable, proton n.m.r. spectra for lone-pair bearing organic compounds with complex spectra is described. Implications for structural studies are discussed. (The SC# indicates that this paper has been cited over 280 times since 1970.)

December 18, 1981

"I moved to Cambridge in October 1969, aged 21, to begin research. My supervisor, Dudley Williams, was excited about a paper which had just been published by Conrad Hinckley. Hinckley had shown that the pyridine adduct of the lanthanide complex Eu(DPM)₃, by complexing with cholesterol, was capable of drastically changing the n.m.r. spectrum of the steroid so as to reveal a tremendous amount of structural information. He called the complex a shift reagent. Hinckley was clearly an inorganic chemist, and apparently not in a position to fully exploit his discovery. Williams, however, as an accomplished steroid chemist and organic spectroscopist, knew the kind of problem which needed this solution and put me to work on the topic.

"Williams felt that the pyridine in Hinckley's complex was getting in the way by competing for the lanthanide. However, as a novice I was uncomfortable with such complex molecules as steroids so I decided to explore the shift reagent's potential by using simple compounds with intratable spectra. N-hexanol was the first; essentially only two protons are normally resolved, but late on the night of January 20, 1970, I added small amounts of Eu(DPM)₃, one signal after another separated until every detail of every proton was resolved. The satisfaction and excitement were extraordinarily intense—but everyone I knew was at home, asleep. Within five weeks we had looked at a range of compound types and submitted this first paper.

"We sent another paper to the same journal soon after, but it was rejected. A referee felt that 'the first...had crystallised all the novelty.' That rejected paper, slightly filled out, was published elsewhere and became the most-cited 1971 paper in both 1971 and 1972. Why was our work highly cited? Our first paper (and Hinckley's) set off an explosion of shift reagent work. Anybody could magically persuade impossibly difficult spectra to reveal a wealth of new information for a trivial cost in chemicals. The intellectual credit belongs to Hinckley. Our role was to demonstrate the power of the technique with a spectacular spectrum every organic chemist could appreciate. I suspect that the long-term importance of this whole area is much less than citation counts would indicate: it was popular because it was easy.

"As a result of this work I was awarded the Meldola Medal of the Royal Institute of Chemistry. The work also helped Williams toward the position of most-cited organic chemist outside the US, 1965-1978."
