Supporting Information: Photochemical Generation and Reactivity of the 5,6-Dihydrouridin-6-yl Radical.

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Contents:

General Methods. Benzoyl chloride, β-mercaptoethanol, and pivaloyl chloride were distilled prior to use. DMF was distilled from CaH_2. CH_3CN was passed through anhydrous $CuSO_4$ prior to distillation from CaH_2. All photolyses were carried out in Pyrex tubes using a Rayonet photoreactor fitted with 16 lamps having an output maximum at 350 nm. All anaerobic photolyses were carried out in sealed Pyrex tubes, which were degassed and sealed using standard freeze-pump-thaw degassing techniques (three cycles, three minutes each).

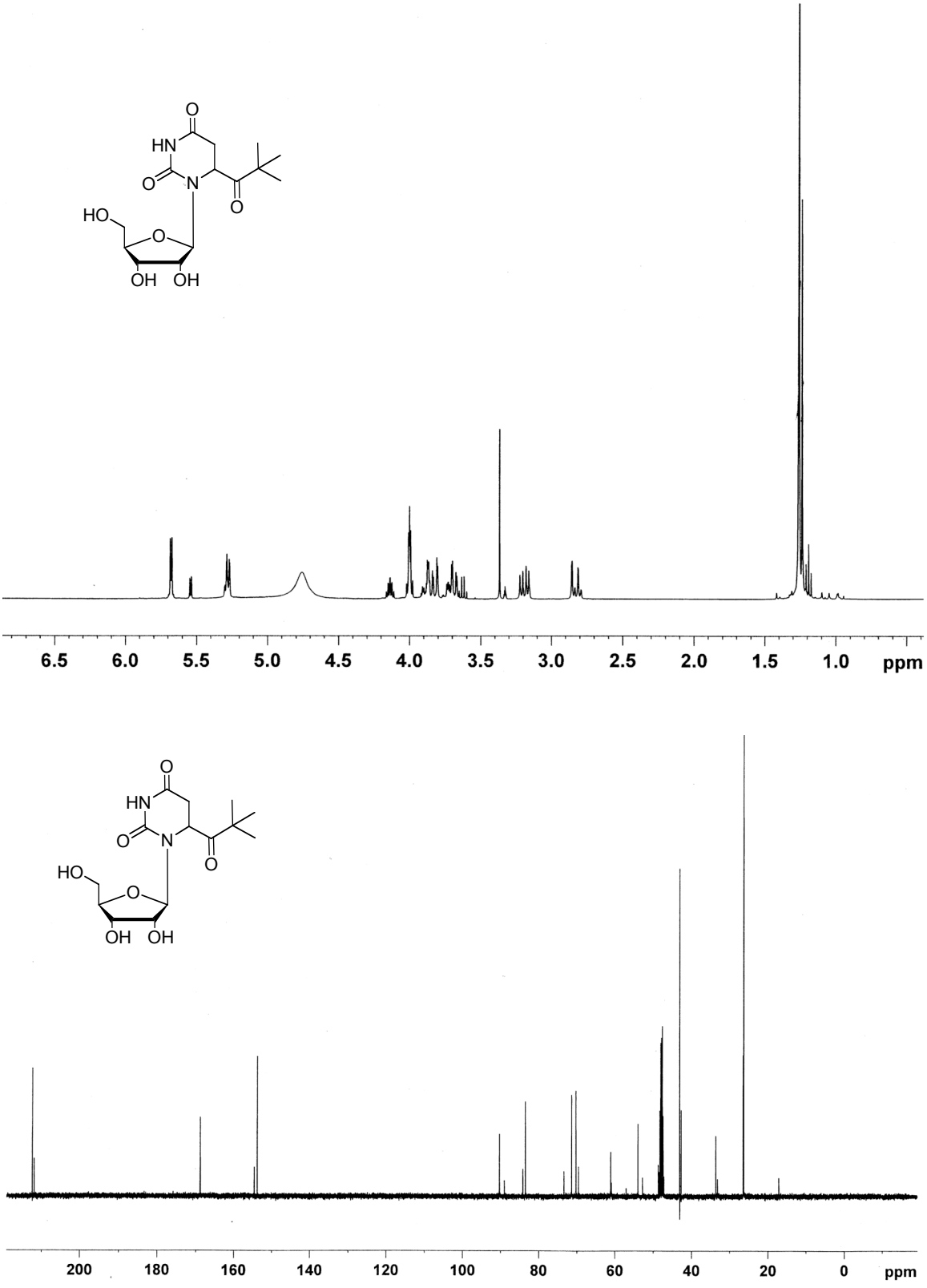
HPLC samples were analyzed with a Microsorb-MV C18 5 μm column (4.6 × 250 mm). Samples were detected at 230 nm using one of the following three gradients. Hold for 1 min. (100% water); then ramp to 20% CH_3CN linearly in 29 min; then ramp to 40% CH_3CN linearly in 5 min; hold at 40% CH_3CN. Dihydrouridine was prepared as previously described.[1]

Determination of response factors. Response factors for **2b**, **4**, **5** and **6** were calculated versus 2'-deoxyuridine (dU) as an internal standard. Response factors were calculated using the following formula: $([X]/[S])=R_f(A(X)/A(S)$, where [X] is the concentration of the compound of interest and [S] is the concentration of the internal standard. A(X) and A(S) are the areas under the peaks corresponding to the compound of interest and the internal standard, respectively (Table 1).

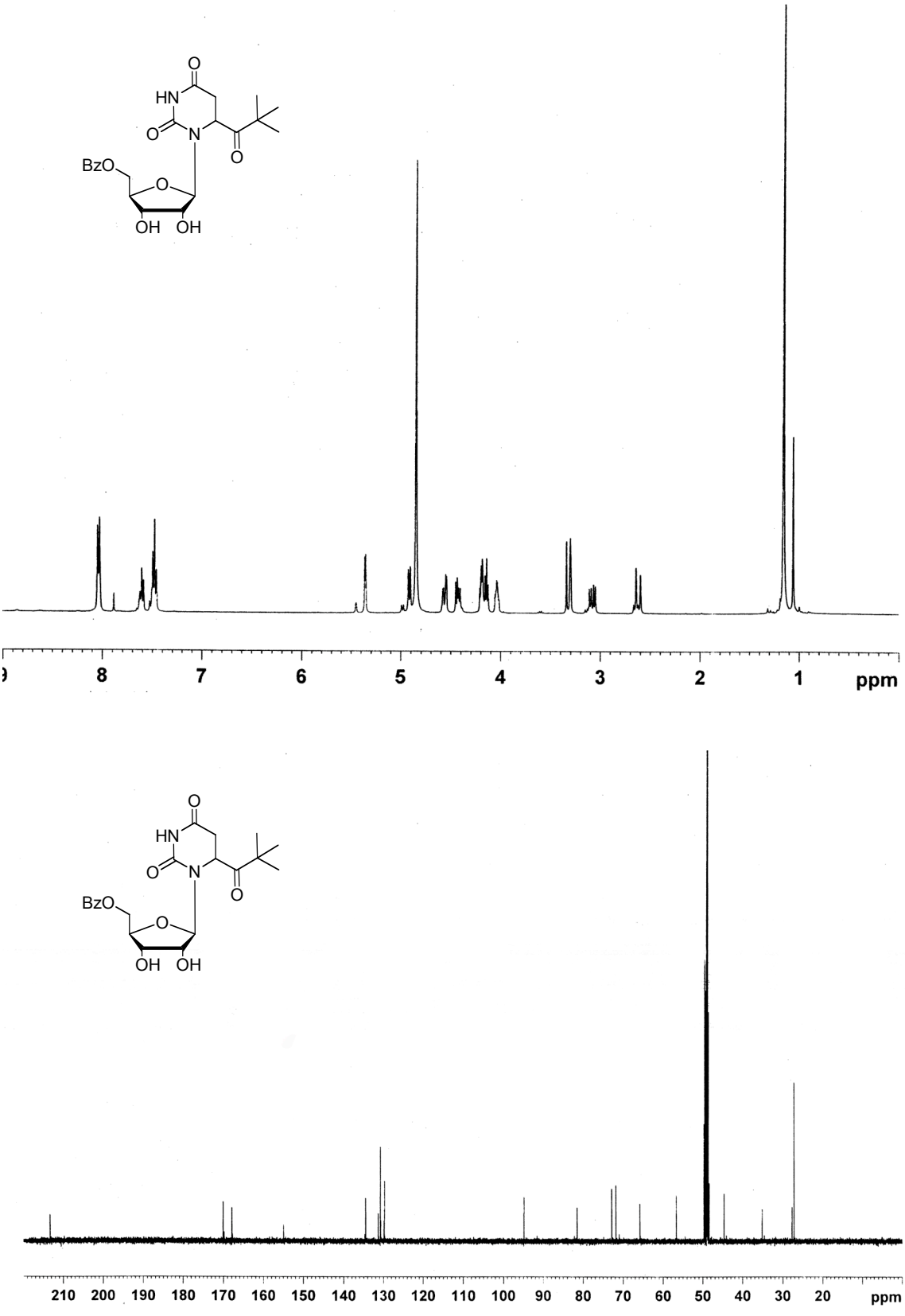
Supporting Information Table 1. Response Factors and retention times using dU as internal standard.

Compound	Retention time (min)	Response Factor
2b	42	4.36
4	38	3.80
5	37	5.67
6	35 and 36	4.03
7	39	0.20

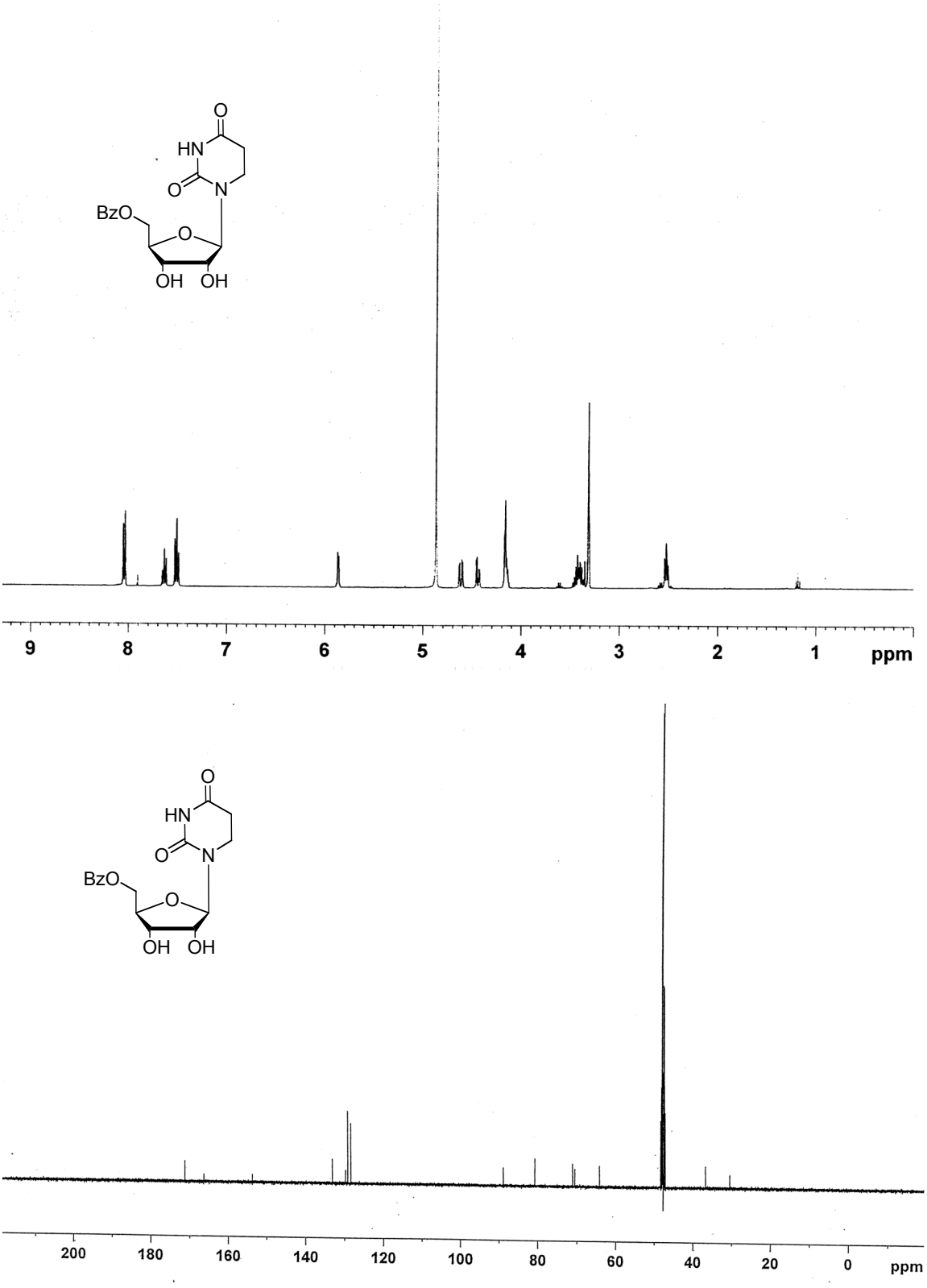
(1) Johnson, D. C. I.; Widlanski, T. S. *Org. Lett.* **2004**, *6*, 4643-4646.



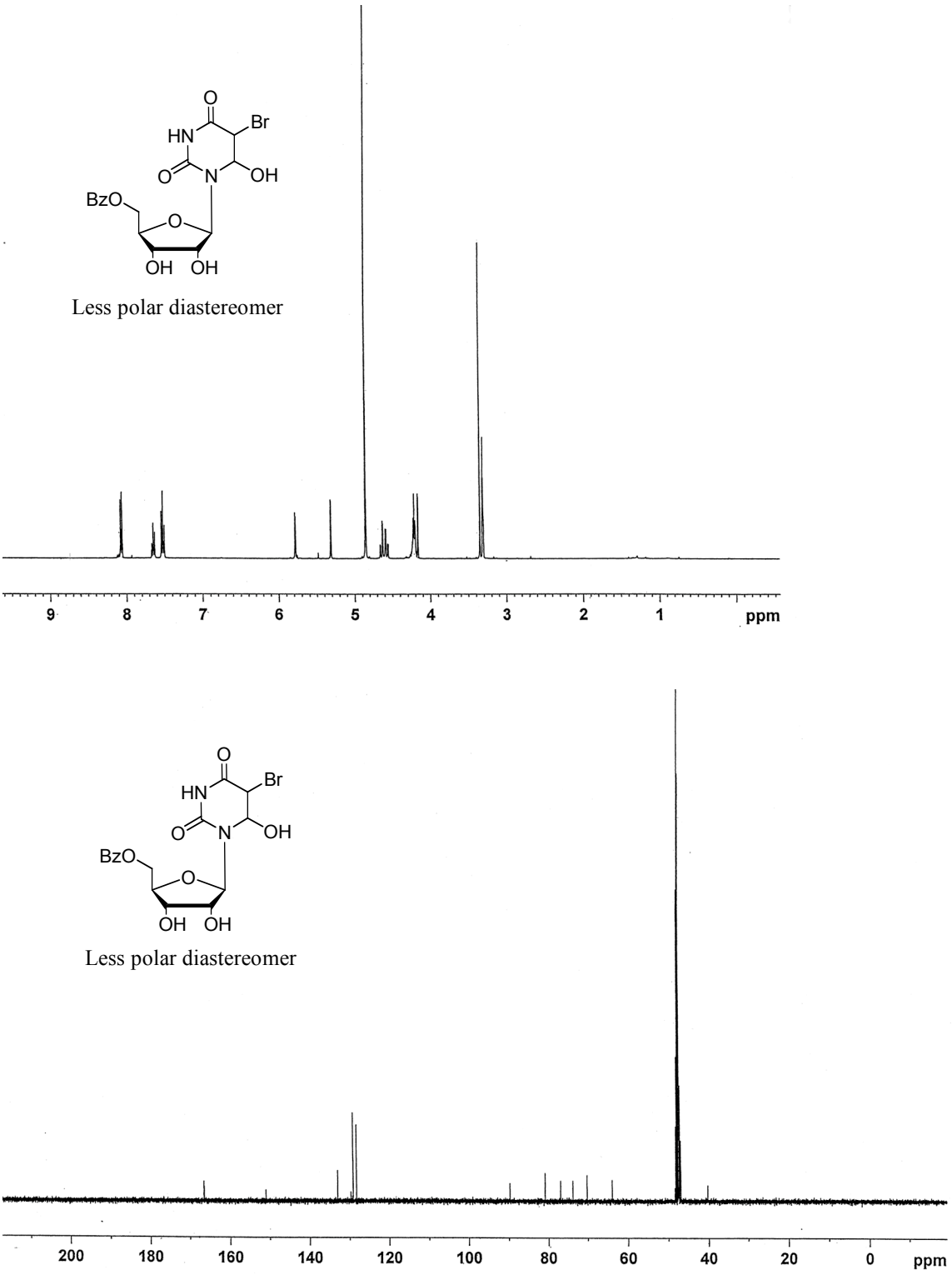
Supporting Information Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2a**.



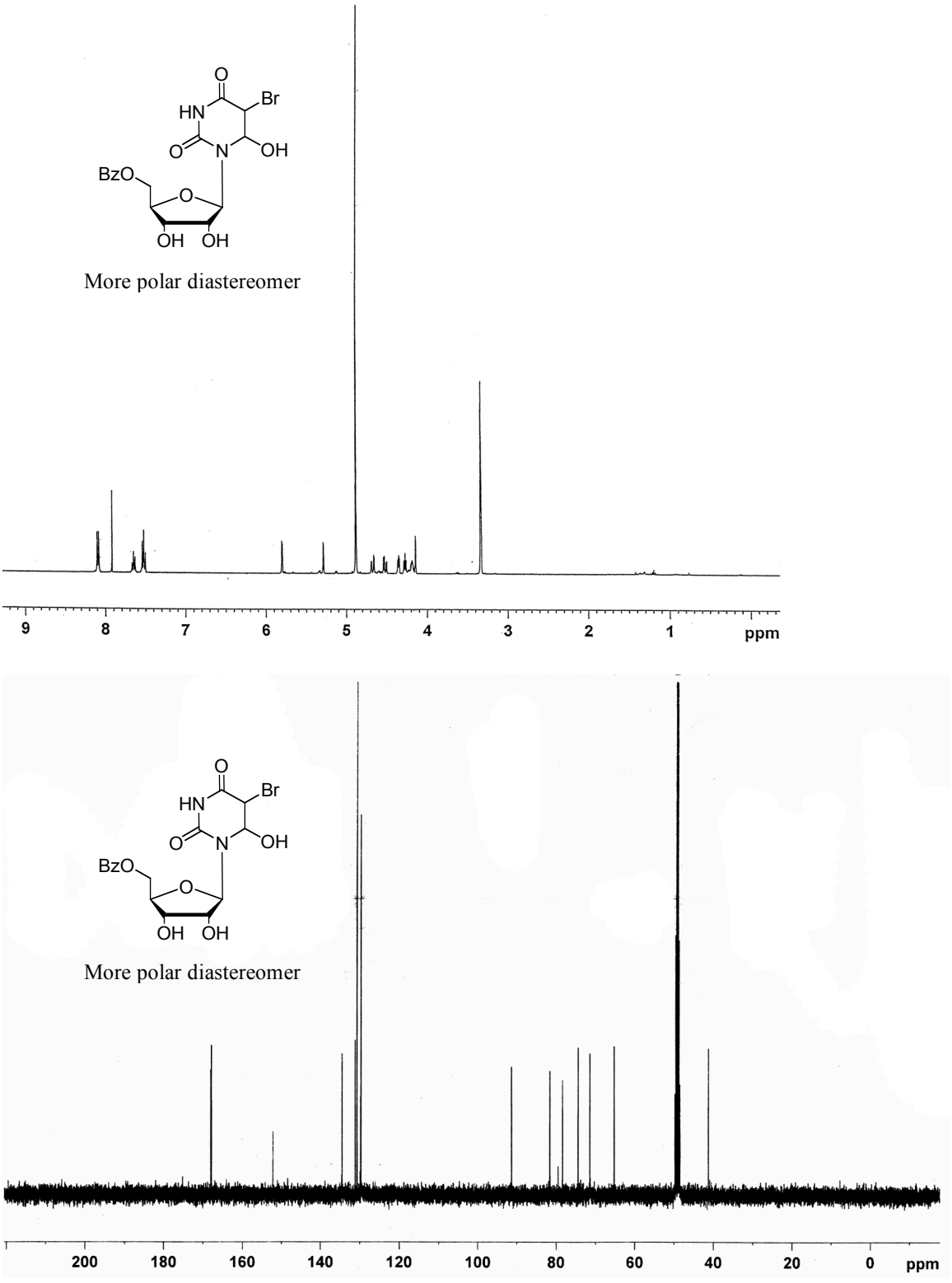
Supporting Information Figure 2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2b**.



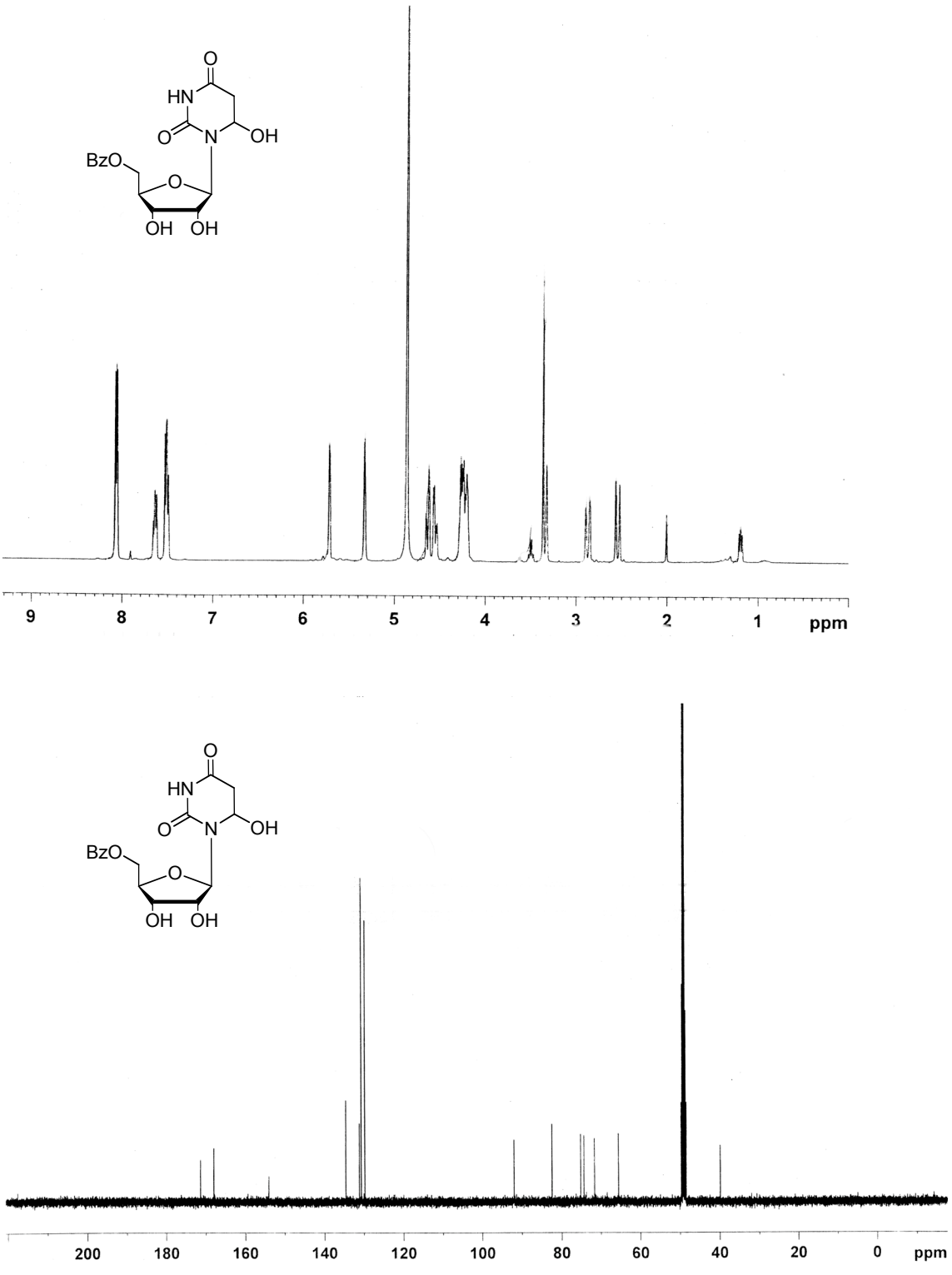
Supporting Information Figure 3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4**.



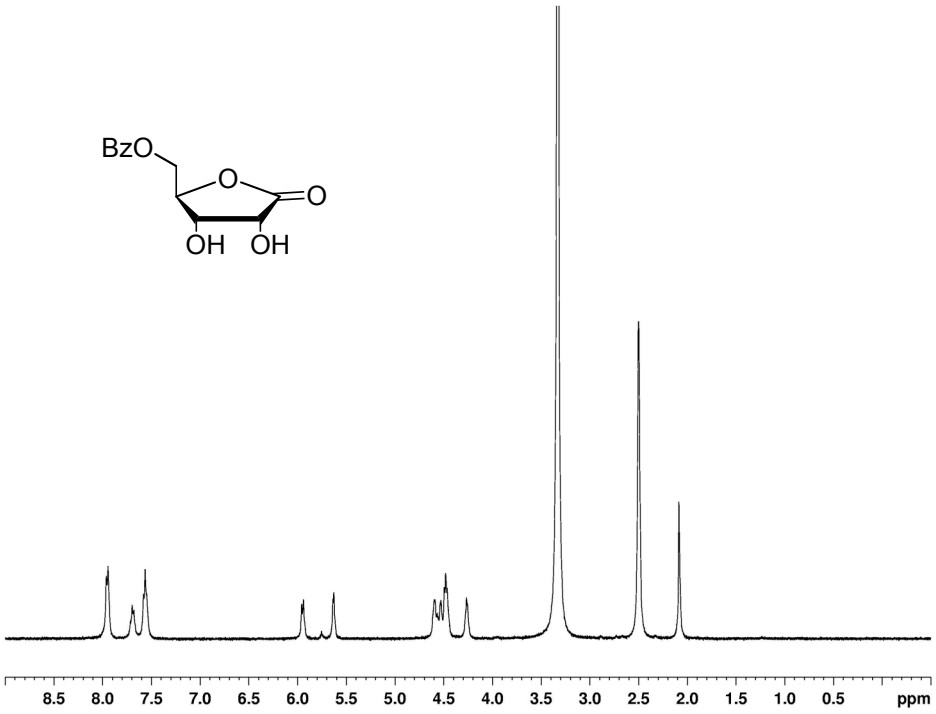
Supporting Information Figure 4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of less polar bromohydrin.



Supporting Information Figure 5. ^{1}H (top) and ^{13}C (bottom) NMR spectra of more polar bromohydrin.



Supporting Information Figure 6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **6**.



Supporting Information Figure 7. ^{1}H NMR spectra of **7 (**d_6-DMSO).