

Supporting Information of

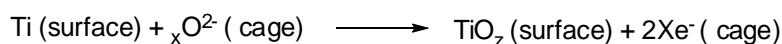
Room-Temperature-Stable Electride as a
Synthetic Organic Reagent: Application to
Pinacol Coupling Reaction in Aqueous Media

*Haritha Buchammagari, Yoshitake Toda, Masahiro Hirano, Hideo Hosono, Daisuke
Takeuchi, and Kohtaro Osakada*

Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama, 226-8503, Japan

General procedure for Preparation of Single Crystal C12A7 electrider

C12A7 single-crystals grown by a CZ (Czochralski) method were subjected to Ti-treatment to dope electrons. The grown single-crystal ingots were sliced into 25 mm ϕ x 1 mm plates or $\sim 10 \times 3 \times 3$ mm³ blocks. These single-crystals were sealed in silica gel glass tube with metal Titanium powders (~ 5 g) under vacuum of $\sim 10^{-3}$ torr. Then the sealed tube was thermally annealed at temperature 1,100°C for 12-13 h. Titanium treatment replaces all or a part of the free oxygen ions with electrons as shown in the following equation, resulted in the formation of $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{68}]^{4+}4\text{e}^-$ electrider.



After the reaction was completed, the surface of the crystal was mechanically polished to remove TiO_x layers. The sample color was changed from transparent orange tint to dark green. The polished crystal ingots were crushed in to fine powder and then used for organic reactions.

General procedure for Preparation Polycrystalline C12A7 electrider

Insulating C12A7 powders, which were synthesized by a conventional solid-state reaction from a stoichiometric mixture of high purity CaCO₃ and γ - Al₂O₃ at 1300°C for 12h in air were melted in a carbon crucible with a carbon cap at 1600°C in air for 1 h and then slowly cooled. The solidified C12A7 melt was the mixed phase of 3CaO.Al₂O₃ + CaO.Al₂O₃ (C3A+CA). The remelt-solidification of the resultant

mixture in the same atmosphere resulted in a dark green C12A7 polycrystalline electride. After completion of the reaction, the surface of the polycrystalline electride was polished manually to remove the carbon impurities then crushed in to fine powder and used in organic reactions.

General procedure for electride mediated pinacol coupling reaction of benzaldehyde derivatives:

To a black suspension of single crystal electride (192 mg, 0.138 mmol, 0.277 mmol of electron) in water (5.0 mL) under nitrogen atmosphere, benzaldehyde (10 mg, 0.094 mmol) was added. The reaction mixture was stirred at room temperature until the reaction mixture becomes milky white gel. After completion of the reaction the gel was quenched with aqueous HCl (1 N, 10 mL) and extracted with diethyl ether (15 mL x 3), organic phase was washed with saturated aqueous NaHCO₃ solution (10 mL) and brine (10 mL), dried over MgSO₄, and filtered. The filtrate was concentrated in vacuo to give a crude 1,2-diphenyl-1,2-ethandiol. 4-Methoxybiphenyl (4.0 mg, 0.022 mmol) was added to the crude product and the conversion yield was estimated by the comparison of the signal due to Me group of the standard and the Ar-CH group of the pinacol by ¹H NMR to be 71%. The dl:meso ratio was determined by the relative intensities of the signals of Ar-CH groups to be 55:45.

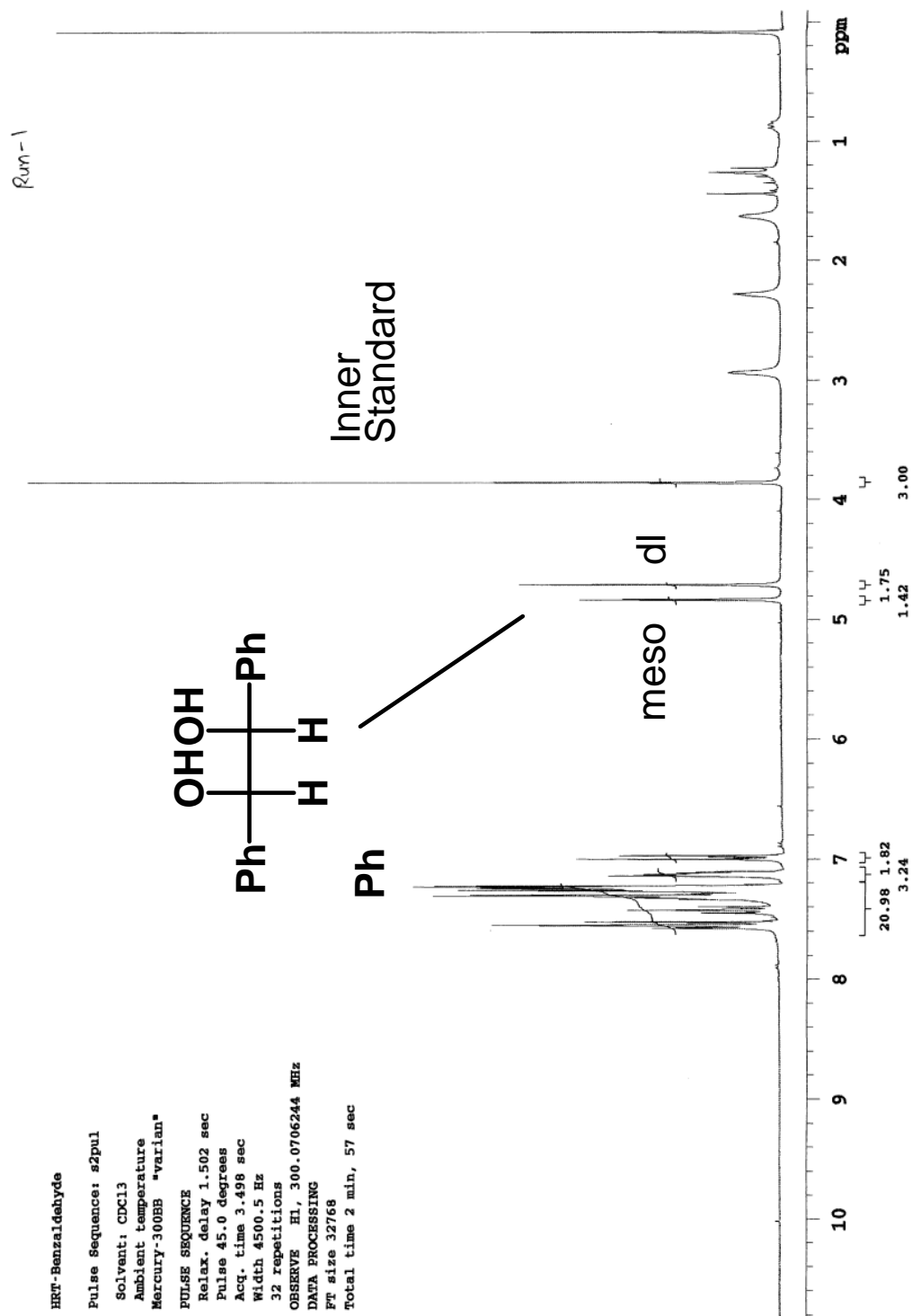


Fig. S1. ¹H NMR spectrum of crude product (Table 1, run 1)

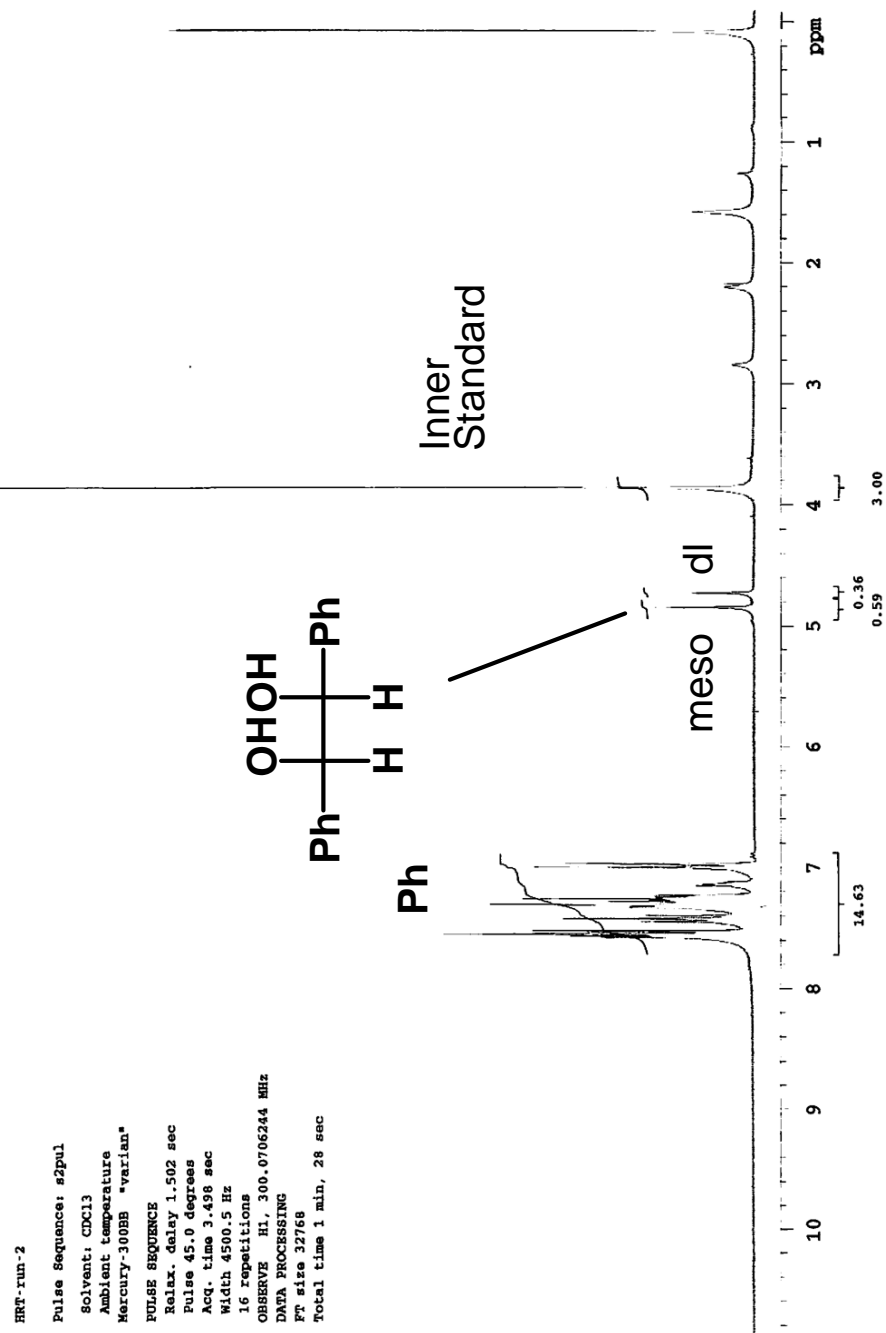


Fig. S2. ¹H NMR spectrum of crude product (Table 1, run 2)

Run 3

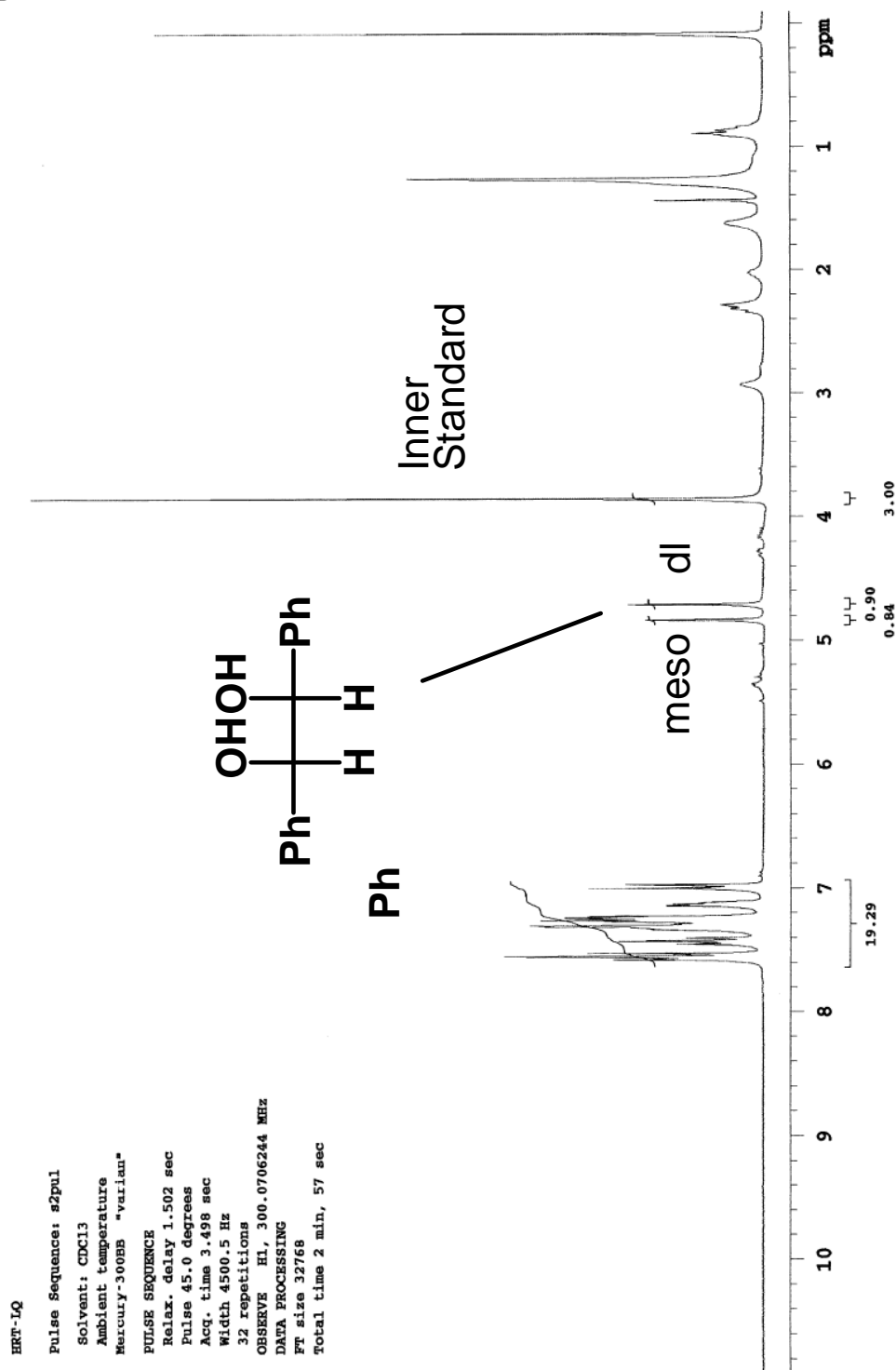


Fig. S3. ¹H NMR spectrum of crude product (Table 1, run 3)

Run 5

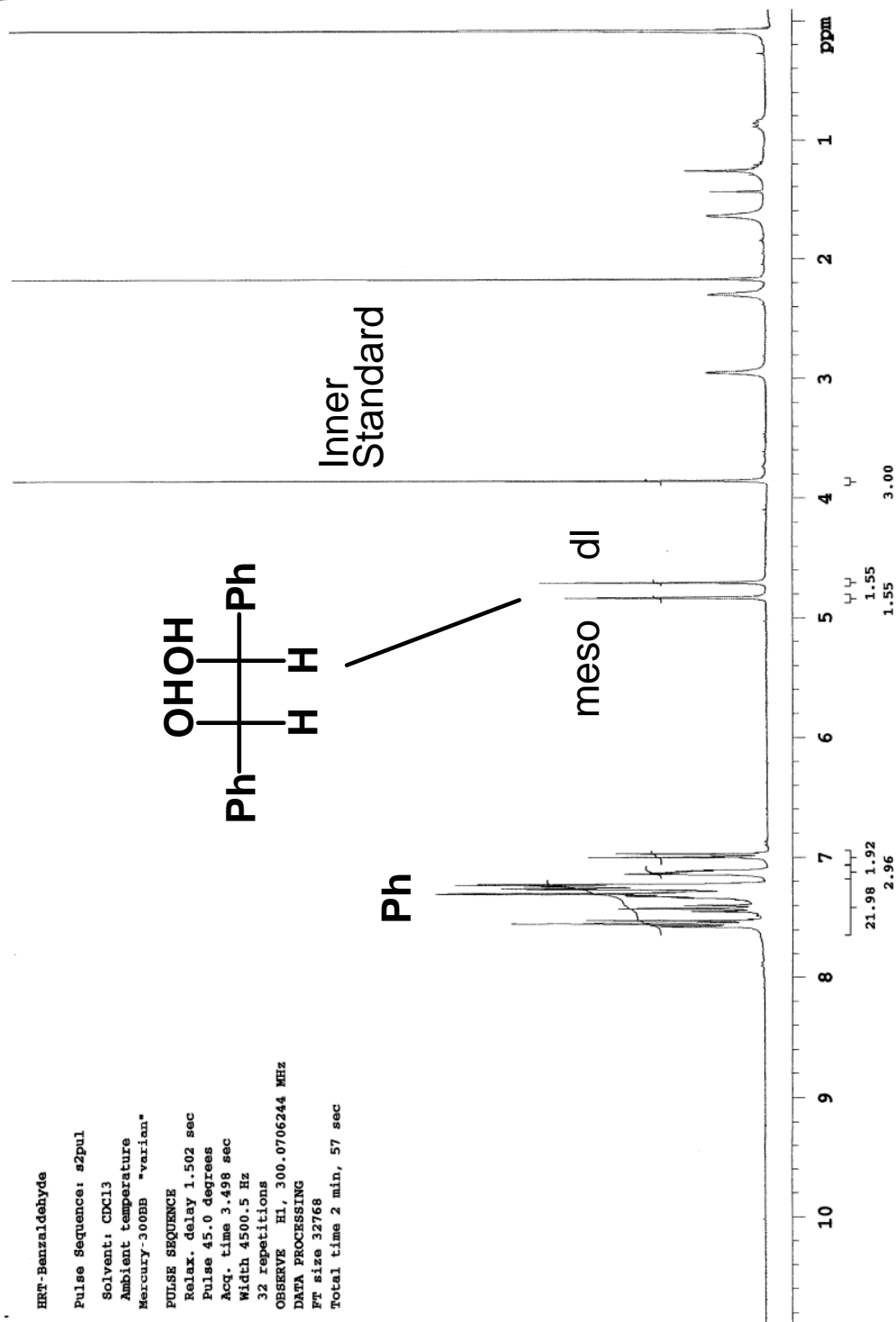


Fig. S4. ¹H NMR spectrum of crude product (Table 1, run 5)

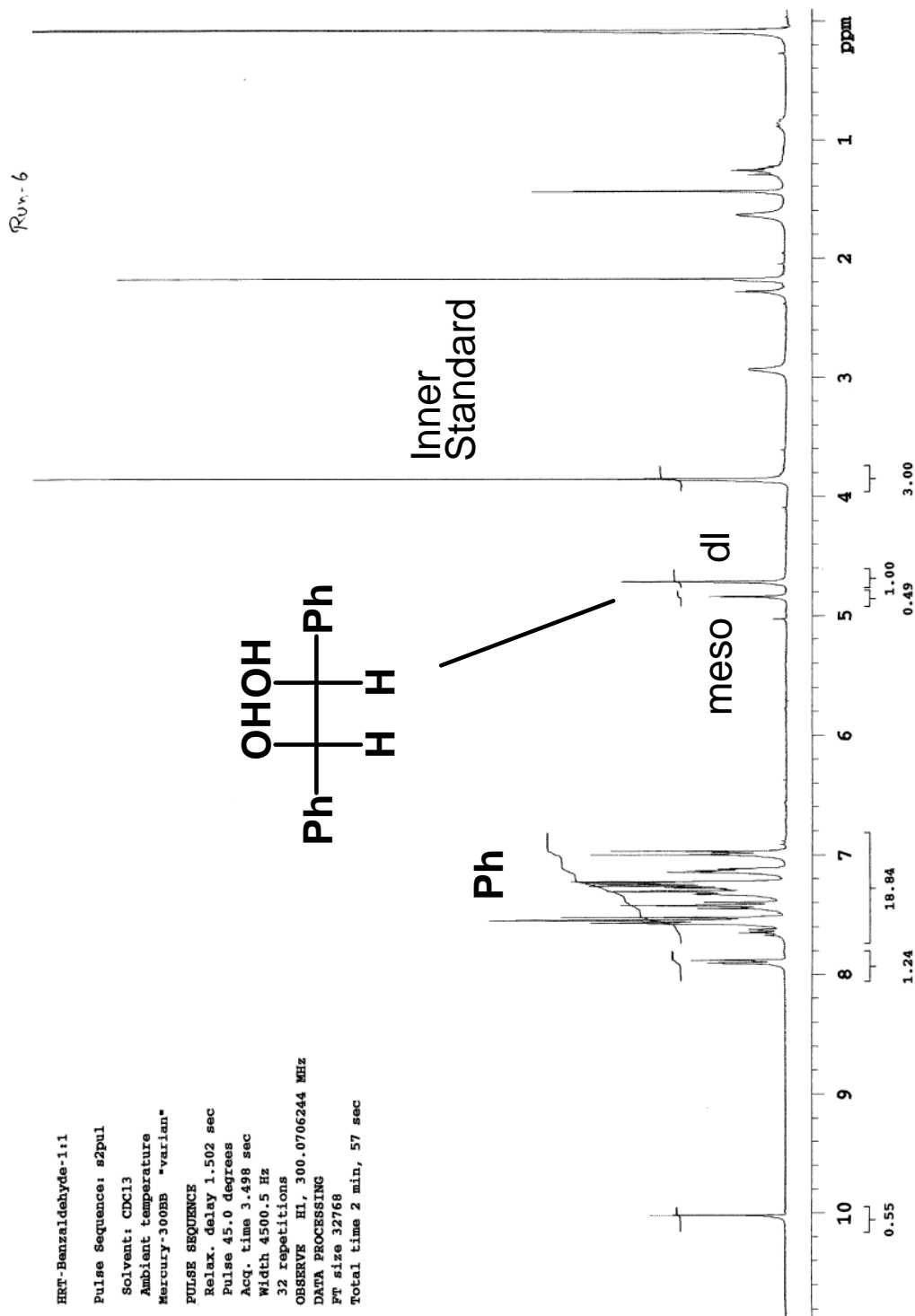


Fig. S5. ^1H NMR spectrum of crude product (Table 1, run 6)

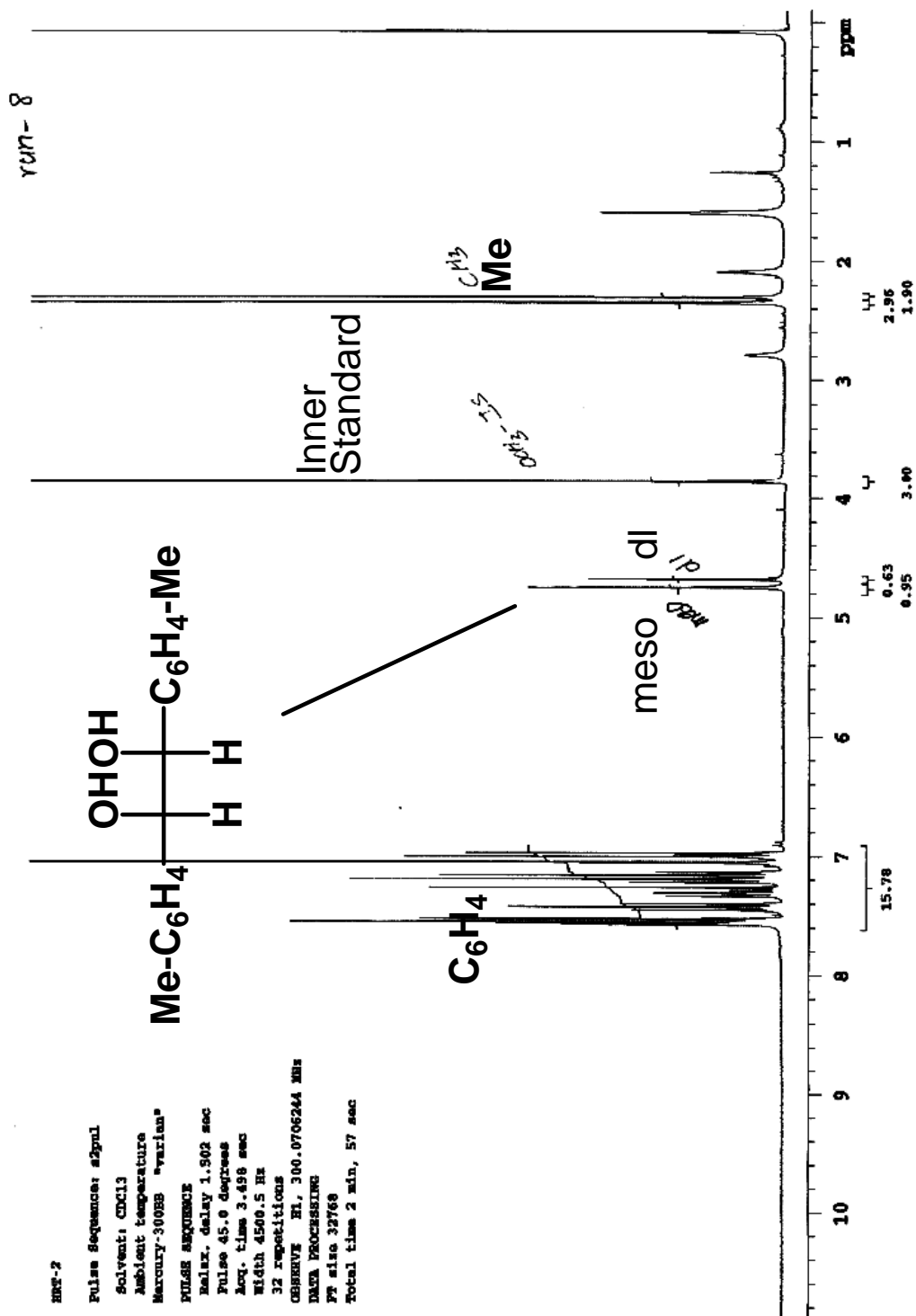


Fig. S6. ¹H NMR spectrum of crude product (Table 1, run 8)

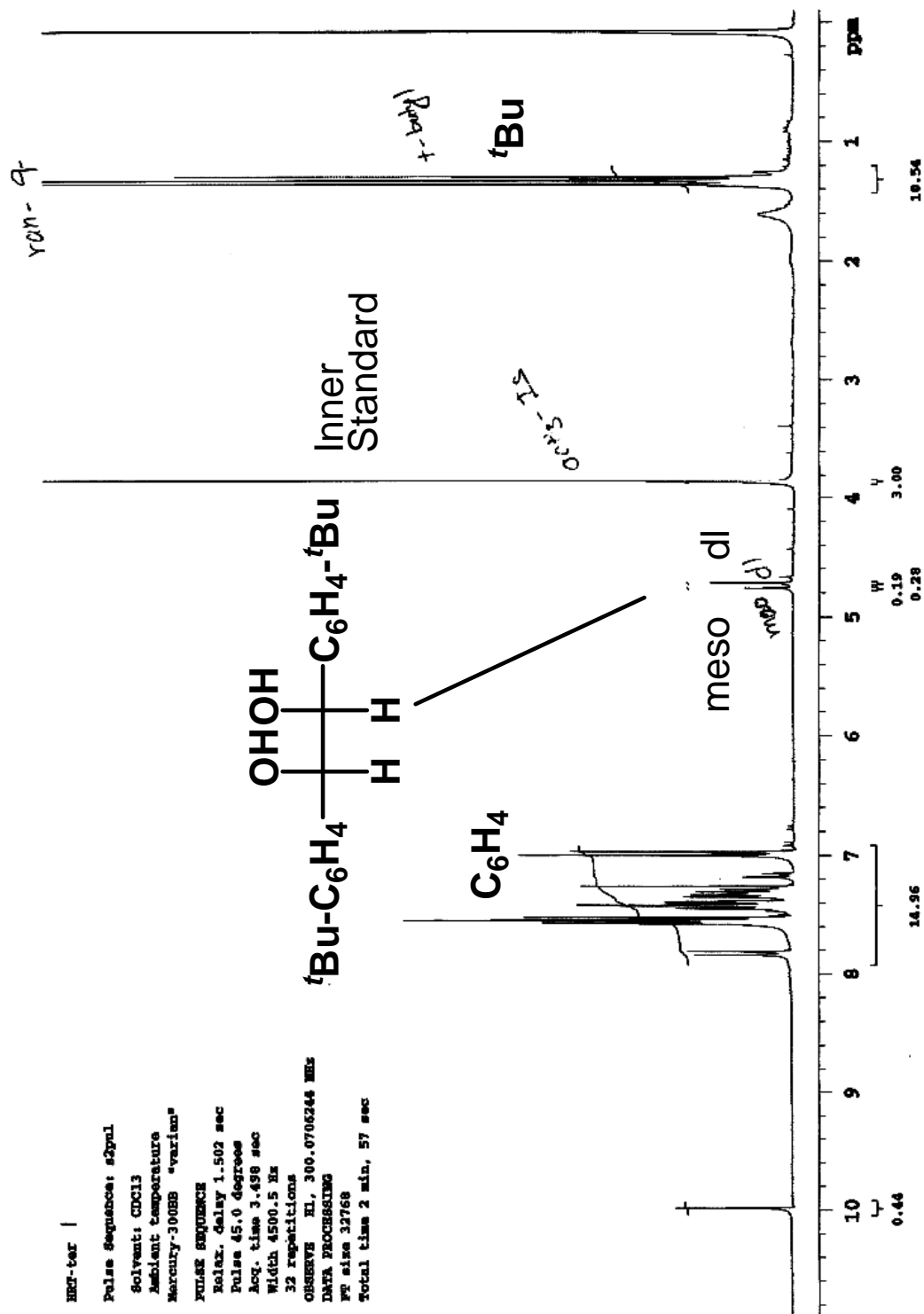


Fig. S7. ¹H NMR spectrum of crude product (Table 1, run 9)

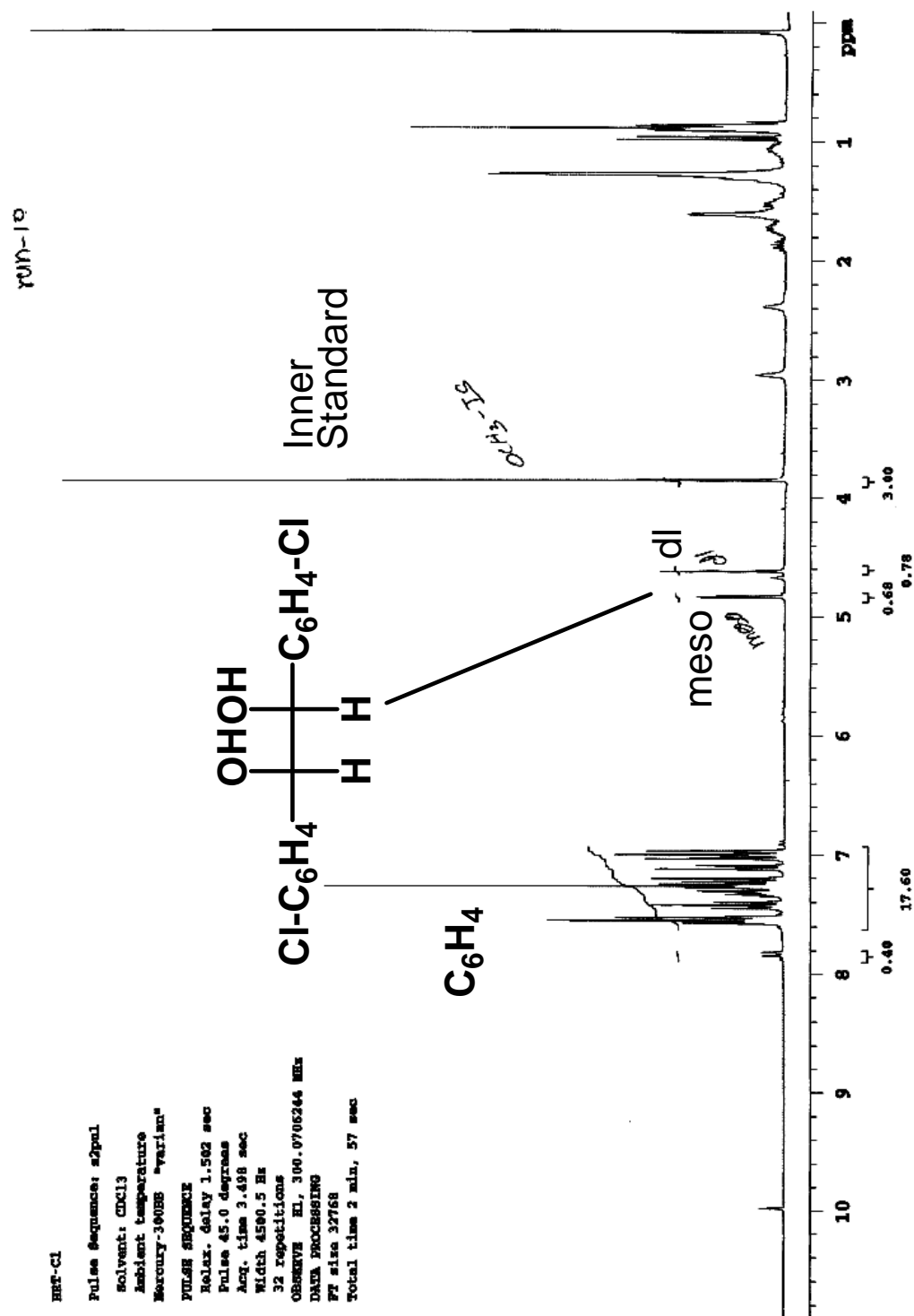


Fig. S8. ¹H NMR spectrum of crude product (Table 1, run 10)

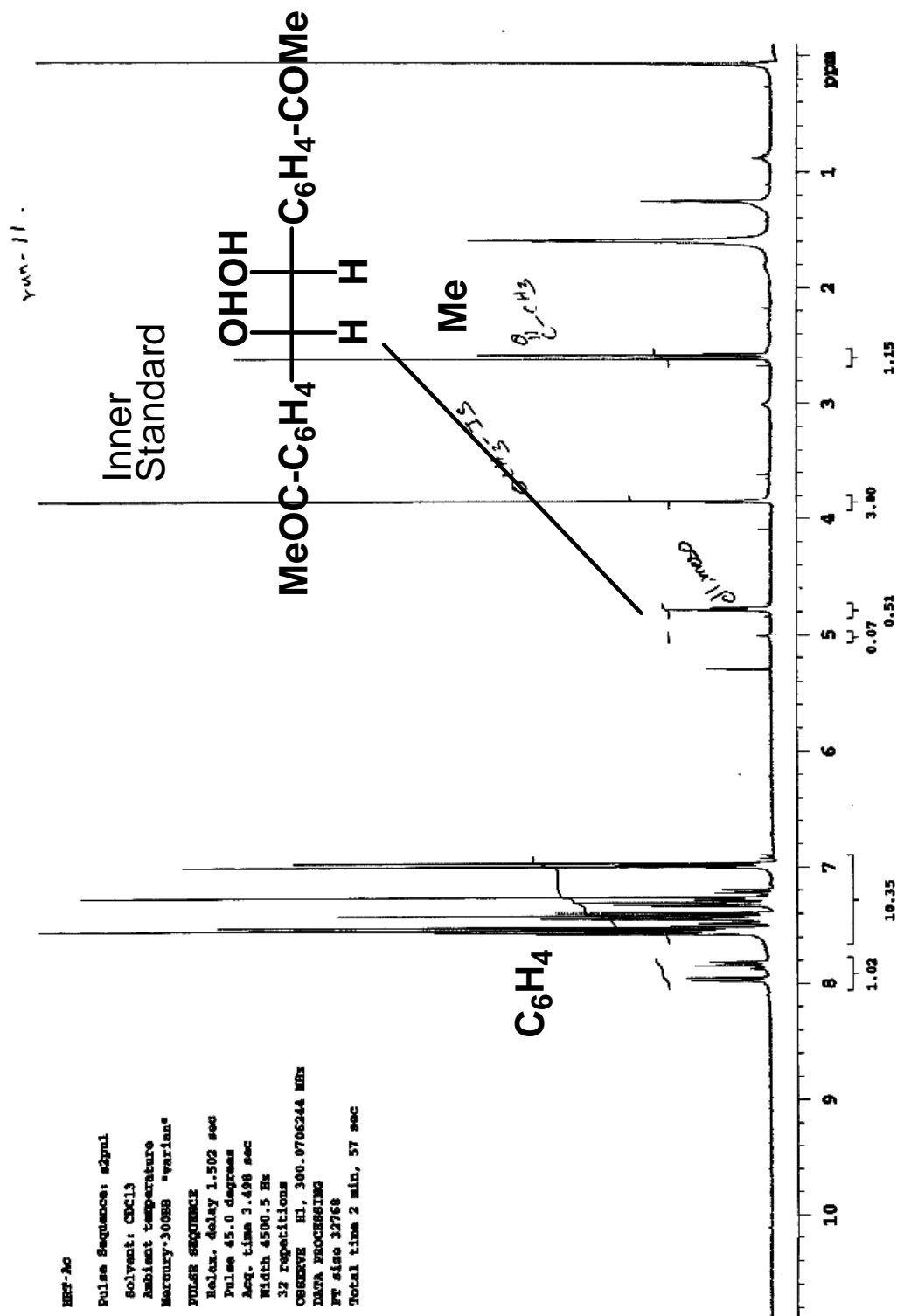


Fig. S9. ¹H NMR spectrum of crude product (Table 1, run 11)