

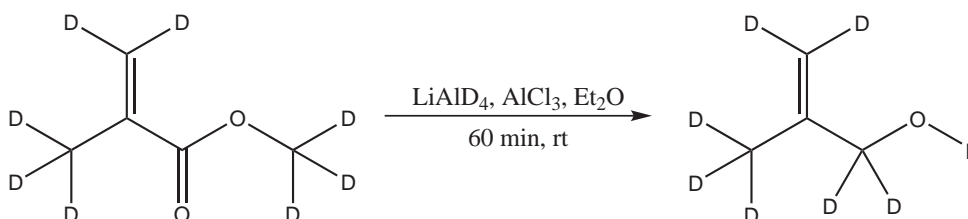
Vibronic structure of the 3s Rydberg state of the 2-methylallyl radical

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1. Precursor synthesis

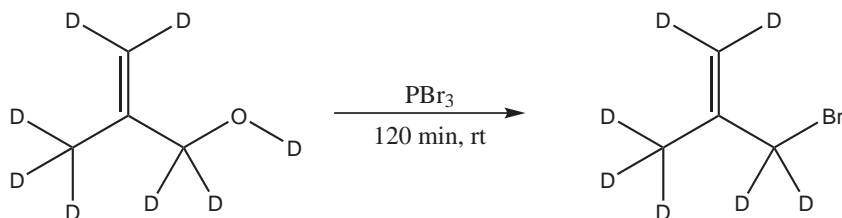
1.1. 2-(²H₃)Methyl(²H₄)prop-2-en-1-(²H)ol



To a stirred, ice-cooled solution of lithium aluminium deuteride (1.9 g, 45 mmol) in ether (200 ml) was added in small portions aluminium chloride (2 g, 15 mmol). After the hydride mixture was stirred at room temperature for 30 minutes and cooled down to 0 °C, (²H₃)Methyl (²H₅)methacrylate (5 g, 50 mmol) in ether (35 ml) were added dropwise and the mixture was stirred for 60 minutes at room temperature before it was quenched with water. To the quenched solution was added a HCl solution (2 M) until the salt was dissolved and then washed with ether. The combined organic phases were washed with brine and dried over MgSO₄ to give the title alcohol (3.49 g, 43.5 mmol, 87 %).

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1.2. 3-Bromo-2-(²H₃)methyl(²H₄)prop-1-ene



2-(²H₃)Methyl(²H₄)prop-2-en-1-(²H)ol (3.27 g, 40.8 mmol) was added to phosphorous tribromide (5 g, 18 mmol) at 0 °C. The mixture was stirred for 120 minutes at room temperature. To the crude mixture was added ether and this solution was washed with ice water and dried over MgSO₄. The solvent was removed under reduced pressure to give the title bromide (3.38 g, 23.8 mmol, 58 %).