Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Reply to the 'Comment on "Zemplén transesterification: a name reaction that has misled us for 90 years"' by G. Poli, C. Pezzetta, I. Leito and S. Tshepelevitsh, Green Chemistry, 2018, 20, DOI: 10.1039/c7gc03795c

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General Methods: All commercially available starting materials and solvents were of reagent grade and used without further purification. 1H NMR spectra were recorded at 298K in CD3OD by a 600 M NMR instrument (JNM-ECZ600R/S3) using the residual signals from CD3OD (1H: δ = 3.31 ppm) as internal standard.

General Method for Measuring the Rate Constant (k): As step b) in Figure **S1** is the rate-determining step, the rate constants (k) can be measured using the following equation: $\ln (B_0/B) = k*A*t$, where A stands for the concentration of base catalysts, B stands for the concentration of esters, k stands for the rate constant, and t is the reaction time. The values of B_0/B can be measured over time using ^{1}H NMR tests. In Figure **S1**, A stands for the concentration of the H-bonding complex and X stands for MeO or OH group. As methanol acts as solvent in the reaction, A equals to the concentration of hydroxyl anion or methoxyl anion and is a constant. Therefore, we can get the differential equation (1) which is related to the rate constant k and the concentration of the esters (B). To solve the differential equation (1) gets equation (2). B_0 stands for the initial concentration of the esters in equation (2). Therefore, the value of k can be measured through recording the concentration of the esters (B) with time (t).

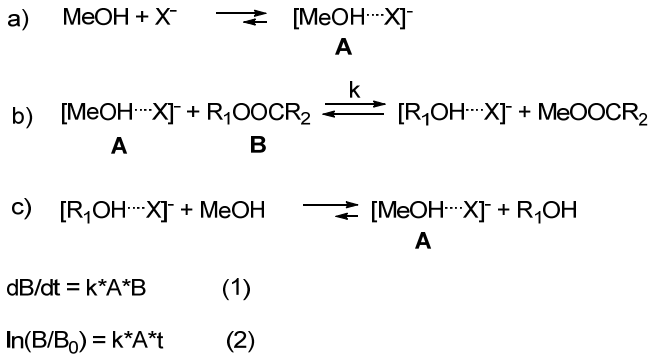

Figure **S1**. The value of k can be measured via recording the concentration of the esters (B) with time (t).

Solution A: NaOH (12 mg) was solved in *d*-methanol (1.2 mL).
Solution B: NaOH (20 mg) was solved in methanol (20 mL). The solution was kept at 70 ^{o}C for 2 h and then was evaporated to removing most of the methanol. The process was repeated for 3 times to obtain fresh MeONa. Then the concentrate (fresh MeONa) was solved in *d*-methanol (2.0 mL).
Solution C: NaOH (12 mg) was solved in D_2O (1.2 mL).
Solution D: NaOH (20 mg) was solved in methanol (20 mL). The solution was kept at 70 ^{o}C for 2 h and then was evaporated to removing most of the methanol. The process was repeated for 3 times to obtain fresh MeONa. Then the concentrate (fresh MeONa) was solved in D_2O (2.0 mL).

The General NMR Experiments for Transesterification of Ethyl Benzoate in *d*-Methanol: a) Ethyl benzoate (10 μL) was solved in *d*-methanol (0.5 mL) and then was added **solution A** (28 μL, 0.1 eq). The NMR spectrum was recorded with times. b) Ethyl benzoate (10 μL) was solved in *d*-methanol (0.5 mL) and then was added **solution B** (28 μL, 0.1 eq). The NMR spectrum was recorded with times.

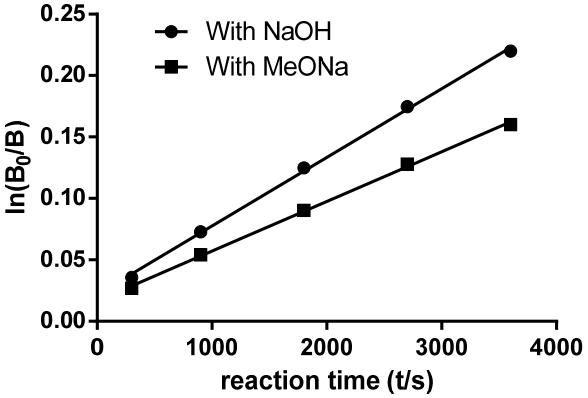

Figure **S2**. The values of k were measured for transesterification of ethyl benzoate in *d*-methanol. a) NaOH (0.1 eq) as catalyst, $k_{OH}*A$ = 5.584 x $10^{-5}\pm$0.116/s, R^2 = 0.9987; b) NaOMe (0.1 eq) as catalyst, $k_{MeO}*A$ = 4.04 x $10^{-5}\pm$0.083/s, R^2 = 0.9987, therefore, ko_H/k_{MeO} = 1.38.

The General NMR Experiments for Transesterification of n-Propyl Acetate in *d*-Methanol: a) n-Propyl acetate (10 μL) was solved in *d*-methanol (0.5 mL) and then was added **solution A** (7 μL, 0.02 eq). The NMR spectrum was recorded with times. b) n-Propyl acetate (10 μL) was solved in *d*-methanol (0.5 mL) and then was added **solution B** (7 μL, 0.02 eq). The NMR spectrum was recorded with times.

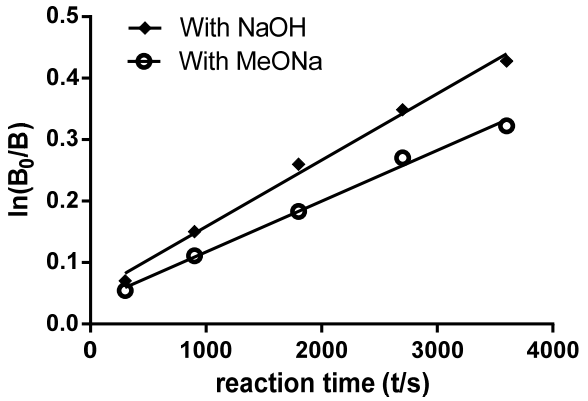

Figure **S3**. The values of k were measured for transesterification of n-Propyl acetate in *d*-methanol. a) NaOH (0.02 eq.) as catalyst, $k_{OH}*A$ = 10.83 x $10^{-5}\pm$0.52/s, R^2 = 0.9932; b) NaOMe (0.02 eq) as catalyst, $k_{MeO}*A$ = 8.261 x $10^{-5}\pm$0.36/s, R^2 = 0.9944, therefore, k_{OH}/k_{MeO} = 1.31.

The General NMR Experiments for Transesterification of Ethyl Benzoate in *d*-Methanol:D_2O (9:1): a) Ethyl benzoate (10 μL) was solved in *d*-methanol:D_2O (9:1) (0.5 mL) and then was added **solution A** (28 μL, 0.1 eq). The NMR spectrum was recorded with times. b) Ethyl benzoate (10 μL) was solved in *d*-methanol:D_2O (9:1) (0.5 mL) and then was added **solution B** (28 μL, 0.1 eq). The NMR spectrum was recorded with times.

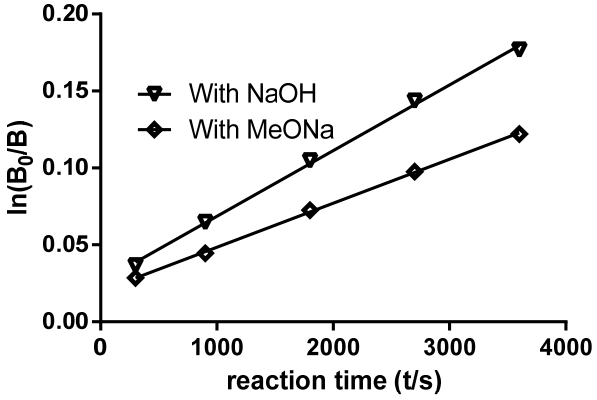

Figure **S4**. The values of k were measured for transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1). a) NaOH (0.1 eq) as catalyst, $k_{OH}*A$ = 4.267 x $10^{-5}\pm0.103$/s, R^2 = 0.9982; b) NaOMe (0.1 eq) as catalyst, $k_{MeO}*A$ = 2.855 x $10^{-5}\pm0.039$/s, R^2 = 0.9994, therefore, ko_H/k_{MeO} = 1.49.

The General NMR Experiments for Transesterification of Ethyl Benzoate in *d*-Methanol:D_2O: a) Ethyl benzoate (10 μL) was solved in *d*-methanol (0.5 mL) and then was added **solution C** (28 μL, 0.1 eq). The NMR spectrum was recorded with times. b) Ethyl benzoate (10 μL) was solved in *d*-methanol (0.5 mL) and then was added **solution D** (28 μL, 0.1 eq). The NMR spectrum was recorded with times.

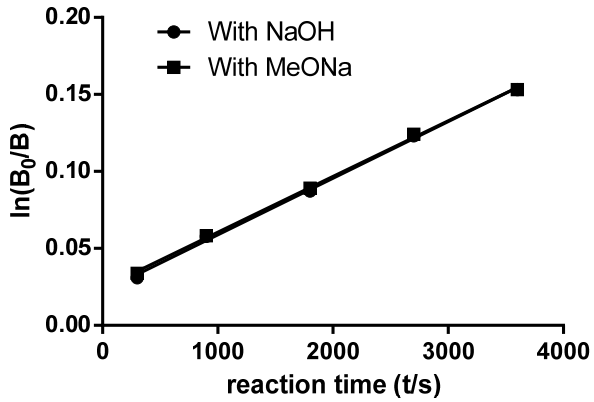

Figure **S5**. The values of k were measured for transesterification of ethyl benzoate in *d*-MeOD:D_2O. a) NaOH (0.1 eq) as catalyst, $k_{OH}*A$ = 3.675 x $10^{-5}\pm0.091$/s, R^2 = 0.9982; b) NaOMe (0.1 eq) as catalyst, $k_{MeO}*A$ = 3.617 x $10^{-5}\pm0.071$/s, R^2 = 0.9988, therefore, ko_H/k_{MeO} = 1.

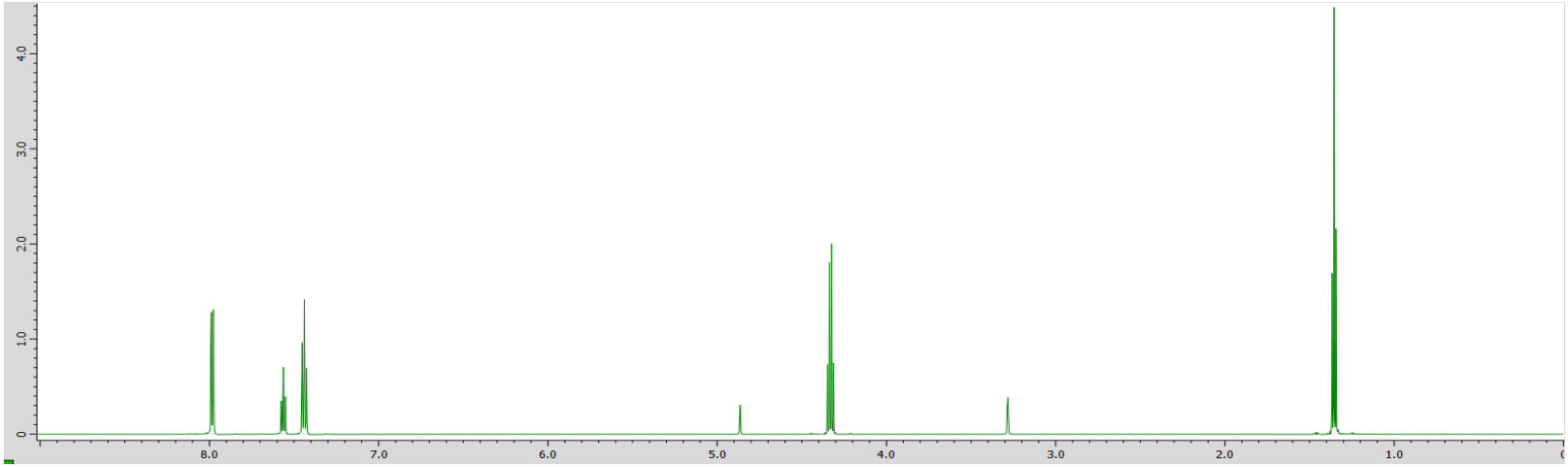

Figure **S6.** Recorded ethyl benzoate in *d*-methanol

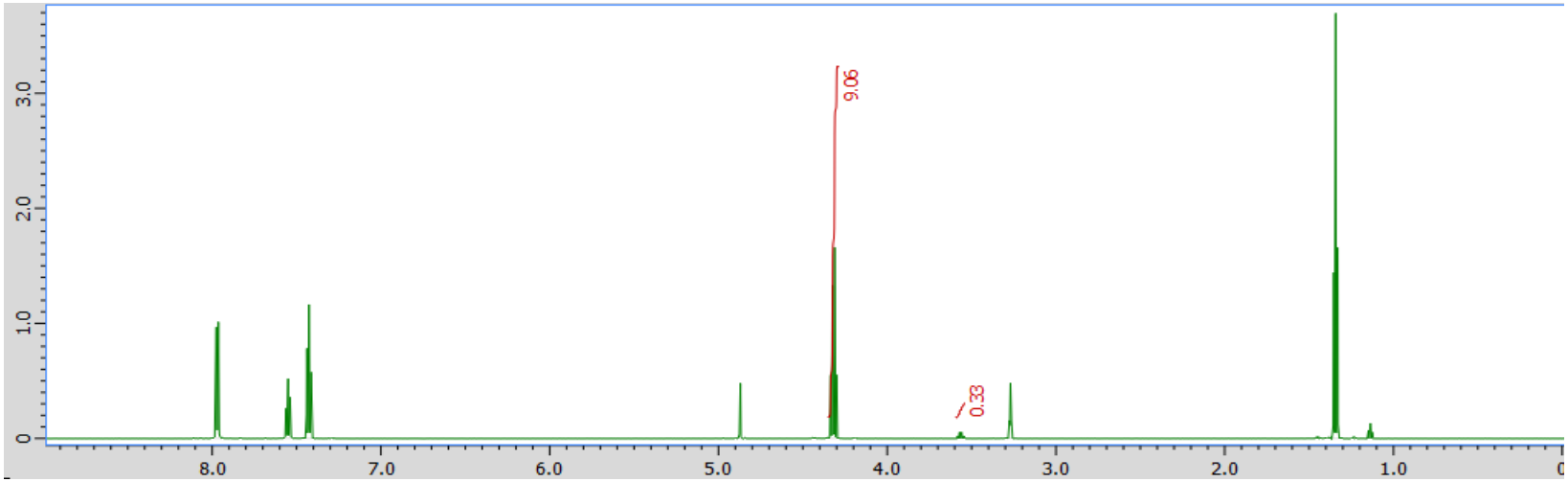

Figure **S6a.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by NaOH in 5 min.

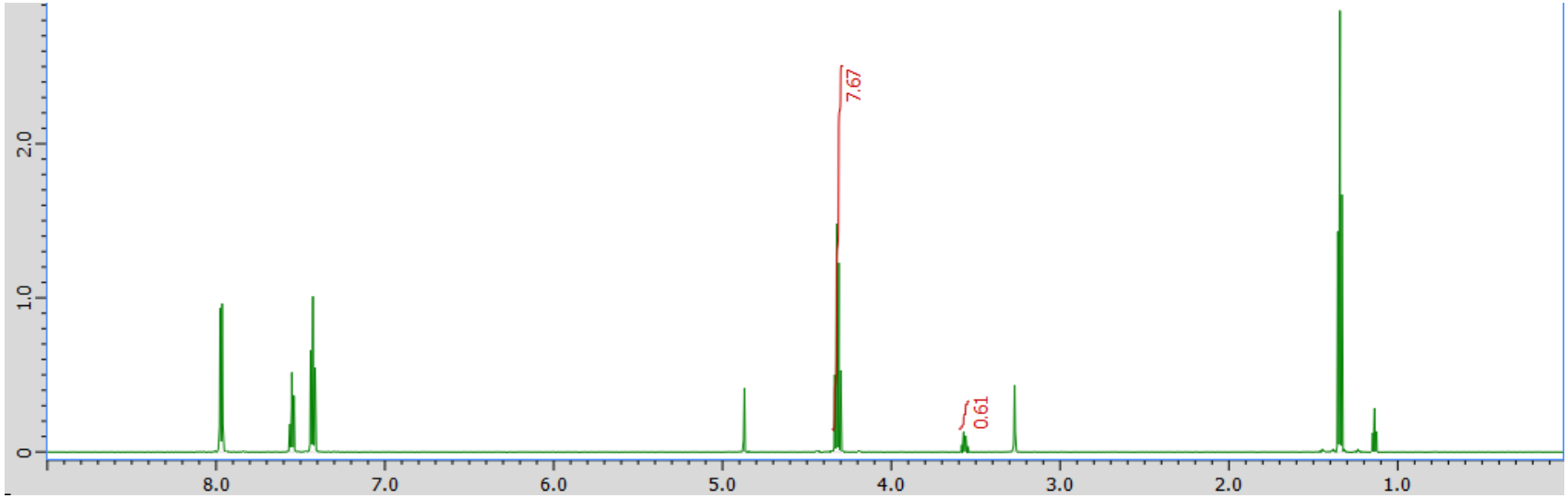

Figure **S6b.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by NaOH in 15 min.

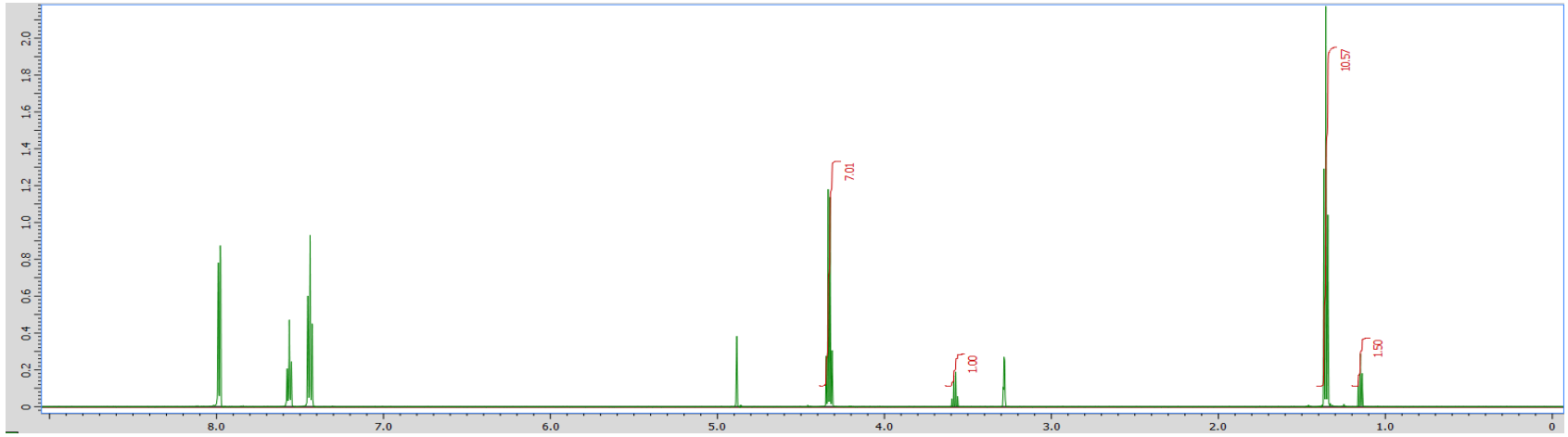

Figure **S6c.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by NaOH in 30 min.

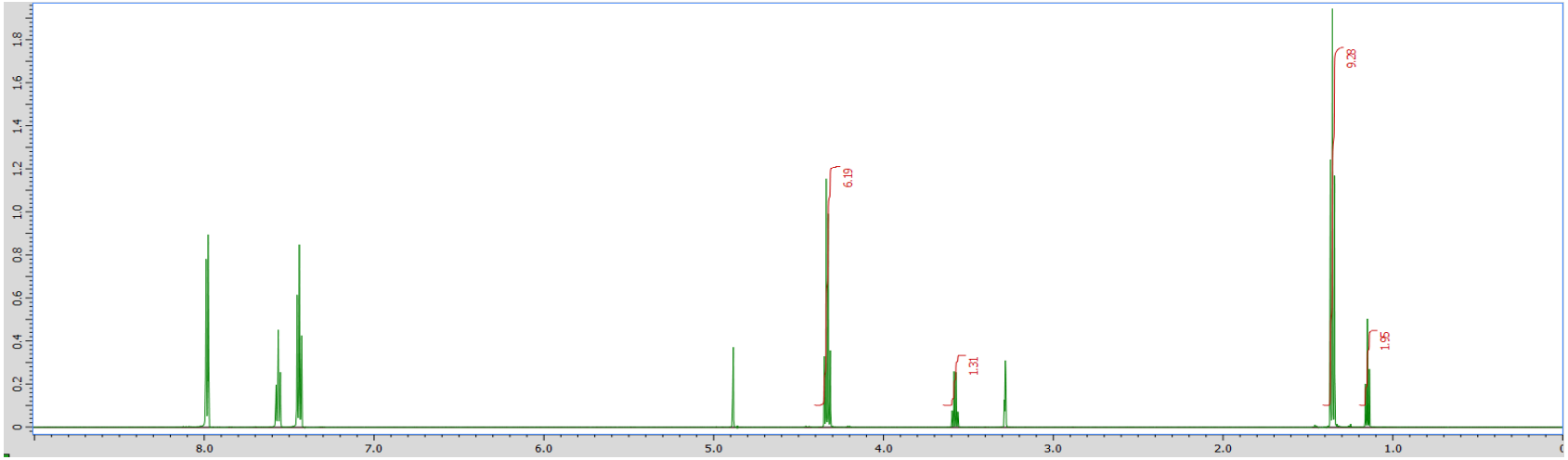

Figure **S6d.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by NaOH in 45 min.

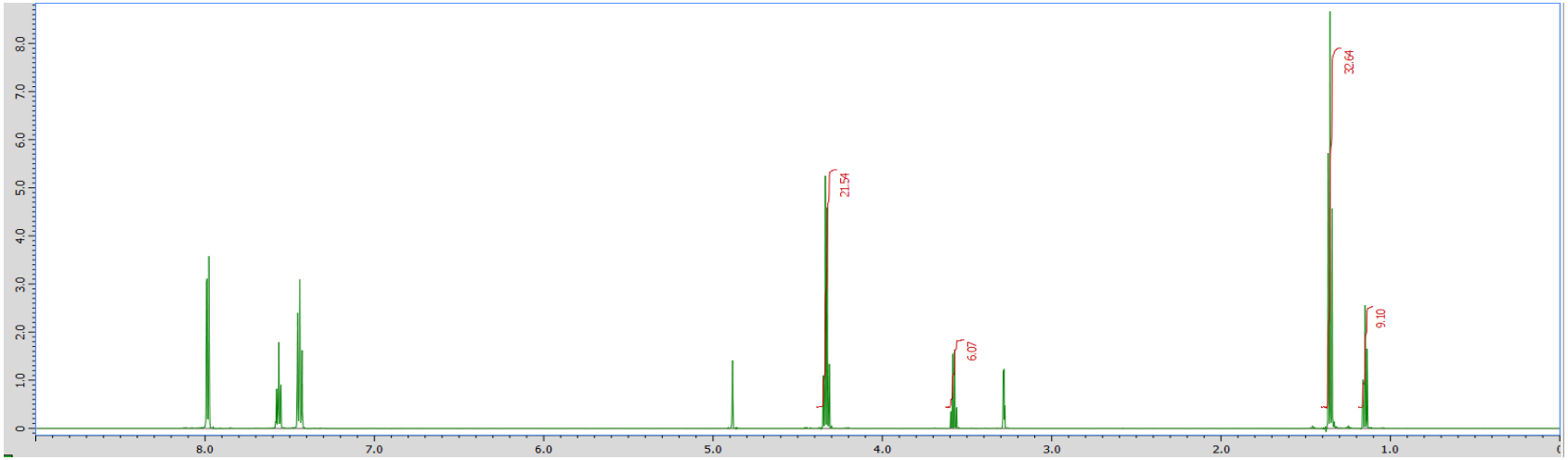

Figure **S6e.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by NaOH in 60 min.

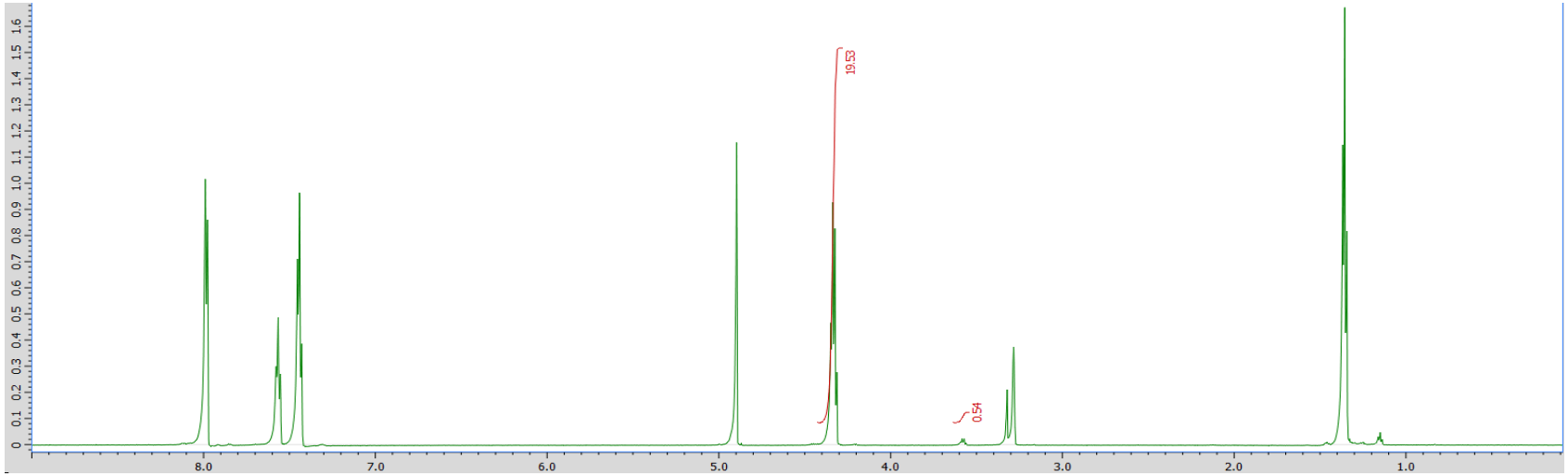

Figure **S7a.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by MeONa in 5 min.

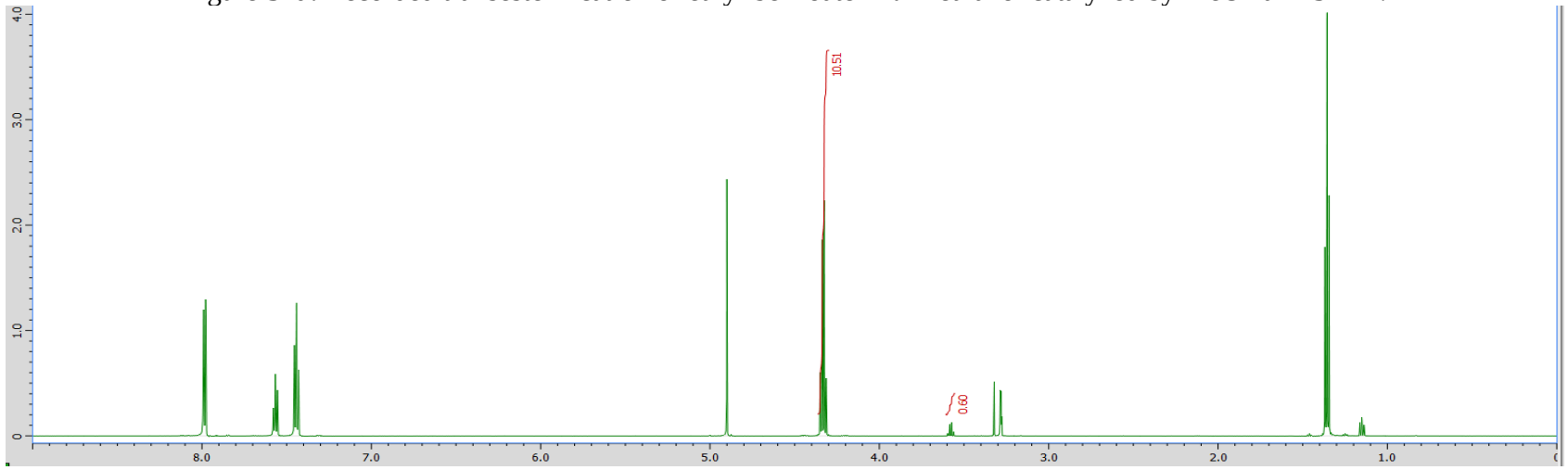

Figure **S7b.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by MeONa in 15 min.

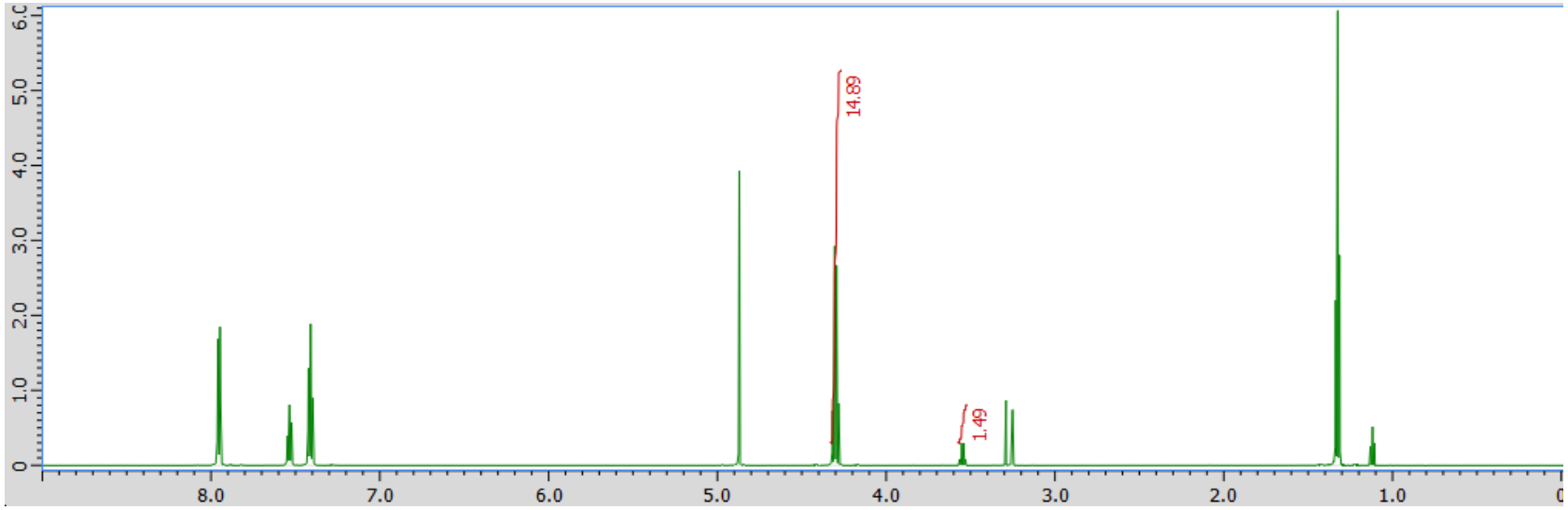

Figure **S7c.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by MeONa in 30 min.

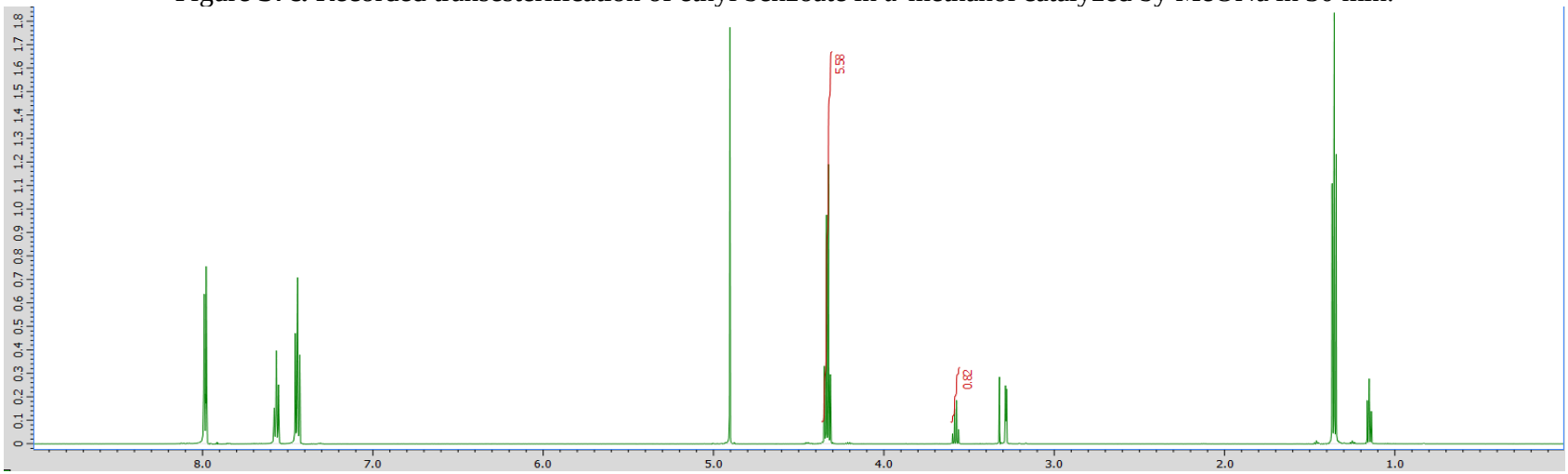

Figure **S7d.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by MeONa in 45 min.

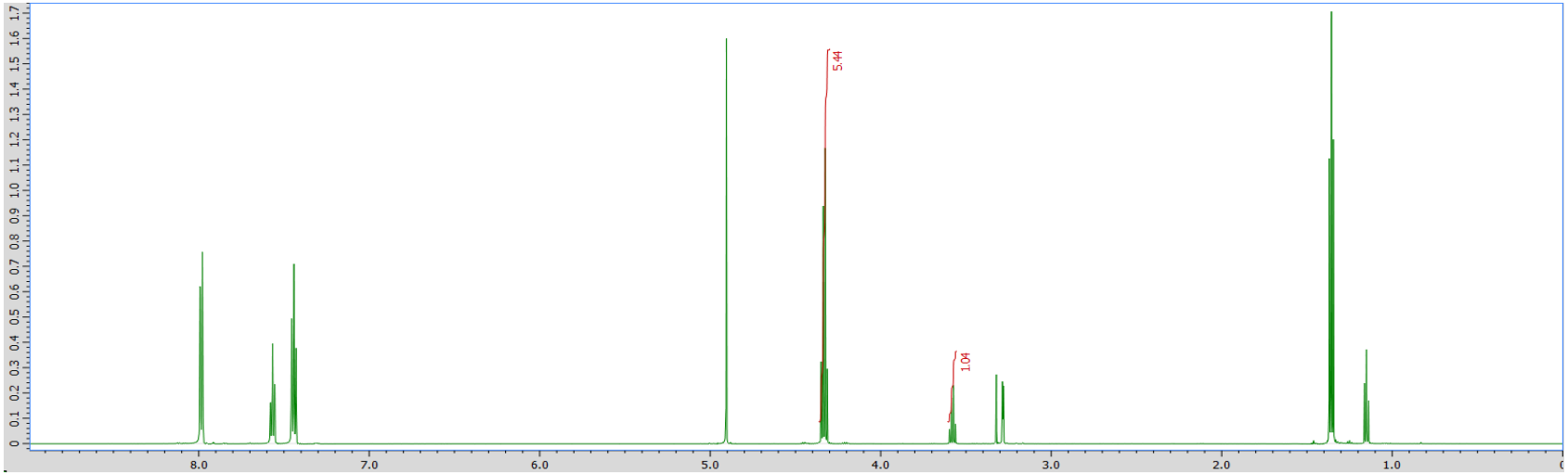

Figure **S7e.** Recorded transesterification of ethyl benzoate in *d*-methanol catalyzed by MeONa in 60 min.

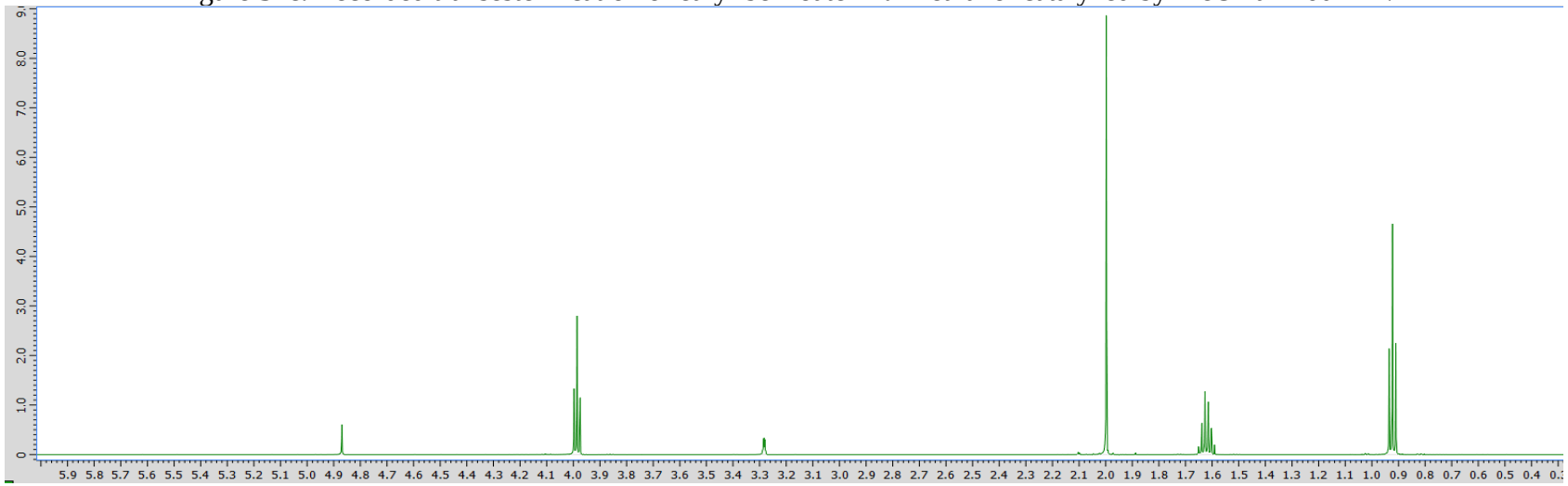

Figure **S8.** Recorded n-Propyl acetate in *d*-methanol

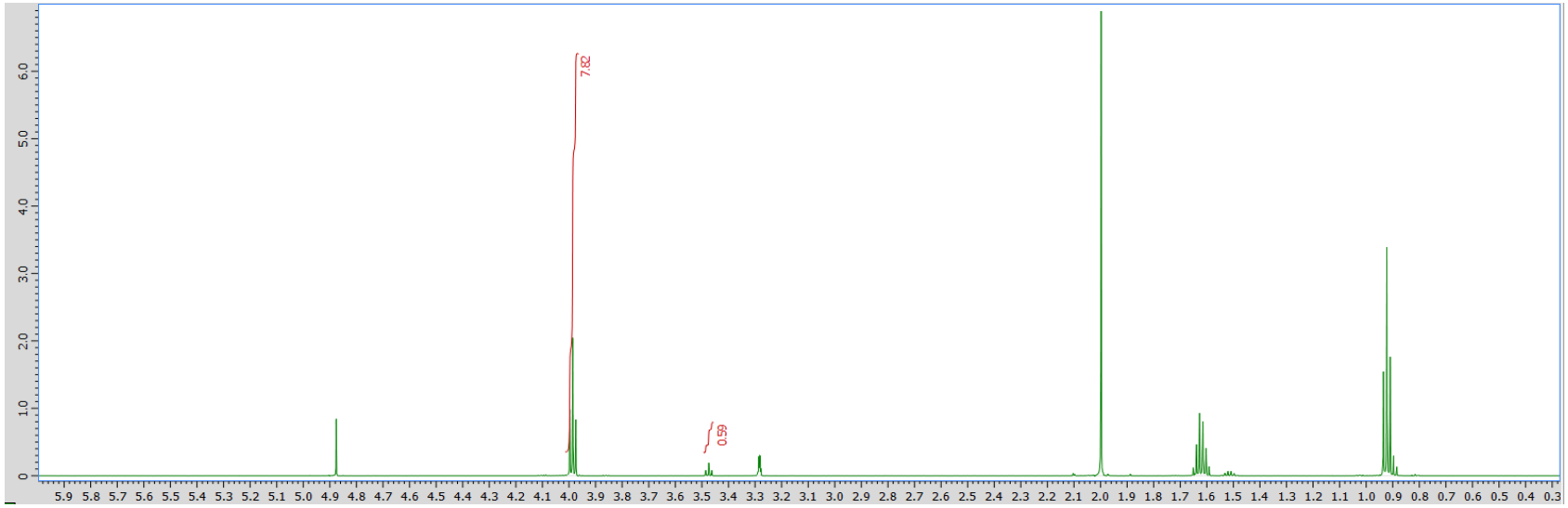

Figure **S8a.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by NaOH in 5 min.

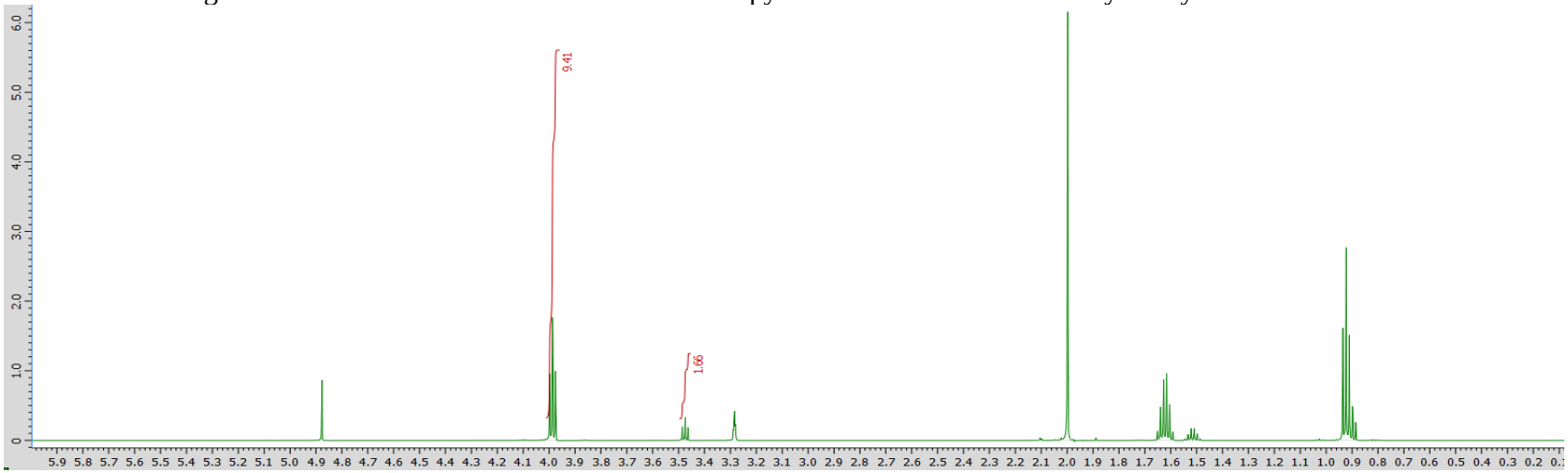

Figure **S8b.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by NaOH in 15 min.

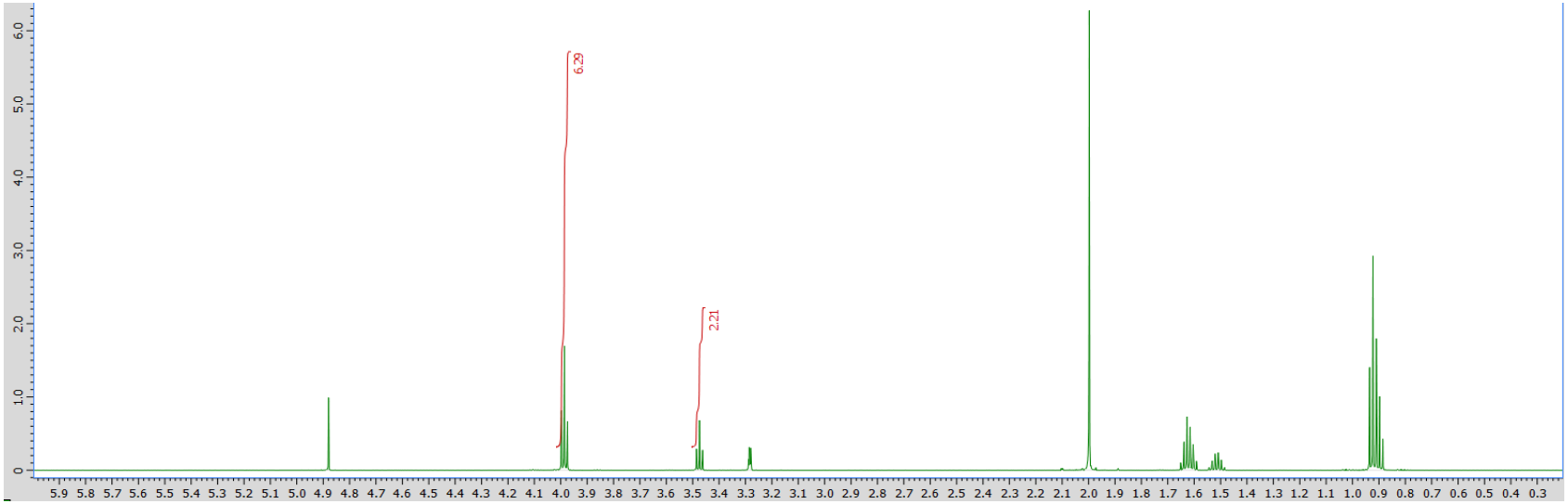

Figure **S8c.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by NaOH in 30 min.

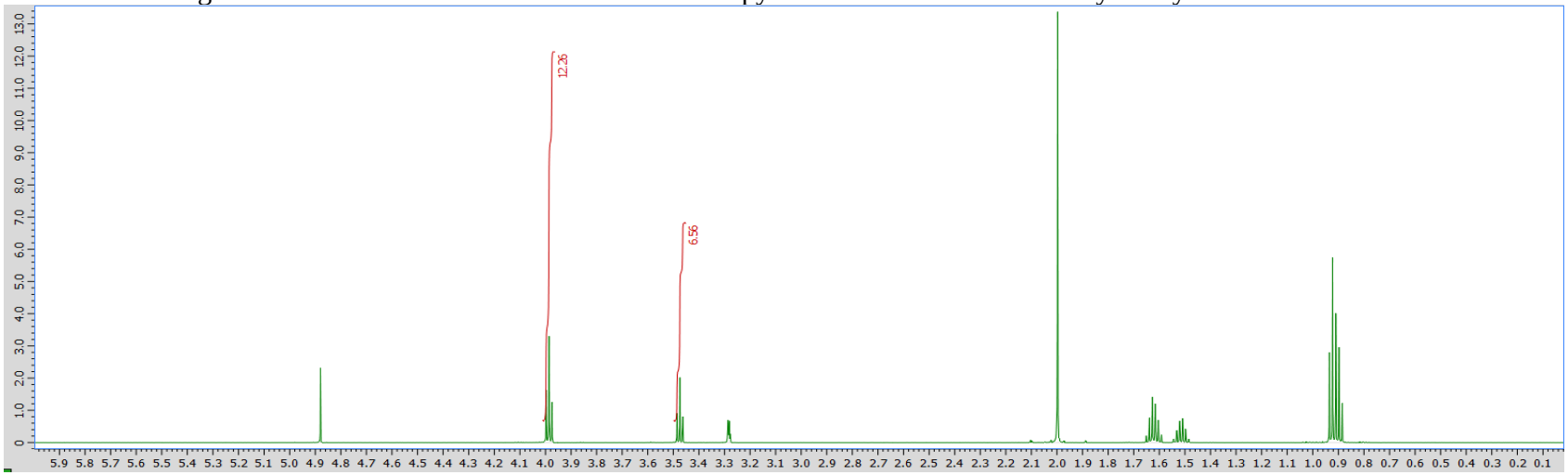

Figure **S8d.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by NaOH in 45 min.

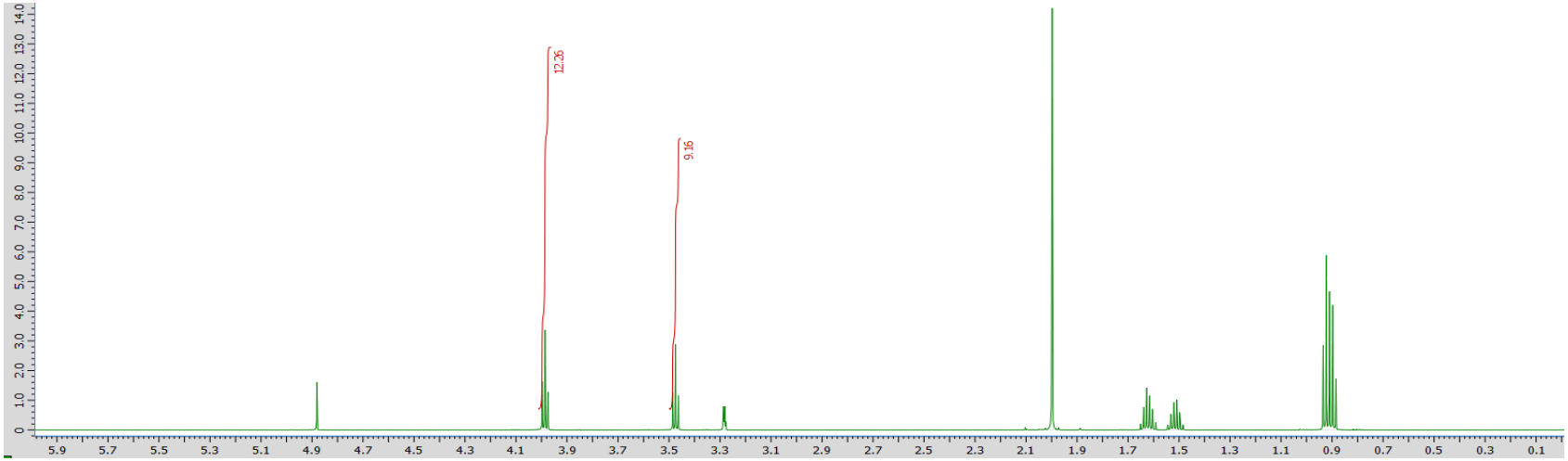

Figure **S8e.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by NaOH in 60 min.

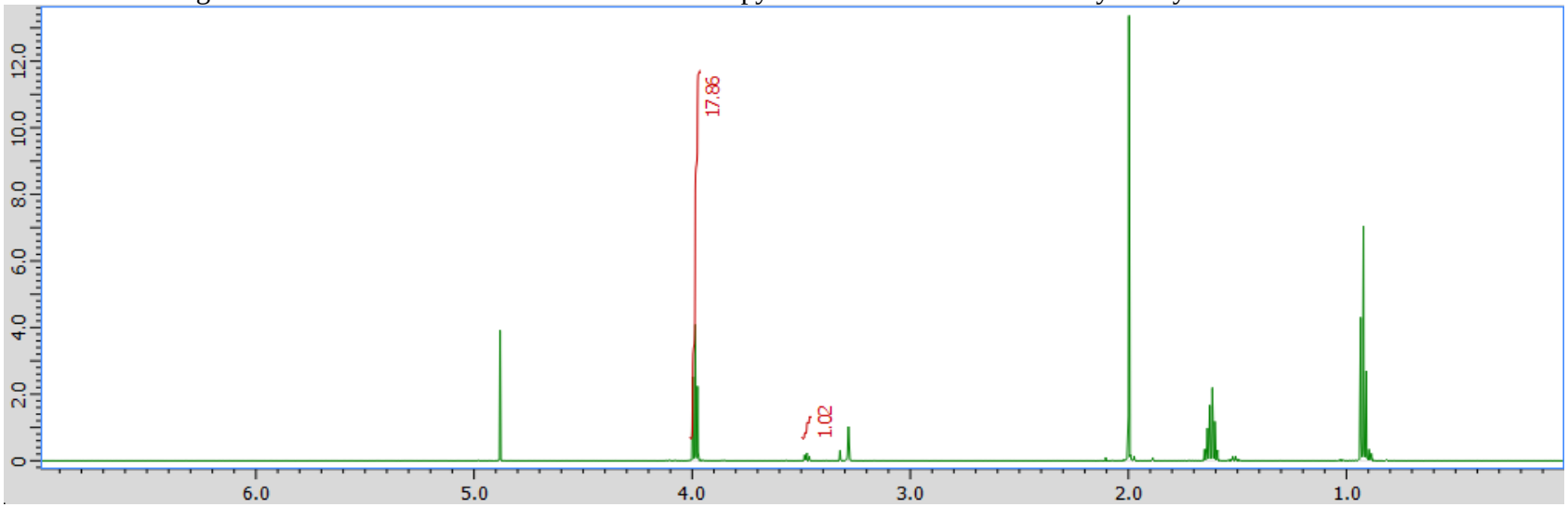

Figure **S9a.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by MeONa in 5 min.

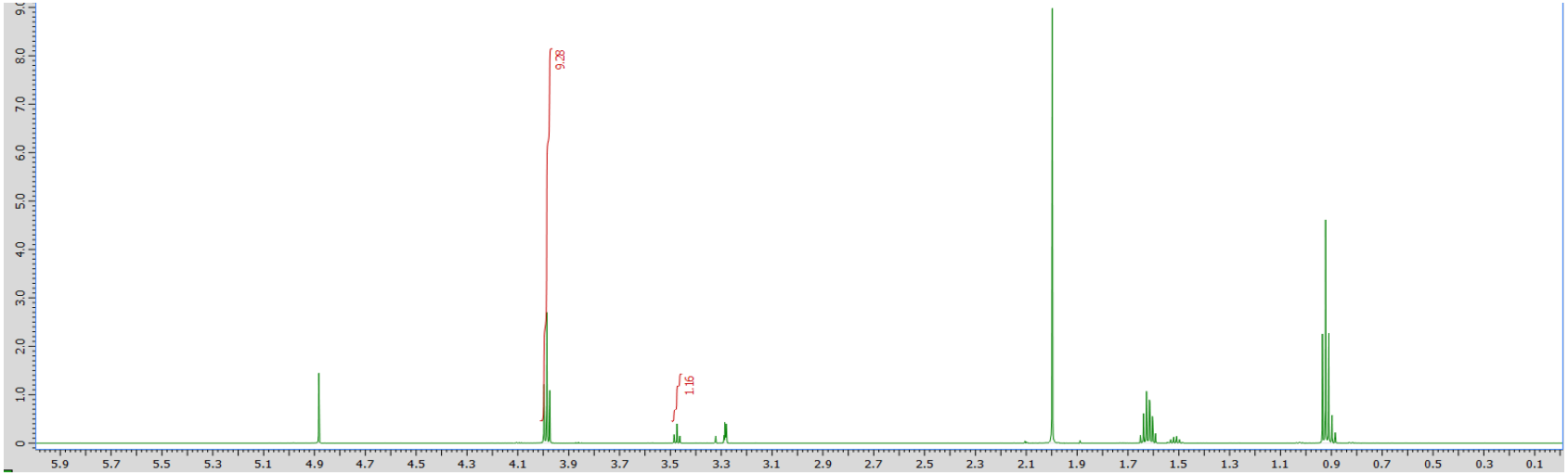

Figure **S9b.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by MeONa in 15 min.

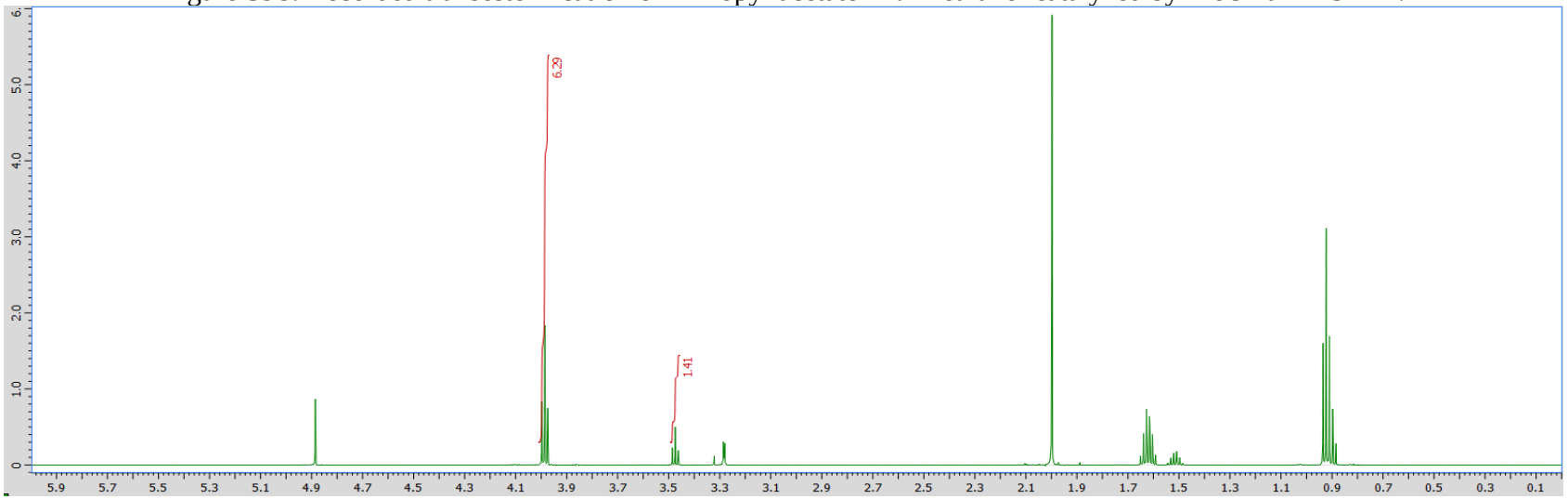

Figure **S9c.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by MeONa in 30 min.

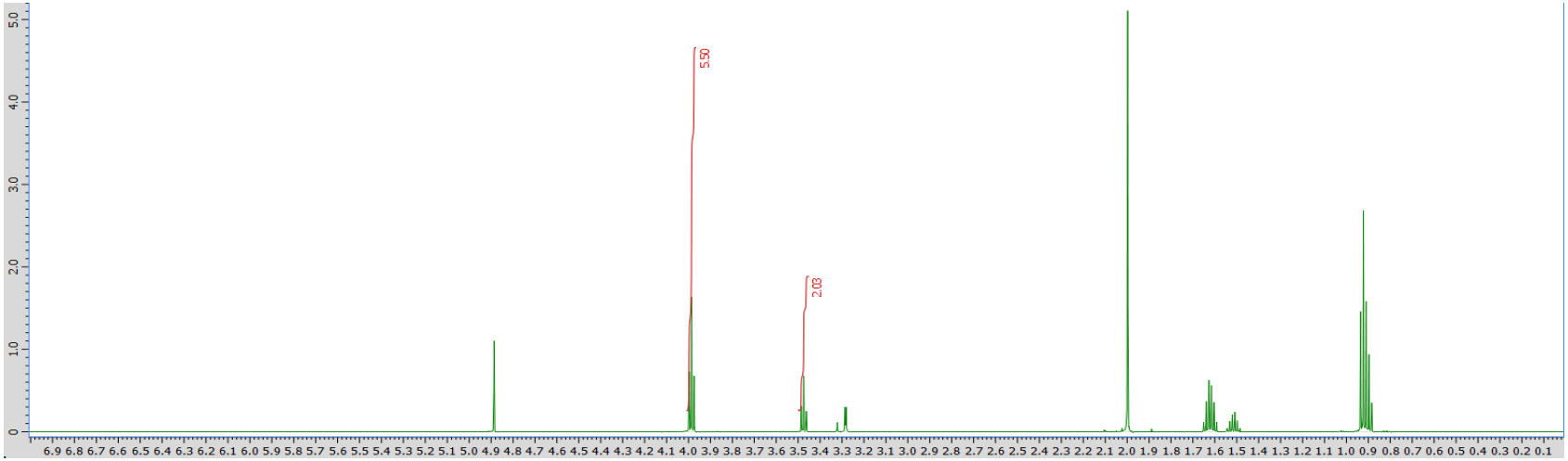

Figure **S9d.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by MeONa in 45 min.

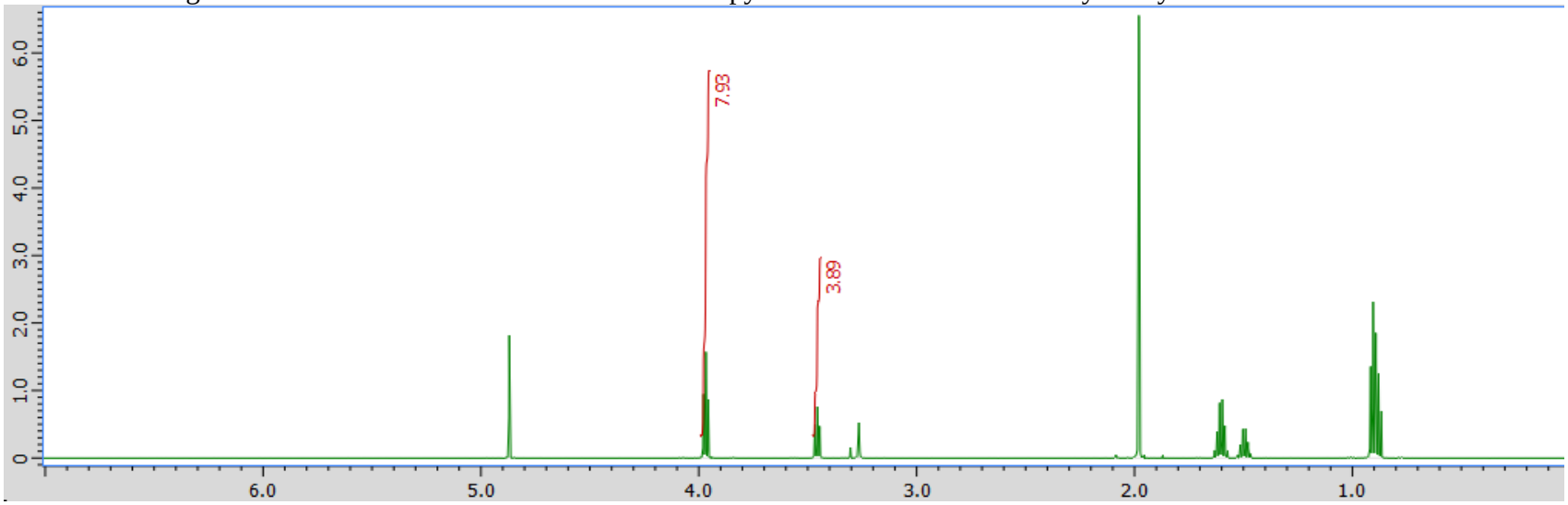

Figure **S9e.** Recorded transesterification of n-Propyl acetate in *d*-methanol catalyzed by MeONa in 60 min.

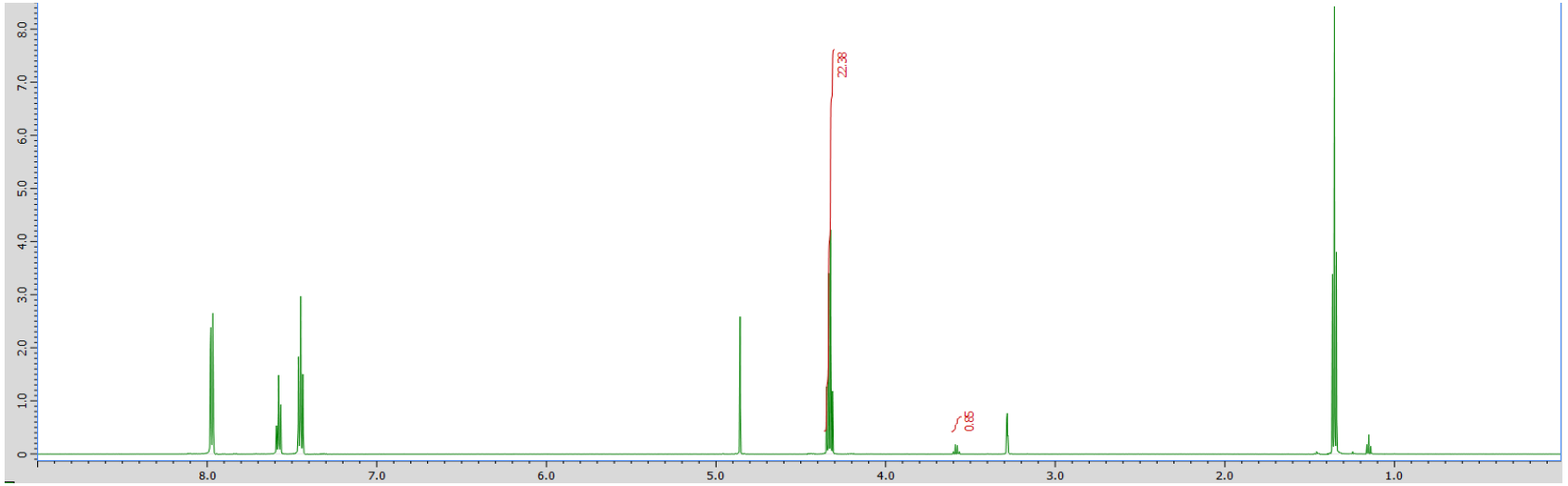

Figure **S10a.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by NaOH in 5 min.

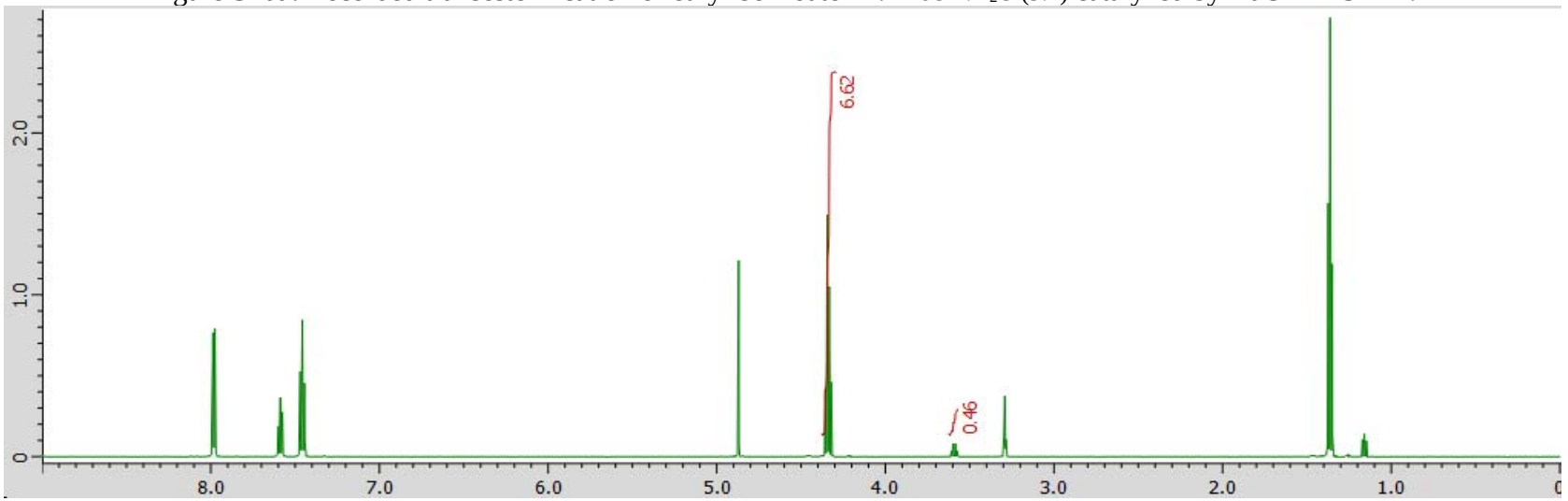

Figure **S10b.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by NaOH in 15 min.

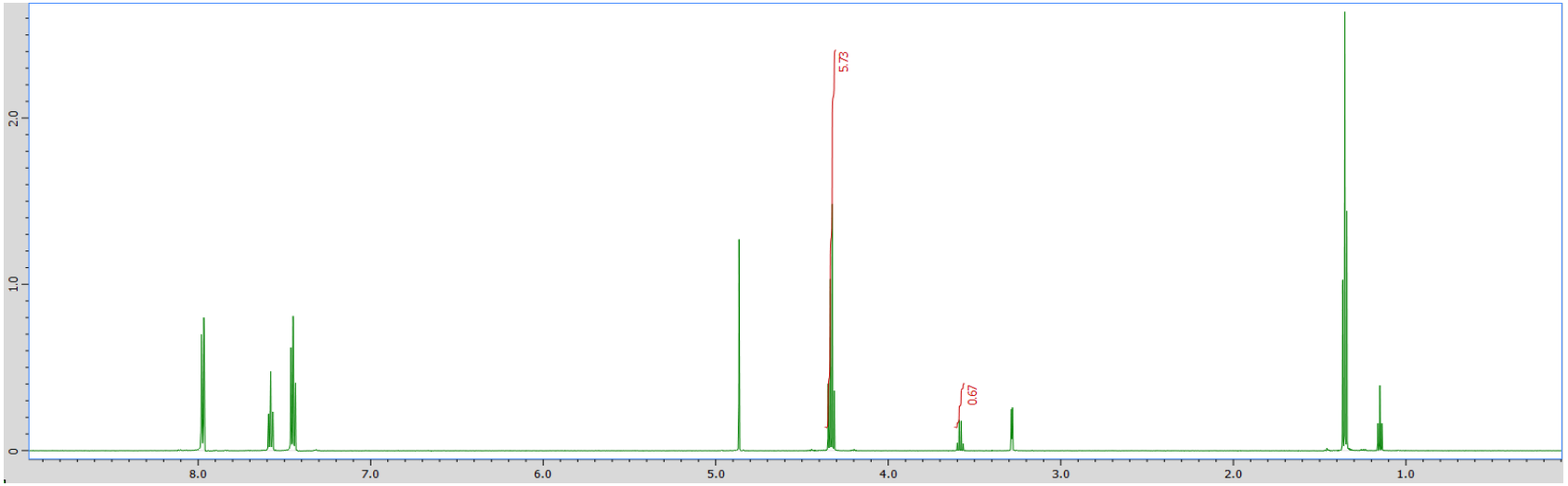

Figure **S10c.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by NaOH in 30 min.

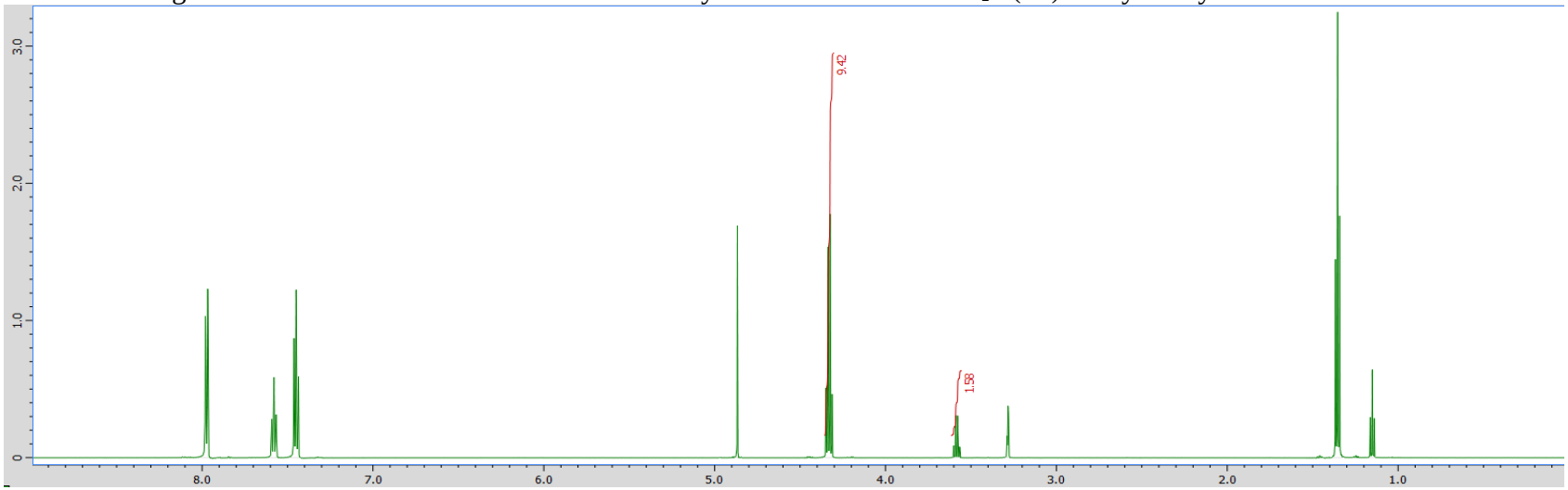

Figure **S10d.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by NaOH in 45 min.

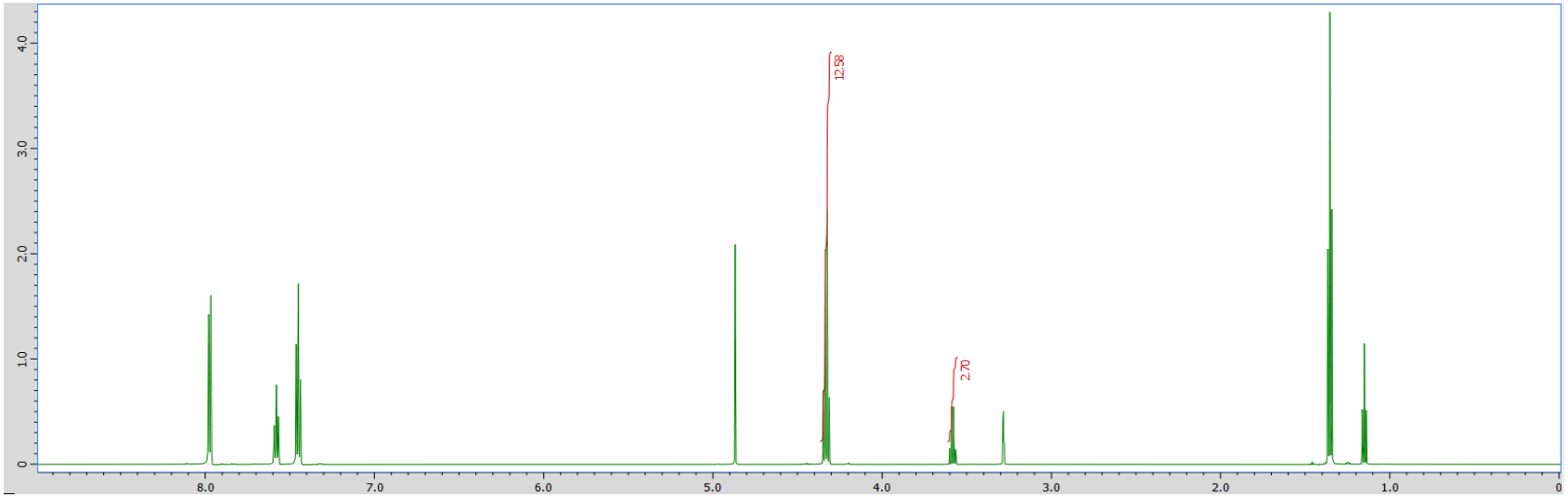

Figure **S10e.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by NaOH in 60 min.

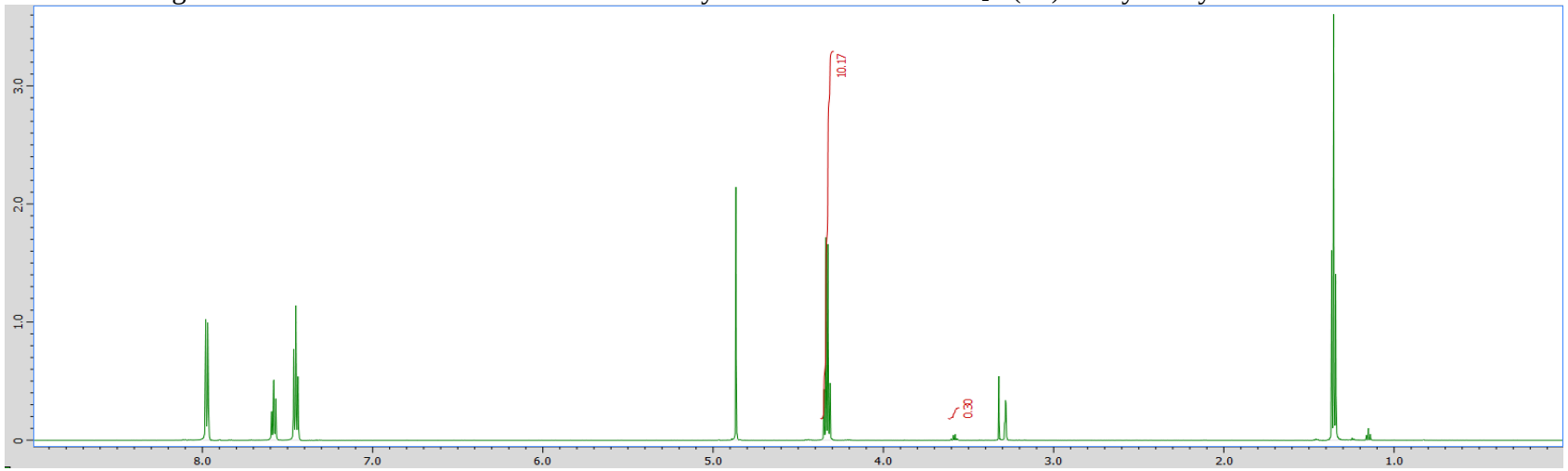

Figure **S11a.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by MeONa in 5 min.

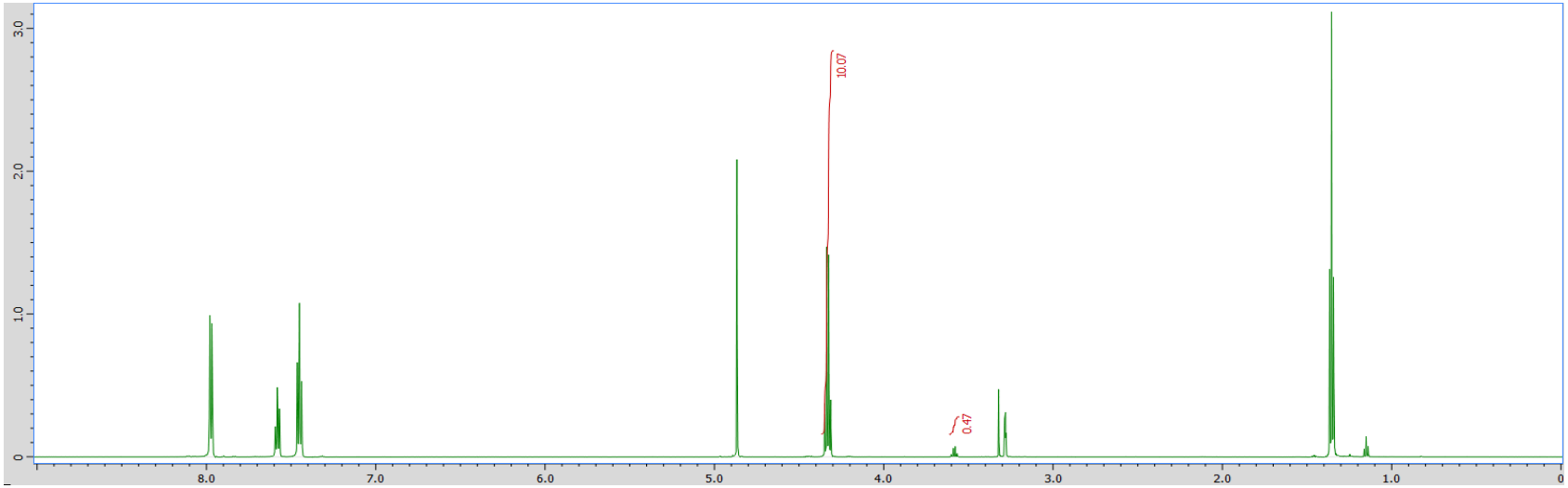

Figure **S11b.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by MeONa in 15 min.

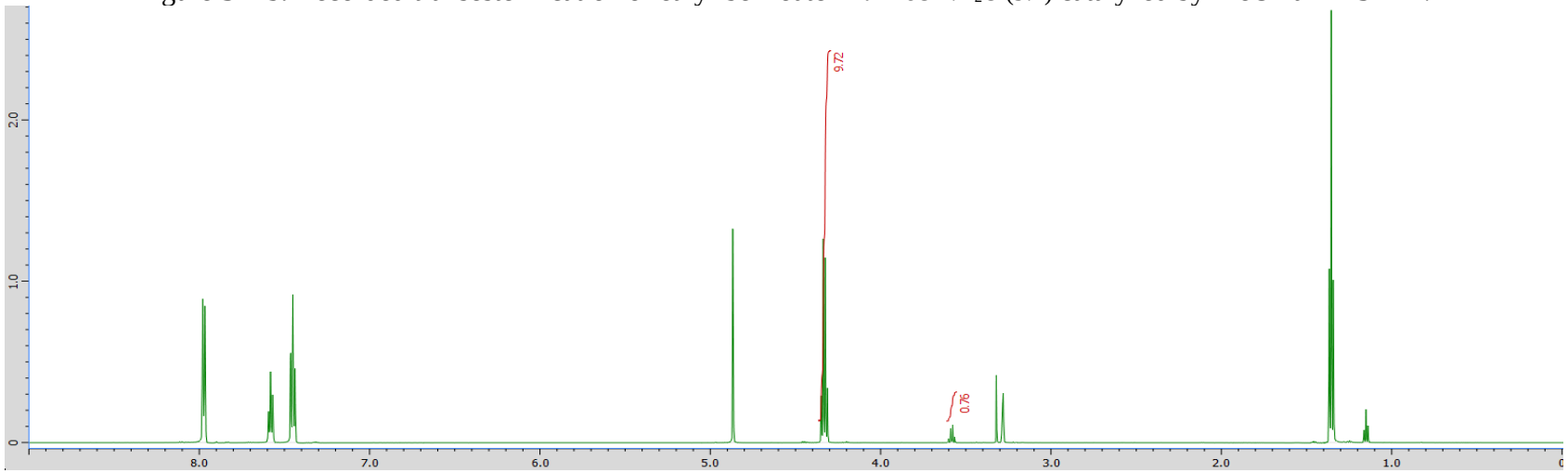

Figure **S11c.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by MeONa in 30 min.

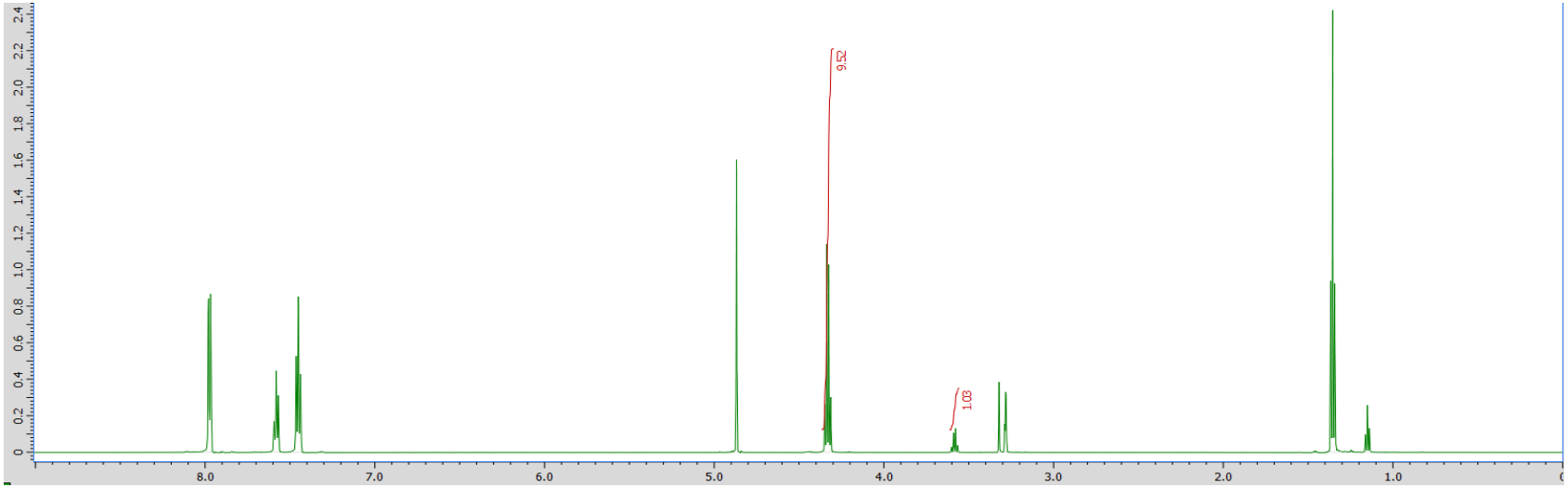

Figure **S11d.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by MeONa in 45 min.

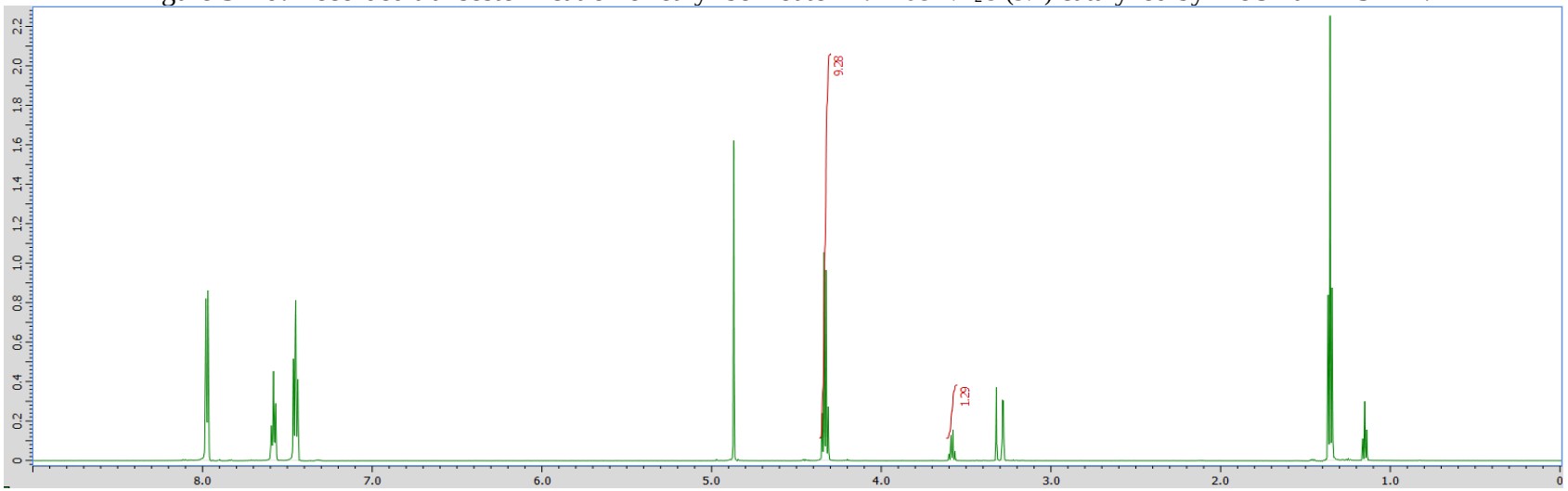

Figure **S11e.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O (9:1) catalyzed by MeONa in 60 min.

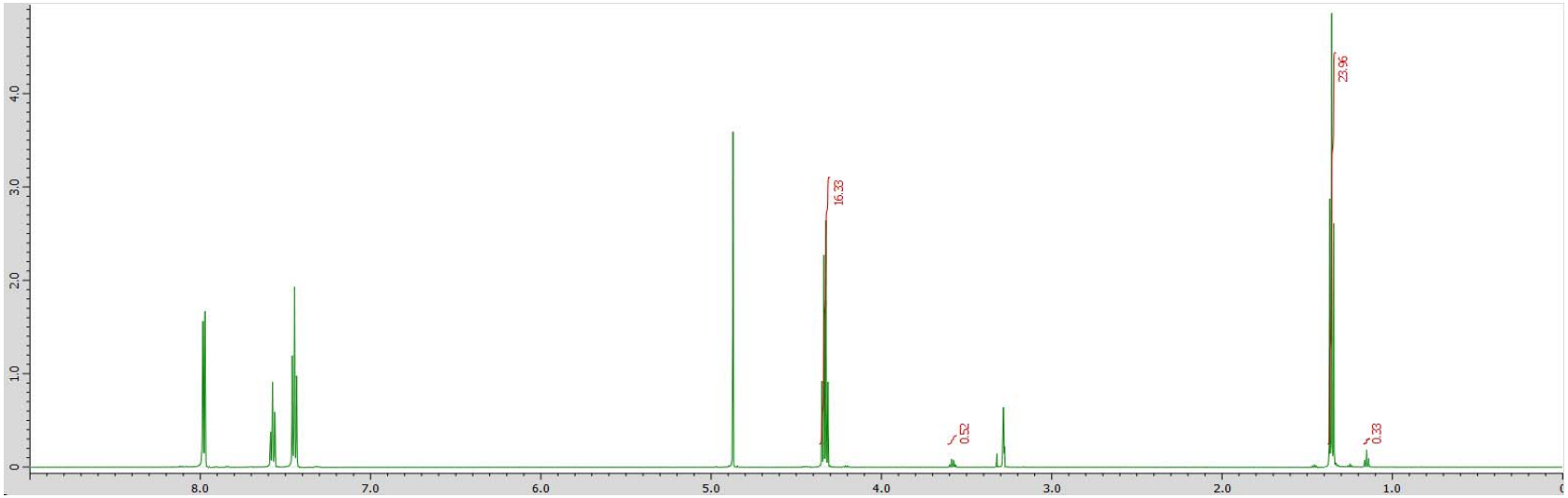

Figure **S12a.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by NaOH in 5 min.

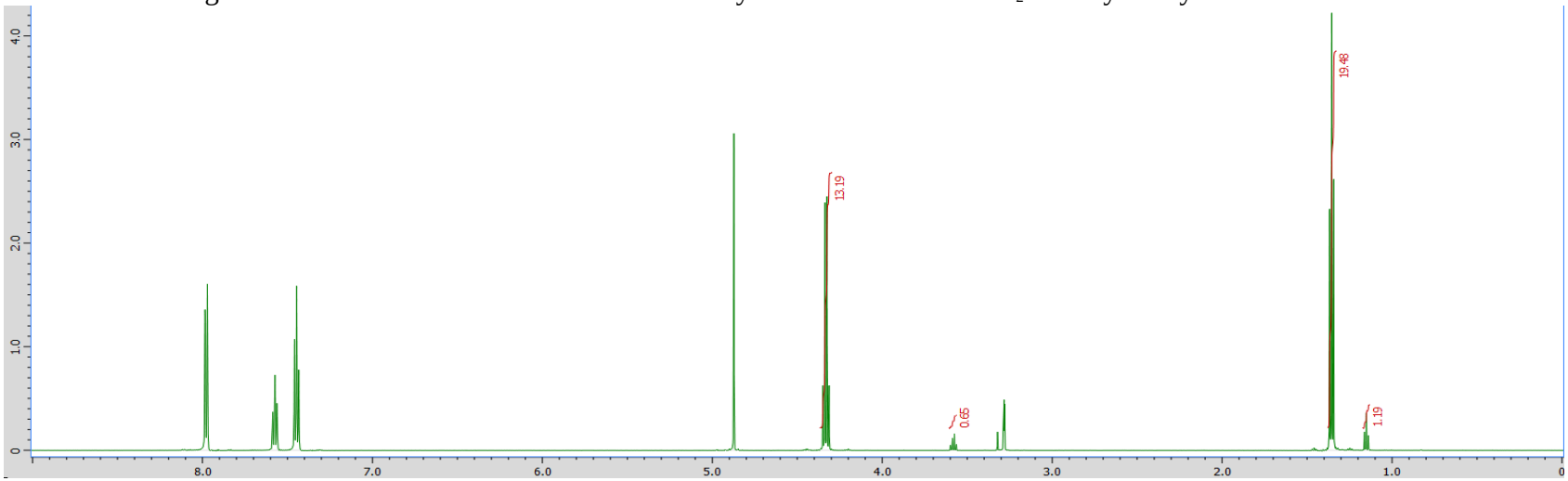

Figure **S12b.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by NaOH in 15 min.

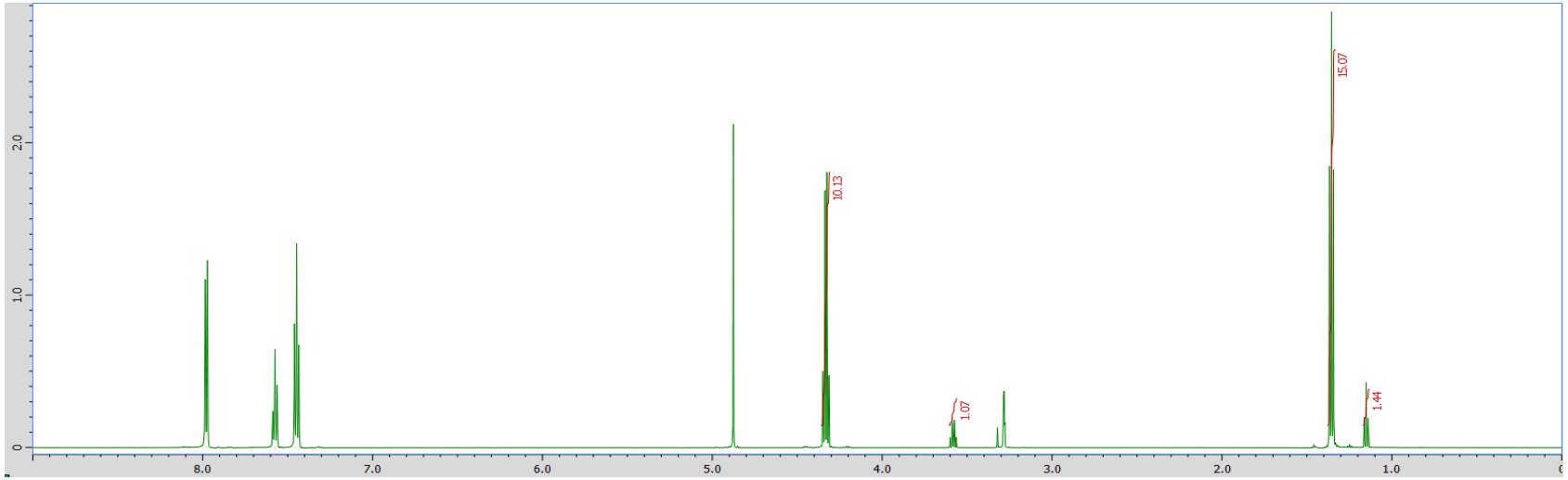

Figure **S12c.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by NaOH in 30 min.

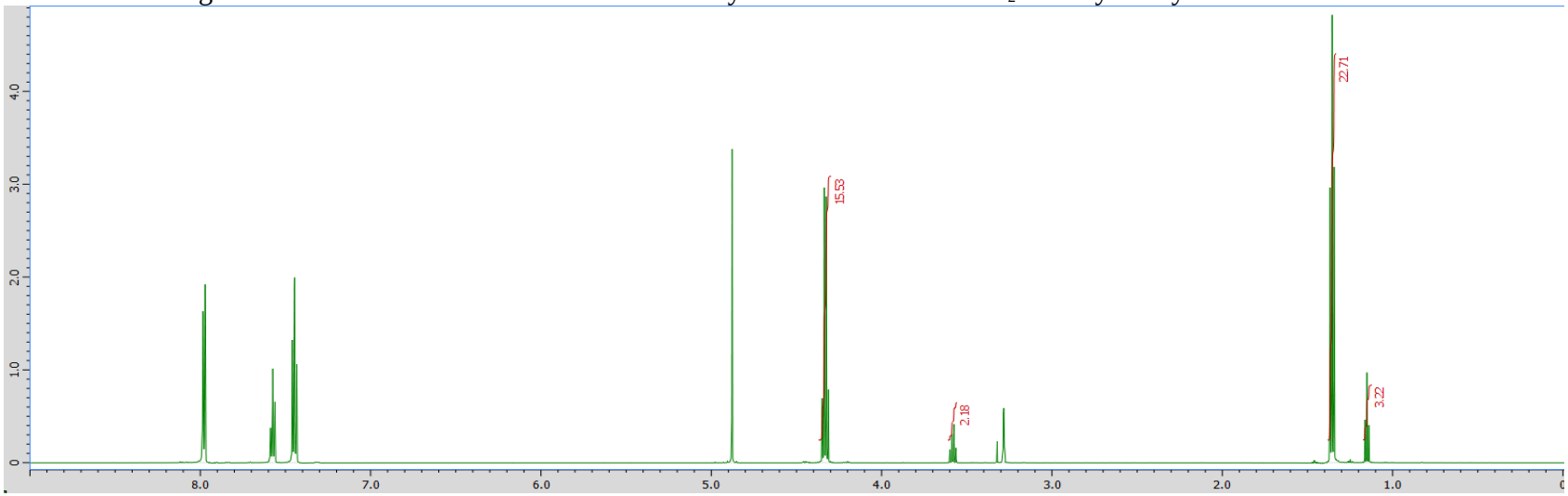

Figure **S12d.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by NaOH in 45 min.

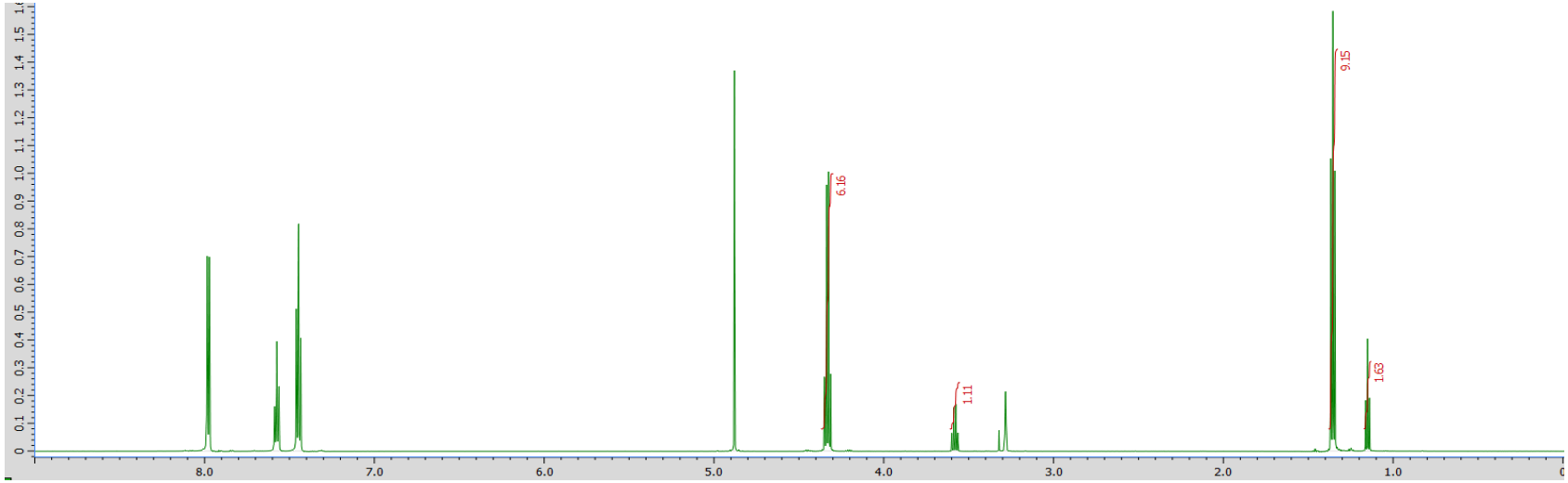

Figure **S12e.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by NaOH in 60 min.

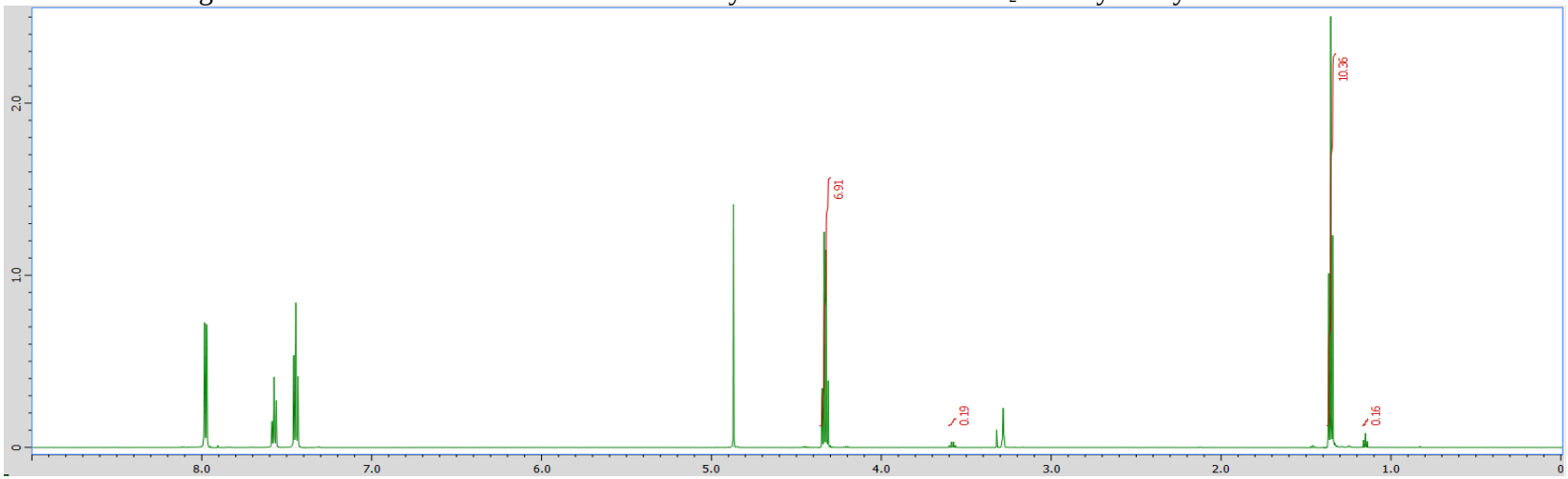

Figure **S13a.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by MeONa in 5 min.

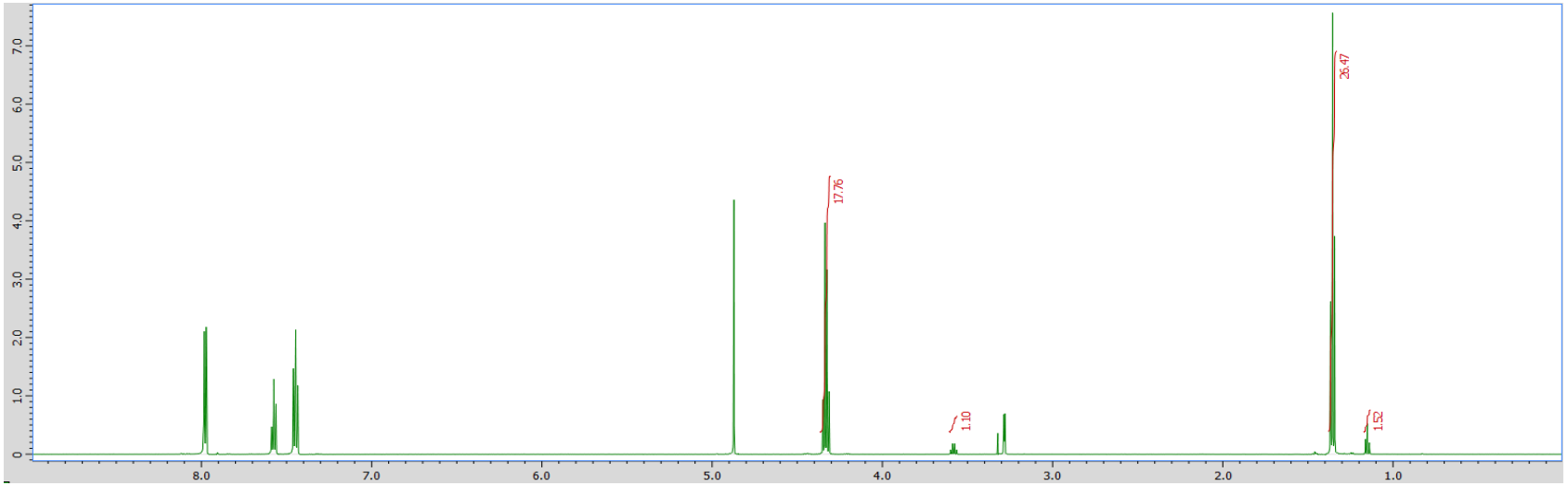

Figure **S13b.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by MeONa in 15 min.

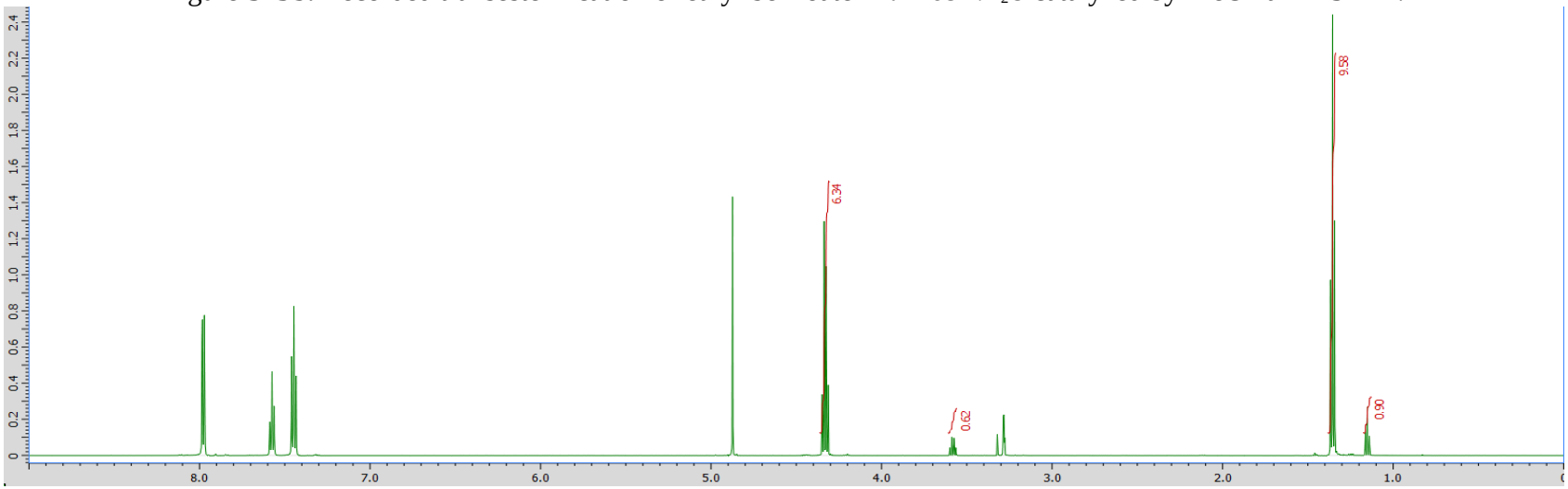

Figure **S13c.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by MeONa in 30 min.

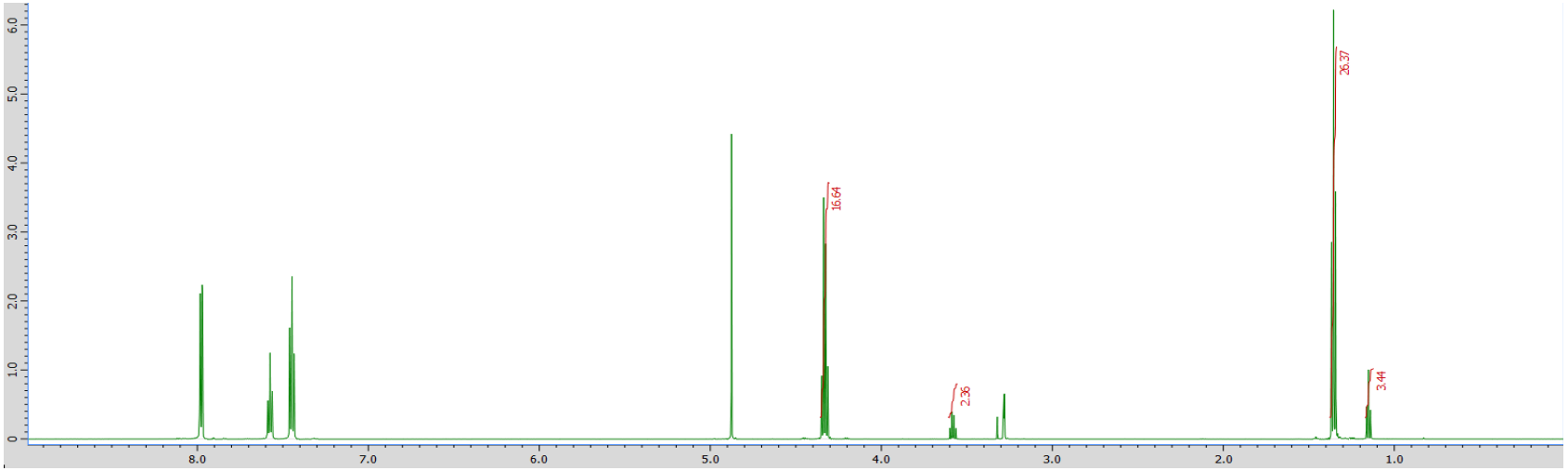

Figure **S13d.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by MeONa in 45 min.

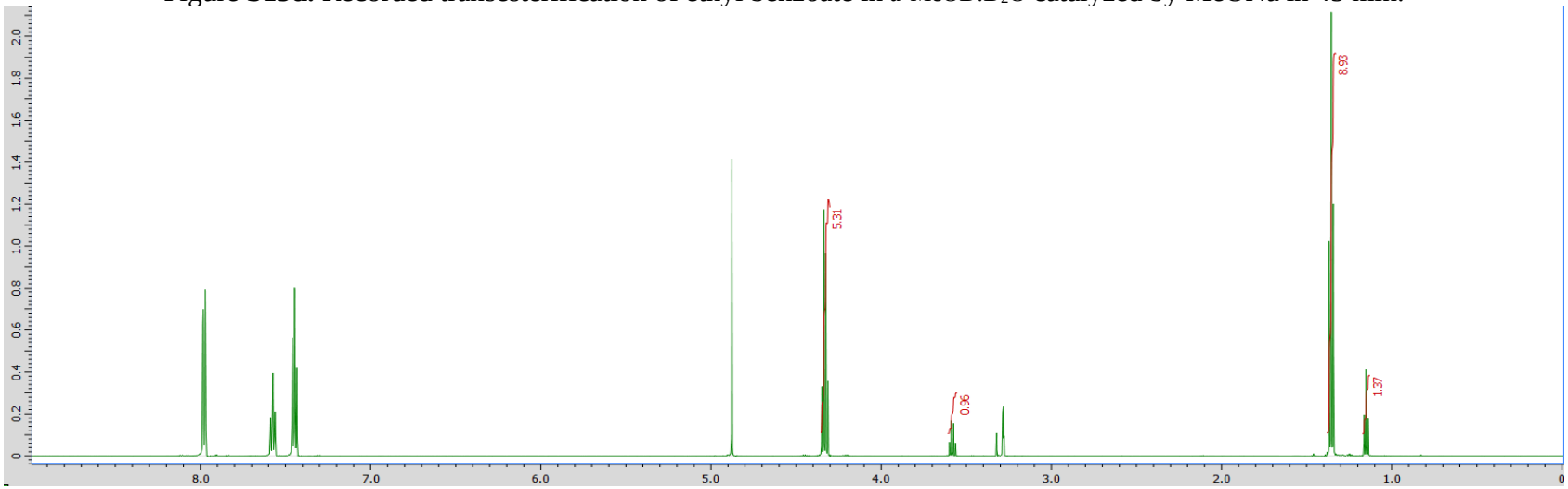

Figure **S13e.** Recorded transesterification of ethyl benzoate in *d*-MeOD:D_2O catalyzed by MeONa in 60 min.