Electronic Supplementary Material (ESI) for Green Chemistry.

Catalyst-Free Lignin Valorization by Acetoacetylation. Structural Elucidation by Comparison with Model Compounds

Eric Krall,[1,3] Eric Serum,[2,3] Mukund P. Sibi, *[,2,3] Dean Webster*[,1,3]

[1]Department of Coatings and Polymeric Materials, [2]Department of Chemistry and Biochemistry, [3]Center for Sustainable Materials Science: All found at North Dakota State University, Fargo, ND 58108-6050

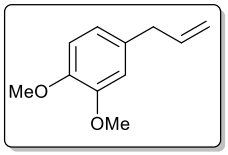
1.0 General Methods

Unless otherwise stated, all commercially procured materials were used as received without further purification. Mass of all reagents, substrates and reaction aliquots was determined on by an Accuris Analytical Series Balance. Melting points were collected on a REACH Devices RD-MP digital melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were collected on a Bruker Avance 400 MHz instrument and processed with Topspin software; Peak shifts were calibrated based on residual solvent peaks[1] and where applicable, the method of Hoye was used to assign coupling constants.[2] Infrared spectra were collected with a Nicolet™ iS™ 10 FTIR Spectrometer using a diamond sample plate for ATR and processed using Omnix. High Resolution Mass Spectra were collected on Waters Synapt G2-Si high definition mass spectrometer and were processed using MassLynx.

2.0 Preparation of Lignin Model Compounds

2.1

4-Allylveratrole or 3-(3,4-Dimethoxyphenyl)-1-propene



CAS# 93-15-2

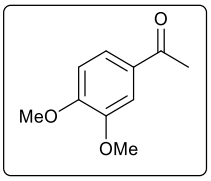
A 250 mL single neck round bottom flask was charged with eugenol (99%, Acros Organics, 16.7881 g, 0.1022 mol, 1 equiv), anhydrous DMF (50 mL) and the light-yellow solution was warmed on an oil bath (40 °C preheated). Potassium carbonate (30.1532 g, 0.2182 mole, 2.13 equiv) was added to the stirring reaction mixture which took on a distinctive amber color which became green as the mixture stirred. Iodomethane (6.5 mL, 14.82 g, 0.1044 g, 1.02 equiv) was added by syringe and the green color rapidly dissipated. The mixture was sealed with a yellow cap-plug and stirred on the warm bath for 17 h. The color of the reaction mixture darkened significantly upon standing. The heterogeneous slurry was poured over ice (400 mL). The mixture was stirred as the ice melted and was partitioned in a 1 L separatory funnel with diethyl ether. The ethereal solution (250 mL light gold colored) was isolated, and the aqueous mixture (400 mL of brown colloidal mixture) was extracted with additional ether (2 X 100 mL). The golden yellow ethereal extracts were combined, backwashed with water (2 X 100 mL), then once with saturated sodium chloride solution (100 mL). The organic solution (350 mL) was dried (sodium sulfate) and concentrated by rotary evaporation under reduced pressure. The mass of crude residue was 20.53 g of brown solution. The mixture was adsorbed onto silica gel, and purified by flash chromatography. The very significant major eluate peak's fractions were combined and concentrated to afford 17.88 g (98%) of colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, J=8.64 Hz, 1H), 6.74-6.68 (m, 2 H), 5.95 (dddd, J=6.68, 6.68, 10.08, 16.8 Hz), 5.13-5.02 (m, 2 H), 3.84 (s, 3 H), 3.83 (s, 3H), 3.32 (d, J=6.68 Hz, 2 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 147.3, 137.6, 132.5, 120.3, 115.5, 111.8, 111.2, 55.76, 55.63, 39.7

FTIR (ATR) cm^{-1} 3017, 2935, 2833, 1637, 1591, 1511, 1464, 1258, 1233, 1139, 1027, 911, 849, 805, 766, 745, 644

2.2 4-Acetylveratrole or 1-(3,4-dimethoxyphenyl)ethanone



CAS# 1131-62-0

A 250 mL single neck round bottom flask was charged with apocynin (acetovanillone, 16.6198, 100 mmol, 1 equiv, Acros Organics) as a tan powder and anhydrous N,N-dimethylformamide (Sigma Aldrich sure seal, 50 mL); the solution which formed was dark brown in color. The solution was capped with a yellow cap-plug and warmed on an oil bath (40 °C). Potassium carbonate (EMD, 30.8369 g, 0.2281 mole, 2.2 equiv) was added to the mixture but did not totally dissolve. The mixture was stirred for 40 minutes and iodomethane (Alfa Aesar, 6.5 mL, 14.82 g, 0.1044 mole, 1.04 equiv) was added to the warmed solution in a steady stream by syringe. The cap-plug was sealed into the neck of the flask. The reaction was stirred; within 10 minutes, the color of the solution had drastically lightened to a straw yellow. Within 2mintues the mixture had thickened with precipitate which continued to develop during the course of the reaction. The mixture was stirred on the warm oil bath for 17 h and was also observed to darken upon standing.

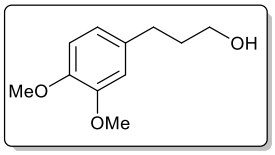
The reaction slurry was poured into a 400 mL beaker charged with ice. Upon contact with the ice, the color of the solution became tan. The contents of the flask were rinsed over with diethyl ether, and the mixture was stirred until the ice had melted then allowed to partition in a 1000 mL separatory funnel. The ethereal solution was isolated (300 mL), and the aqueous phase was extracted with additional ether (2X100 mL). The organic extracts were combined (500 mL), backwashed with distilled water (2 X100 mL) then saturated sodium chloride solution (100 mL) and the first wash took on a slightly pink color. The isolated organic solution (450 mL of amber color) was dried (sodium sulfate). TLC indicated predominately one motile spot with an orange residue at the baseline. The combined extract solution was concentrated by rotary evaporation under reduced pressure. The residue was a brown oil with a mass of 15.48 g (85% crude yield). The residue was adsorbed onto silica gel and purified by flash chromatography. The very major eluate fractions were combined and concentrated to afford a clear and colorless viscous oil. The viscous oil was heated by heat gun to assist transfer to an Erlenmeyer flask. Upon cooling to room temperature, the residual material crystalized. The mass of the white crystalline material was 15.4216 g: isolated yield of 85%. The melting point of the white crystalline solid was 53.6 to 55.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J*=2.04, 8.32 Hz), 7.44 (d, *J*=1.96 Hz, 1 H), 6.80 (d, *J*=8.36 Hz, 1 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 2.48 (s, 1 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 148.9, 130.4, 123.2, 110.0, 109.9, 56.0, 55.9, 26.1

FTIR (ATR) cm^{-1} 3002, 2938, 1669, 1586, 1510, 1415, 1262, 1078, 1019, 876, 807, 766, 568

2.3 3-(3,4-Dimethoxyphenyl)-1-propanol



CAS# 3929-47-3

A single neck round bottom flask was charged with 4-allylveratrole (17.88 g, 100.3 mmol, colorless oil) and a large PTFE coated magnetic football was sealed with a white serum septum and flushed with nitrogen. To that oil was added tetrahydrofuran (100 mL, HPLC grade), and the solution was stirred magnetically while chilling on an ice bath beneath an argon balloon. A disposable polypropylene syringe and 18 gauge stainless steel needle was used to draw up 50 mL of borane-tetrahydrofuran complex (Alfa Aesar, 1 M solution in THF, stabilized with 5 mmol sodium borohydride, LOT: T02A053), and that solution was added dropwise to the ice-cold 4-allylveratrole solution from 40 minutes. The mixture was stirred overnight as the ice bath thawed.

A solution of sodium hydroxide (2.49 g, 62.25 mmol, dissolved in 30 mL water) was prepared. To the clear and colorless reaction mixture was added acetone (100 mL), and distilled water (100 mL) followed by the alkaline solution; all additions were made by syringe under an argon balloon. The mixture was slightly turbid. Hydrogen peroxide (50 mL of 30% solution, EMD Scientific) was dispensed into a beaker, then drawn up into a syringe and added dropwise to the stirring reaction mixture. The reaction mixture became turbid during the addition of peroxide solution. The oxidation was determined to be exothermic by observing the temperature of the outer wall of the flask with an infrared thermometer which rose from ambient to 33 °C. The water was wiped from the flask which was transferred to an oil bath (preheated to 65 °C) and fitted with a tall West condenser. The mixture was refluxed from 1.66 h under atmosphere. The mixture was translucent, but upon resting partitioned to afford a clear upper layer. As the reaction mixture stirred above the oil bath, a small amount of manganese dioxide (~50 mg) was added bit by bit to destroy any residual hydrogen peroxide. The decomposition hydrogen peroxide was exothermic, so the reflux condenser was reattached, and the mixture was stirred 40 min. The silicone oil was cleaned from the flask with hexanes, then the reaction mixture was concentrated by rotary evaporation under reduced pressure.

The concentrate was gravity filtered through a pad of Celite 545 filteraid into a 1000 mL separatory funnel. The filter was rinsed heavily with diethyl ether, then ethyl acetate. The filtrate was shaken then allowed to partition. The organic solution was isolated and the lower aqueous solution was extracted with 2 X 100 mL of ethyl acetate. The organic extracts were combined and backwashed with 100 mL of saturated sodium chloride solution in water. The combined organic solution was isolated and dried (sodium sulfate) and concentrated by rotary evaporation under reduced pressure. Upon concentration, the clear colorless light oil had a mass of 18.60 g, or 95% crude yield. The mixture was chromatographed using a Combiflash RF 200, and the major eluate fractions were combined and concentrated by rotary evaporation under reduced pressure to afford 15.84 g (81%) of clear, colorless oil which was characterized as a mixture of primary and secondary alcohol (10 mol%). The

material was used as a mixture of regioisomers since preliminary experiment had indicated a similar reactivity between secondary and primary aliphatic alcohols under the conditions of neat acetoacetylation.

1-(3,4-Dimethoxyphenyl)-2-propanol or 3,4-dimethoxy-α-methylbenzene ethanol could be identified in the ^{1}H NMR spectrum but was not fully resolved while it was clearly resolved in the ^{13}C NMR spectrum.

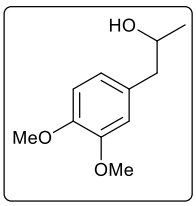
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82-6.67 (m, 3 H), 3.85 (s, 3 H), 3.83 (s, 3 H) 3.65 (t, *J*=6.4 Hz, 2 H), 2.64 (t, *J*=7.7, 2 H), 1.93-1.77 (m, 3 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 147.3, 134.7, 120.3, 111.9, 111.4, 62.3, 56.1, 56.0, 34.5, 32.8

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.83 (d, *J*=8.2 Hz, 1 H), 6.78 (d, *J*= 1.9 Hz, 1 H), 6.68 (dd, *J*= 2.0, 8.1 Hz, 1 Hz), 4.43 (t, *J*=5.1 Hz, 1 H) 3.73 (s, 3 H), 3.70 (s, 3 H) 3.4 (q, *J*=6.0 Hz, 2 H), 2.53 (t, *J*=7.8, 2 H), 1.69 (p, *J*=7.1 3 H)

^{13}C NMR (101 MHz, DMSO-d_6) δ 148.6, 146.8, 134.7, 120.0, 112.3, 111.9, 60.1, 55.5, 55.4, 34.5, 31.2

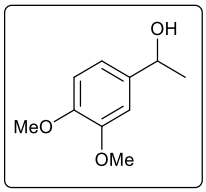
FTIR (ATR) cm^{-1} 3497, 3366, 2935, 1591, 1514, 1258, 1233, 1138, 1025, 807, 763



CAS# 19578-92-8

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 147.9, 131.2, 121.5, 112.7, 111.5, 69.1, 56.1, 56.0, 45.5, 22.85

2.4 1-(3,4-Dimethoxyphenyl)ethan-1-ol or α-methylveratryl alcohol or 1-(3,4-Dimethoxyphenyl)-1-ethanol or 3,4-Dimethoxy-α-methylbenzenemethanol



CAS# 5653-65-6

A 500 mL Erlenmeyer flask was charged with 4-acetylverarole (14.4214 g, 0.0800 mole, 1 molar equivalent) with the aid of a heat gun, and the viscous oil began to crystalize on the inside of the flask upon cooling. Absolute ethanol was added, and the material was noted to fully crystalize (it lost all gooeyness) and resisted dissolution. A large-flat PTFE coated magnetic spinbar was added to the reaction flask and the mixture was stirred for 5 minutes. The solid dissolve except for a few large chunks to afford a clear and colorless solution. Sodium borohydride (0.9820g, 0.02593 mole, 32 mol%), was added as white granular solid without noticeable change. The flask was submerged in a room temperature water bath and stirred under an argon balloon for 17 h.

Silica gel was added to the faintly hazy reaction solution while it stirred in a well-ventilated fume hood. As the silica gel was added, there was noticeable outgassing. When the slurry had stopped effervescing, it was transferred to a 500 mL single neck RBF with the aid of 95% ethanol for concentration. The mixture was adsorbed onto silica gel by rotary evaporation under reduced pressure, then chromatographed by Combiflash: Hex/EtOAc. The very major fractions were combined and concentrated by rotary evaporation under reduced pressure to a constant mass. The mass of the colorless oil which crystallized in the freezer but thawed at room temperature was 13.60 g, 74.62 mmol, 93% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J*=1.9 Hz, 1 H), 6.78 (dd, *J*=8.2, 1.7 Hz, 1 H), 6.73 (d, *J*=8.2 Hz, 1 H), 4.7 (q, *J*=6.4 Hz, 1 H), 3.78 (s, 3 H), 3.77 (s, 3H), 2.68 (s, 1 H), 1.38 (d, *J*=6.5 Hz, 3 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 148.2, 138.7, 114.5, 111.0, 108.7, 69.9, 55.9, 55.8, 25.1

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.93 (d, *J*=1.7 Hz, 1 H), 6.87 (d, *J*=8.2 Hz, 1 H), 6.83 (dd, *J*= 1.7, 8.1 Hz, 1 H), 5.02 (d, *J*=4.2 Hz, 1 H), 4.71-4.59 (m, 1 H), 3.74 (s, 3 H), 3.72 (s, 3 H), 1.30 (d, *J*=6.5 Hz, 3 H)

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.0, 148.0, 140.6, 117.6, 112.0, 109.8, 68.3, 56.1, 55.9, 26.5

FTIR (ATR) cm^{-1} 3518, 2968, 2834, 1593, 1514, 1463, 1416, 1257, 1229, 1138, 1092, 1023, 860, 808, 764

3.0 Acetoacetylation of Lignin Model Compounds

General procedure for acetoacetylation of lignin model compounds:

A 25 mL single neck conical flask was charged with substrate (4 mmol) and t-butyl acetoacetate (4.4 mmol) along with a PTFE coated magnetic spinbar. The flask was fitted with a short path distillation apparatus built from a 75° side arm, Vigruex column (as an extension), a 105° vacuum take off adaptor, and a 100 mL single neck round bottom flask which was submerged in ice to freeze t-butanol in the distillate. The top neck of the 75° side arm was sealed with a red rubber serum septum. Nitrogen was injected into the reaction mixture by modifying a nitrogen line (dried by passage through a column of indicated Drierite) with a disposable polypropylene syringe terminated by a long stainless-steel needle (20 gauge) which was inserted through the septum. The depth of the submerged needle below the surface of the reaction mixture was carefully set to avoid interference with the spinbar. The vacuum take-off was connected to an air-free bubbler. Nitrogen was bubbled through the reaction system as such for 20 minutes at a rate of circa 1 bubble/second.

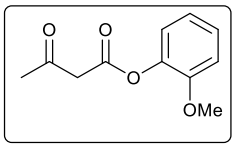
An aliquot (~0.1 g, determined exactly by analytical balance) of the homogenous reaction solution was pulled and dispensed directly into a tared NMR tube (disposable polypropylene syringe and long stem stainless-steel needle: 20 gauge) for the initial (time=0 min) ^{1}H NMR. The stirring reaction mixture was lowered into a preheated (130 °C oil bath) and a stopwatch was started. Note: The reactions were completely thermally equilibrated with the oil bath during the initial 5 minutes. Aliquots were pulled in similar fashion at regular intervals (with the spacing between increasing after the first hour of the reaction) while the mixtures were heated, and t-butanol was collected as white solid in the ice-chilled catch flask.

The aliquot charged NMR tubes were prepared for analysis by addition of ~30 µL of nitromethane (Acros Organics, 99% pure, Lot: A0349318): actual mass determined by change in mass of the charged tube upon an Accuris Analytical Series Balance. To each tube was added roughly 0.6 mL of $CDCl_3$ (Acros Organics, 99.8 atom% D, stabilized with silver foil, Lot A0372356), the tubes were capped and the mixtures were shaken to homogeneity. Initial experiments indicated that there was not a detectable change in a sample's mass during the course of the 3 h of the reaction.

The standard proton experiment (Topspin command: rpar PROTON) was modified slightly (D1 = 20 seconds, number of scans = 8) to establish good agreement between the determined and known concentrations of the time=0 aliquots. As many species as possible were identified and quantified by relation to the internal standard: nitromethane to calculate weight percentages and molalities.

Following 3 h of reaction, the mixtures were allowed to cool and the products were isolated for characterization (^{1}H & ^{13}C NMR, FTIR, HRMS).

3.1 2-Acetoacetoxyanisole



CAS# 5653-65-6

HRMS $C_{11}H_{12}O_4Na$ Calc.: 231.0633, Found: 231.0646

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 1 H), 7.07 (dd, *J*=1.6, 7.8 Hz, 1 H), 7.01-6.93 (m, 2 H), 3.83 (s, 3 H), 3.69 (s, 2 H), 2.39 (s, 3 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 165.33, 151.1, 139.5, 127.4, 122.8, 121.0, 112.6, 55.9, 50.0, 30.1

^{1}H NMR (400 MHz, DMSO d_6) δ 7.25 (td, *J*=1.7, 7.8 Hz, 1 H), 7.14 (dd, *J*=1.4, 8.3 Hz, 1 H), 7.09 (dd, *J*=1.7, 7.9 Hz, 1 H), 6.97 (td, *J*=1.4, 7.6 Hz, 1 H), 3.85 (s, 2 H), 3.77 (s, 3 H), 2.28 (s, 3 H)

^{13}C NMR (101 MHz, DMSO d_6) δ 201.3, 168.9, 151.2, 139.5, 127.7, 123.2, 121.1, 113.4, 56.2, 49.7, 30.4

FTIR (ATR) cm^{-1} 2946, 1760, 1717, 1606, 1500, 1309, 1255, 1196, 1134, 1109, 1042, 1024, 750, 511

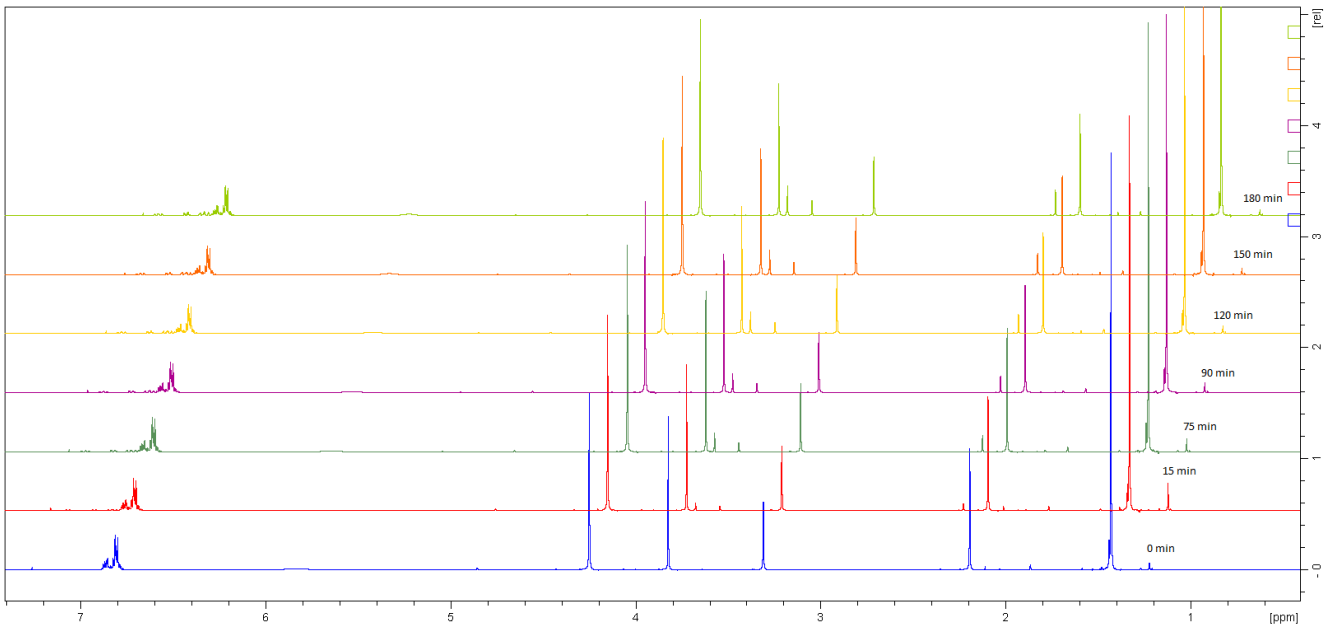


Figure S 1 **2-Aceacetoxyanisole** ^{1}H NMR stacked over time

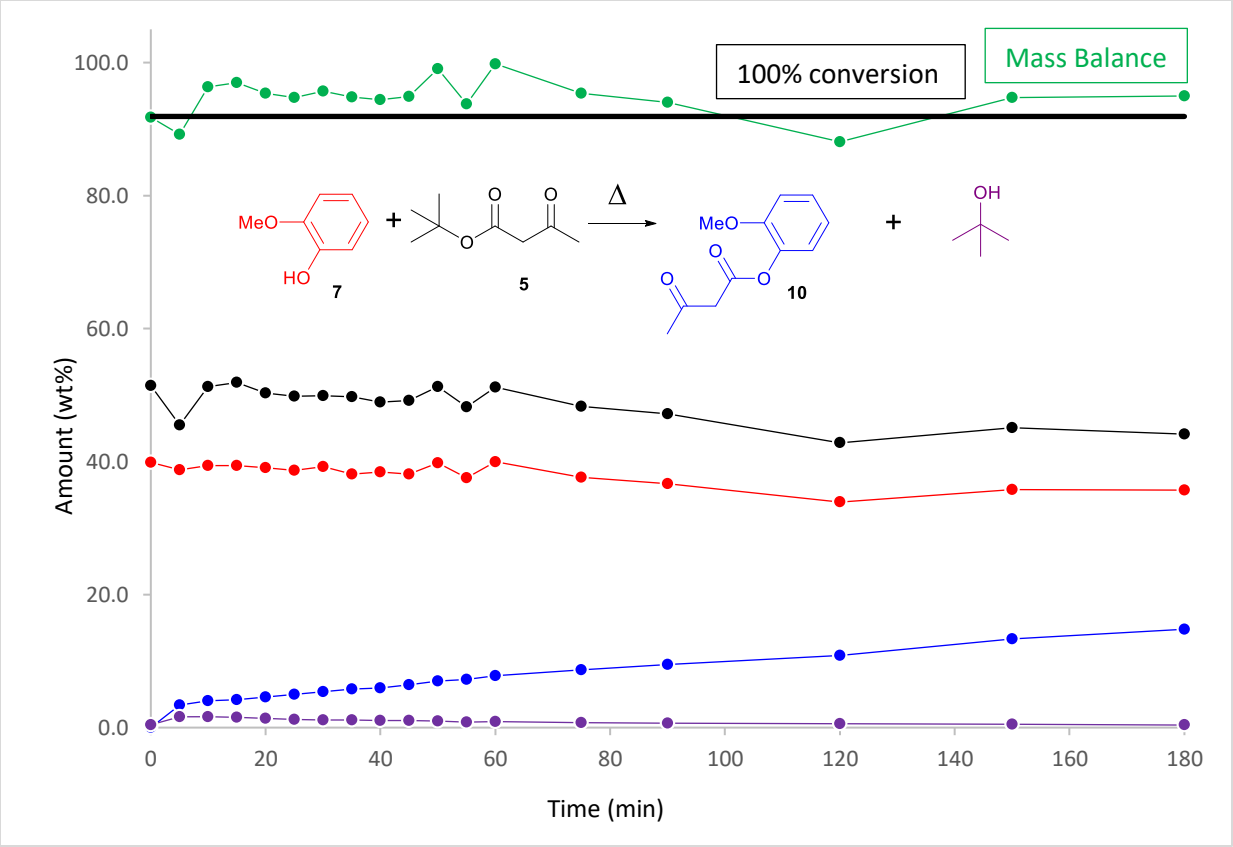


Figure S 2 **Plot of 2-acetoacetoxyanisole reaction cross sections**

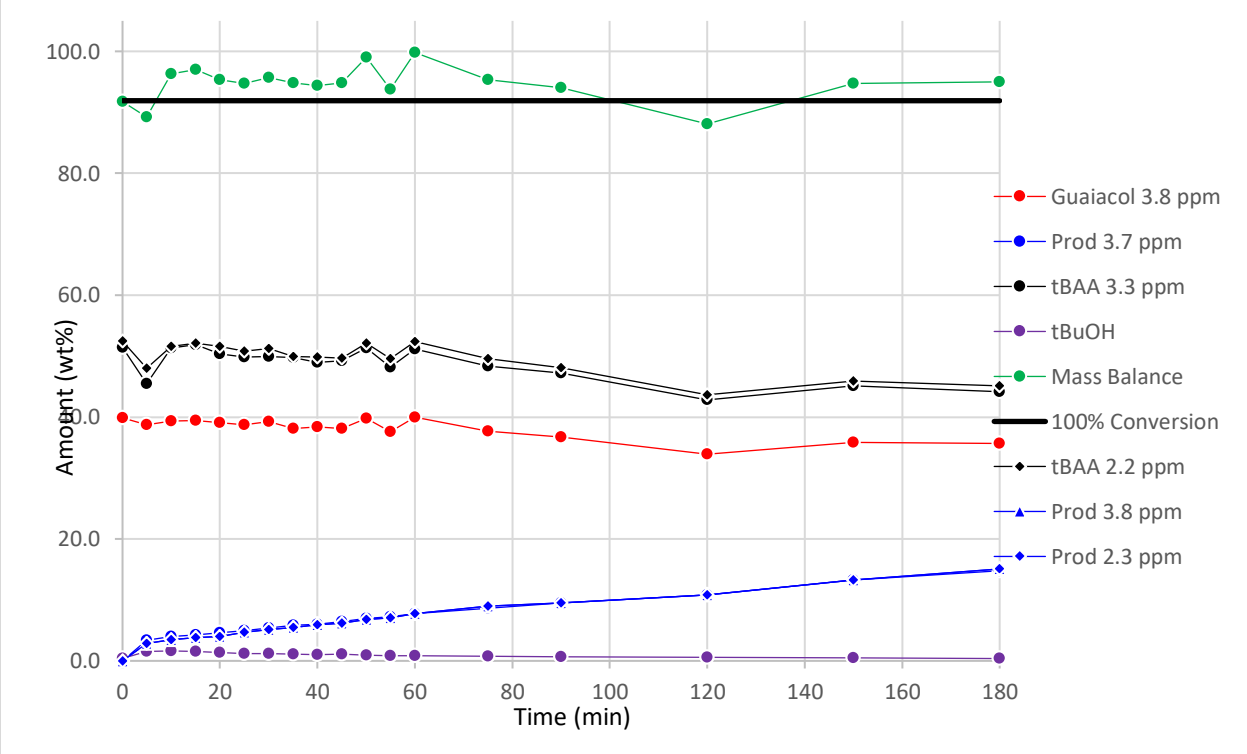
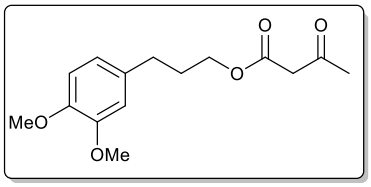


Figure S 3 **Plot of 2-acetoacetoxyanisole reaction cross sections with additional determinations**

3.2 1-Acetoacetoxy-3-(3,4-dimethoxyphenyl)propane or 1-Acetoacetoxy-3-(3,4-dimethoxyphenyl)propane or 3-(3,4-Dimethoxyphenyl)prop-1-yl-acetoacetate



CAS# 100303-78-4

HRMS $C_{15}H_{20}O_5Na$ Calc.: 303.1208, Found: 303.1210

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72, (d, *J*=8.6 Hz, 1 H), 6.72 (d, *J*=8.1 Hz, 1 H), 6.71 (s, 1 H), 4.16 (t, *J=6.7* Hz, 2 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.46 (s, 2 H), 2.63 (t, *J*=7.6 Hz, 2 H), 2.28 (s, 3 H), 2.02-1.91 (m, 2 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 167.3, 149.0, 147.5, 133.7, 120.4, 111.9, 111.4, 64.8, 56.1, 56.0, 50.2, 31.7, 30.4, 30.3

^{1}H NMR (400 MHz, DMSO d_6) δ 6.83 (d, *J*=8.1 Hz, 1 H), 6.79 (d, *J*=2.0 Hz, 1 H), 6.68 (dd, *J*=2.0, 8.0 Hz, 1 H), 4.02 (t, *J*=6.5 Hz, 2 H), 3.72 (s, 3 H), 3.69 (s, 3 H), 3.60 (s, 2 H), 2.55 (d, *J*=7.6 Hz, 2 H), 2.17 (s, 3 H), 1.84 (p, *J*=7.1 Hz, 2 H)

^{13}C NMR (101 MHz, DMSO d_6) δ 202.1, 167.8, 149.1, 147.5, 134.0, 120.5, 112.4, 64.2, 56.0, 55.8, 50.0, 31.3, 30.6, 30.3

FTIR (ATR) cm^{-1} 2939, 1740, 1714, 1515, 1260, 1236, 1154, 1028, 809, 764, 542

Calculated final wt% should be 8.4096 g out of 8.8842 g or 94.6%, but then corrected based on actual starting materials used and we find that the final wt% should be 92%

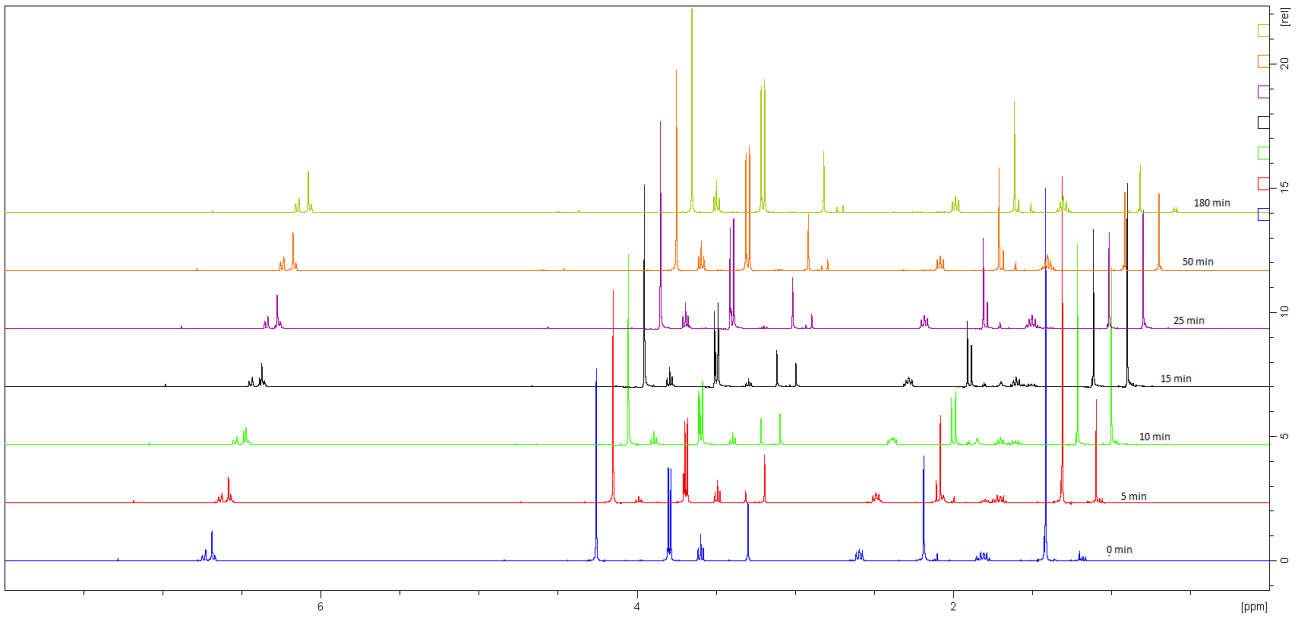


Figure S 4 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: Selected Reaction Cross Sections ($CDCl_3$, ^1H NMR)

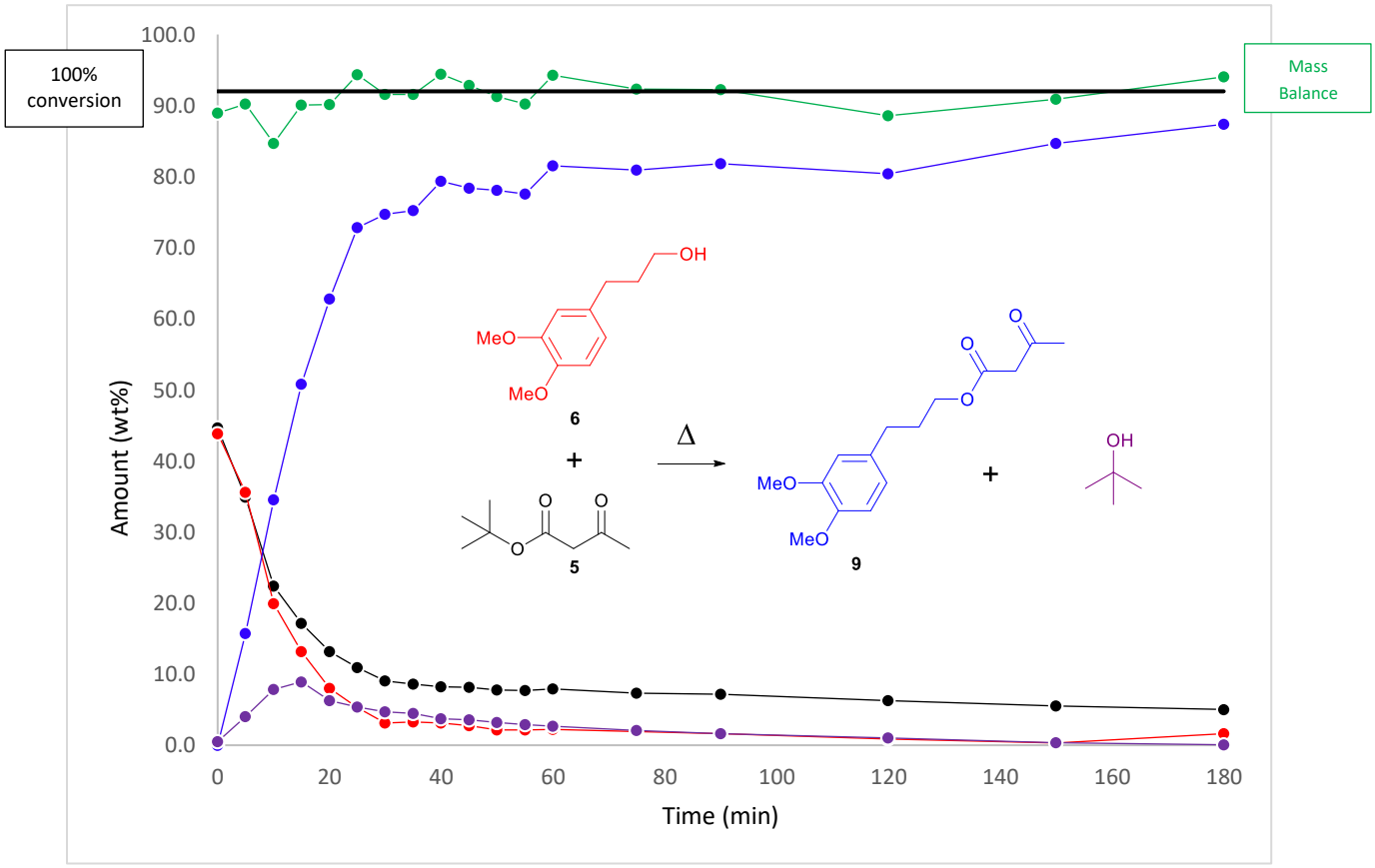
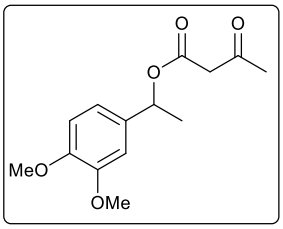


Figure S 5 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**

3.3 1-Acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane



HRMS $C_{14}H_{18}O_5Na$ Calc.: 289.1052, Found: 289.1057

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (dd, *J*= 1.8, 8.2 Hz, 1H), 6.89 (d, *J*=1.9 Hz, 1H), 6.84 (d, *J*=8.2 Hz, 1H), 5.9 (q, *J*=6.6 Hz, 1 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 3.45 (s, 2 H), 2.22 (s, 3 H), 1,56 (d, *J*=6.6 Hz, 1 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 166.4, 149.0, 148.9, 133.4, 118.7, 111.0, 106.6, 73.4, 55.9, 50.4, 30.1, 21.7

^{1}H NMR (400 MHz, DMSO d_6) δ 6.92-6.85 (m, 2 H), 6.94 (d, *J*=1.6 Hz, 1 H), 5.78 (q, *J*=6.6 Hz, 1 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 3.60 (s, 2 H), 2.15 (s, 3 H), 1.46 (d, *J*=6.5 Hz, 3 H)

^{13}C NMR (101 MHz, DMSO d_6) δ 202.0, 167.0, 149.1, 148.9, 134.1, 118.7, 112.0, 110.4, 72.8, 56.0, 55.9, 50.2, 30.6, 22.3

FTIR (ATR) cm^{-1} 2935, 1736, 1712, 1517, 1256, 1233, 1141, 1064, 1024, 806, 765

Final wt% should be 7.988 g out of 8.4626 g or 94.3%

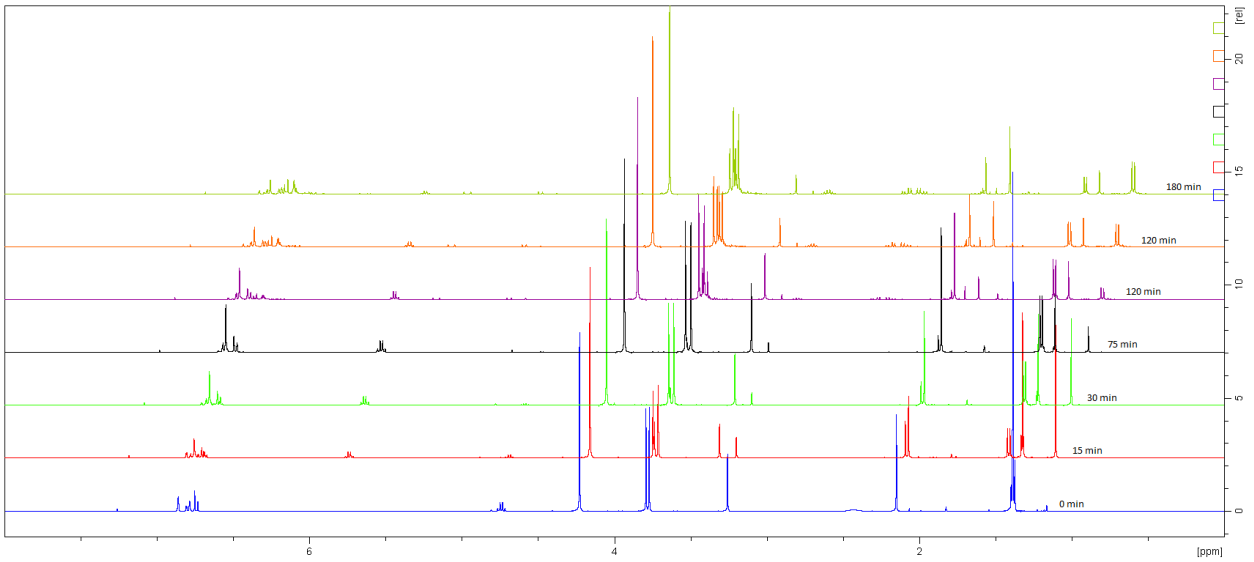


Figure S 6 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol: Stacked ^{1}H NMR Over Time**

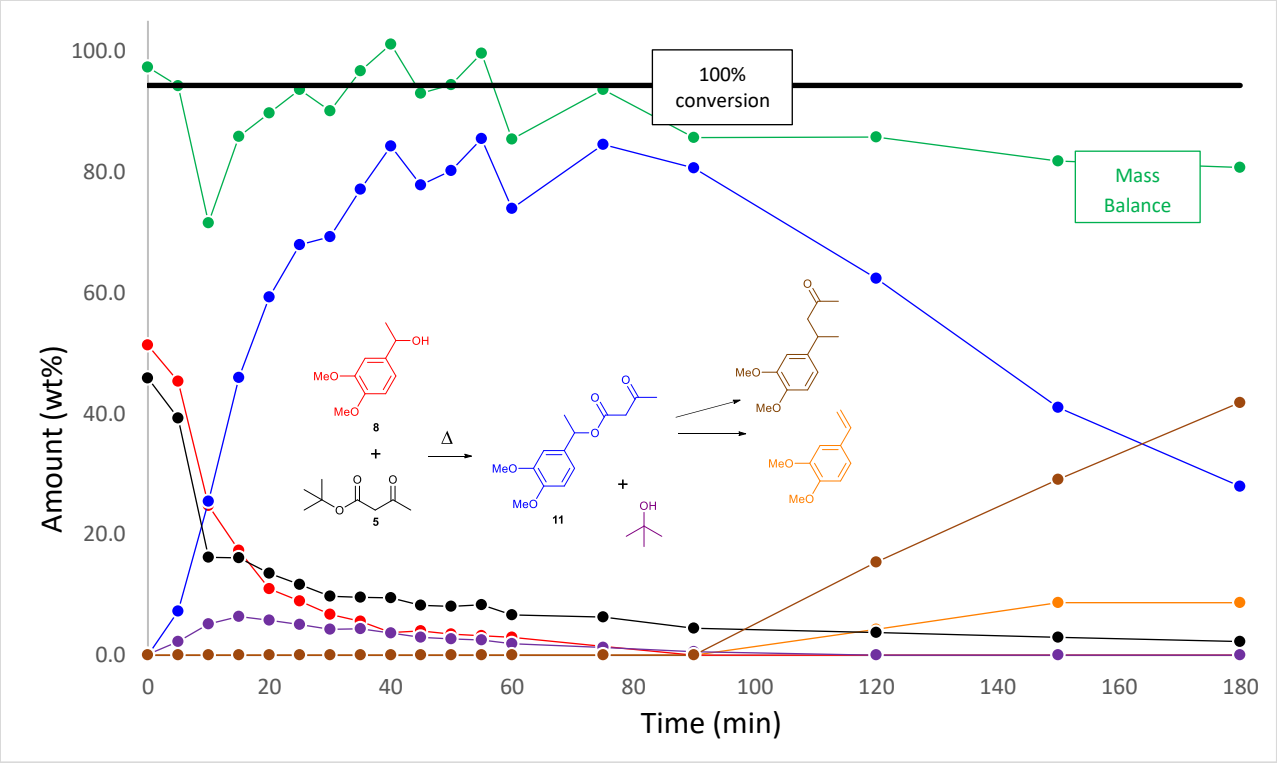


Figure S 7 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**

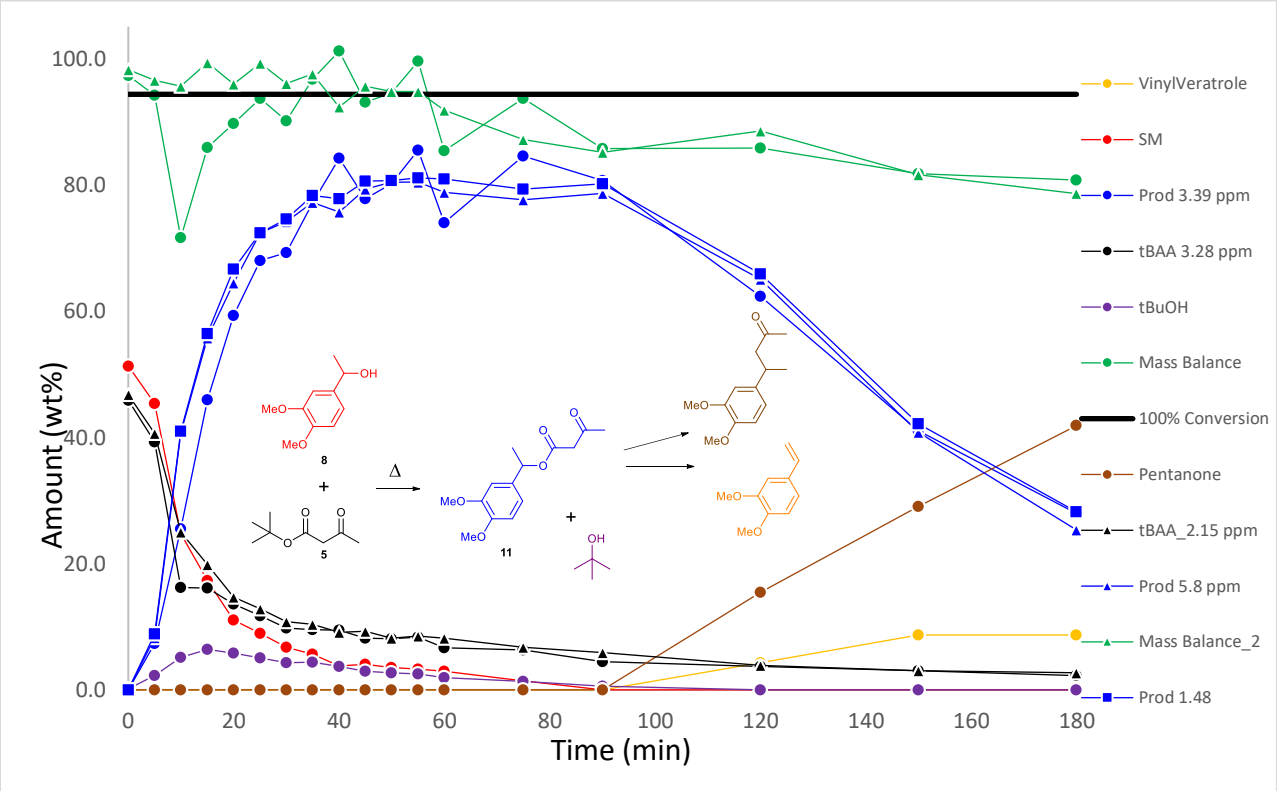
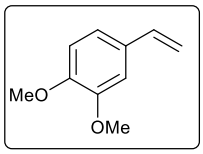


Figure S 8 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol with amount determinations made from multiple peaks**

3.4 4-Vinylveratrole or 1-(3,4-dimethoxyphenyl)ethene or 3,4-dimethoxystyrene



CAS# 6380-23-0

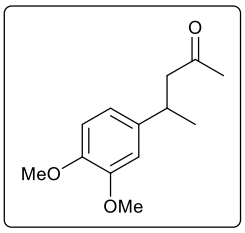
Reportedly prepared and characterized by Chun *et al.* from 4-acetylveratrol by sodium borohydride reduction and acid catalyzed dehydration.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.0-6.90 (m, 2 H), 6.82 (d, *J*=8.2 Hz, 1 H), 6.65 (dd, *J*=10.9, 17.6 Hz, 1 H), 5.61 (dd, *J*=0.8 17.6 Hz, 1 H), 5.15 (dd, *J*=0.7, 10.9 Hz, 1 H), 3.90 (s, 3 H), 3.88 (s, 3 H)

^{1}H NMR (400 MHz, DMSO d_6) δ 7.09 (d, *J*=1.8 Hz, 1 H), 6.96 (dd, *J*=1.9, 8.3 Hz, 1 H), 6.90 (d, *J*=8.2 Hz, 1 H), 6.65 (dd,
J=10.9, 17.6 Hz, 1 H), 5.71 (dd, *J*=1.0, 17.6 Hz, 1 H), 5.13 (dd, *J*=1.0, 10.9 Hz, 1 H) 3.78 (s, 3 H), 3.75 (s, 3 H)

^{13}C NMR (101 MHz, DMSO d_6) δ 149.4, 149.3, 137.0, 130.6, 119.8, 112.36, 112.1, 109.5, 55.92, 55.89

3.5 4-(3,4-Dimethoxyphenyl)-pentan-2-one or 4-(3,4-Dimethoxyphenyl)-2-pentanone



CAS# 1017130-45-8

HRMS $C_{13}H_{18}O_3Na$ Calc.: 245.1154, found: 245.1164

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, *J*=8.0 Hz, 1 H), 6.77-6.72 (m, 2 H), 3.88 (s, 3 H), 3.85 (s, 3 H), 3.26 (h, *J*=7.04 Hz, 1 H), 2.73 (dd, J=6.6, 16.1 Hz, 1 H), 2.63 (dd, *J*=7.8, 16.1 Hz, 1 H), 2.06 (s, 1 H), 1.25 (d, *J=7.0 Hz*, 1 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 1149.0, 147.6, 139.0, 118.5, 111.4, 110.5, 56.03, 56.00, 52.4, 35.3, 30.8, 22.3

^{1}H NMR (400 MHz, DMSO d6) δ 6.84-6.81 (m, 2H), 6.73 (dd, *J*=8.2,2.1 Hz, 1 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 3.14 (h, *J*=7.0 Hz, 1 H), 2.71 (dd, *J*=7.0, 14.2 Hz, 1 H), 2.69 (dd, *J*=7.0, 14.5 Hz, 1 H), 2.03 (s, 3 H), 1.15 (d, *J*=6.9 Hz, 3 H)

^{13}C NMR (101 MHz, DMSO d6) δ 208.0, 149.1, 147.6, 139.4, 118.8, 112.3, 111.32, 56.0, 55.9, 51.5, 34.9, 30.6, 22.7

FTIR (ATR) cm^{-1} 2960, 1713, 1518, 1464, 1419, 1361, 1261, 1142, 1028, 809, 765

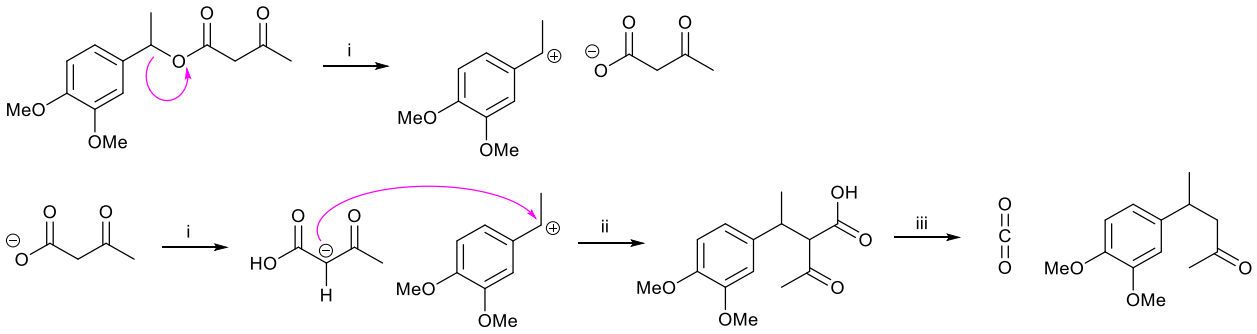


Figure S 9 **Proposed Mechanism for Generation of 4-(3,4-Dimethoxyphenyl)-pentan-2-one from 1-acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane**

3.6 Additional side products of benzylic alcohol acetoacetylation

Sample: 0919680528 | Rf 200 : NDSU | Friday 26 January 2018 12:10AM

RediSep Column: Silica 80g
Flow Rate: 60 ml/min
Equilibration Volume: 2.0 CV
Initial Waste: 0.0 CV
Air Purge: 0.0 min
Solvent: A1 hexane
Solvent: B1 ethyl acetate

Peak Tube Volume: Max.
Non-Peak Tube Volume: Max.
Loading Type: Solid
Wavelength 1 (red): 254nm
Peak Width: 2 min
Threshold: 0.02 AU
Wavelength 2 (purple): 280nm
Peak Width: 2 min
Threshold: 0.02 AU

Run Notes:

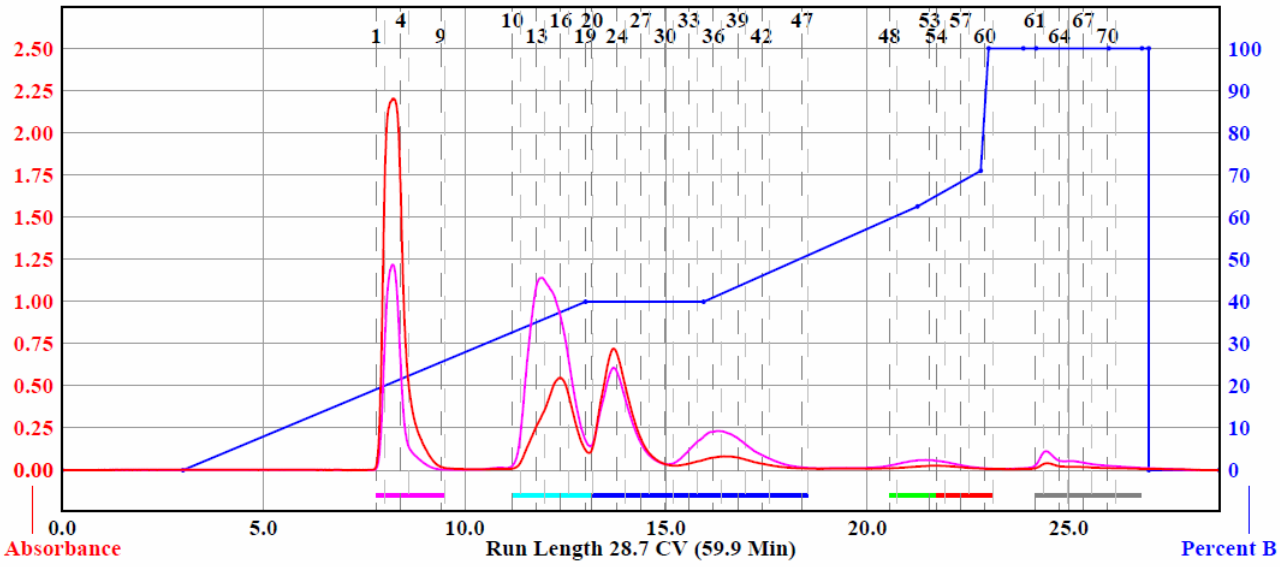


Figure S 10 **Flash chromatogram of additional degradations products observed in the preparation of1-acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane**

Fractions 1-9: 4-vinylveratrole

Fractions 10-18: 4-(3,4-dimethoxyphenyl)-2-pentanone

Fractions 20-27: 1-acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane

Fractions 31-47: Other products from the degradation and recombination of 1-acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane

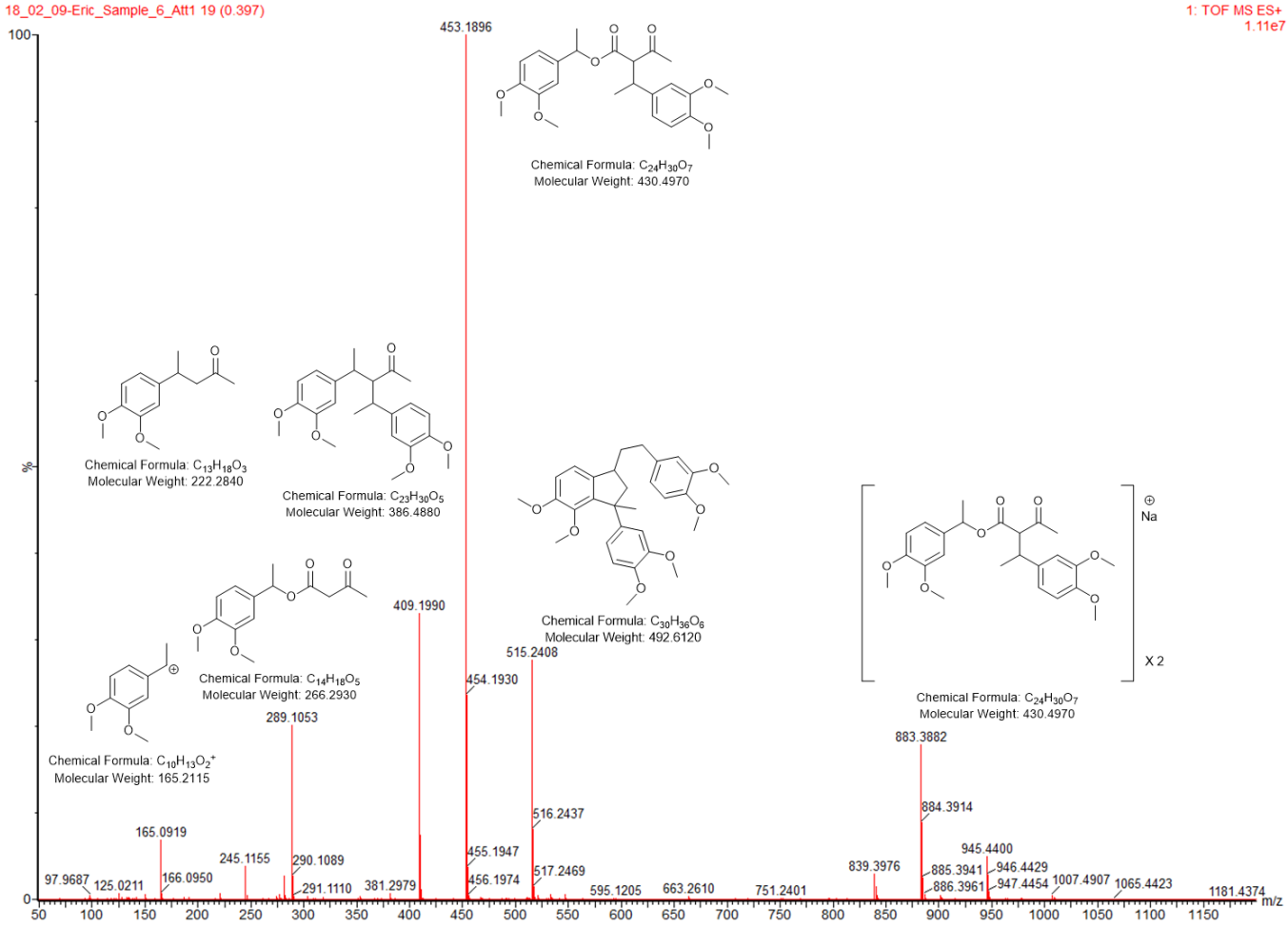


Figure S 11 **HRMS of additional degradations products observed during the preparation of 1-acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane**

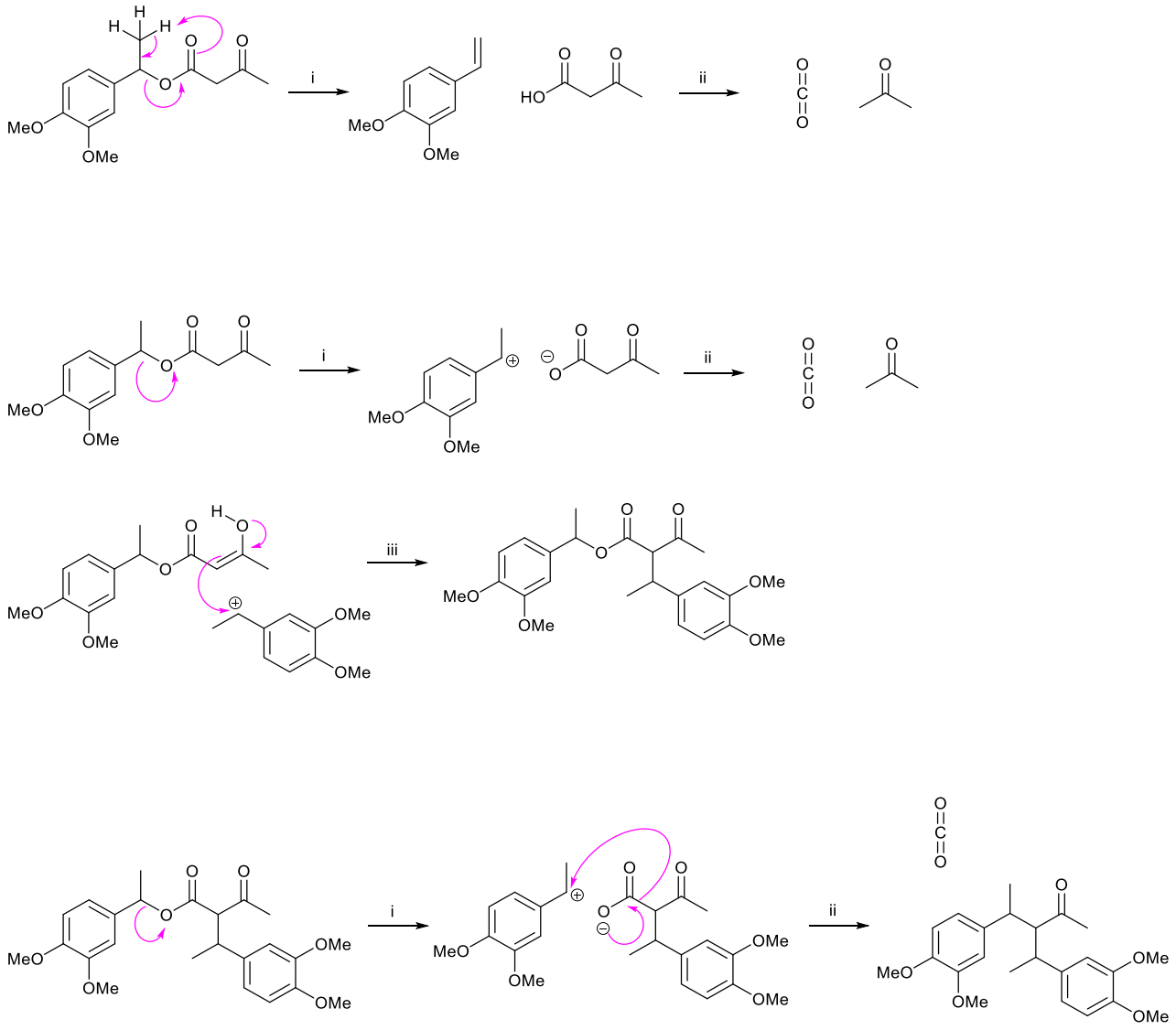


Figure S 12 **Proposed Mechanism for the Degradation of 1-acetoacetoxy-1(3,4-dimethoxyphenyl)ethane into Ketones**

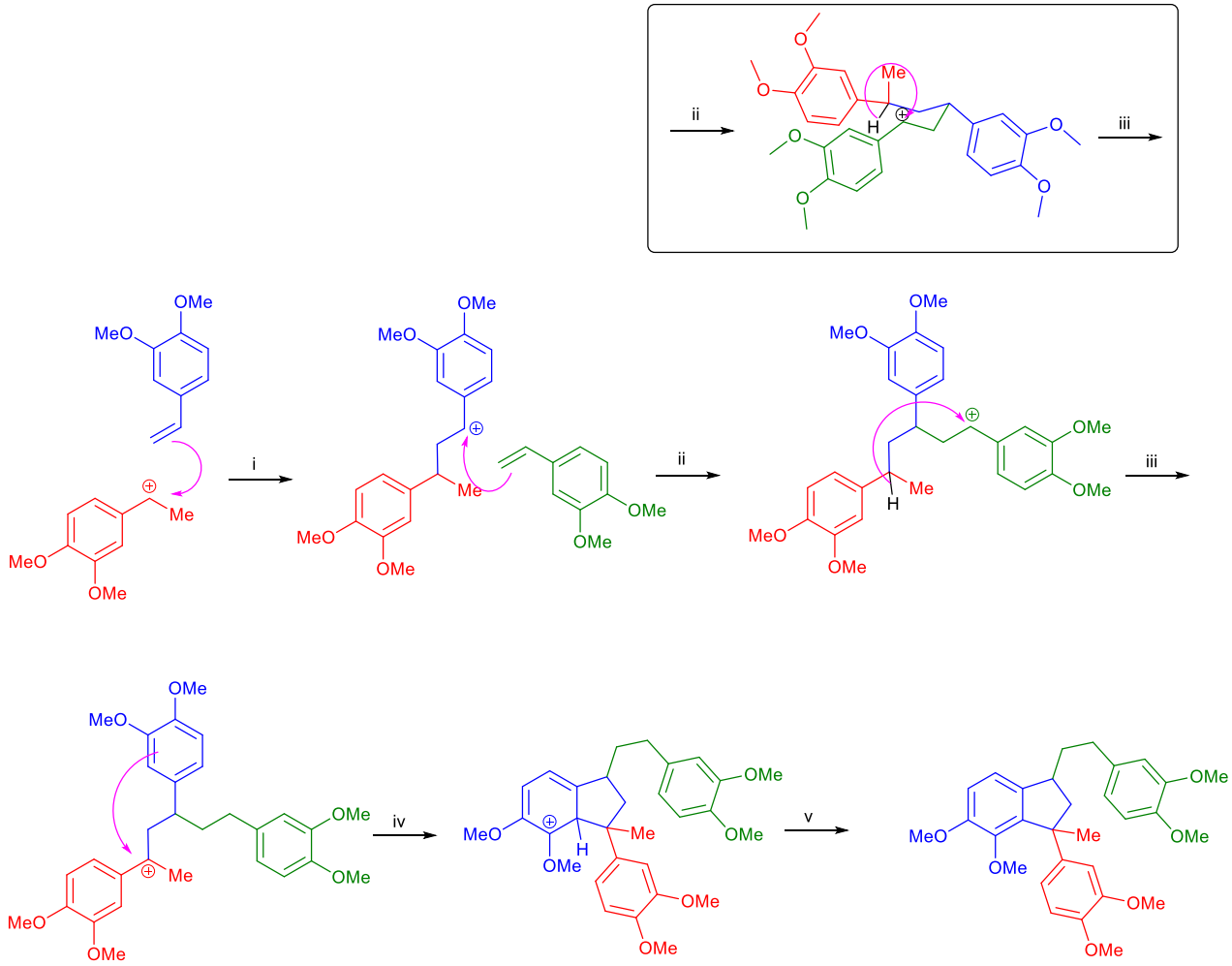
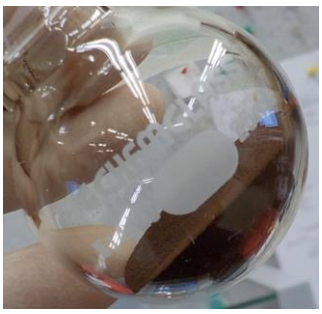
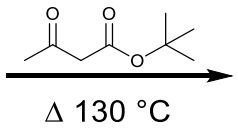


Figure S 13 **Proposed Mechanism for the Generation of 4-Vinylveratrole Trimers**

4.0 Acetoacetylation of (Indulin AT) Kraft Lignin





A 25 mL single neck round bottom flask (14/20) was charged with Kraft lignin (indulin AT, provided by by Ingevity (formerly MeadWestvaco) 2.5004 g), 1,4-dioxane (Sigma-Aldrich, >99%, 7.5 g), and t-butyl acetoacetate (provided by Eastman Chemical Company, 2.454 g). To the flask was added a magnetic spinbar. The flask was fitted beneath a short path distillation apparatus. The reaction was heated in a 130 °C oil bath with nitrogen sparging through the dark reaction mixture. Several aliquots were collected during the reaction mixture for analysis by ^{1}H There was significant difficulty encountered in removing aliquots during the acetoacetylation reaction as the dioxane was removed by distillation and the viscosity of the black liquid resin increased. The reaction was aged open in a well-ventilated fume hood for 6 weeks.

A portion of the vitreous black residue (1.4897 g) was chipped out of the flask and triturated with isopropyl alcohol. A fine tan solid was isolated by suction filtration and vacuum drying to afford a free flowing brown solid (1.1690 g). The amount of acetoacetylation was determined to be 2.05 *m*, as described in the manuscript with the spectral data found in Fig. S21

$$molality_{OAcAc} = m_{OAcAc} = \frac{OAcAc_{mole}}{modified\ lignin_{kg}} =$$

$$\frac{\left(\frac{mass_{NO_2Me(g)}}{molar\ mass_{\frac{NO_2Me(g)}{NO_2Me(mole)}}}\right)_{NO_2Me(mole)} \times \left(\frac{OAcOAc_{integration}}{NO_2Me_{integration}}\right)_{\frac{OAcOAc_{mole}}{NO_2Me_{mole}}}}{\left(\frac{sample\ mass_g}{1000\ \frac{g}{kg}}\right)} =$$

$$\frac{\left(\frac{0.0152_{NO_2Me(g)}}{61.04_{\frac{NO_2Me(g)}{NO_2Me(mole)}}}\right)_{NO_2Me(mole)} \times \left(\frac{3.00}{(9.37-0.89)}\right)_{\frac{OAcOAc_{mole}}{NO_2Me_{mole}}}}{\left(\frac{0.0428_g}{1000\ \frac{g}{kg}}\right)} = 2.05\ _{\frac{OAcAc_{mole}}{modified\ lignin_{kg}}}$$

5.0 Equations

The following equation was used to determine the masses of reaction components during the reaction cross sectioning based on: (1) mass of standard, (2) mass of aliquot and (3)relative integration values of the standard compared with individual peaks absolutely assigned to the reaction components.

Equation 1

$$reaction\ component(g) = \frac{reaction\ component\ \left(\frac{g}{mol}\right) \times standard\ (g)}{standard\left(\frac{g}{mol}\right)} \times \left(\frac{\left(\frac{reaction\ component(integration)}{number\ of\ protons\ per\ molecule\ of\ reaction\ compoent}\right)}{\left(\frac{standard(integration)}{number\ of\ protons\ per\ molecule\ of\ standard}\right)} \right)$$

Equation 2

$$amount\ of\ reaction\ component\ (wt.\%) = \frac{reaction\ component(g)}{aliquot\ (g)}$$

6.0 References

1. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.
2. T. R. Hoye and H. Zhao, *J. Org. Chem.*, 2002, **67**, 4014-4016.
3. C. Mi, X.-G. Meng, X.-H. Liao and X. Peng, *RSC Adv.*, 2015, **5**, 69487-69492.

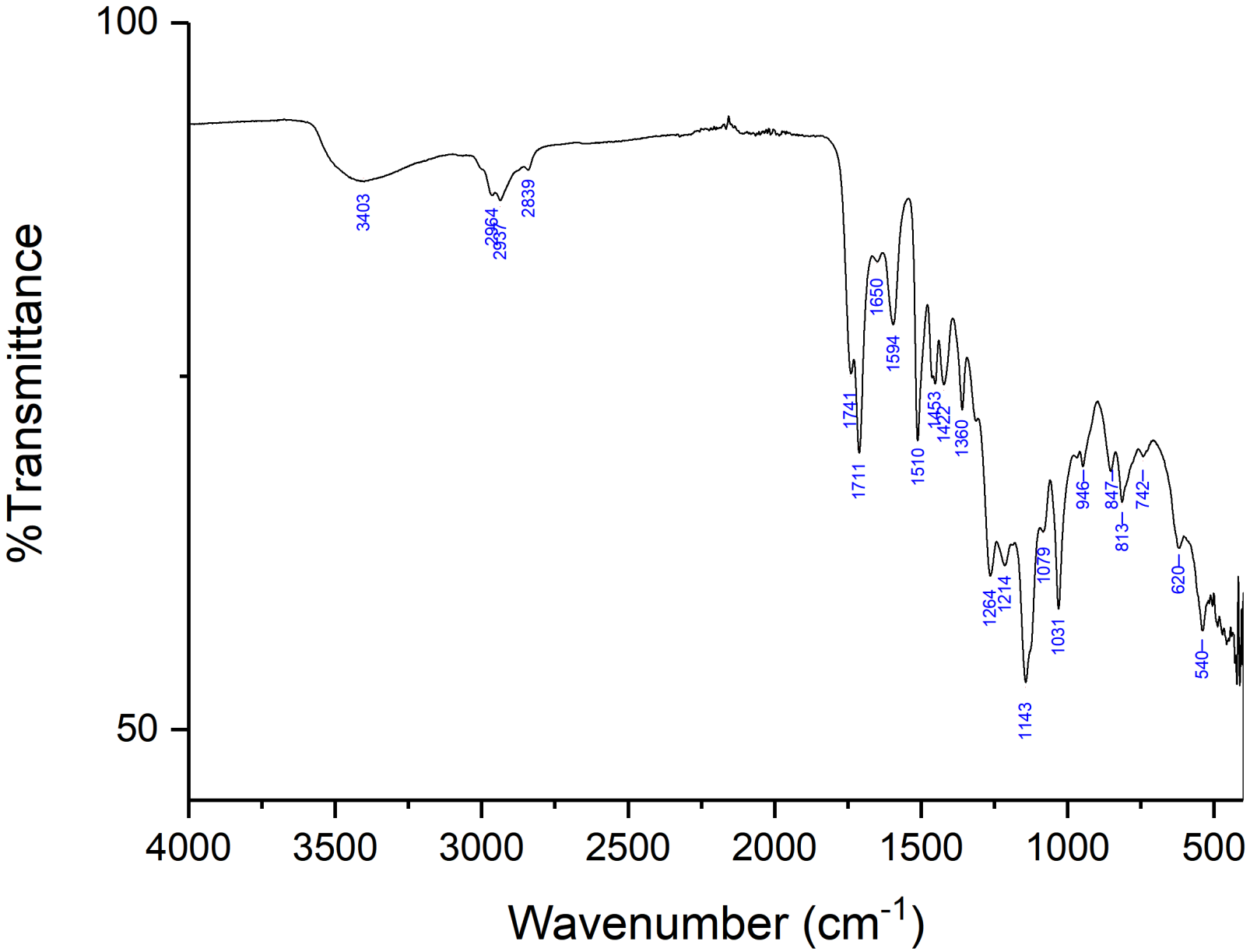


Figure S 14 **Acetoacetylated (Indulin AT) Kraft Lignin (washed with IPA and vacuum dried)** FTIR (ATR, powder)

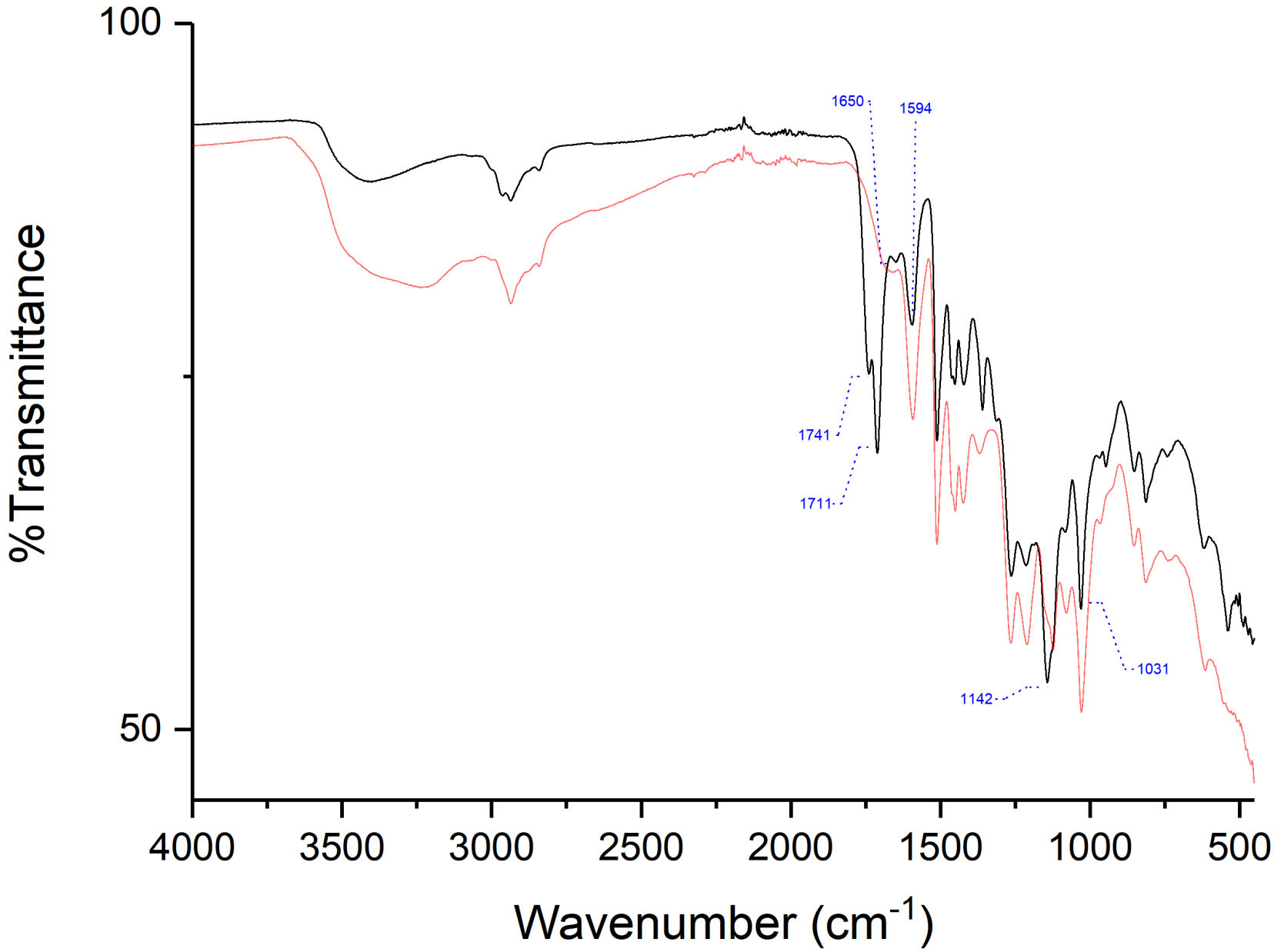


Figure S 15 **Acetoacetylated (Indulin AT) Kraft Lignin (washed with IPA and vacuum dried):** **Acetoacetylated (Indulin AT) Kraft Lignin** FTIR (ATR, powder)

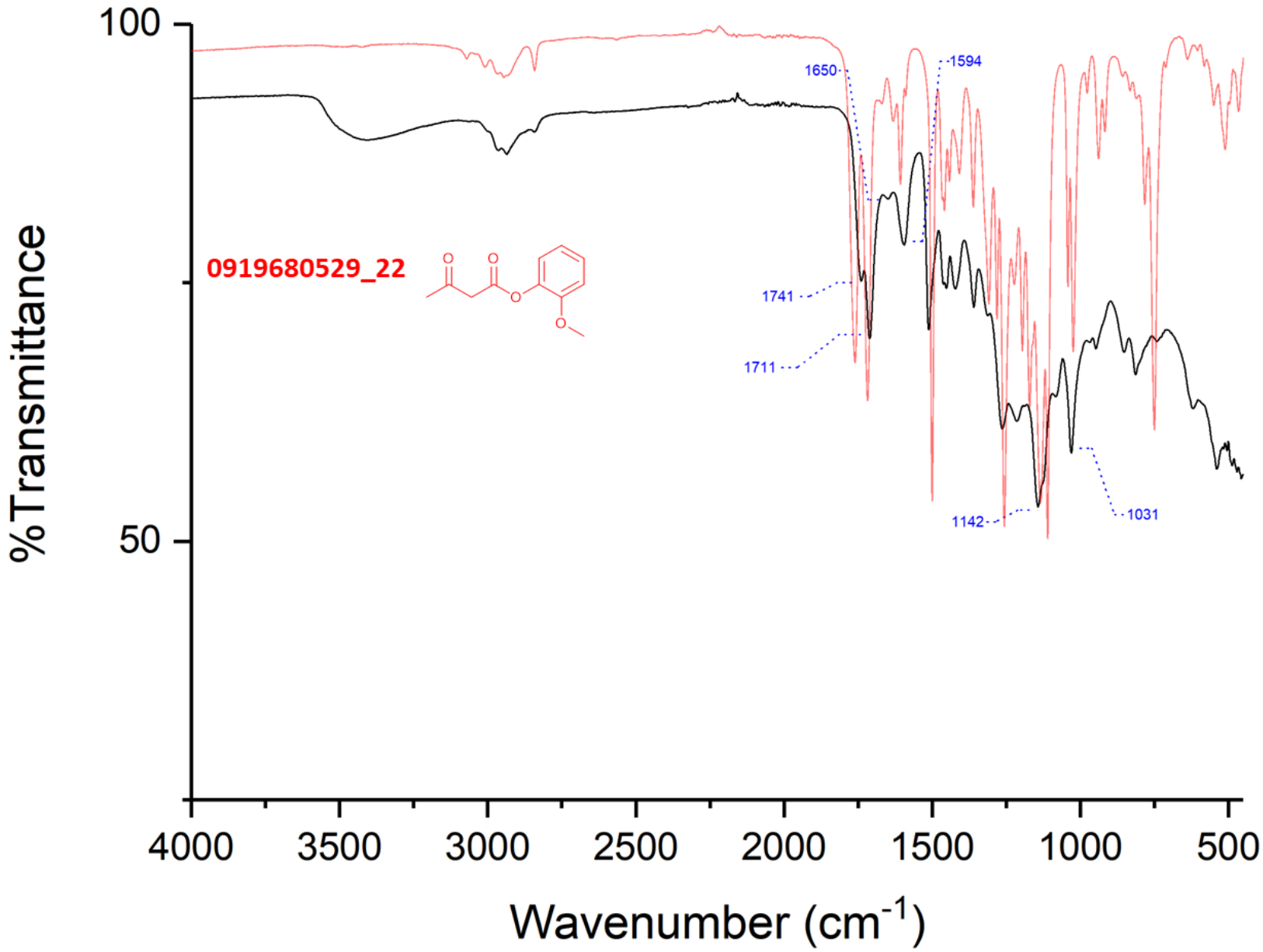


Figure S 16 **Acetoacetylated (Indulin AT) Kraft Lignin (Washed with IPA and Vacuum Dried) Overlaid with 2-Acetoacetoxyanosole** FTIR (ATR)

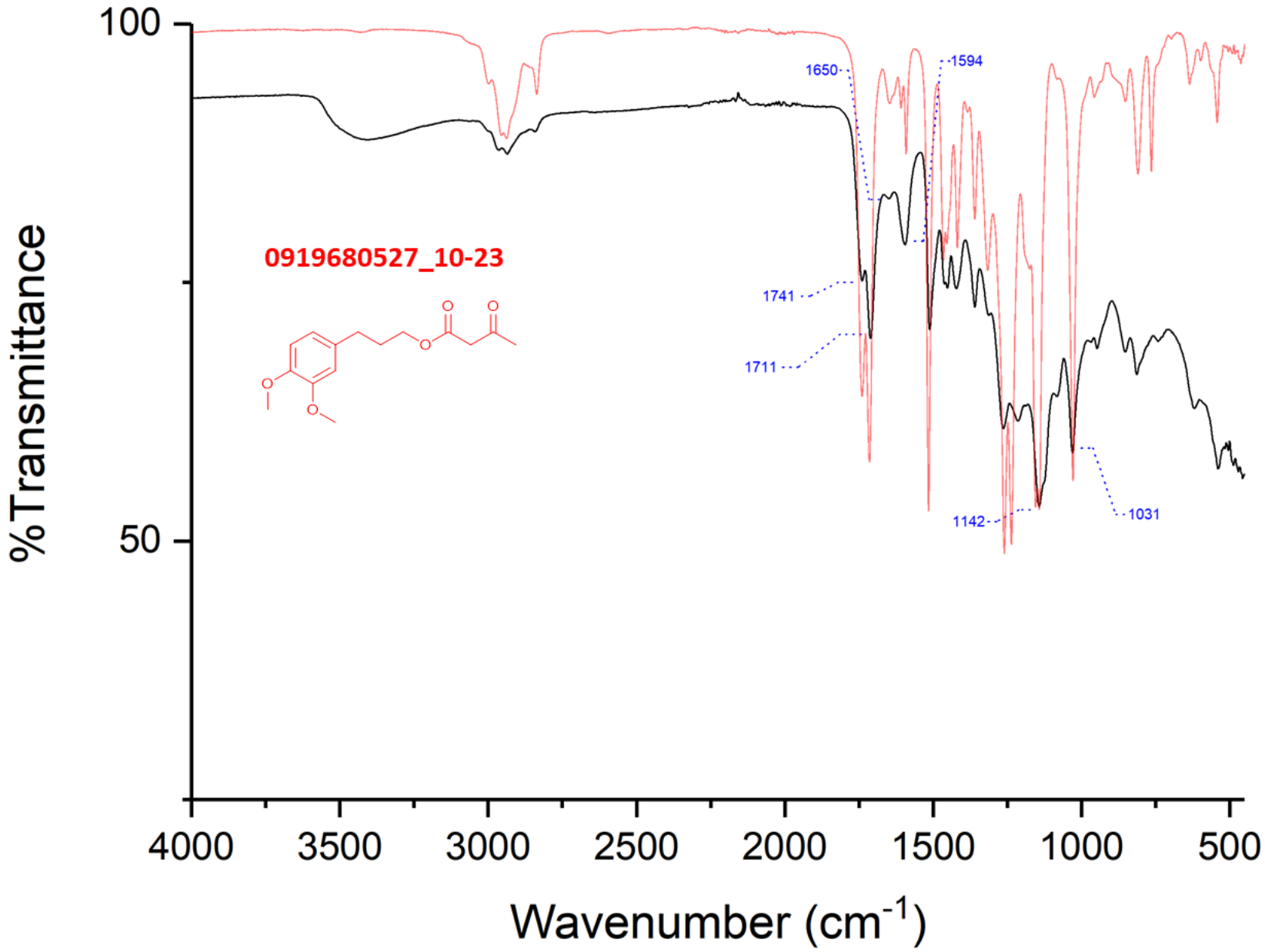


Figure S 17 **Acetoacetylated (Indulin AT) Kraft Lignin (Washed with IPA and Vacuum Dried) Overlaid with 1-Acetoacetoxy-3-(3,4-dimethoxyphenyl)propane** FTIR (ATR)

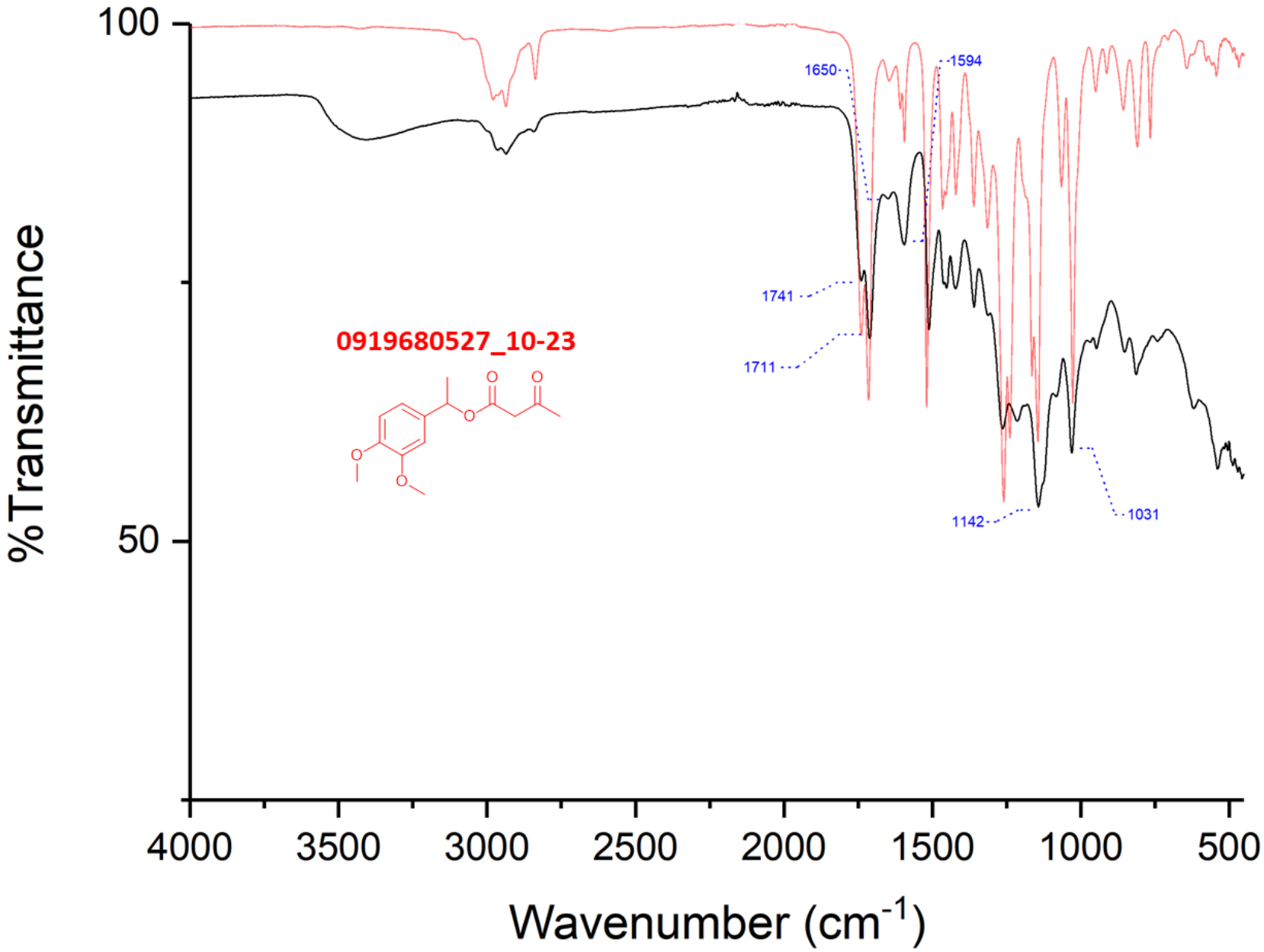


Figure S 18 **Acetoacetylated (Indulin AT) Kraft Lignin (Washed with IPA and Vacuum Dried) Overlaid with 1-Acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane** FTIR (ATR)

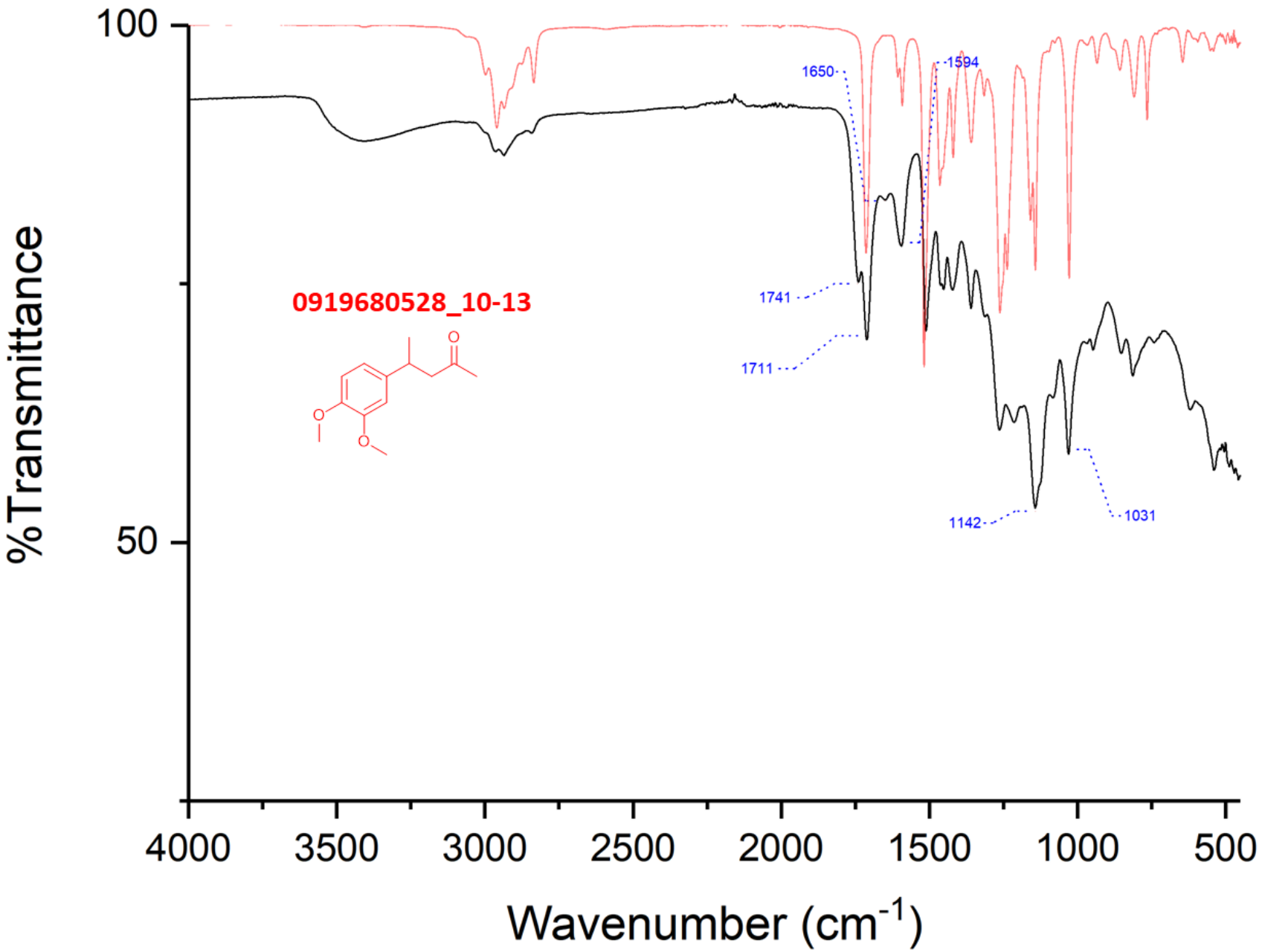


Figure S 19 **Acetoacetylated (Indulin AT) Kraft Lignin (Washed with IPA and Vacuum Dried) Overlaid with Degradation Product** FTIR (ATR)

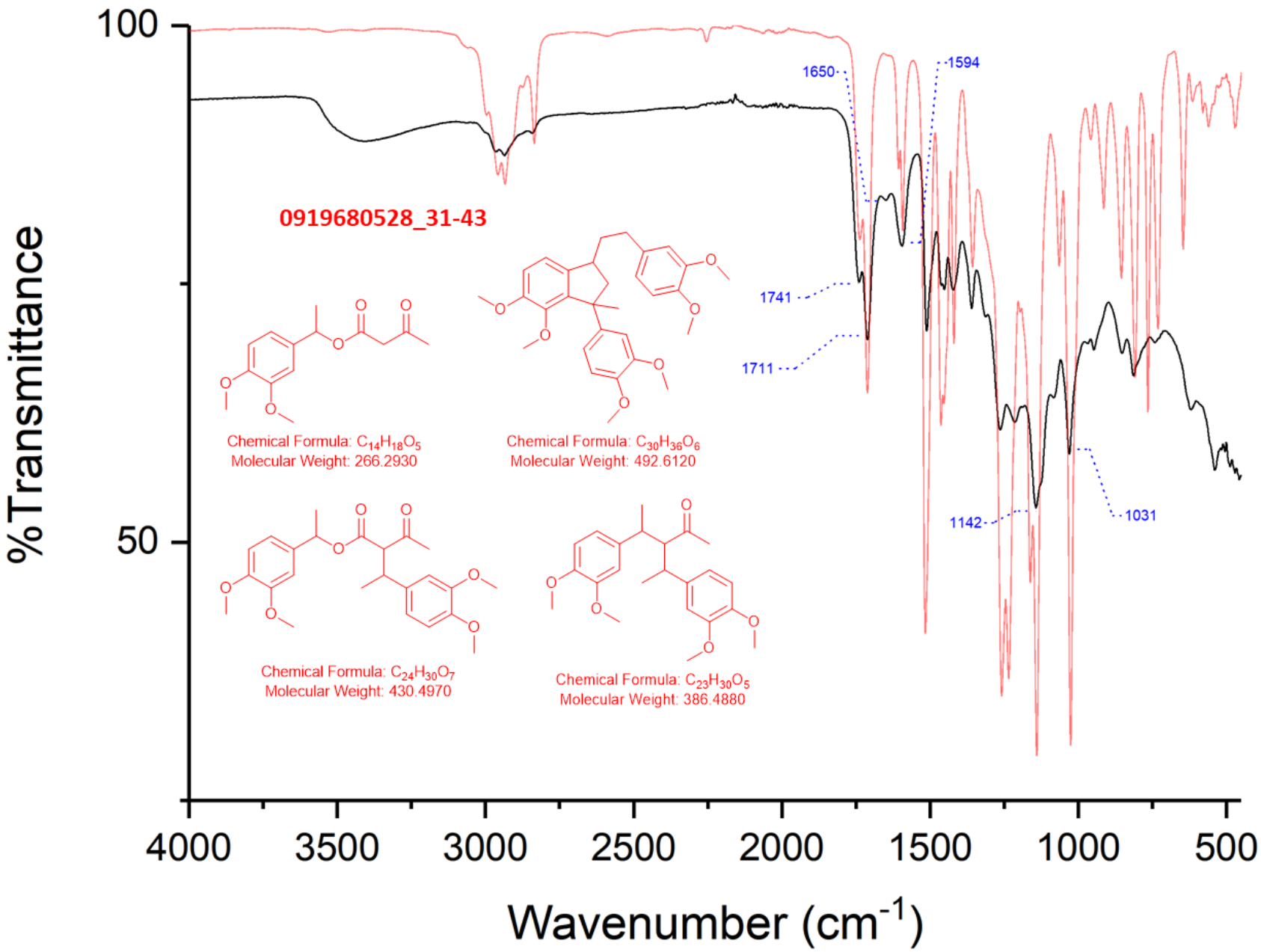


Figure S 20 **Acetoacetylated (Indulin AT) Kraft Lignin (Washed with IPA and Vacuum Dried) Overlaid with Degradation Products** FTIR (ATR)

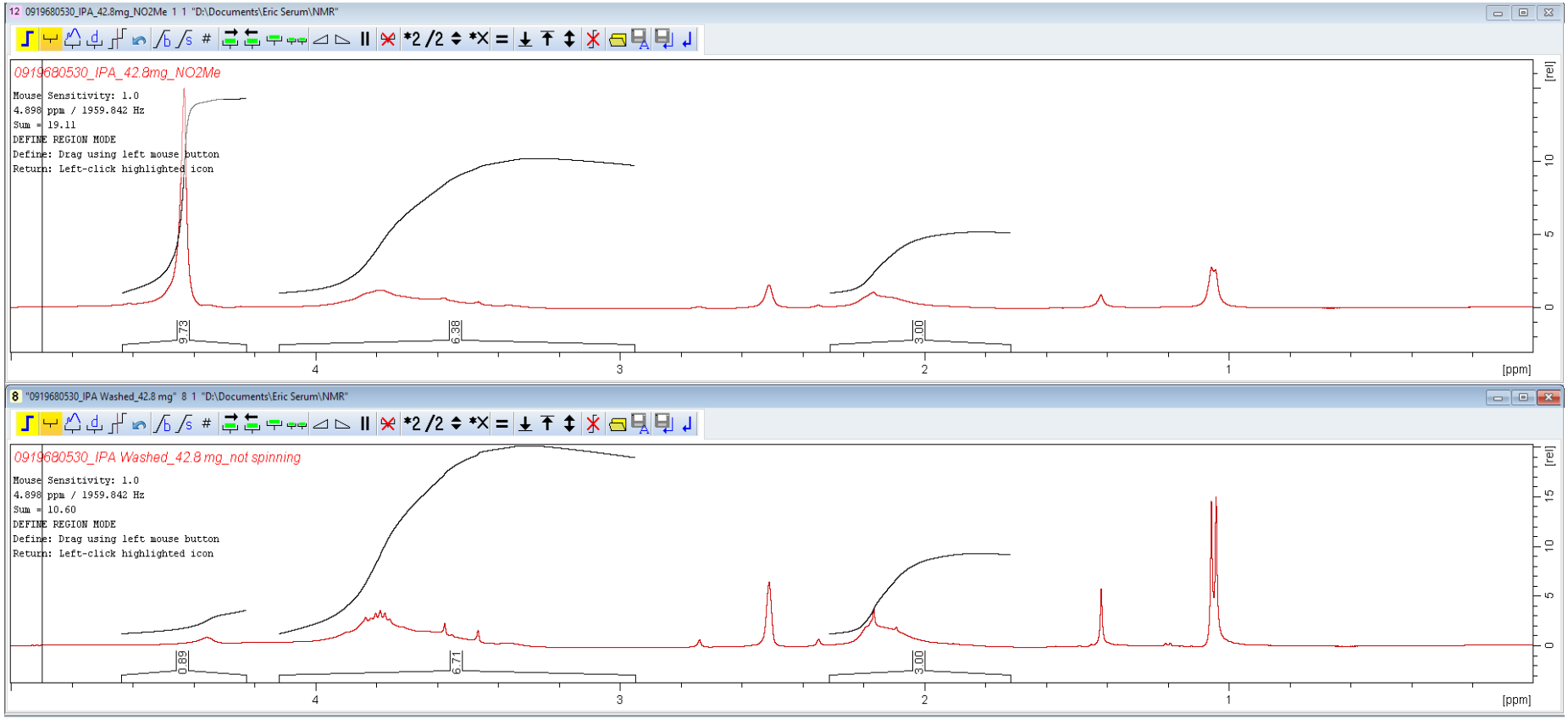


Figure S 21 **Quantification of Acetoacetylated lignin (DMSO d6, nitromethane standard)**

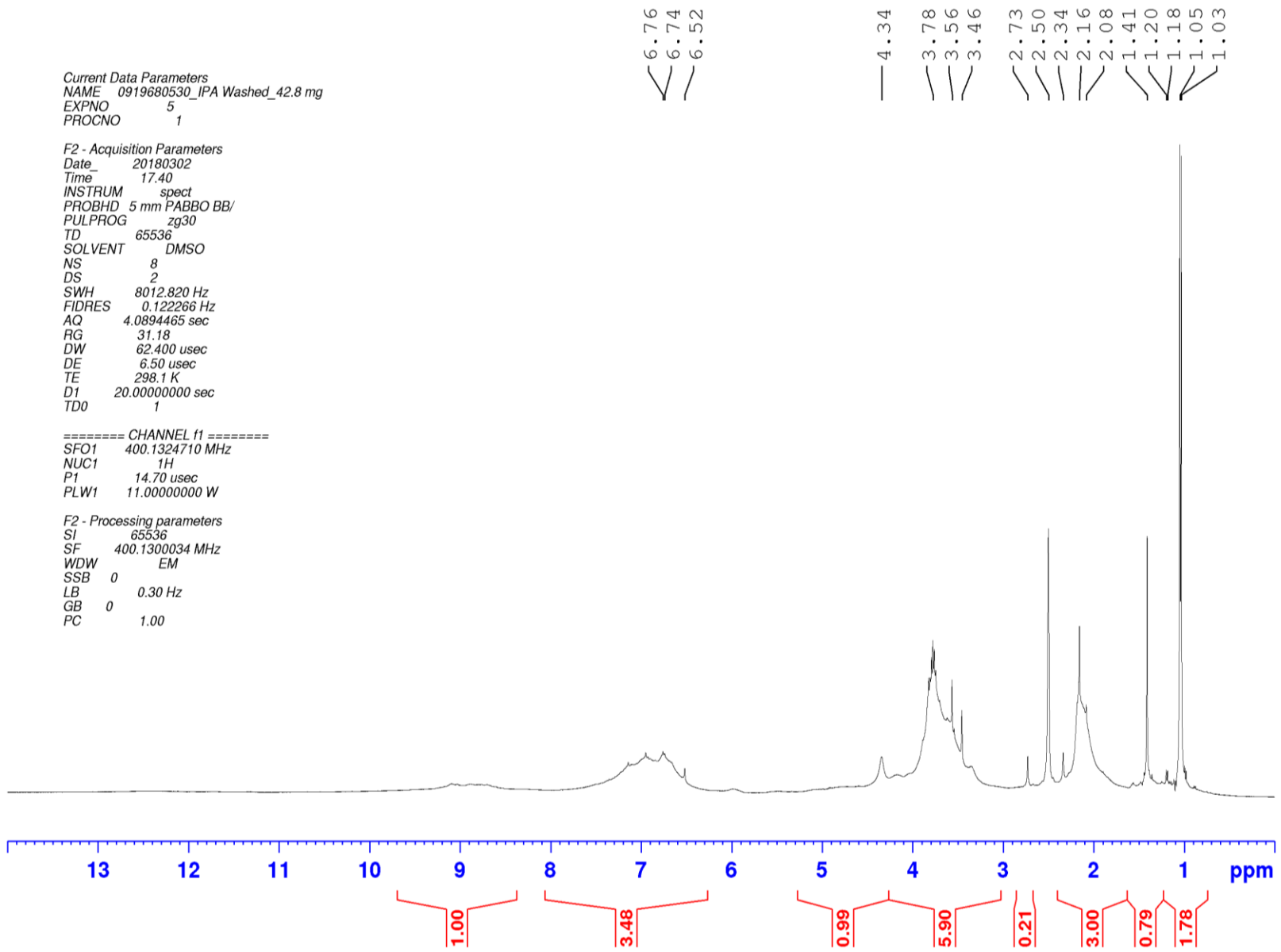


Figure S 22 **Acetoacetylated (Indulin AT) Kraft Lignin (Washed with IPA and Vacuum Dried)** ^{1}H NMR (DMSO-d_6)

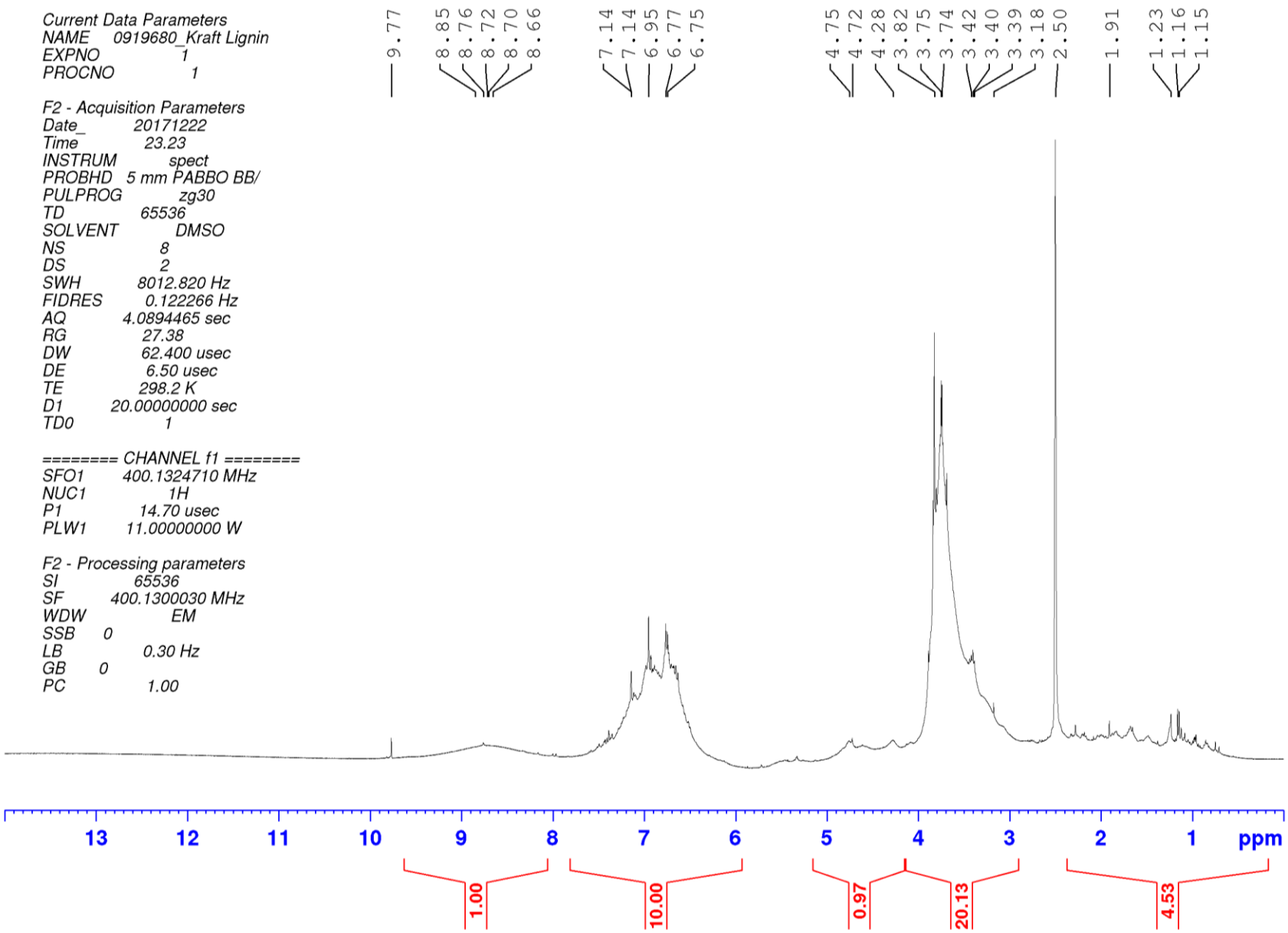


Figure S 23 **(Indulin AT) Kraft Lignin** ^{1}H NMR (DMSO-d_6)

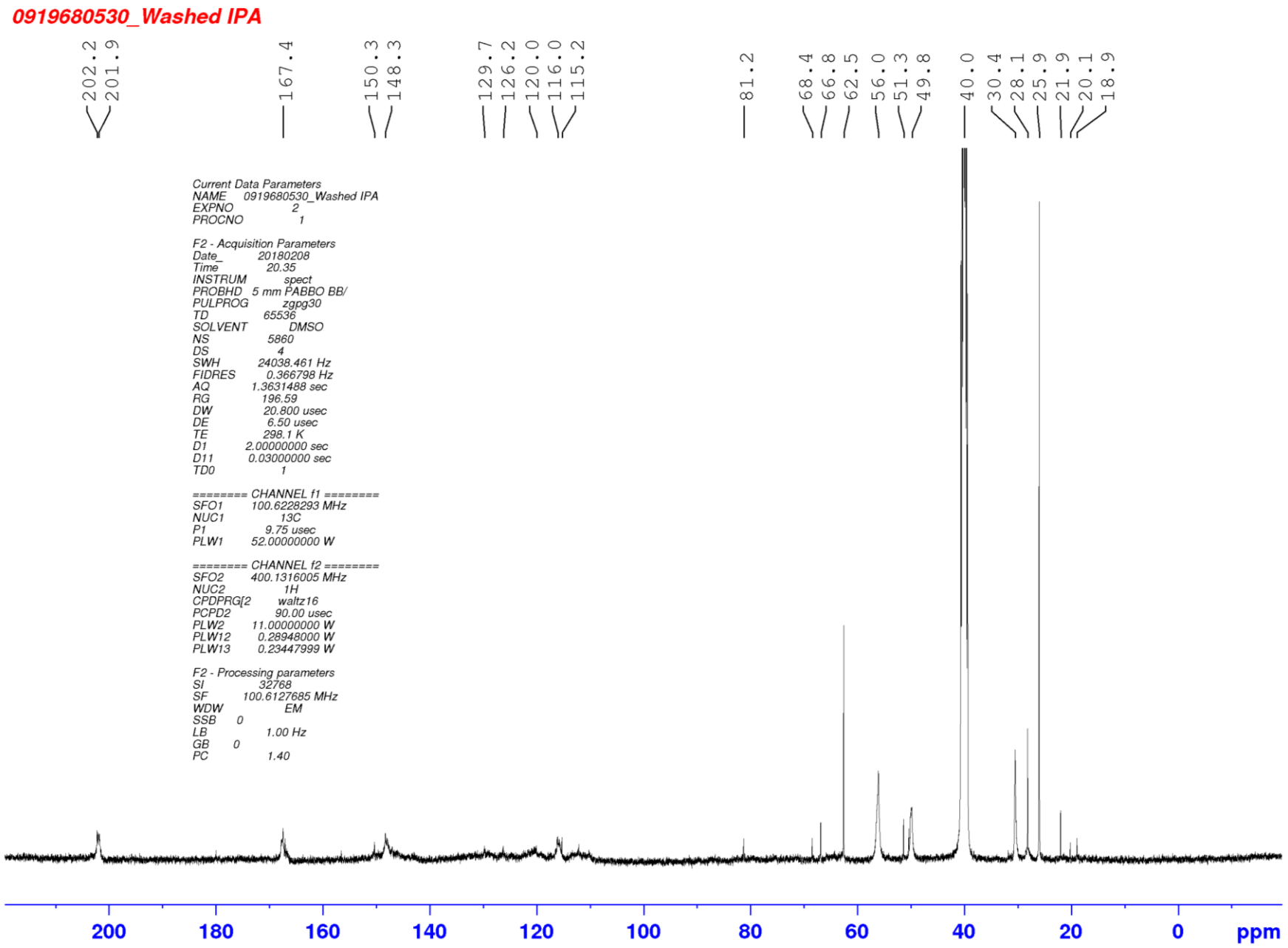


Figure S 24 **Acetoacetylated (Indulin AT) Kraft Lignin (Washed with IPA and Vacuum Dried)** ^{13}C NMR (DMSO-d_6)

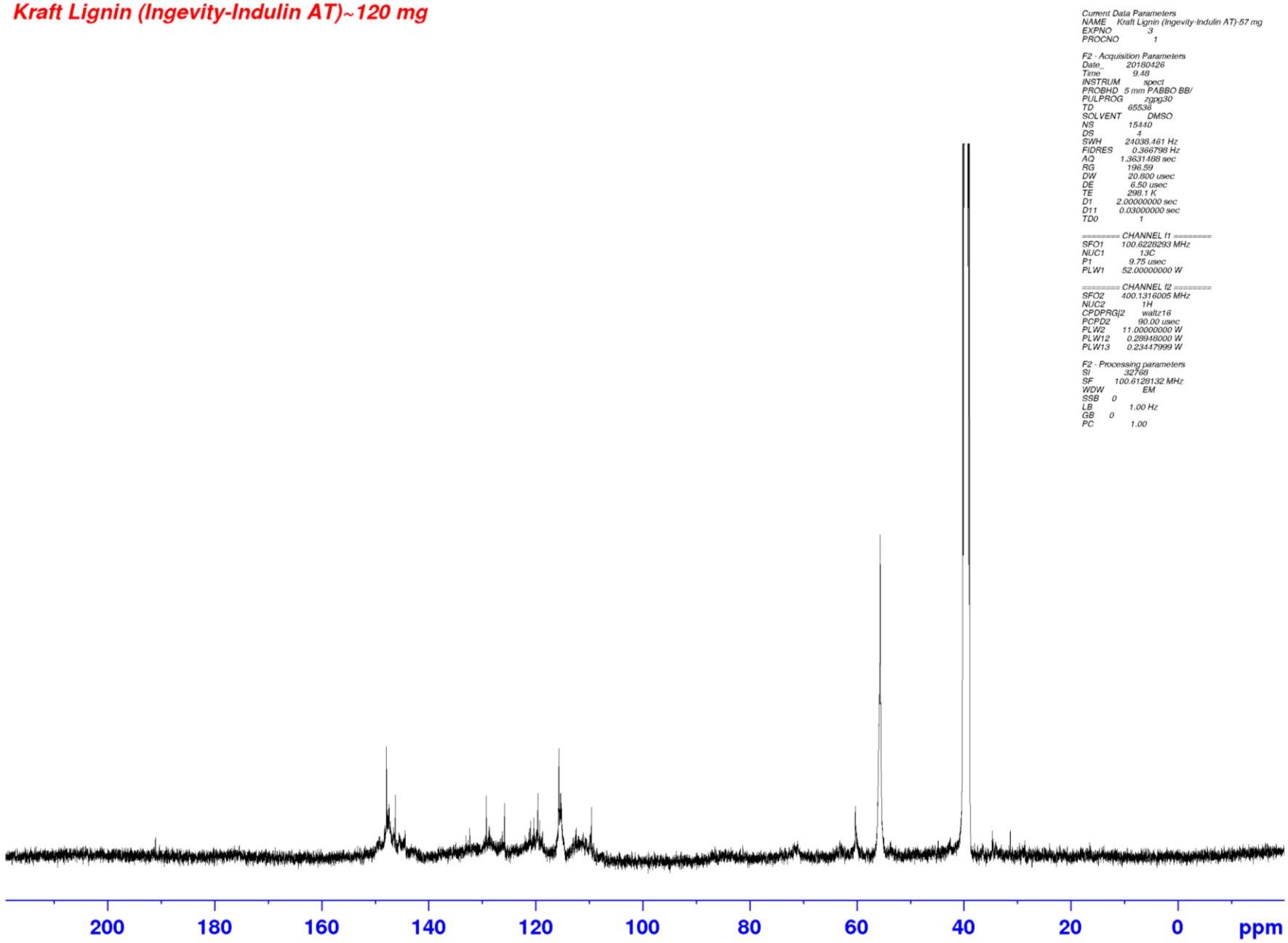


Figure S 25 **(Indulin AT) Kraft Lignin** ^{13}C NMR (DMSO-d_6)

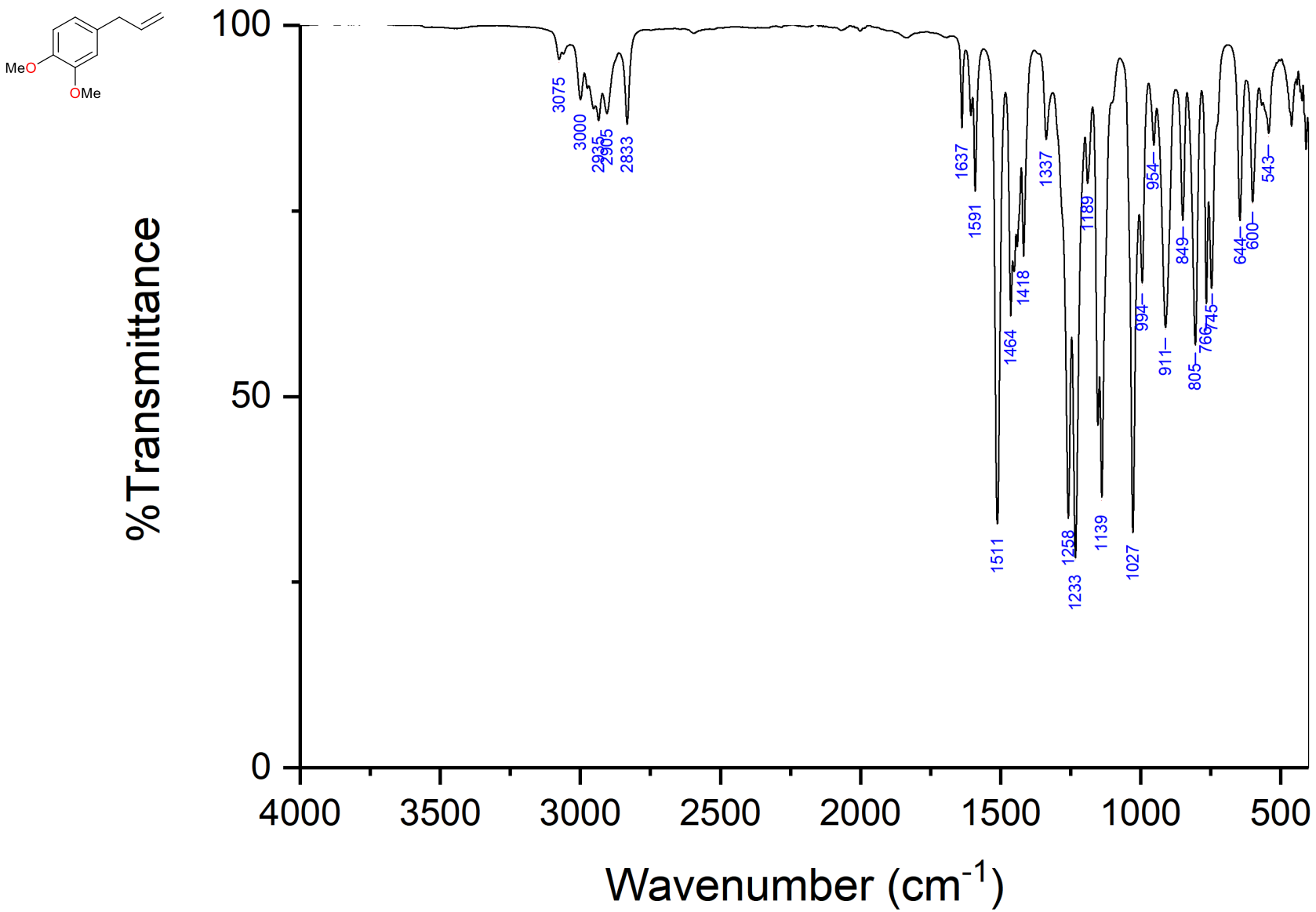


Figure S 26 **4-Allylveratrole** FTIR (ATR, thin film from evaporation of $CDCl_3$)

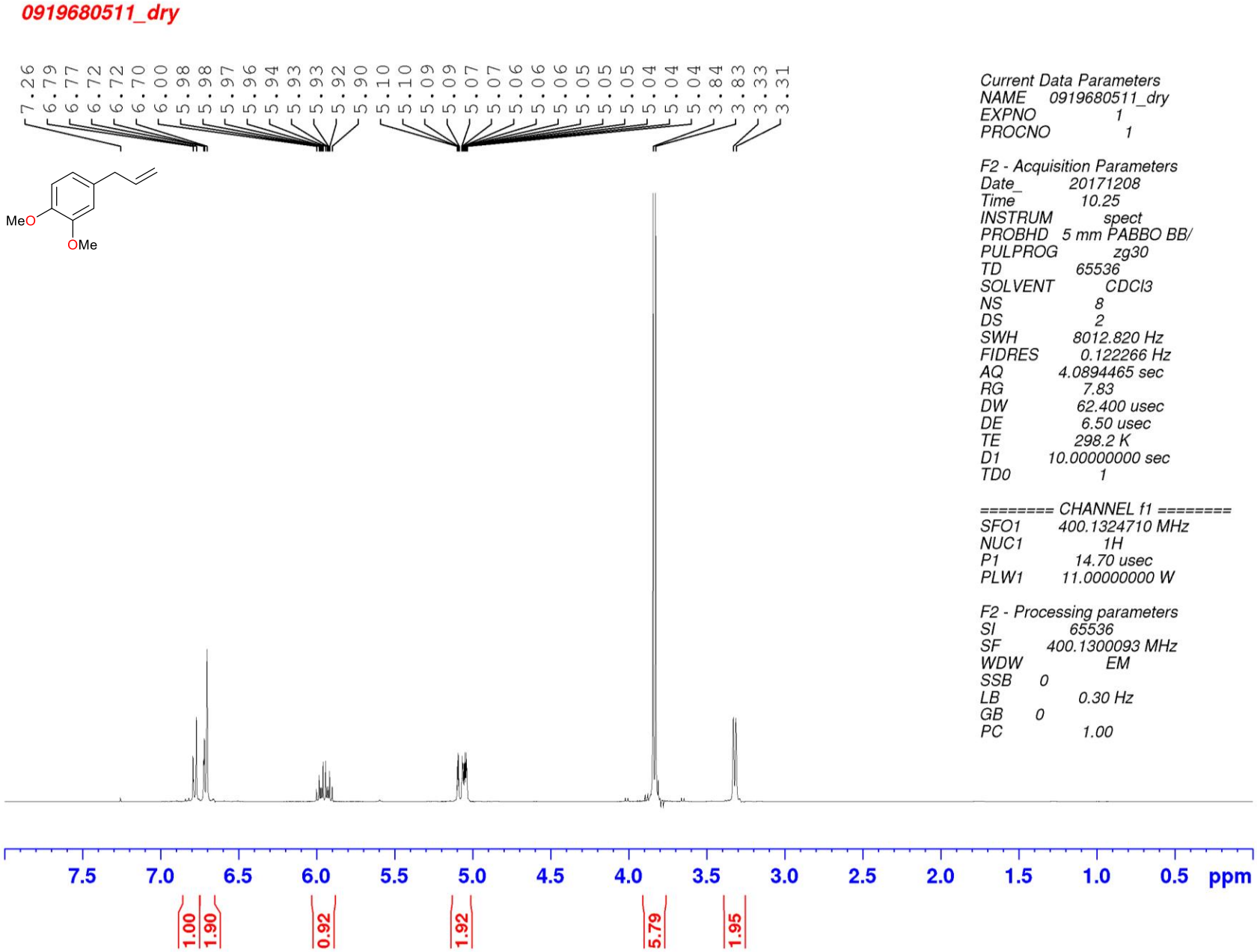


Figure S 27 **4-Allylveratrole** ^{1}H NMR ($CDCl_3$)

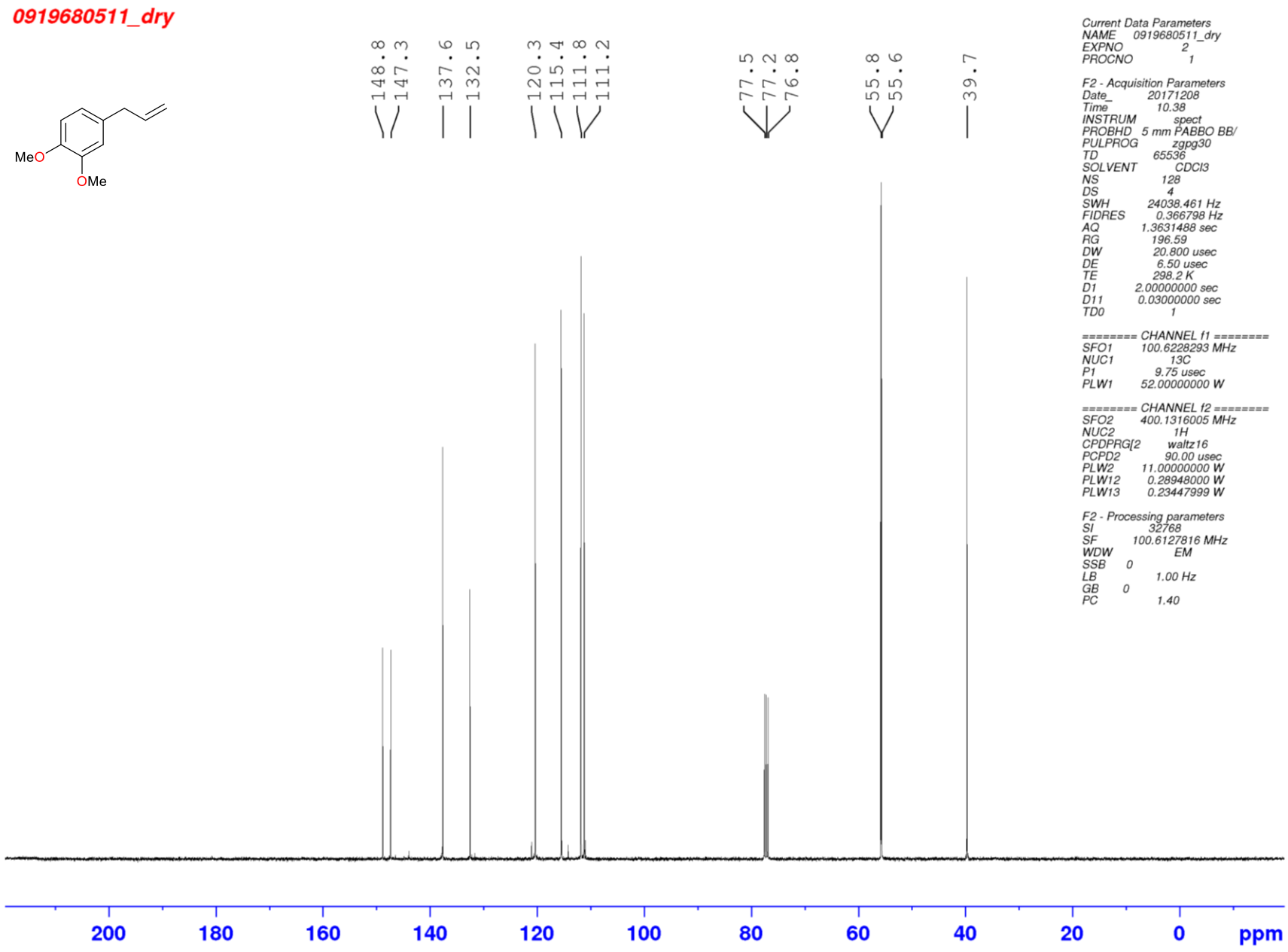


Figure S 28 **4-Allylveratrole** ^{13}C NMR ($CDCl_3$)

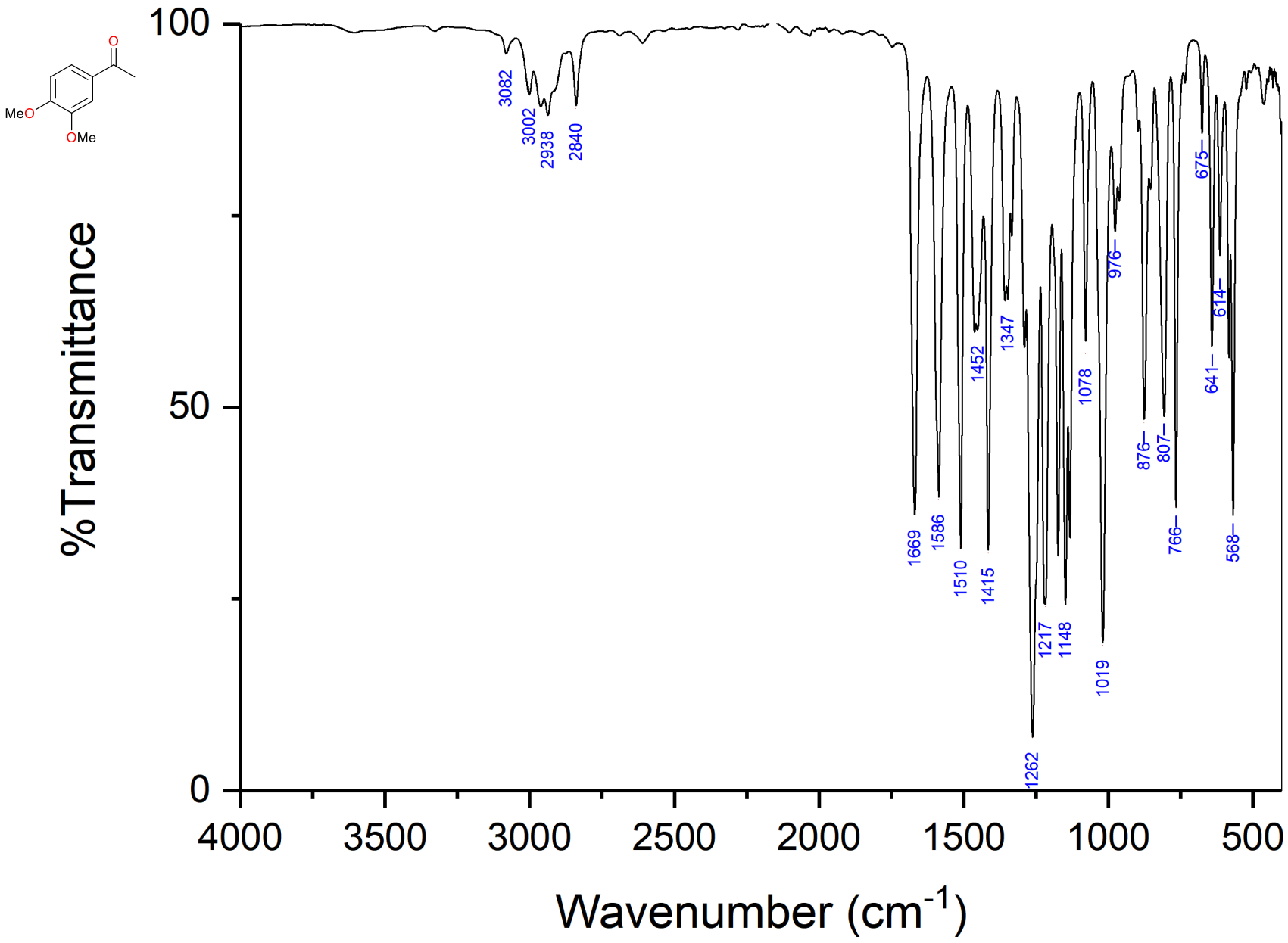


Figure S 29 **4-Acetylveratrole** FTIR (ATR, thin film from evaporation of $CDCl_3$)

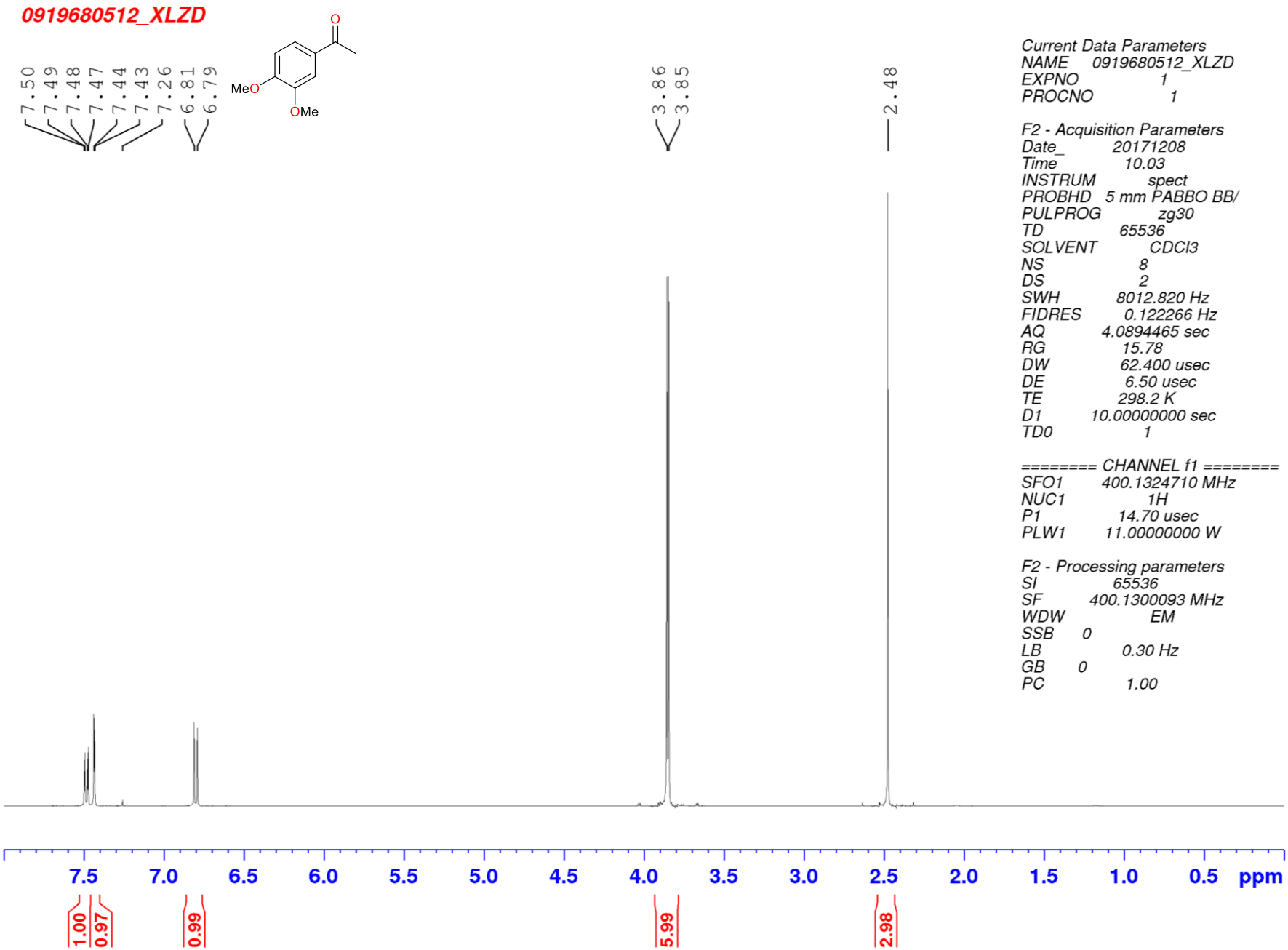


Figure S 30 **4-Acetylveratrole** ^{1}H NMR ($CDCl_3$)

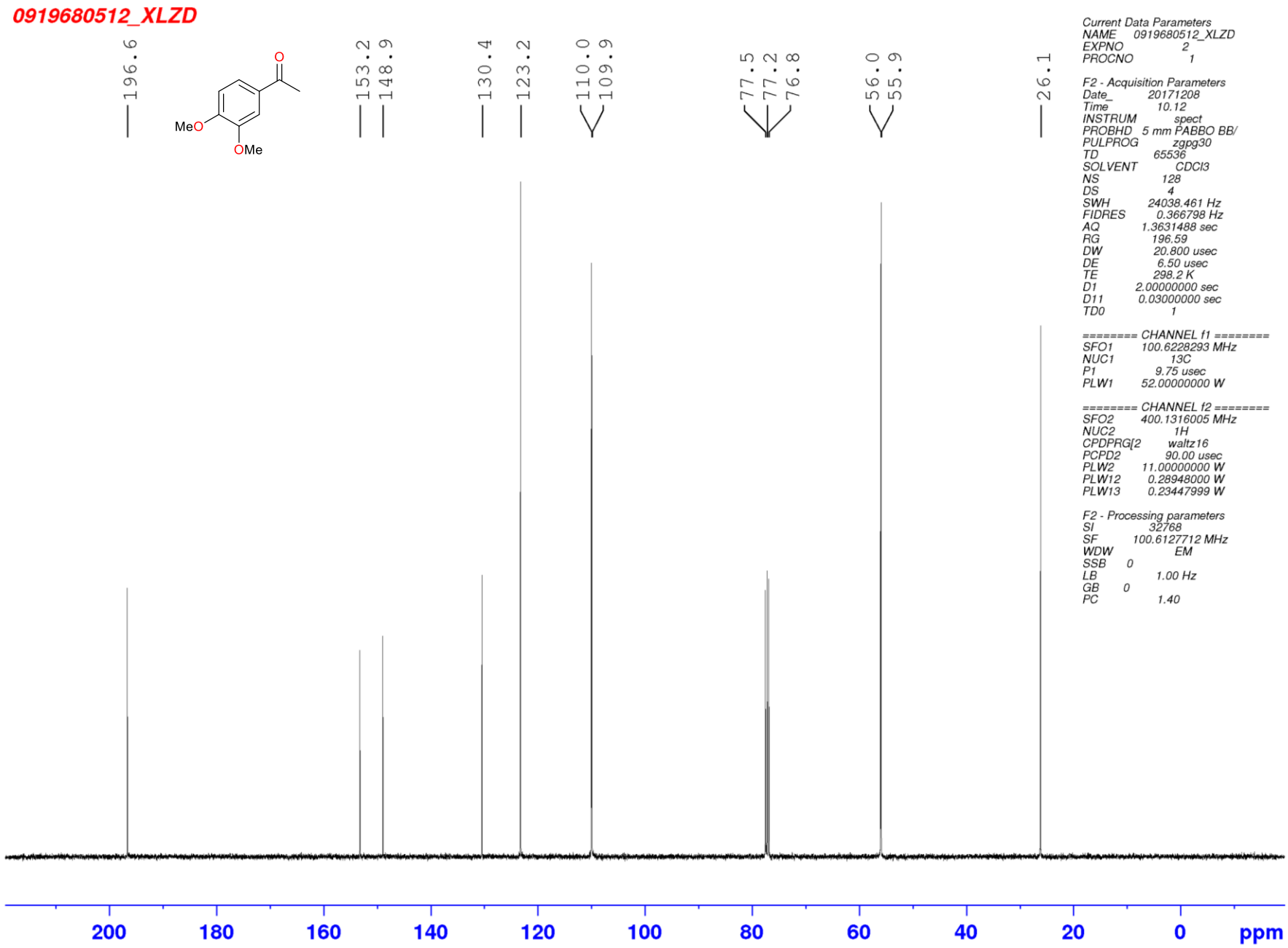


Figure S 31 **4-Acetylveratrole** ^{13}C NMR ($CDCl_3$)

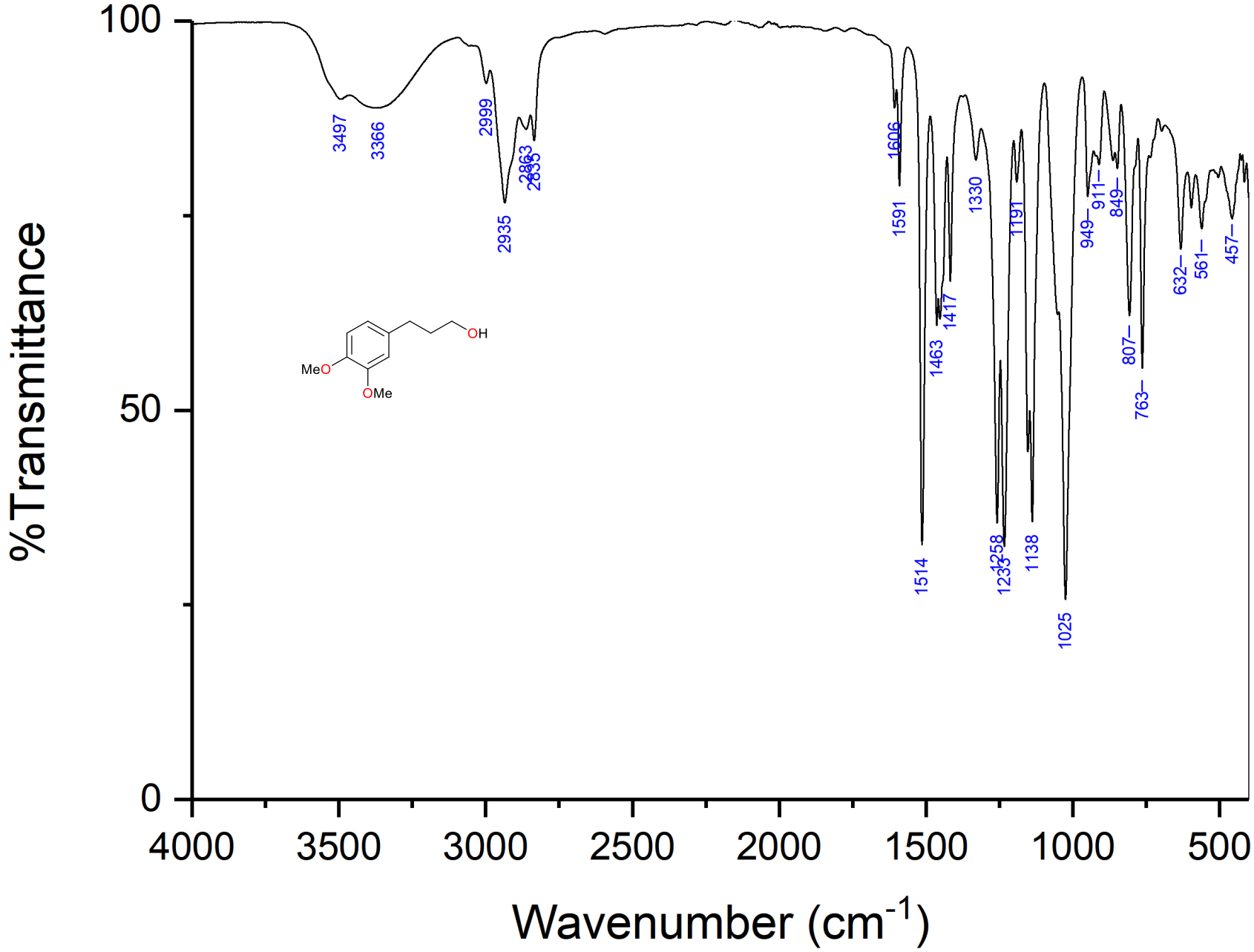


Figure S 32 **3-(3,4-Dimethoxyphenyl)-1-propanol** FTIR (ATR, thin film from evaporation of $CDCl_3$)

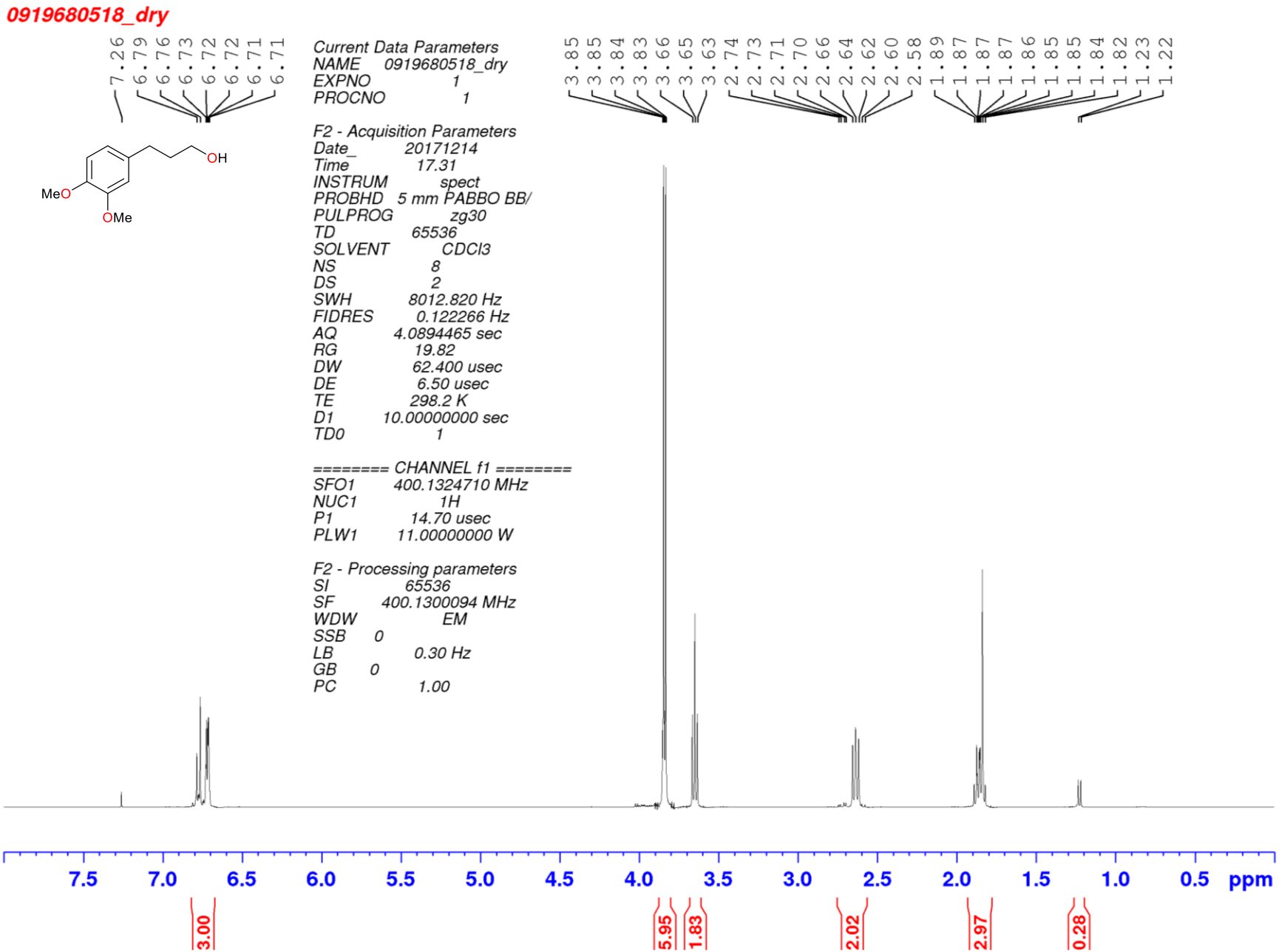


Figure S 33 **3-(3,4-Dimethoxyphenyl)-1-propanol** ^{1}H NMR ($CDCl_3$)

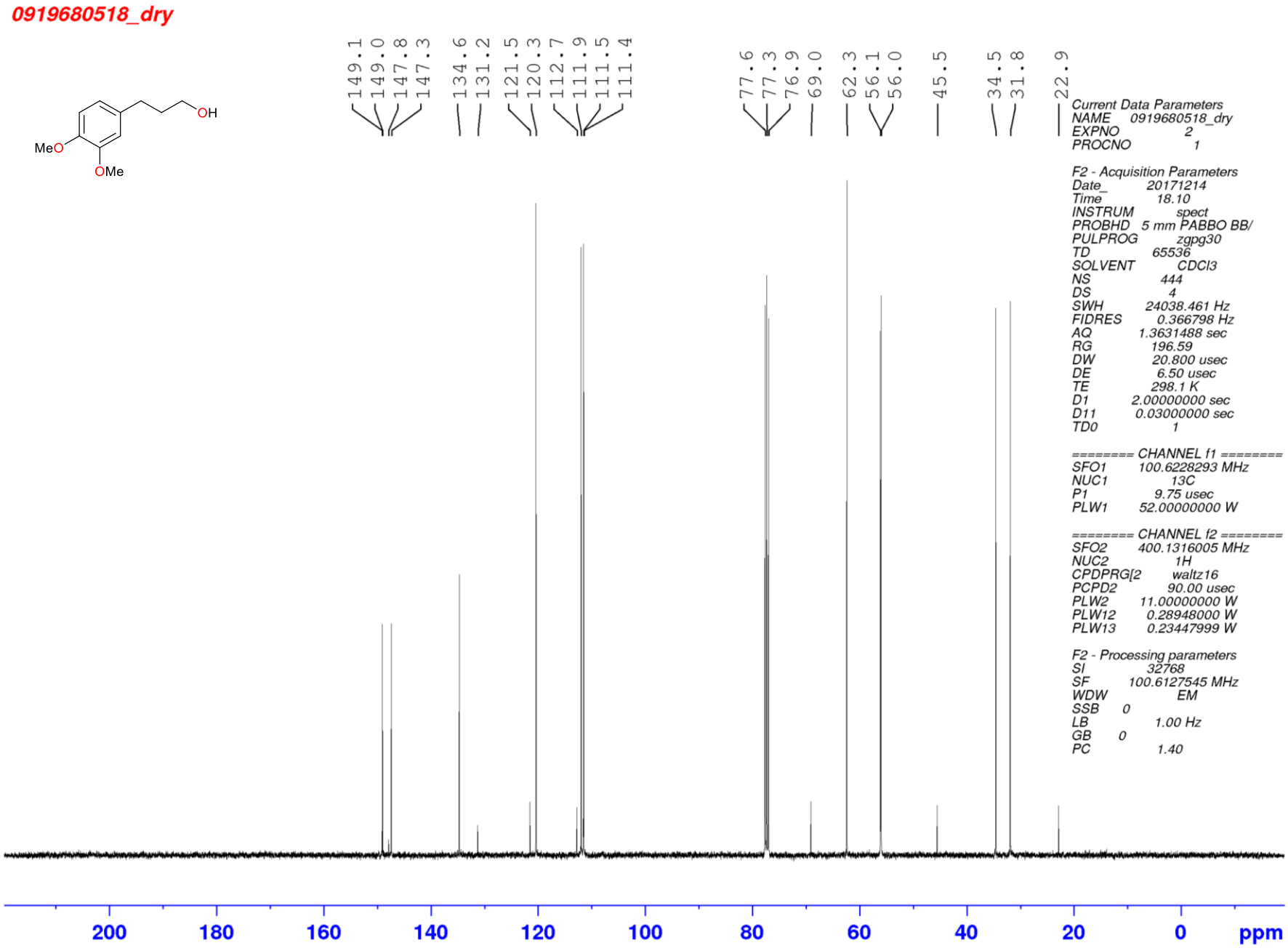


Figure S 34 **3-(3,4-Dimethoxyphenyl)-1-propanol** ^{13}C NMR ($CDCl_3$)

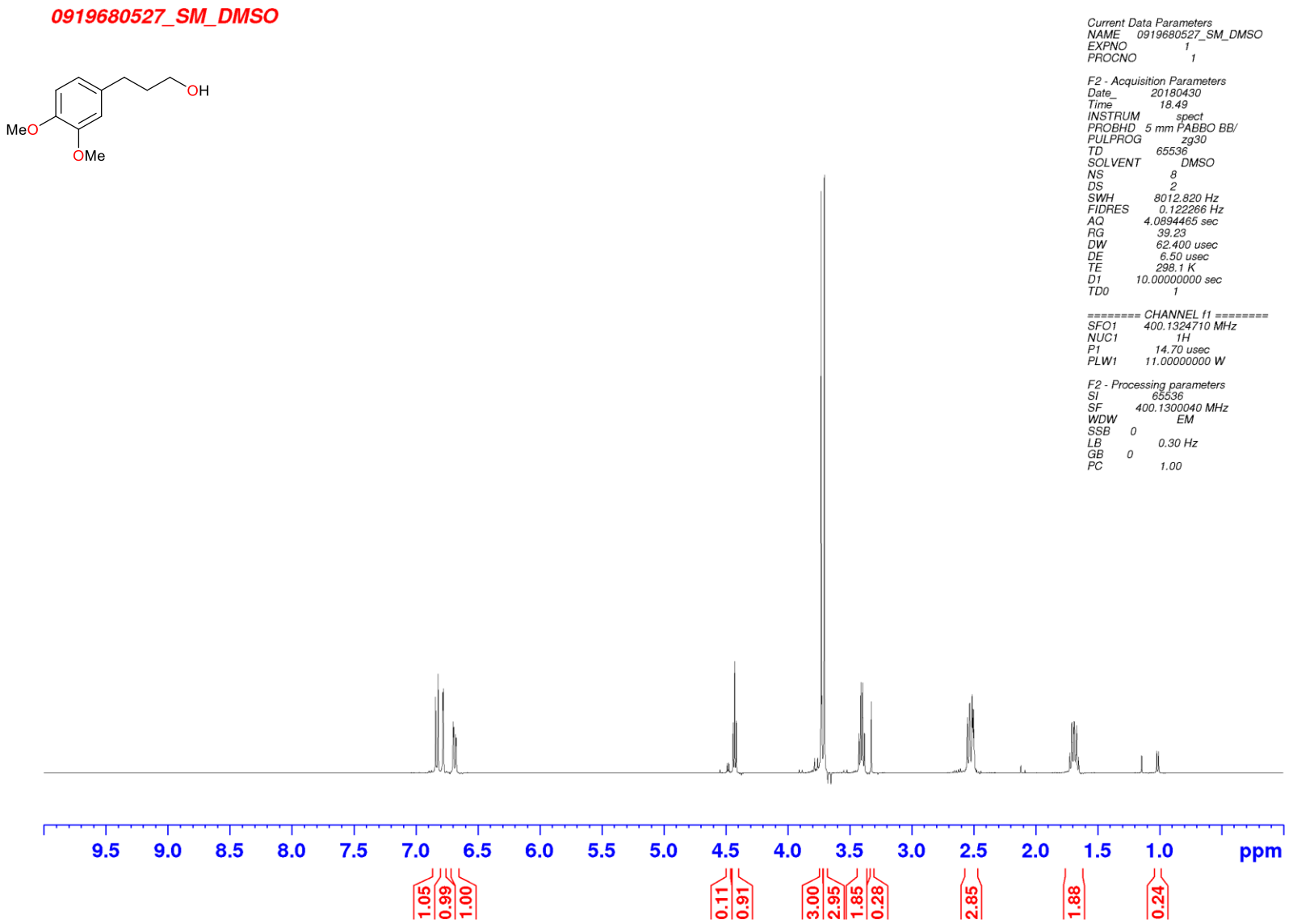


Figure S 35 **3-(3,4-Dimethoxyphenyl)-1-propanol** ^{1}H NMR (DMSO-*d6*)

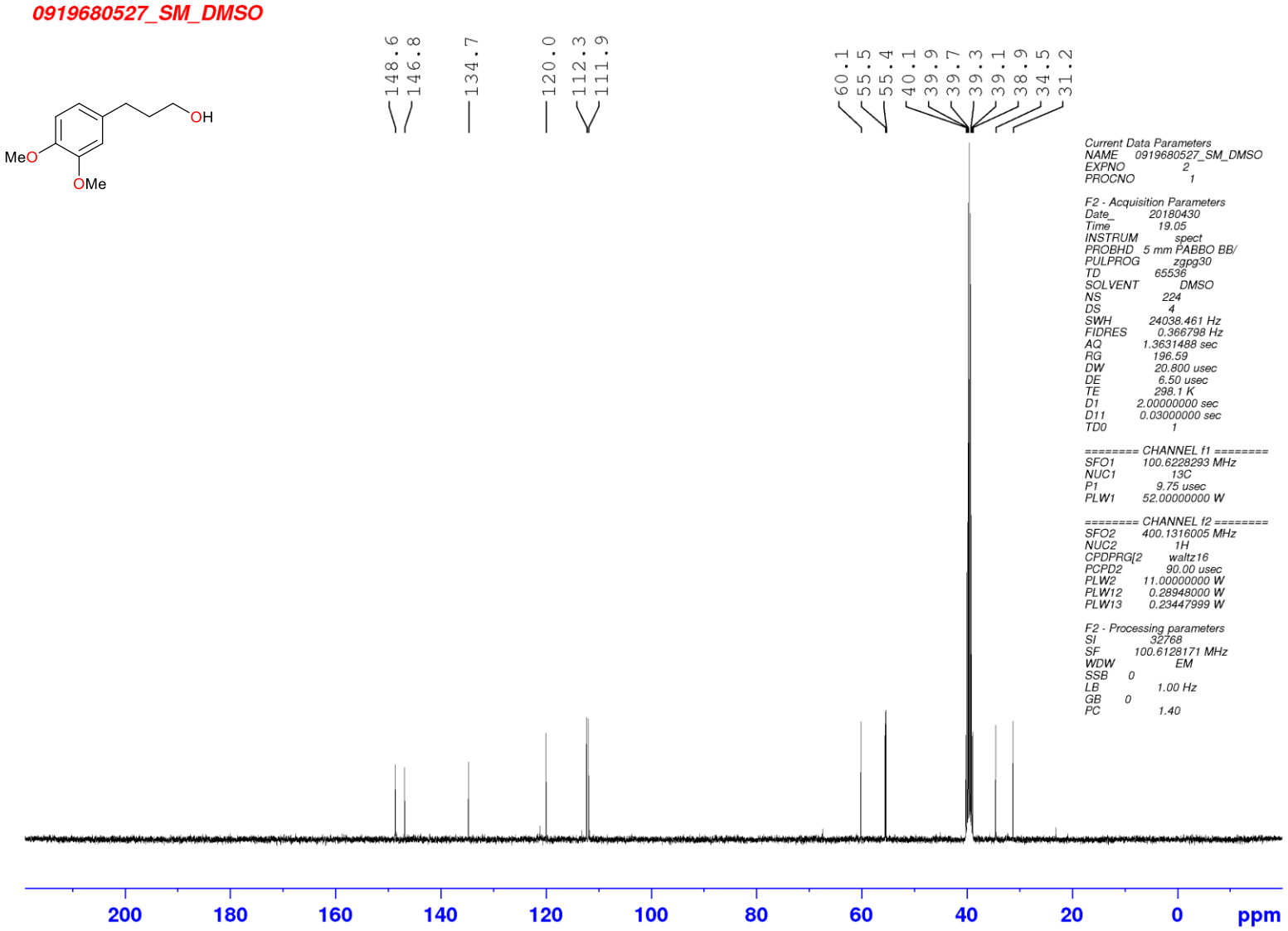


Figure S 36 **3-(3,4-Dimethoxyphenyl)-1-propanol** ^{13}C NMR (DMSO-*d6*)

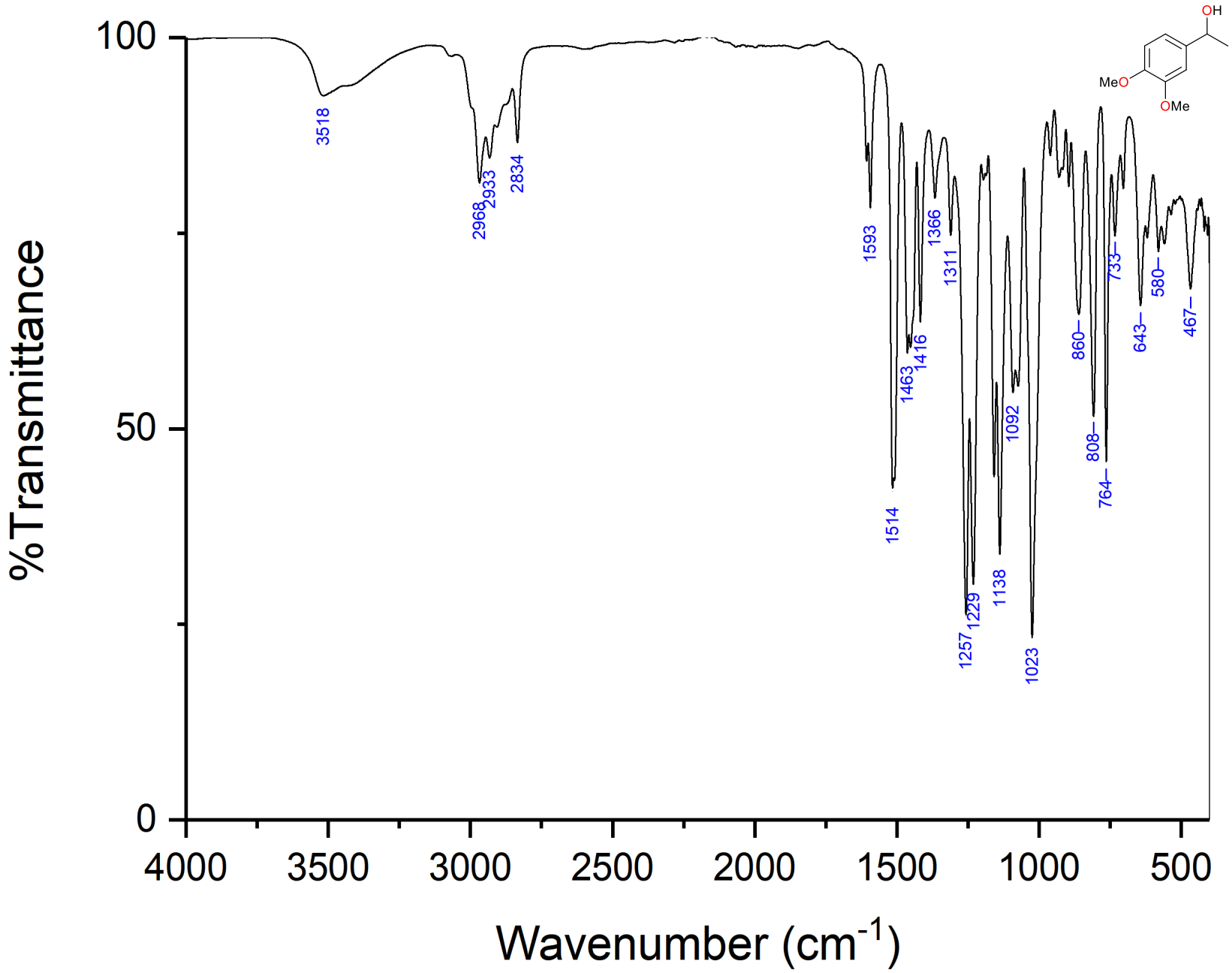


Figure S 37 **1-(3,4-Dimethoxyphenyl)ethan-1-ol** FTIR (ATR, thin film from evaporation of $CDCl_3$)

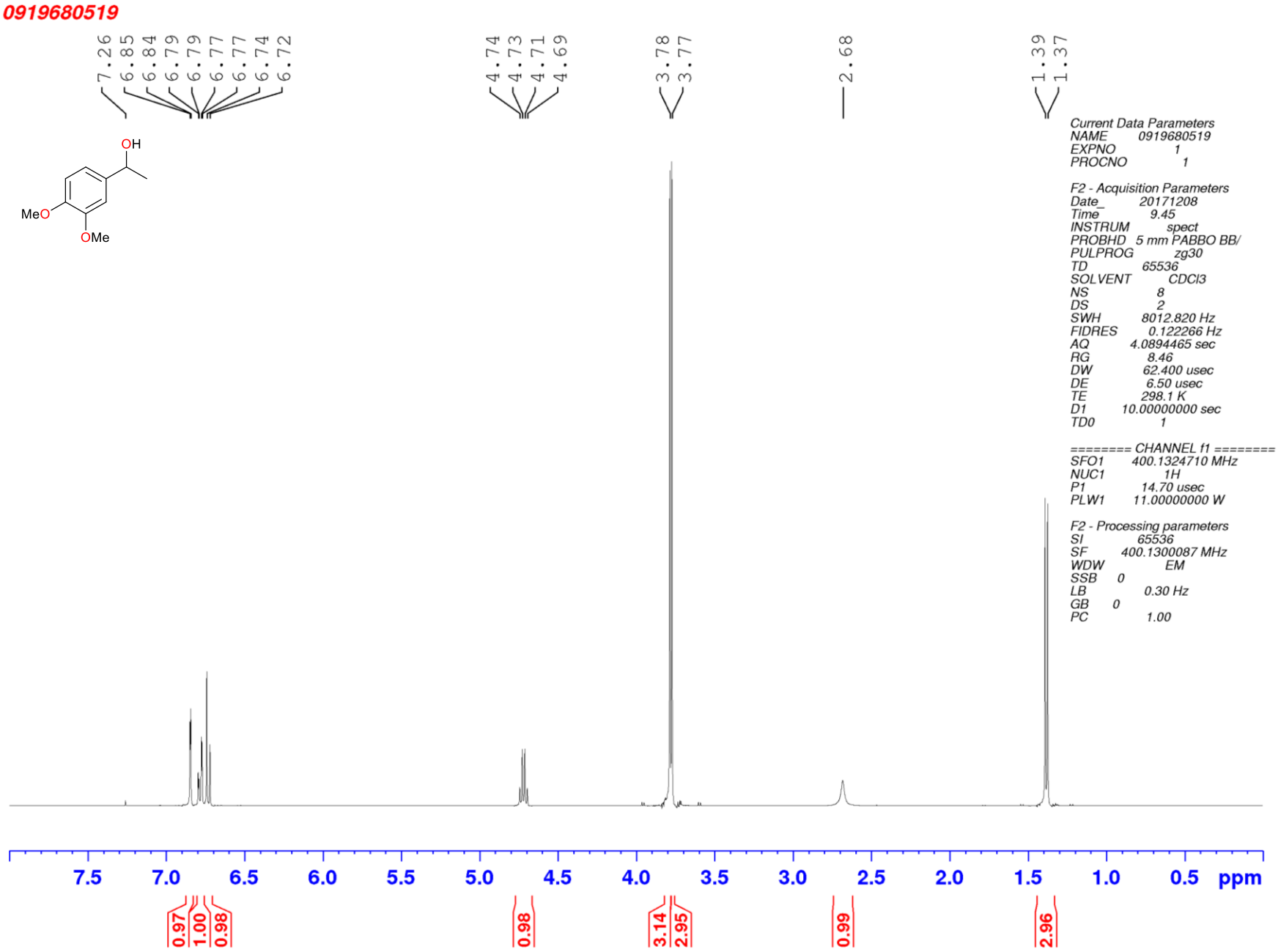


Figure S 38 **1-(3,4-Dimethoxyphenyl)ethan-1-ol** ^{1}H NMR ($CDCl_3$)

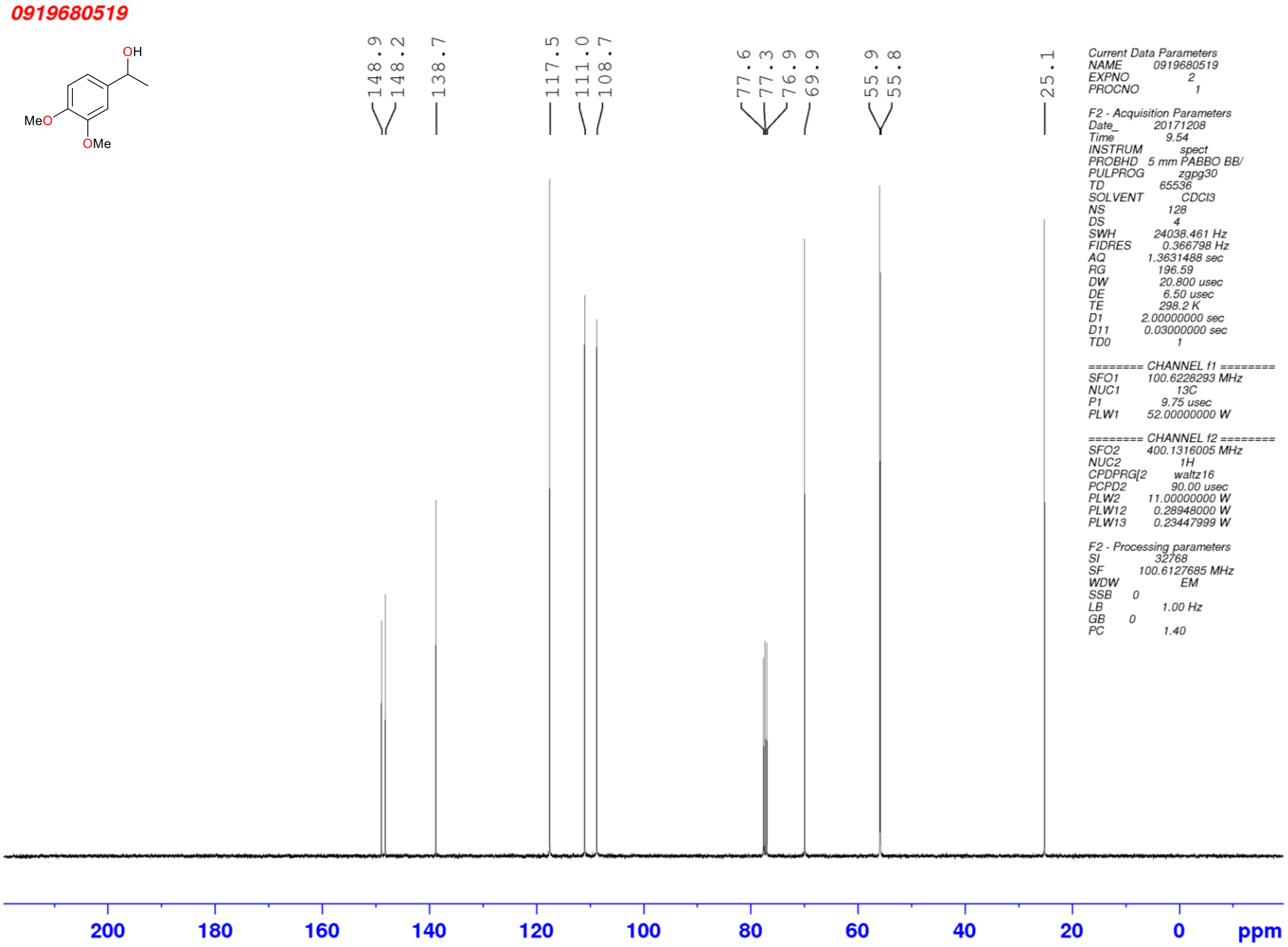


Figure S 39 **1-(3,4-Dimethoxyphenyl)ethan-1-ol** ^{13}C NMR ($CDCl_3$)

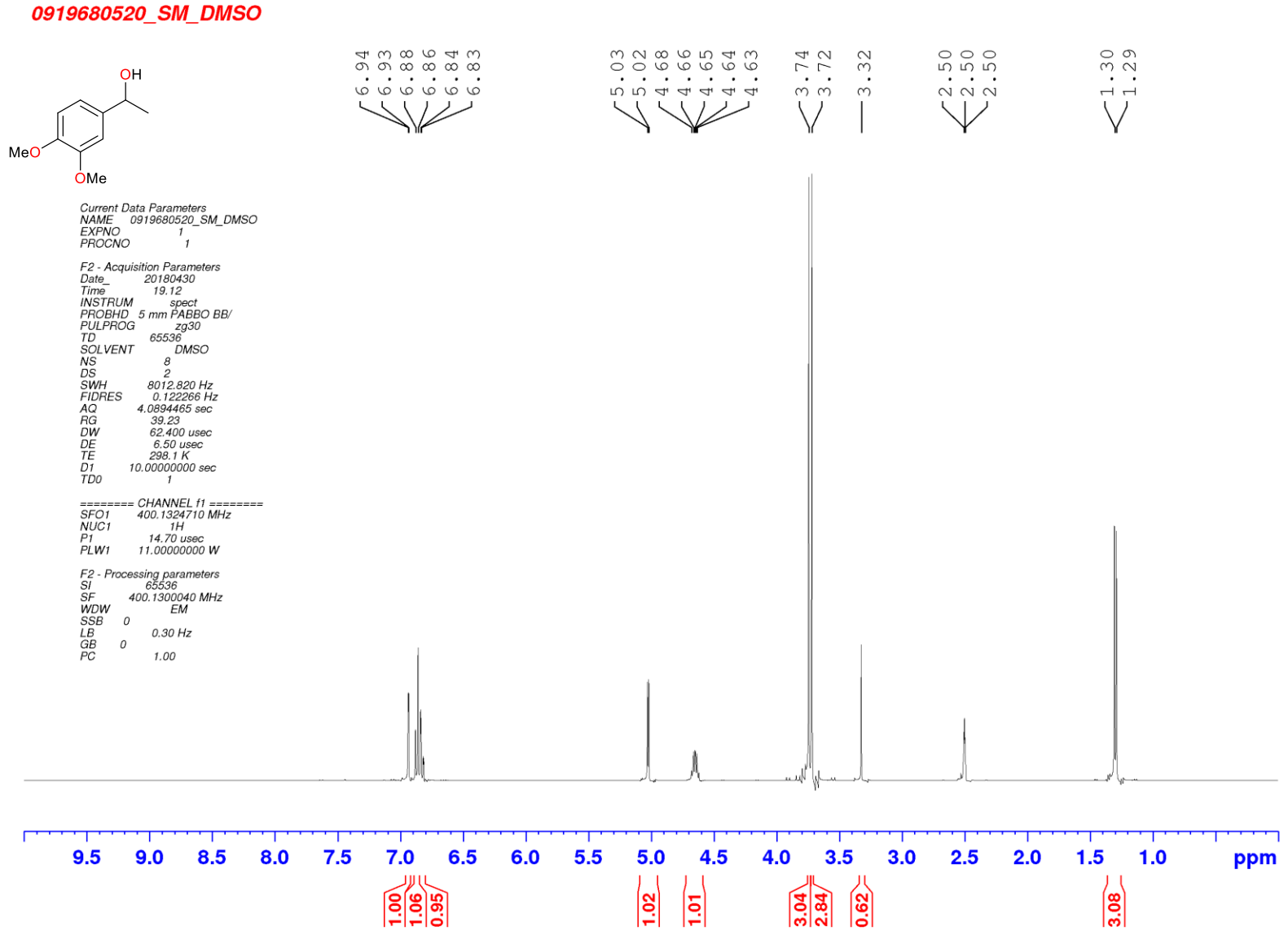


Figure S 40 **1-(3,4-Dimethoxyphenyl)ethan-1-ol** ^{1}H NMR (DMSO-d_6)

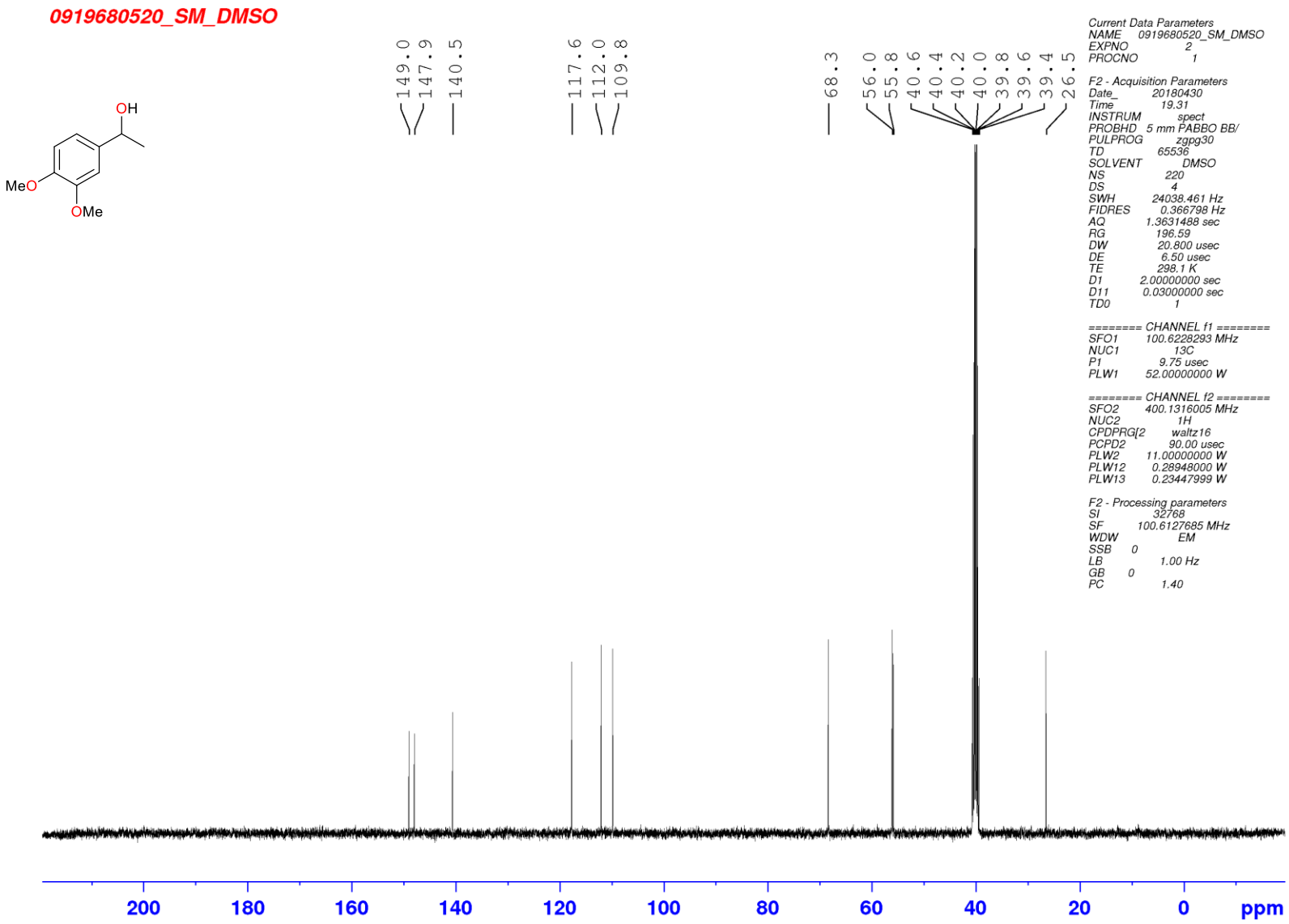


Figure S 41 **1-(3,4-Dimethoxyphenyl)ethan-1-ol** ^{13}C NMR (DMSO-d_6)

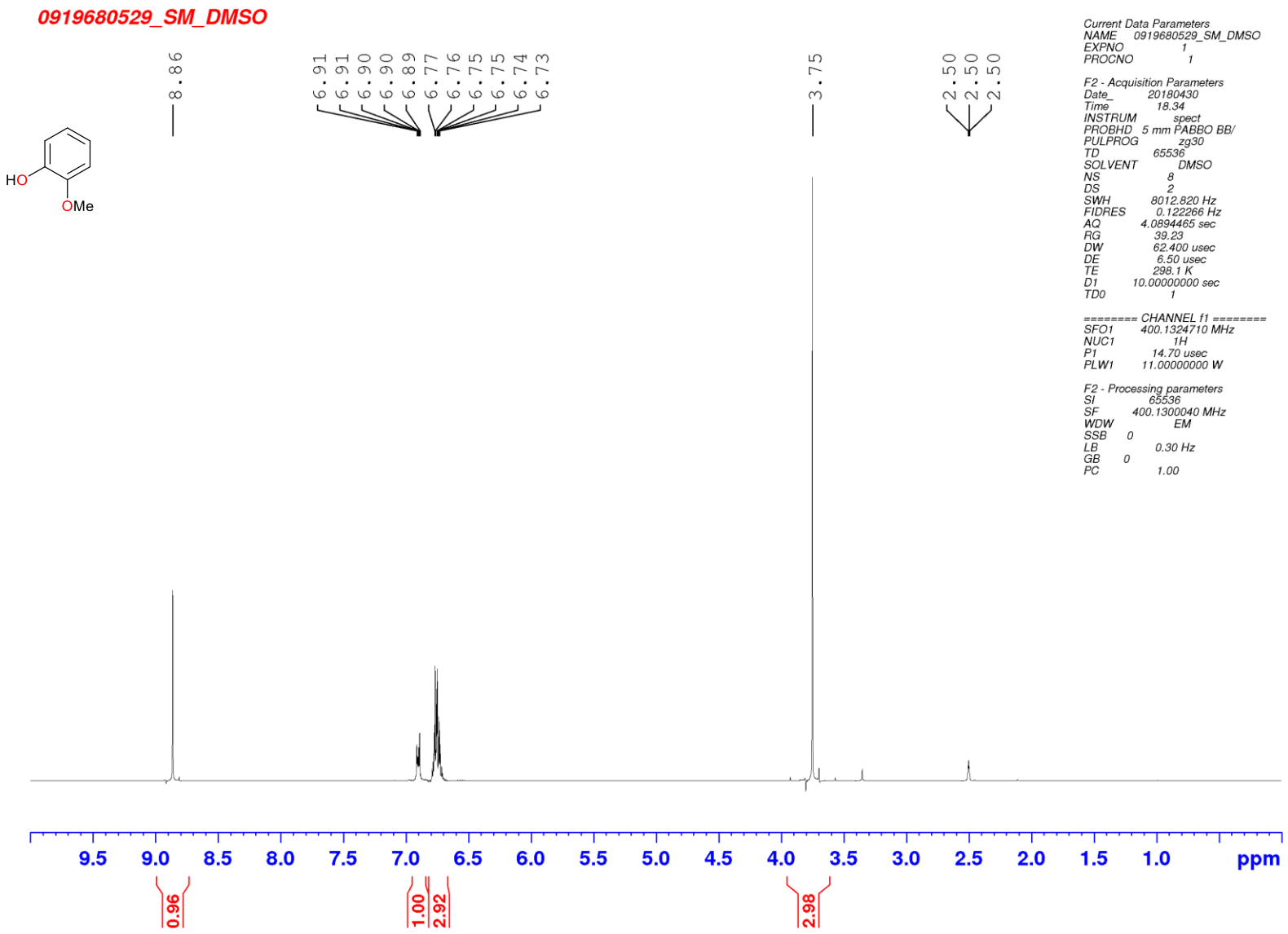


Figure S 42 **Guaiacol** ^{1}H NMR (DMSO-d_6)

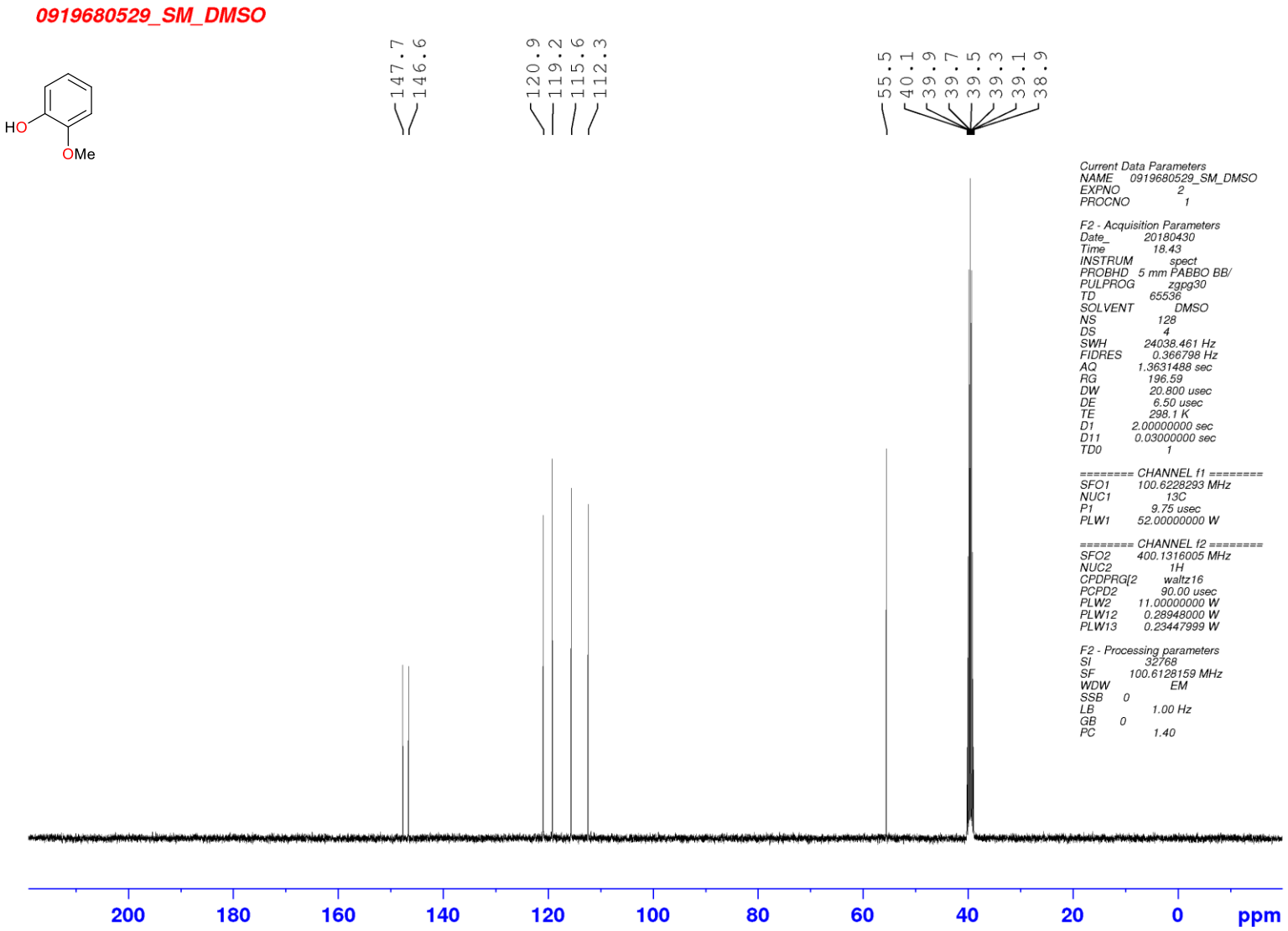


Figure S 43 **Guaiacol** ^{13}C NMR (DMSO-d_6)

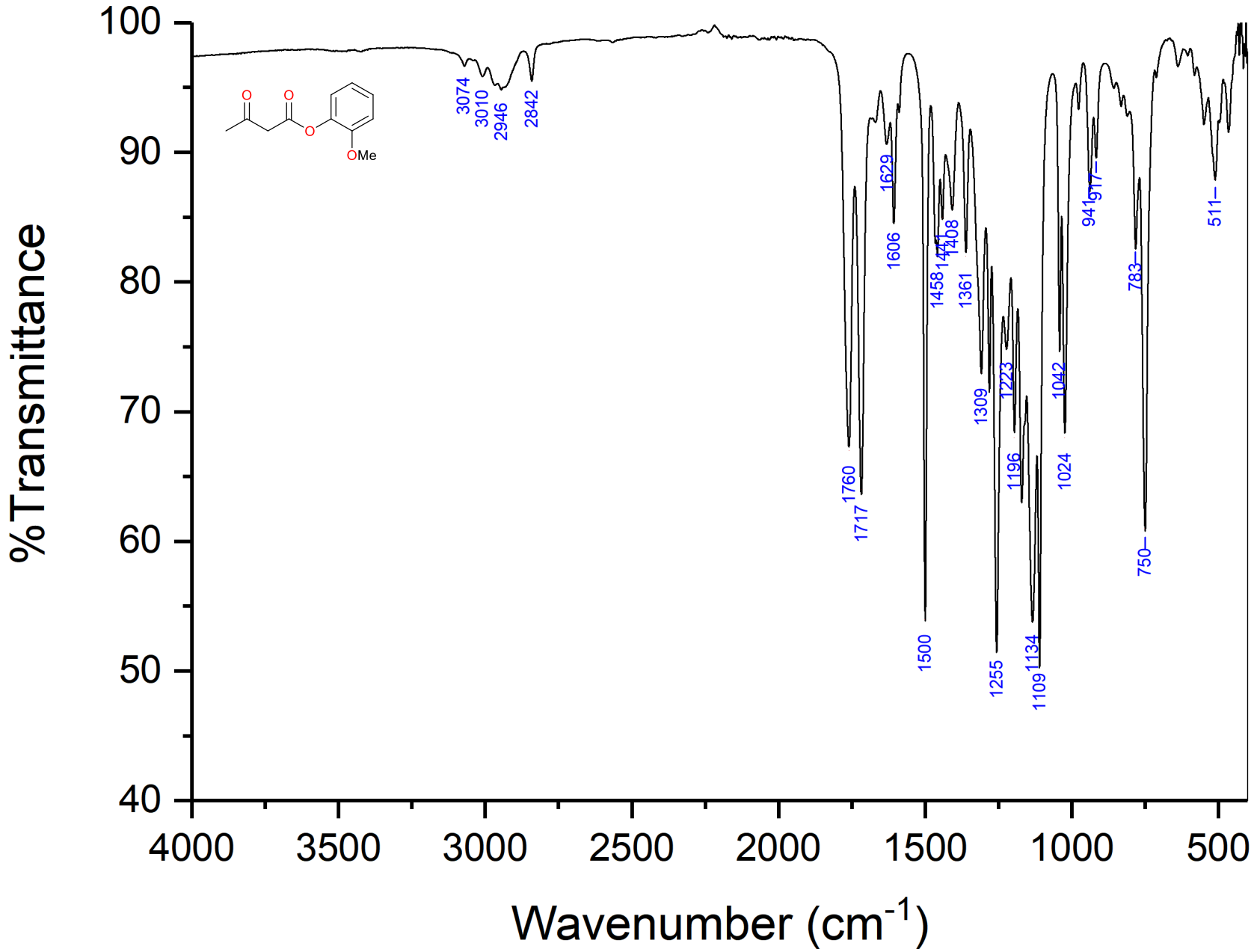


Figure S 44 **2-Acetoacetoxyanisole** FTIR (ATR, thin film from evaporation of $CDCl_3$)

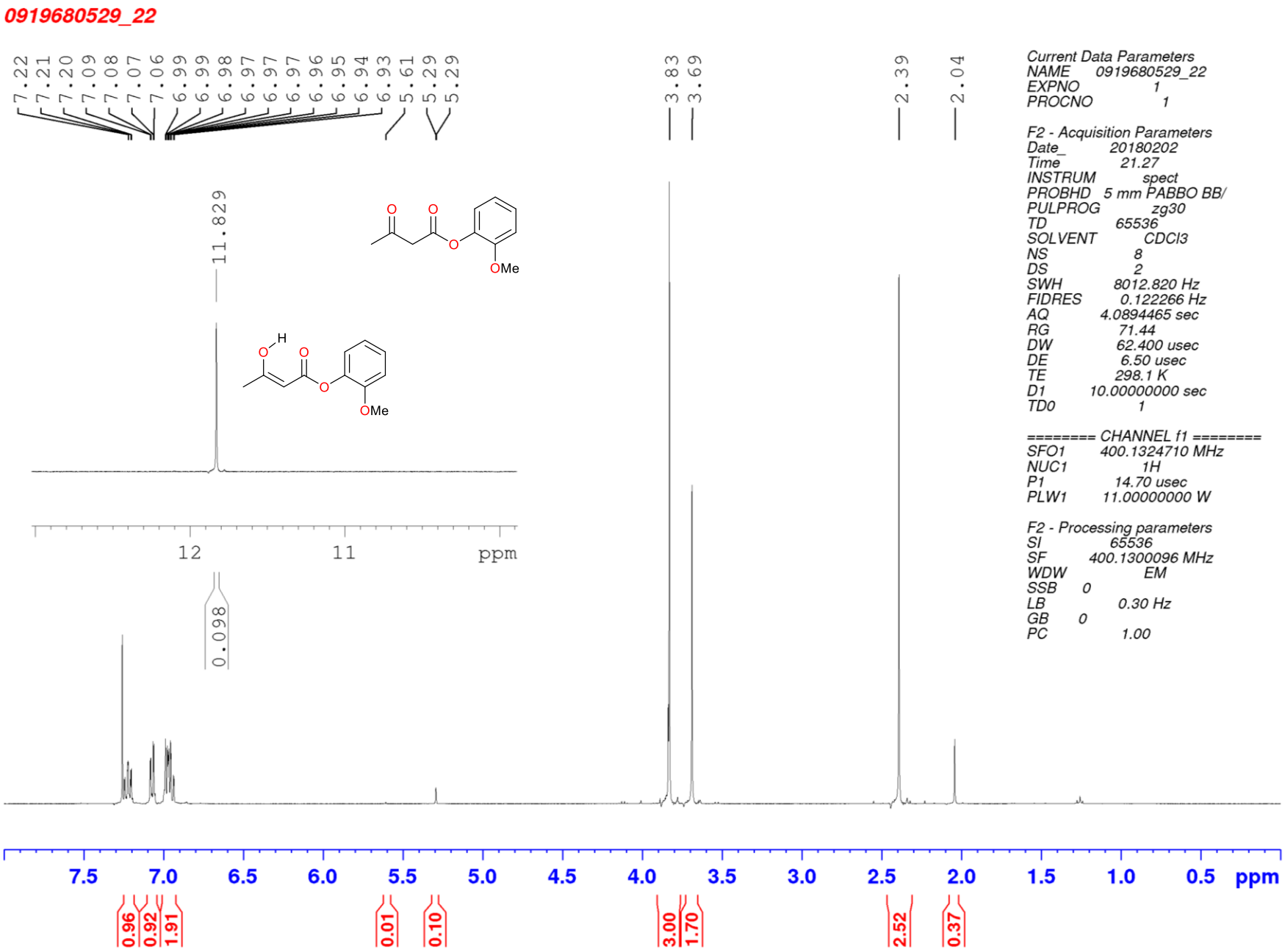


Figure S 45 **2-Acetoacetoxyanisole** illustrating enolization ^{1}H NMR ($CDCl_3$)

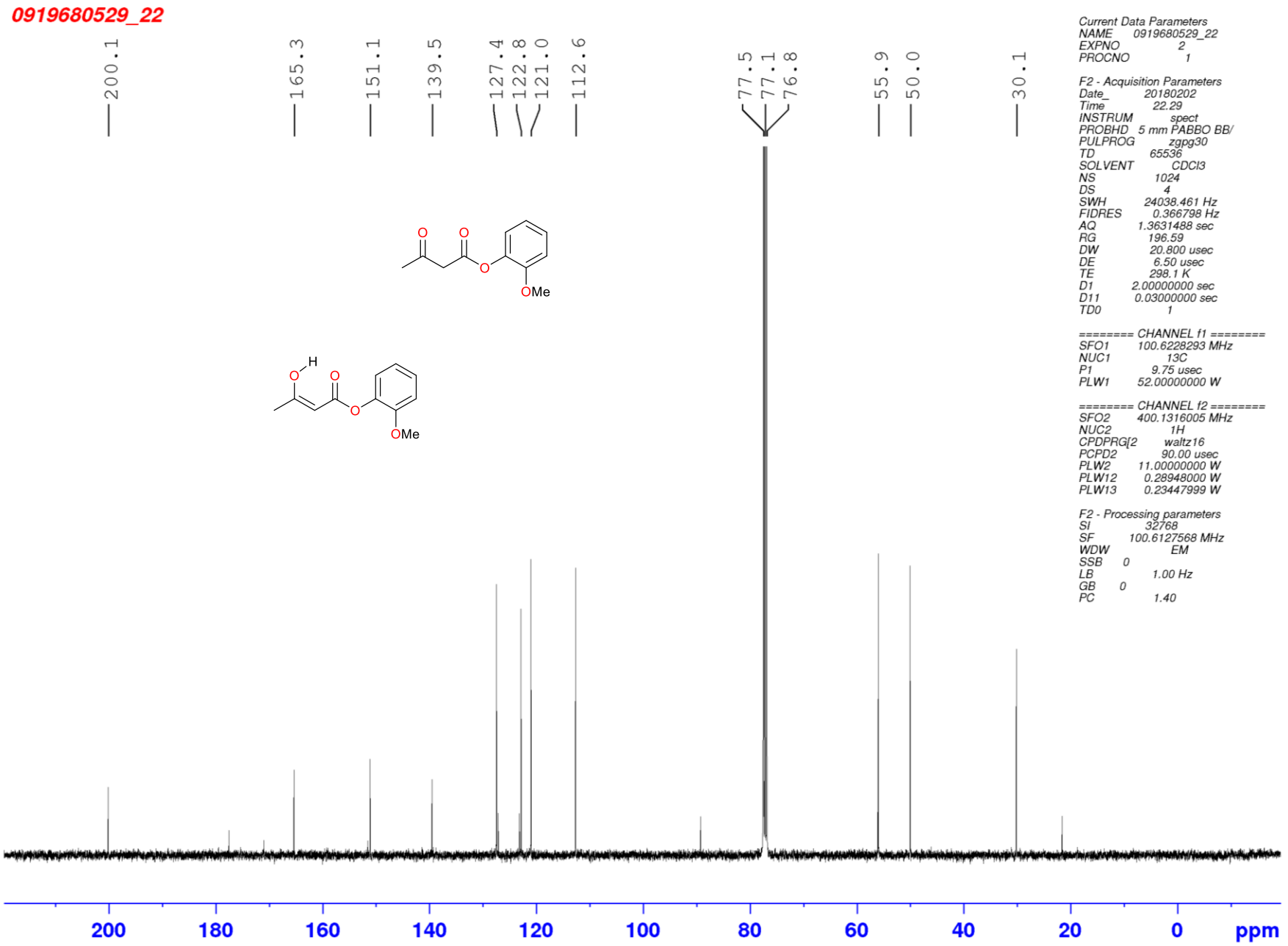


Figure S 46 **2-Acetoacetoxyanisole** ^{13}C NMR ($CDCl_3$)

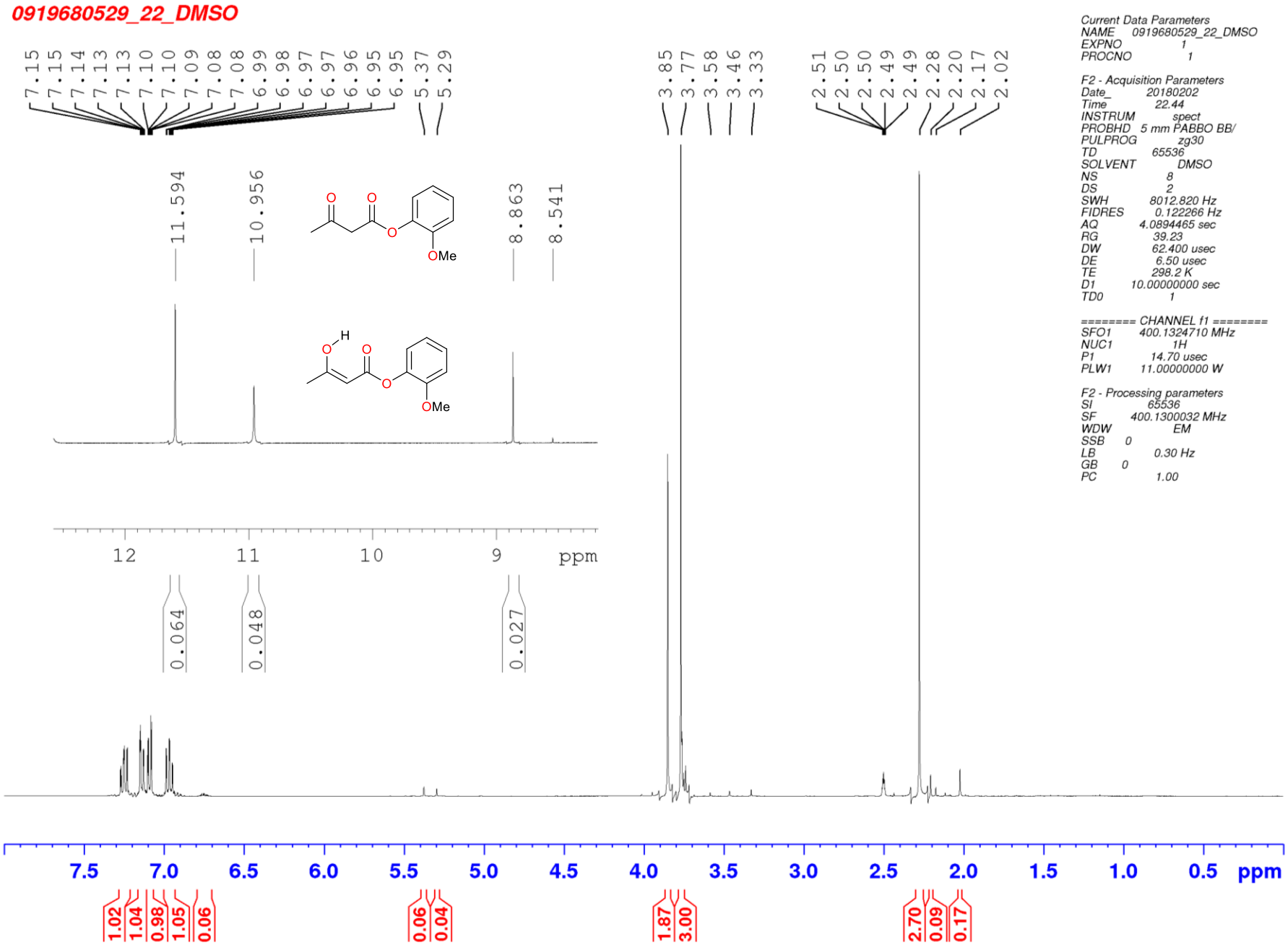


Figure S 47 **2-Acetoacetoxyanisole** illustrating diminished enolization ^{1}H NMR (DMSO-*d6*)

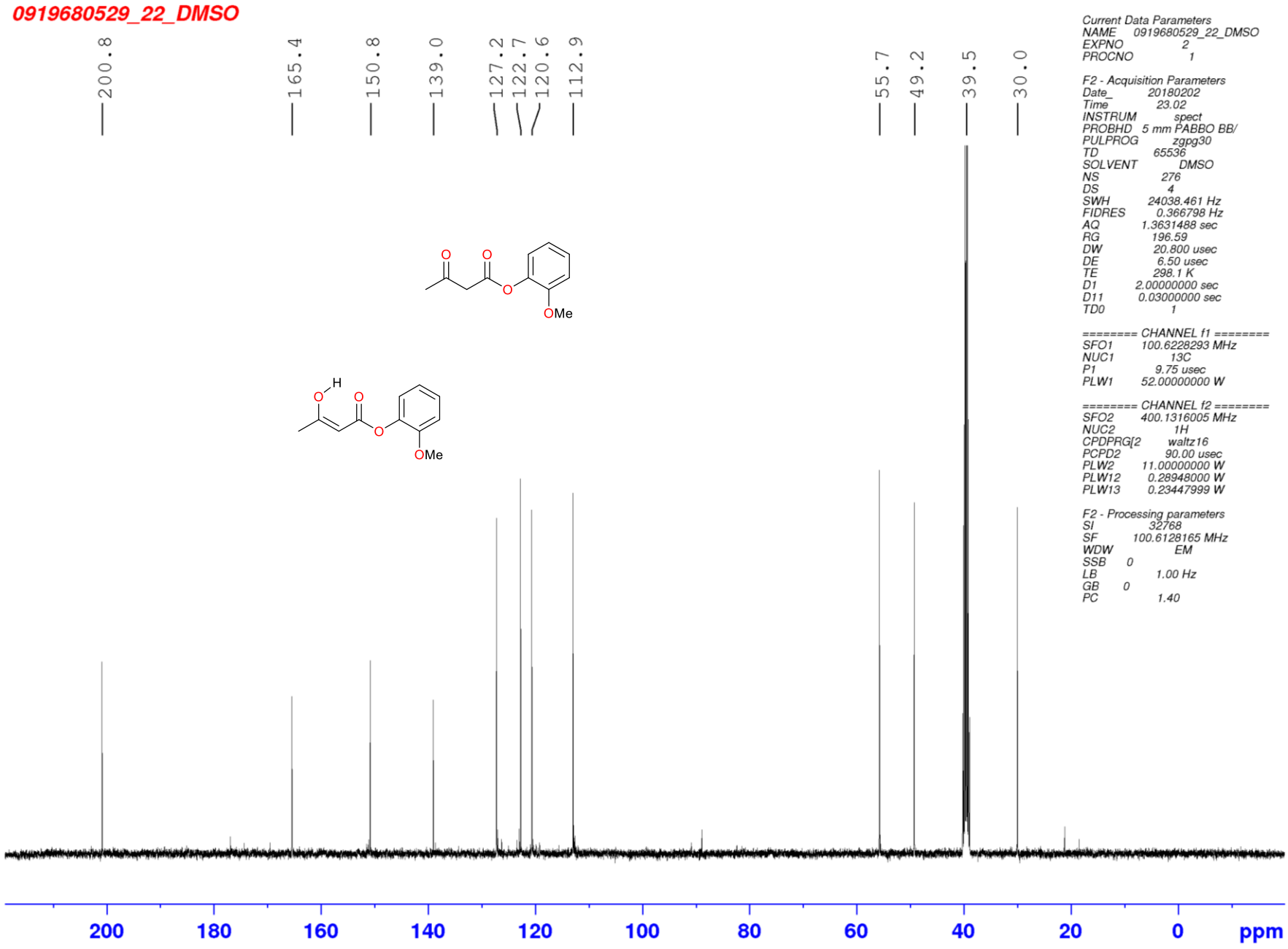


Figure S 48 **2-Acetoacetoxyanisole** ^{13}C NMR (DMSO-*d6*)

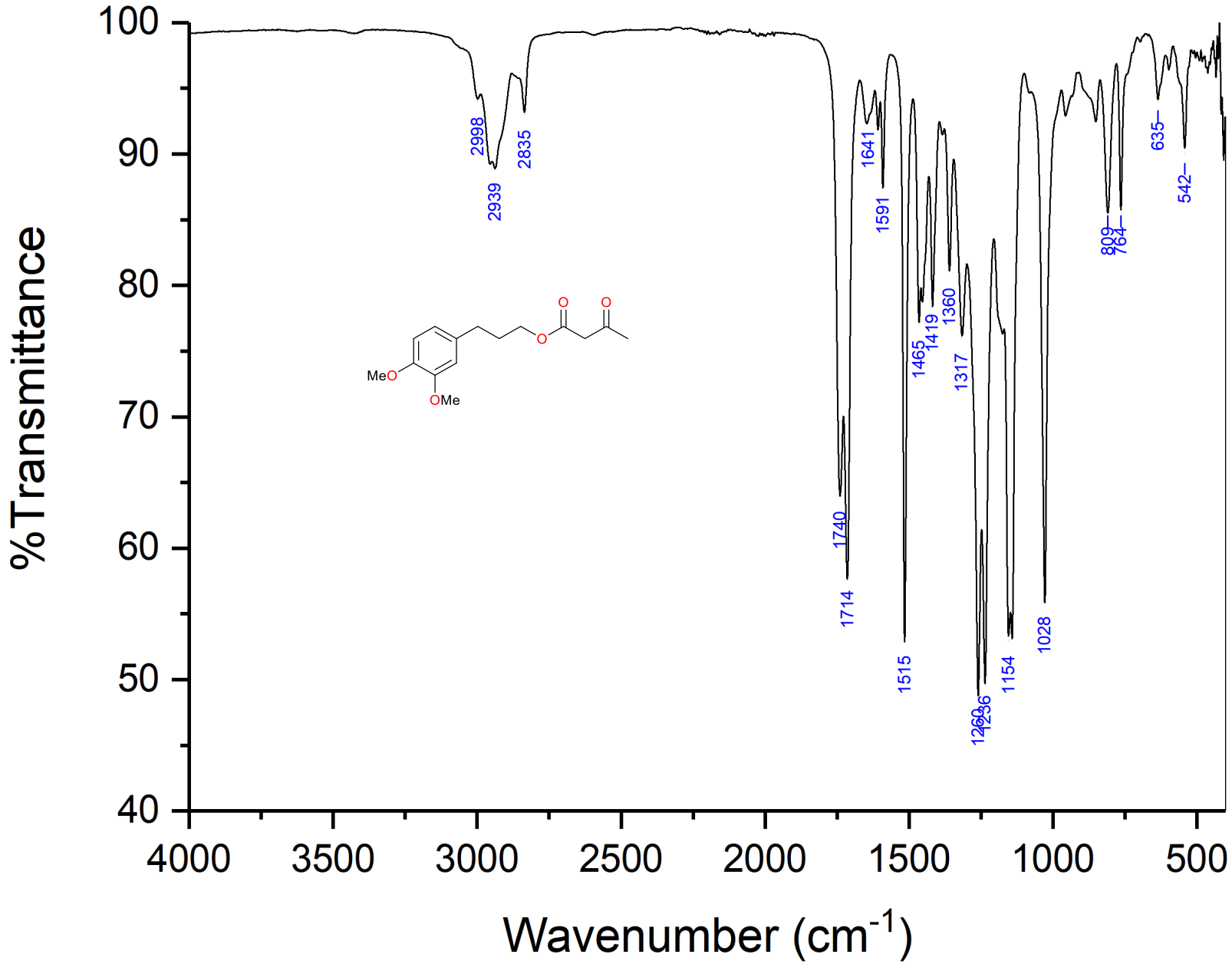


Figure S 49 **1-Acetoacetoxy-3(3,4-dimethoxyphenyl)propane** FTIR (ATR, thin film from evaporation of $CDCl_3$)

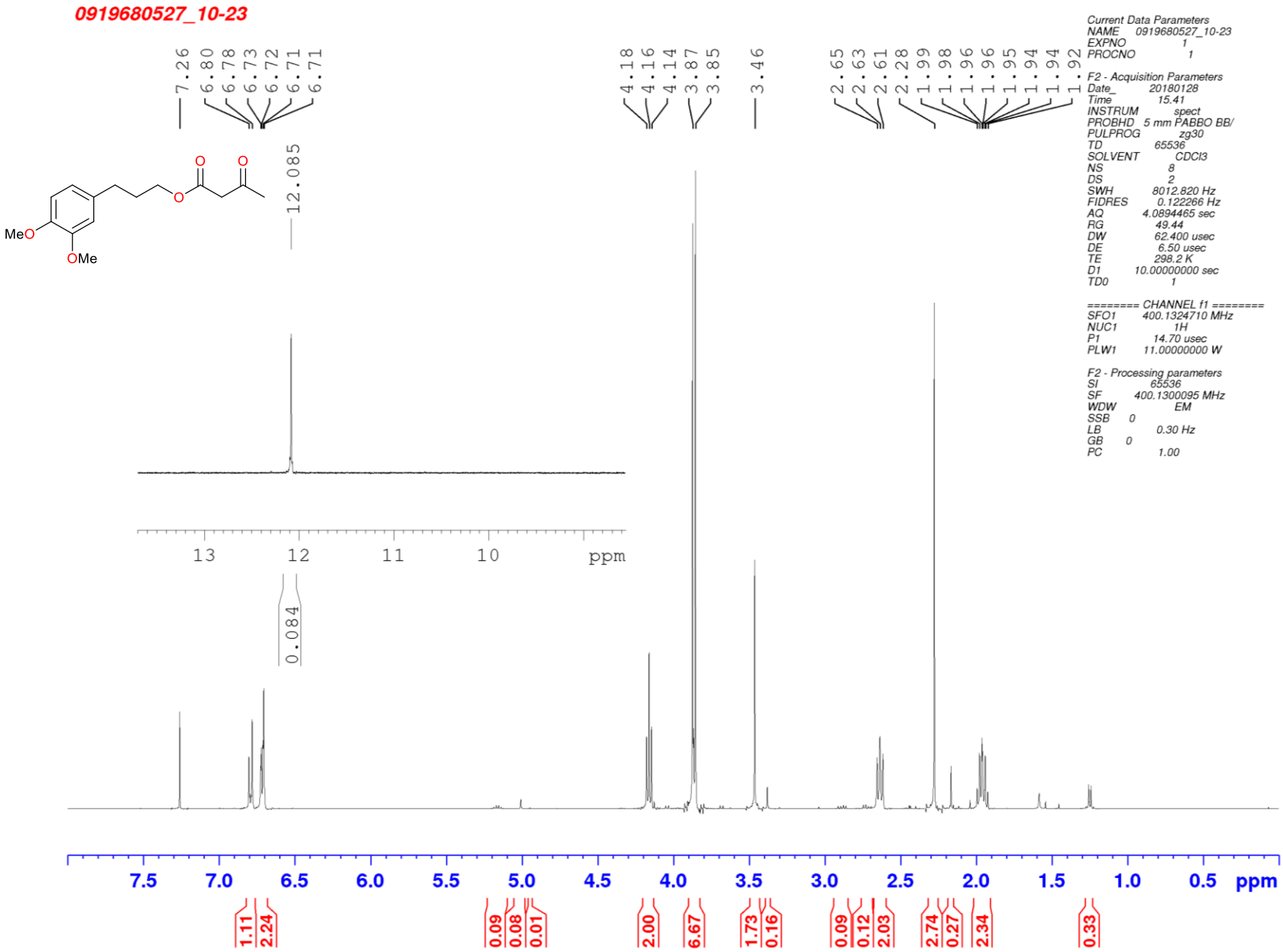


Figure S 50 **1-Acetoacetoxy-3(3,4-dimethoxyphenyl)propane** ^{1}H NMR ($CDCl_3$)

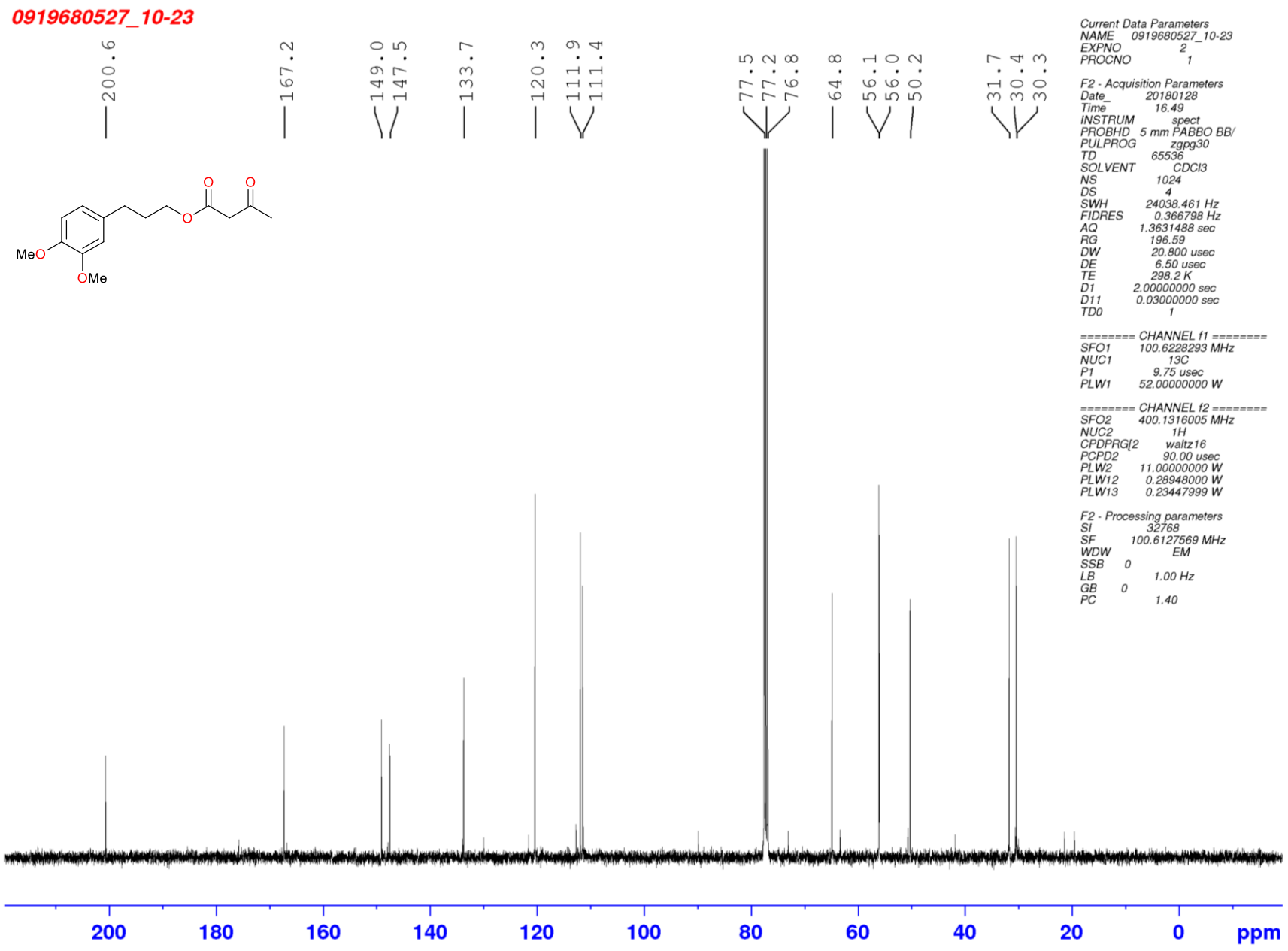


Figure S 51 **1-Acetoacetoxy-3(3,4-dimethoxyphenyl)propane** ^{13}C NMR ($CDCl_3$)

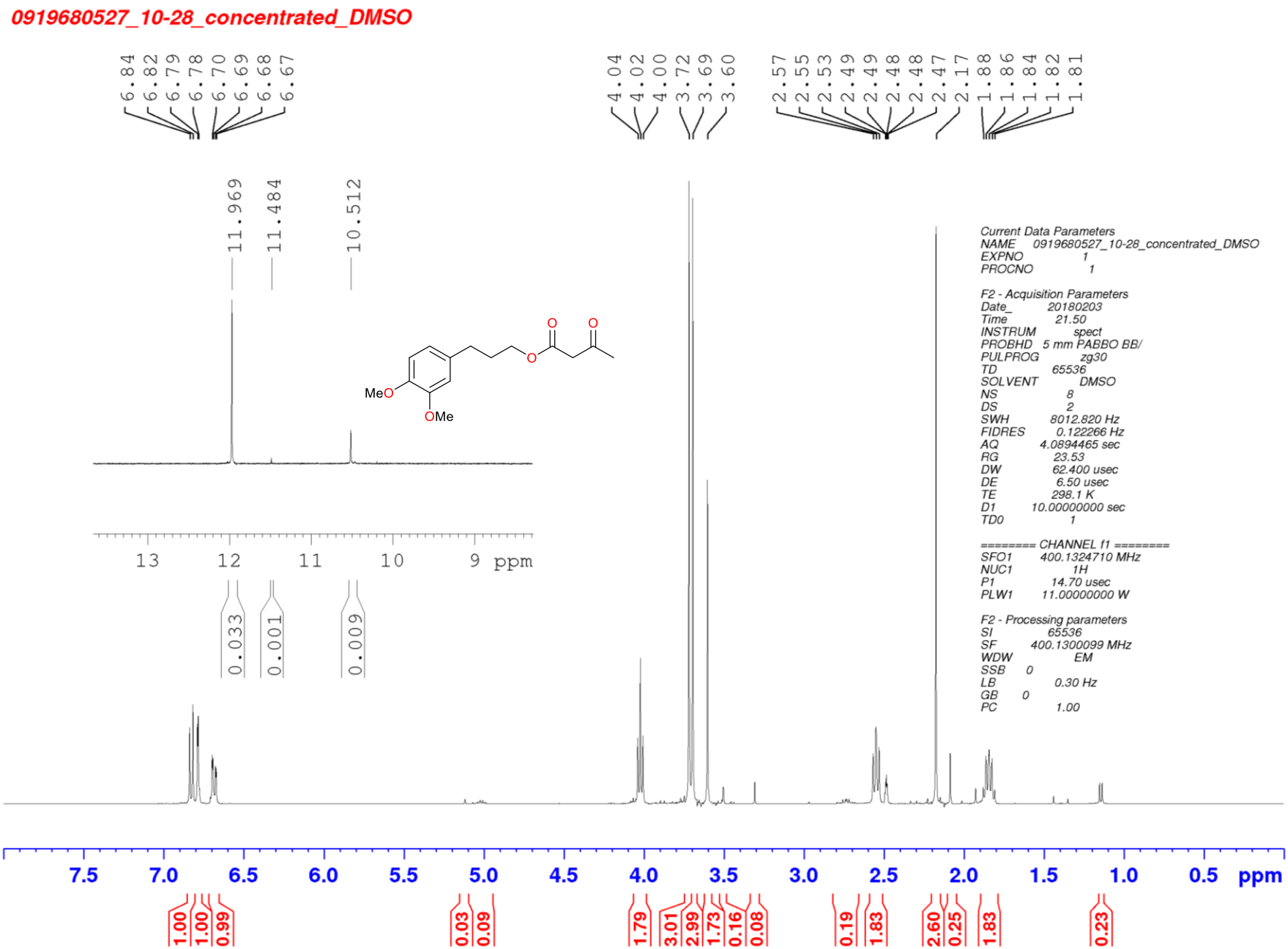


Figure S 52 **1-Acetoacetoxy-3(3,4-dimethoxyphenyl)propane** ^{1}H NMR (DMSO-d_6)

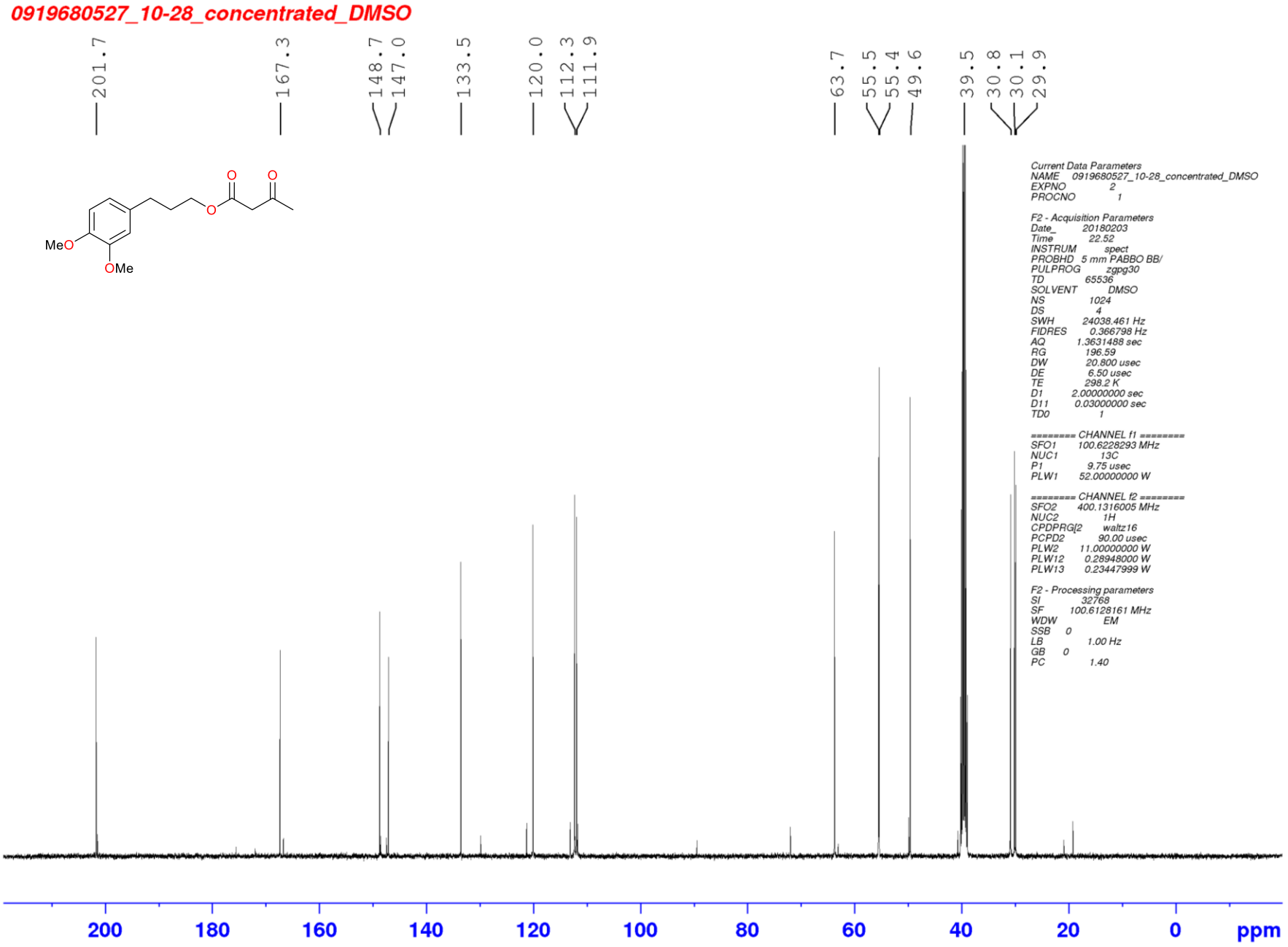


Figure S 53 **1-Acetoacetoxy-3(3,4-dimethoxyphenyl)propane** ^{13}C NMR (DMSO-d_6)

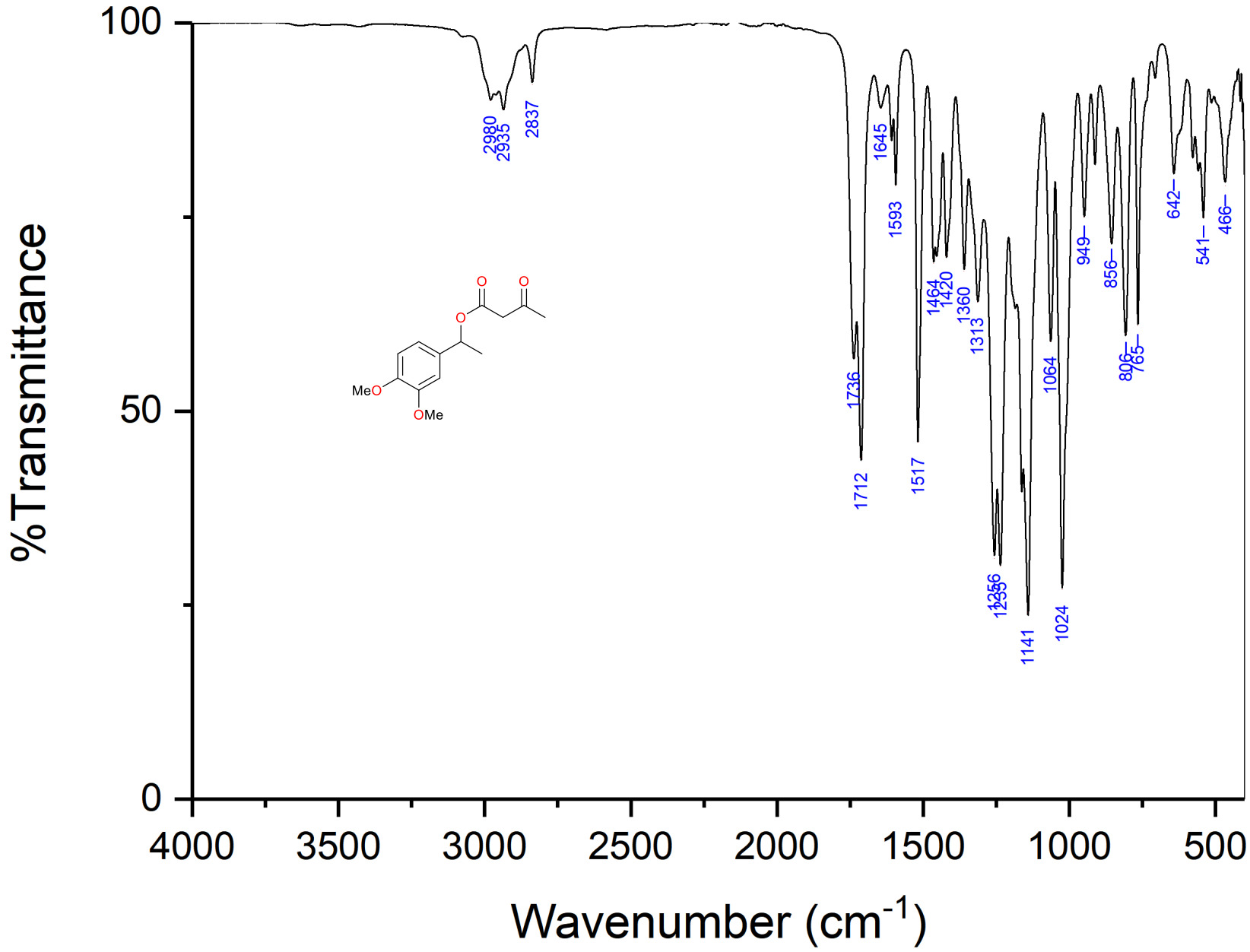


Figure S 54 **1-Acetoacetoxy-1(3,4-dimethoxyphenyl)ethane** FTIR (ATR, thin film from evaporation of $CDCl_3$)

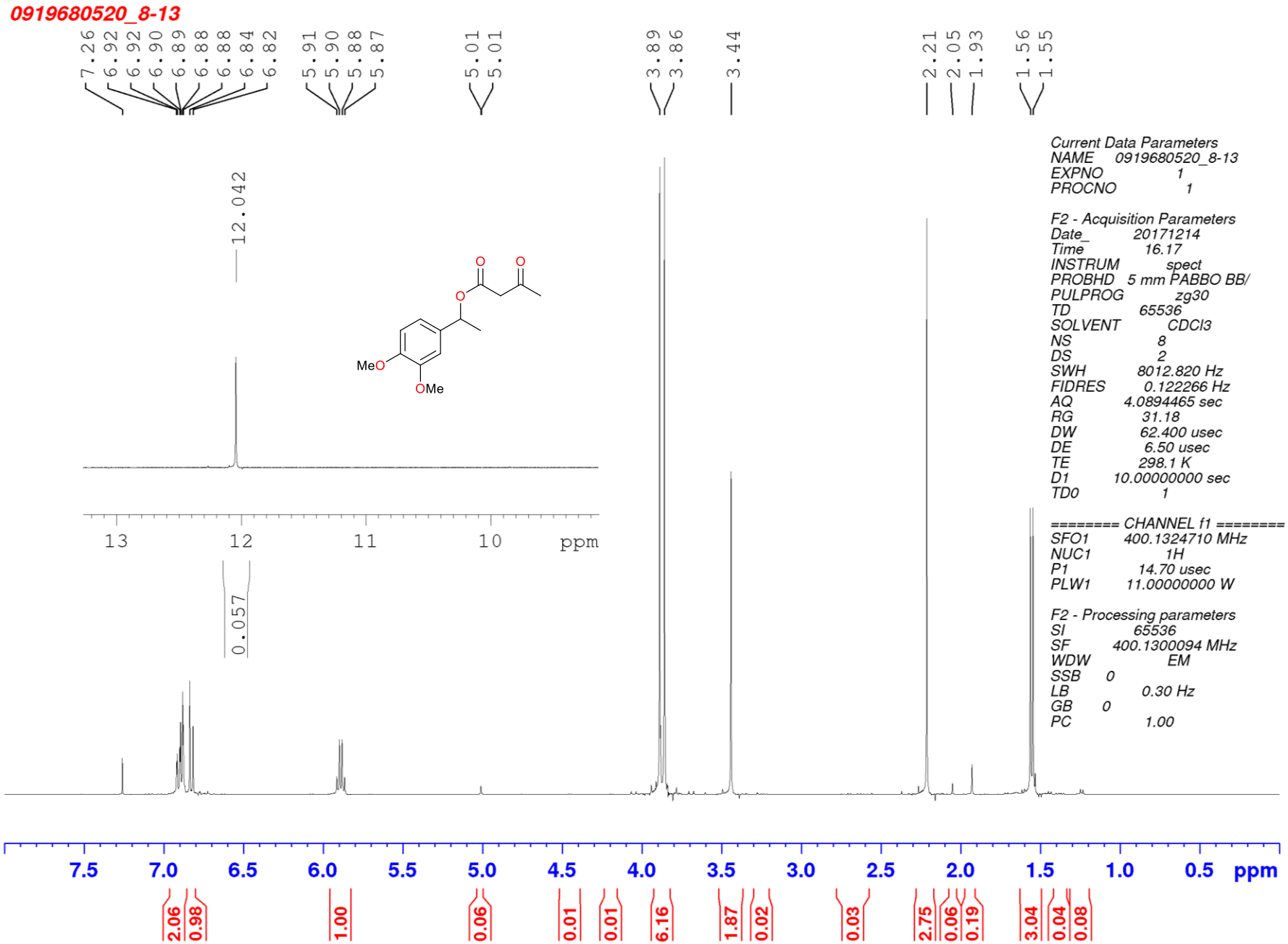


Figure S 55 **1-Acetoacetoxy-1(3,4-dimethoxyphenyl)ethane** ^{1}H NMR ($CDCl_3$)

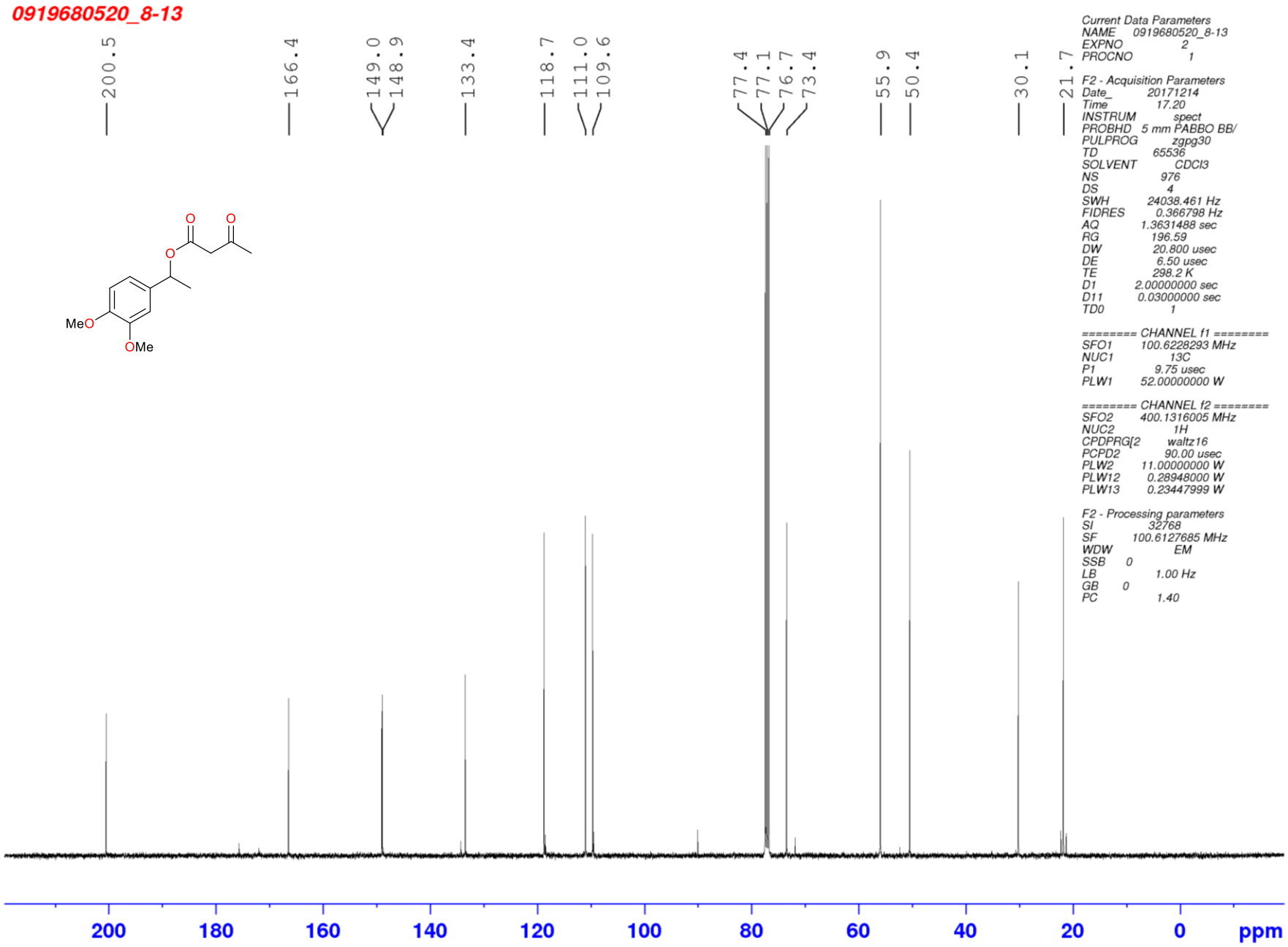


Figure S 56 **1-Acetoacetoxy-1(3,4-dimethoxyphenyl)ethane** ^{13}C NMR ($CDCl_3$)

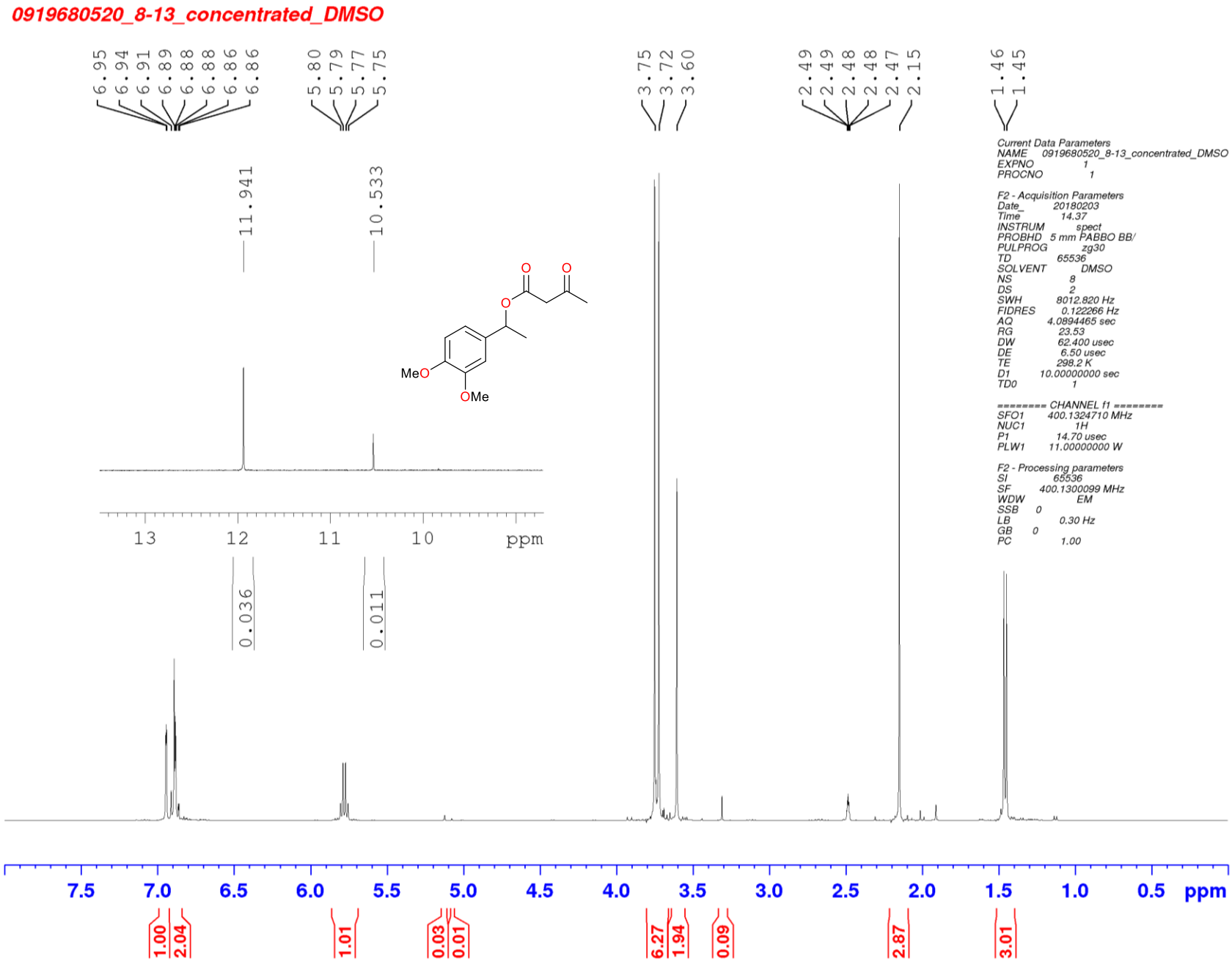


Figure S 57 **1-Acetoacetoxy-1(3,4-dimethoxyphenyl)ethane** ^{1}H NMR (DMSO-d_6)

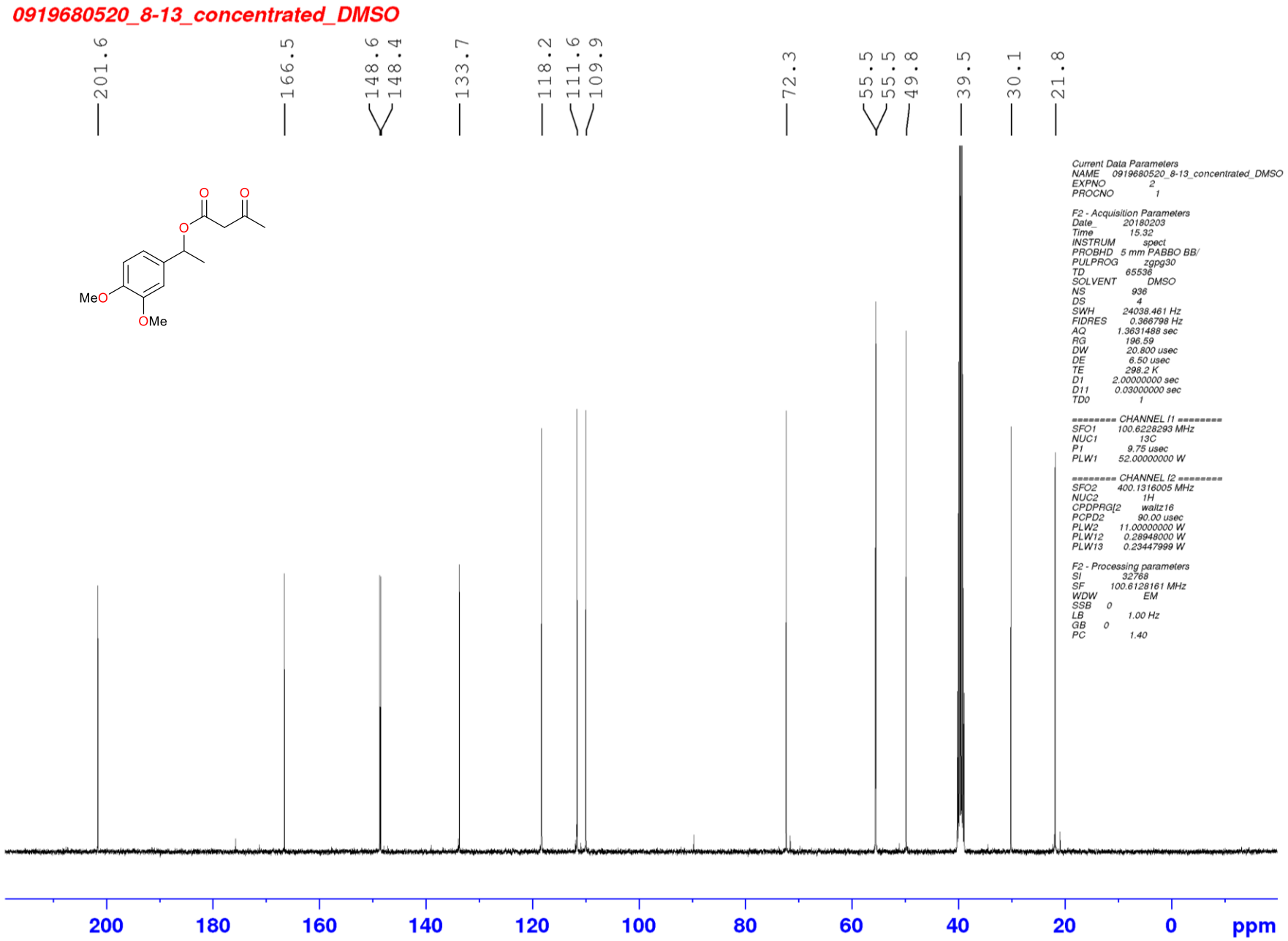


Figure S 58 **1-Acetoacetoxy-1(3,4-dimethoxyphenyl)ethane** ^{13}C NMR (DMSO-d_6)

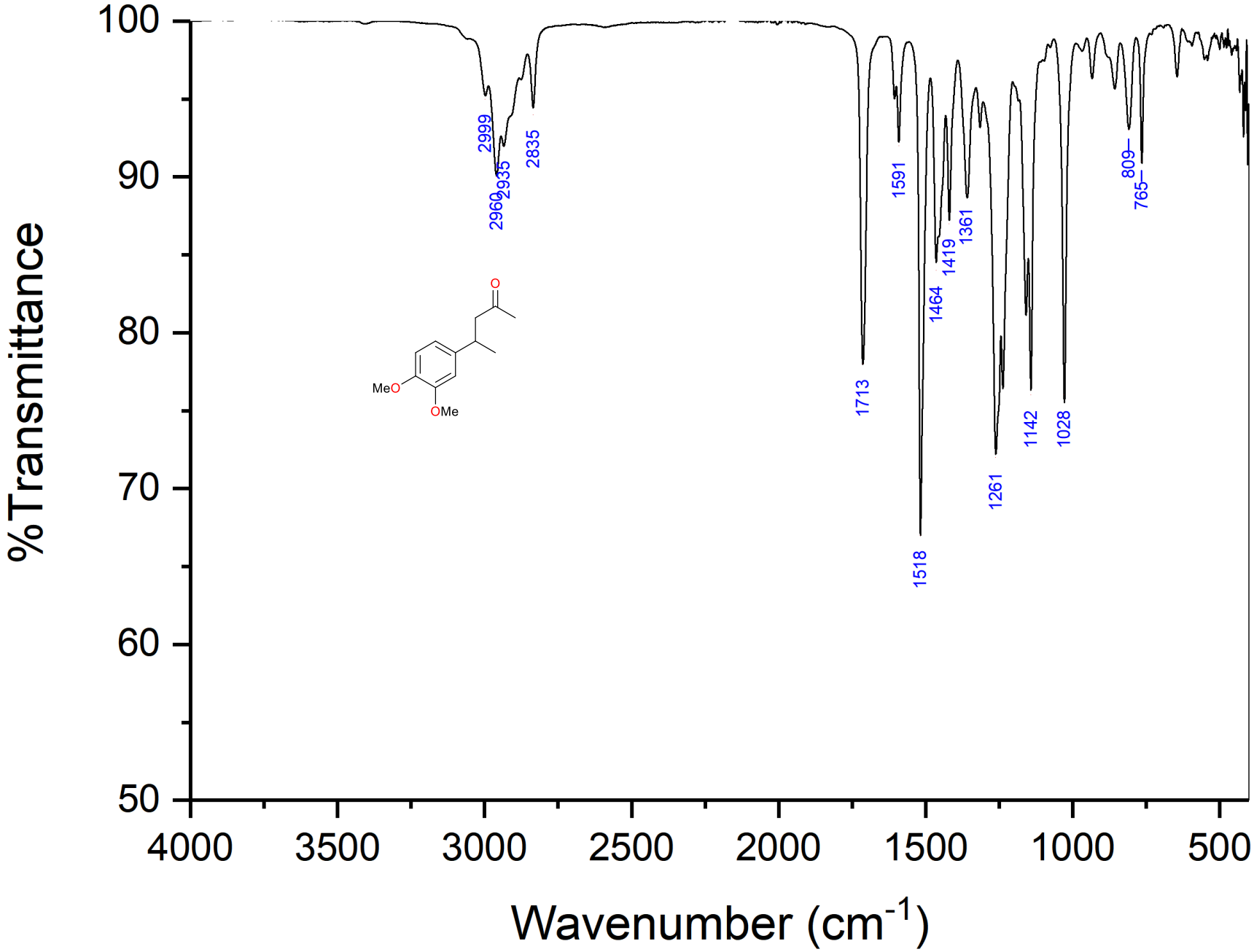


Figure S 59 **4-(3,4-dimethoxyphenyl)-pentan-2-one** FTIR (ATR, thin film from evaporation of $CDCl_3$)

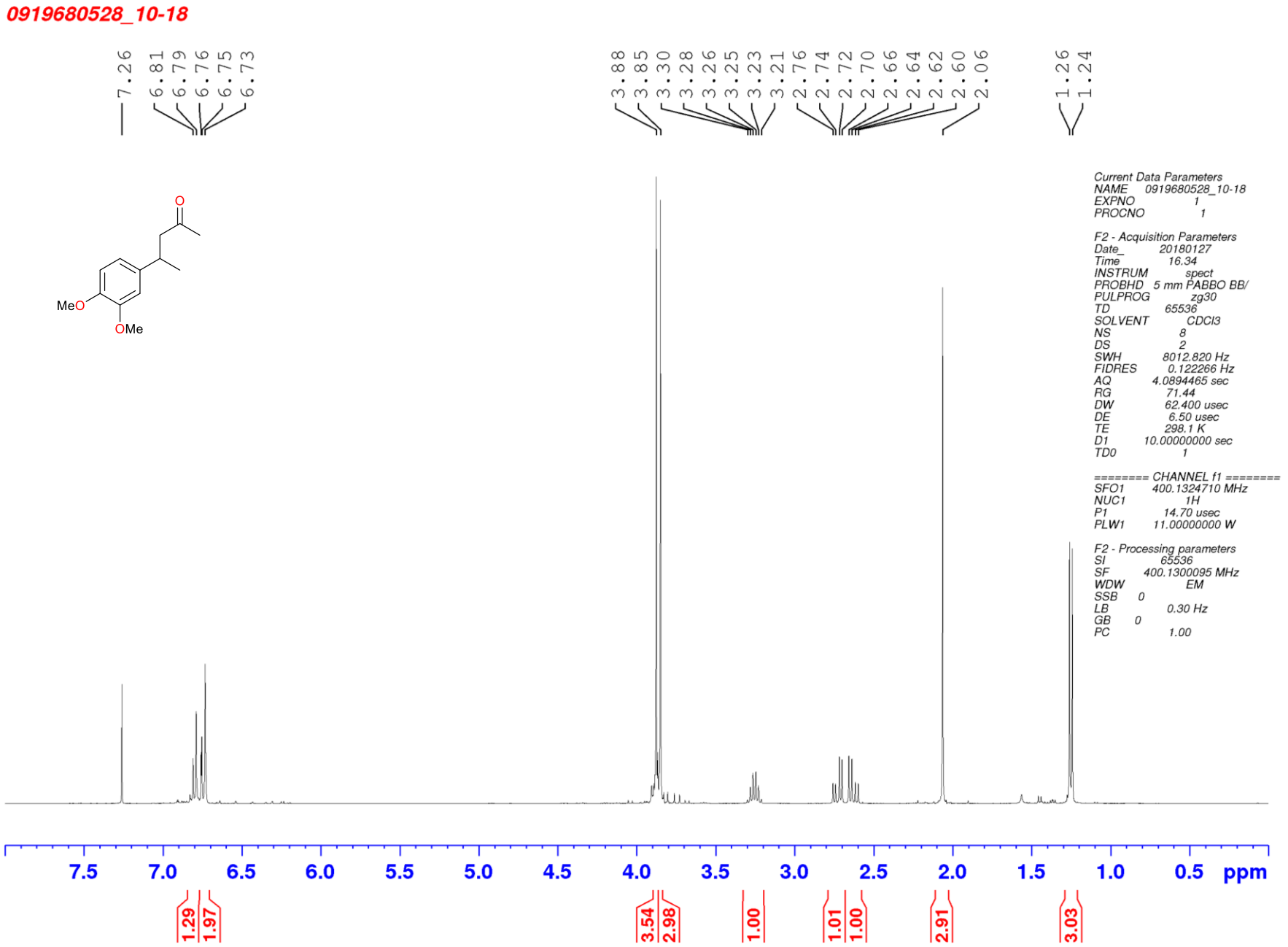


Figure S 60 **4-(3,4-dimethoxyphenyl)-pentan-2-one** ^{1}H NMR ($CDCl_3$)

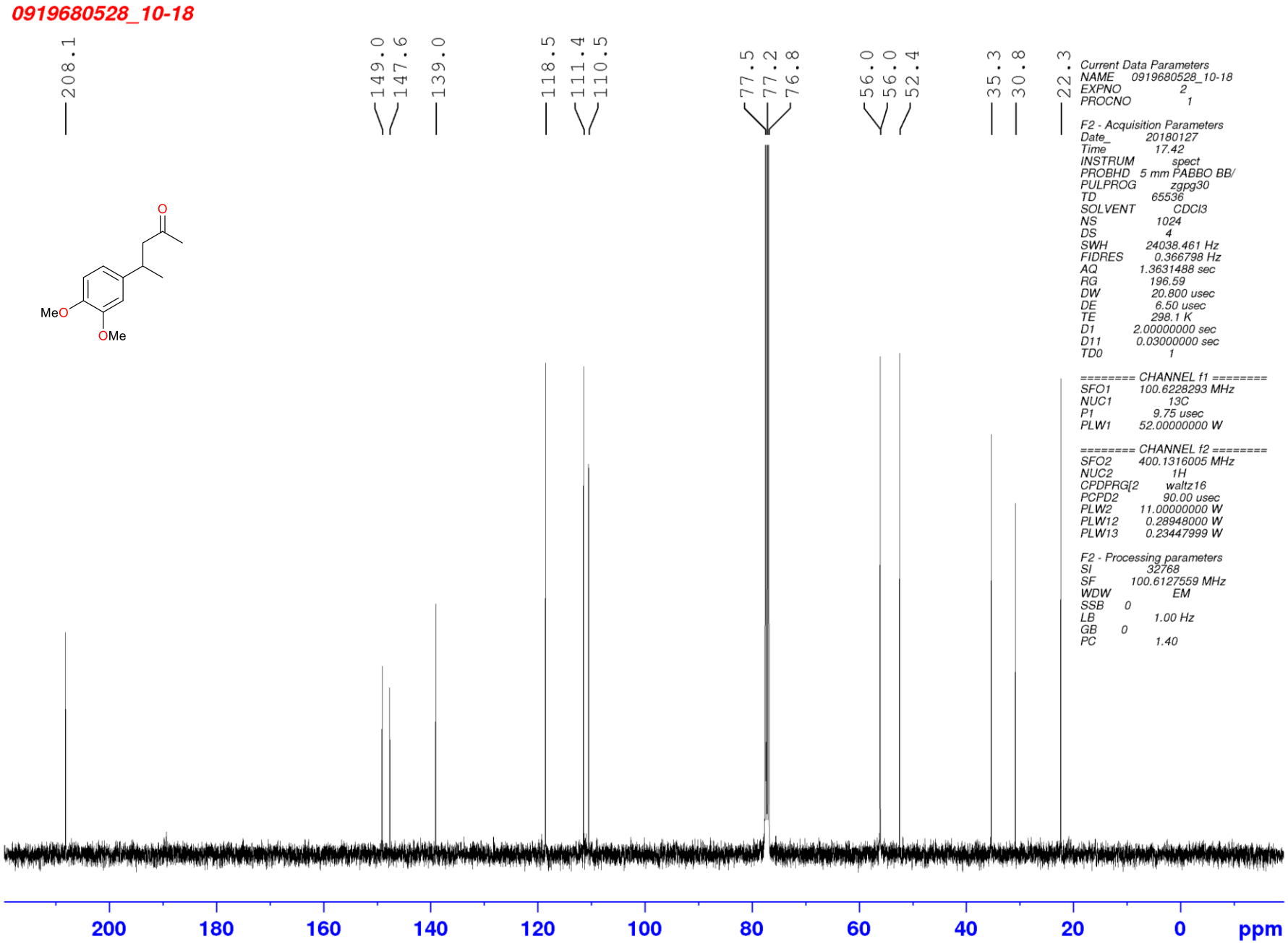


Figure S 61 **4-(3,4-dimethoxyphenyl)-pentan-2-one** ^{13}C NMR ($CDCl_3$)

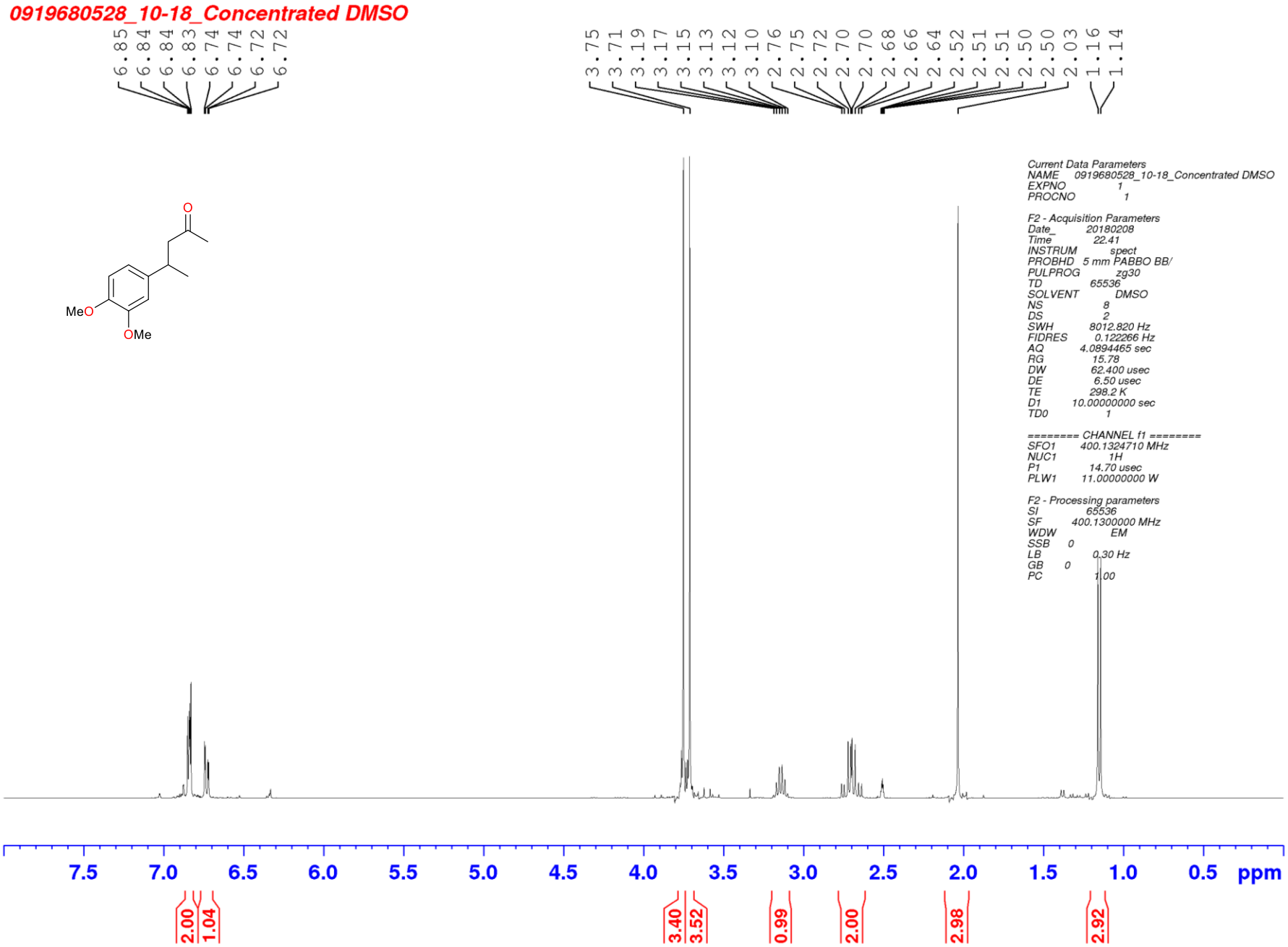


Figure S 62 **4-(3,4-dimethoxyphenyl)-pentan-2-one** ^{1}H NMR (DMSO d_6)

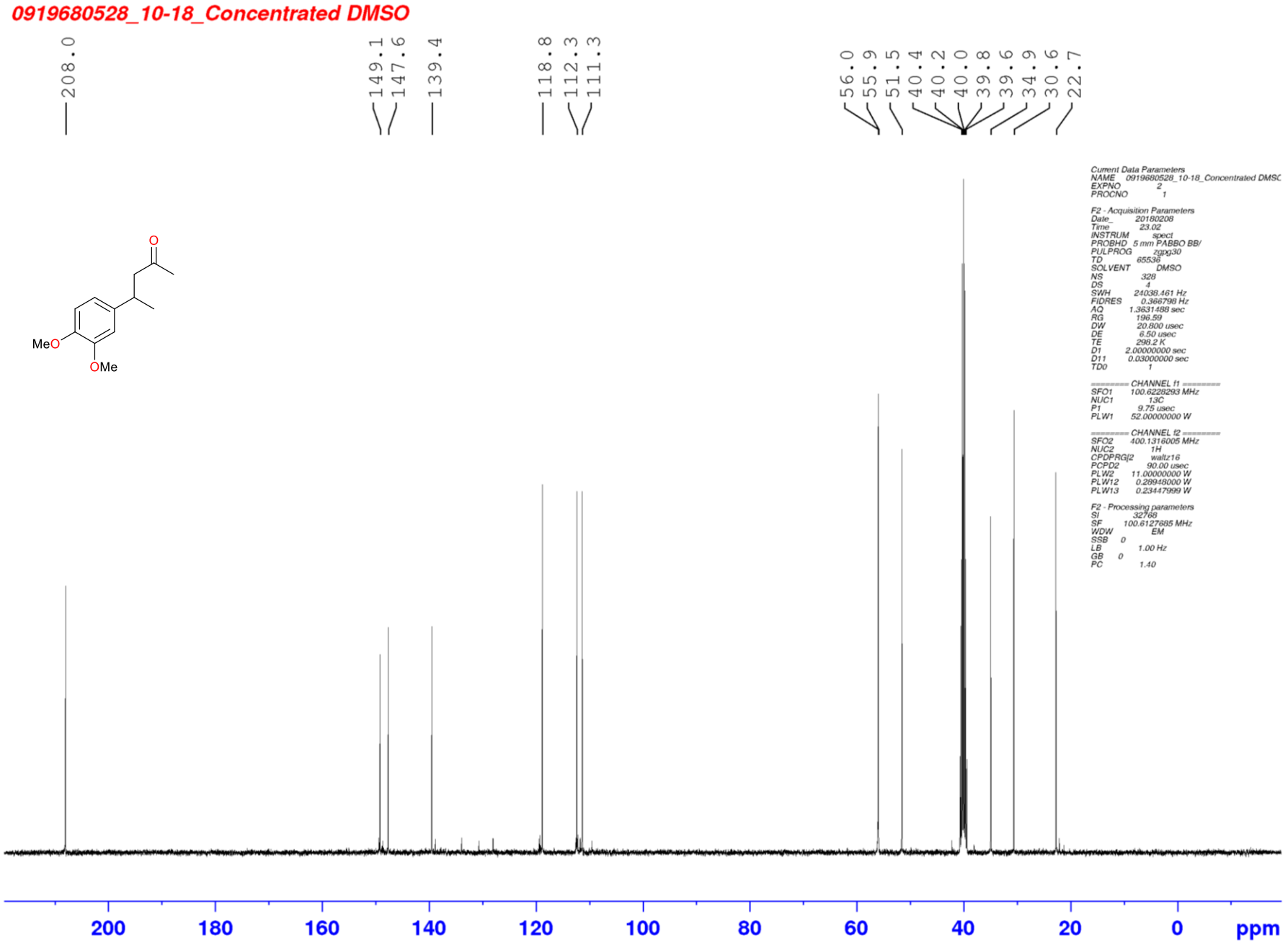


Figure S 63 **4-(3,4-dimethoxyphenyl)-pentan-2-one** ^{13}C NMR (DMSO d_6)

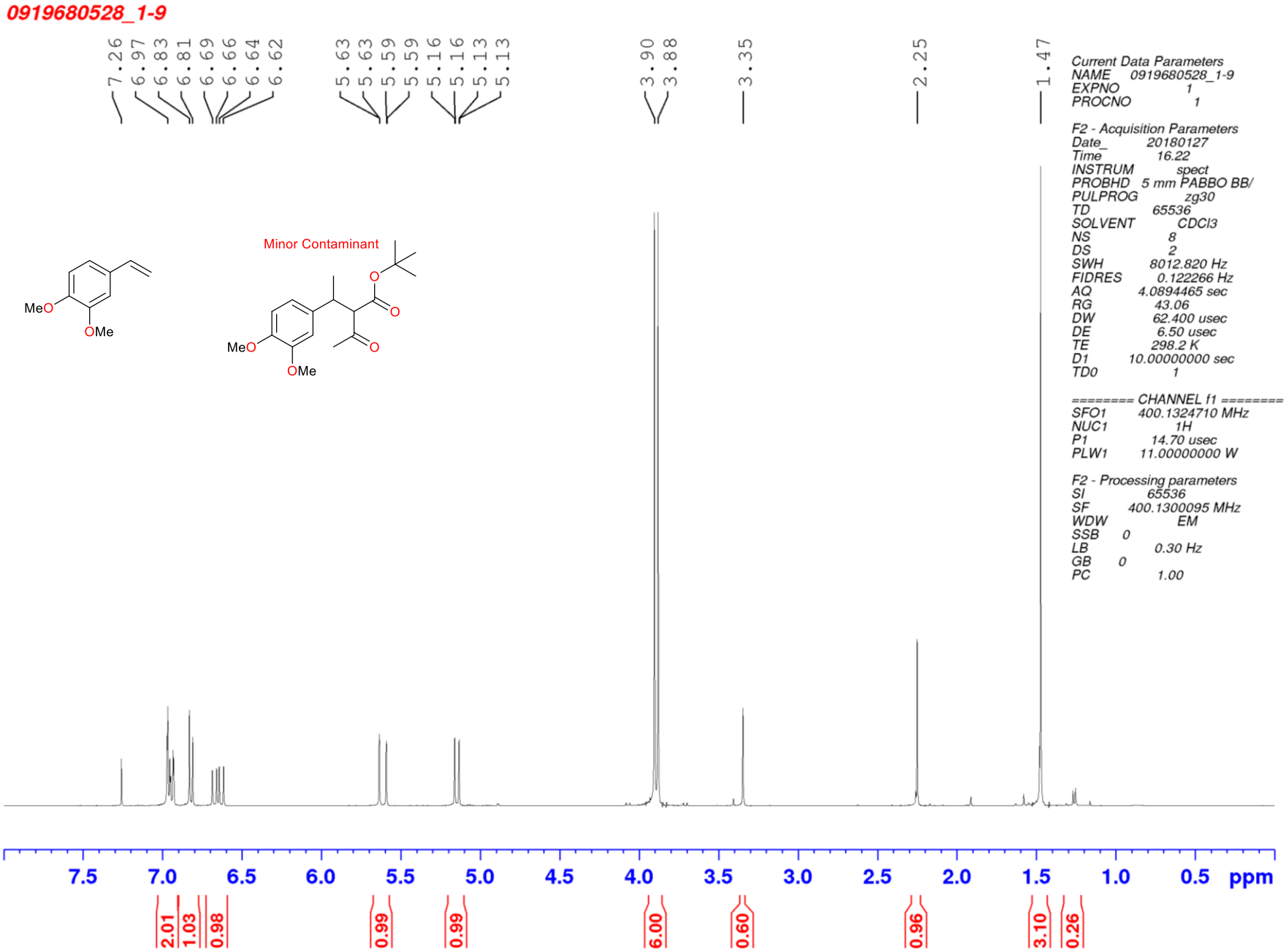


Figure S 64 4-**Vinylveratrole & t-butyl acetoacetate** ^{1}H NMR ($CDCl_3$)

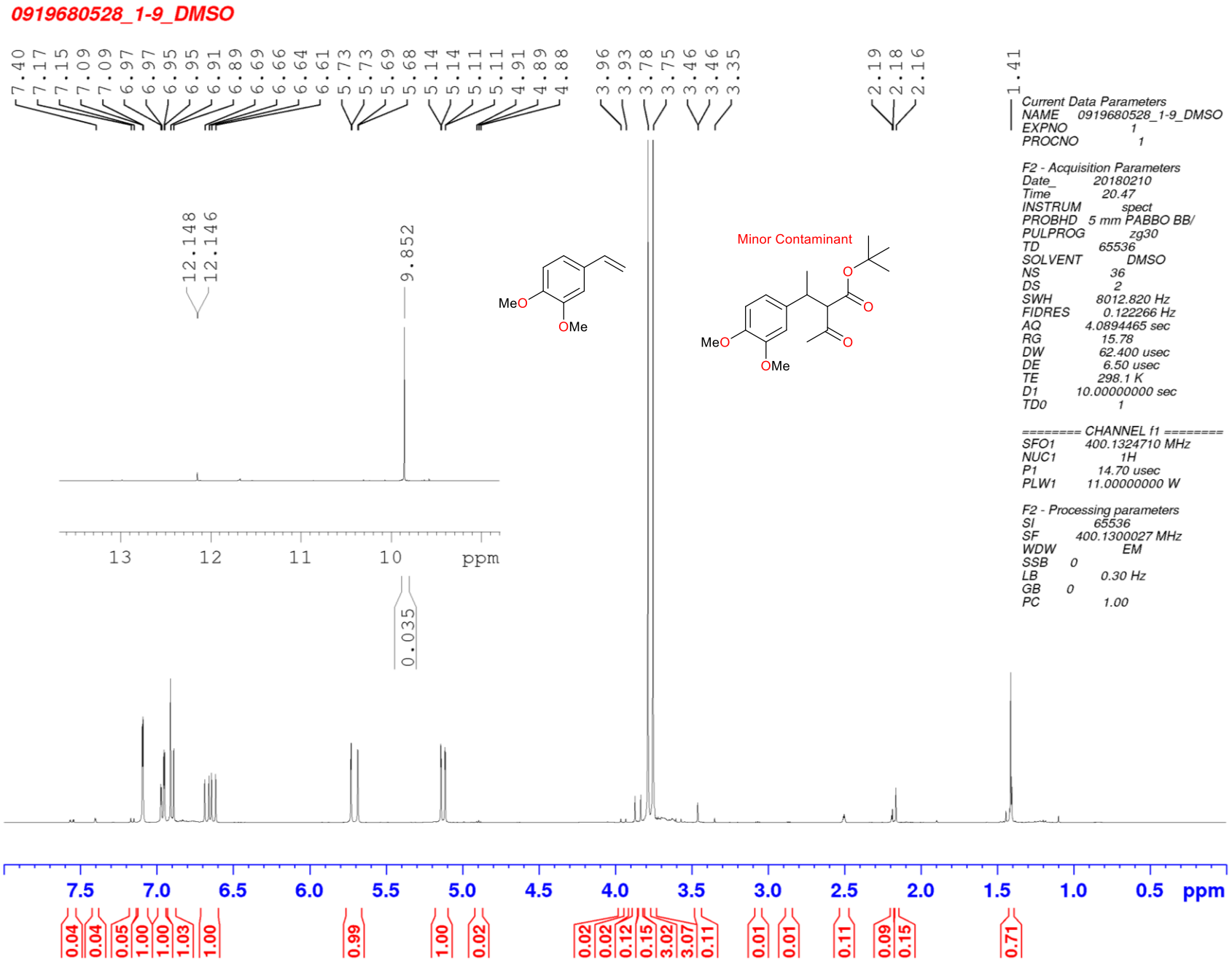


Figure S 65 **4-Vinylveratrole & t-butyl acetoacetate** ^{1}H NMR (DMSO d_6)

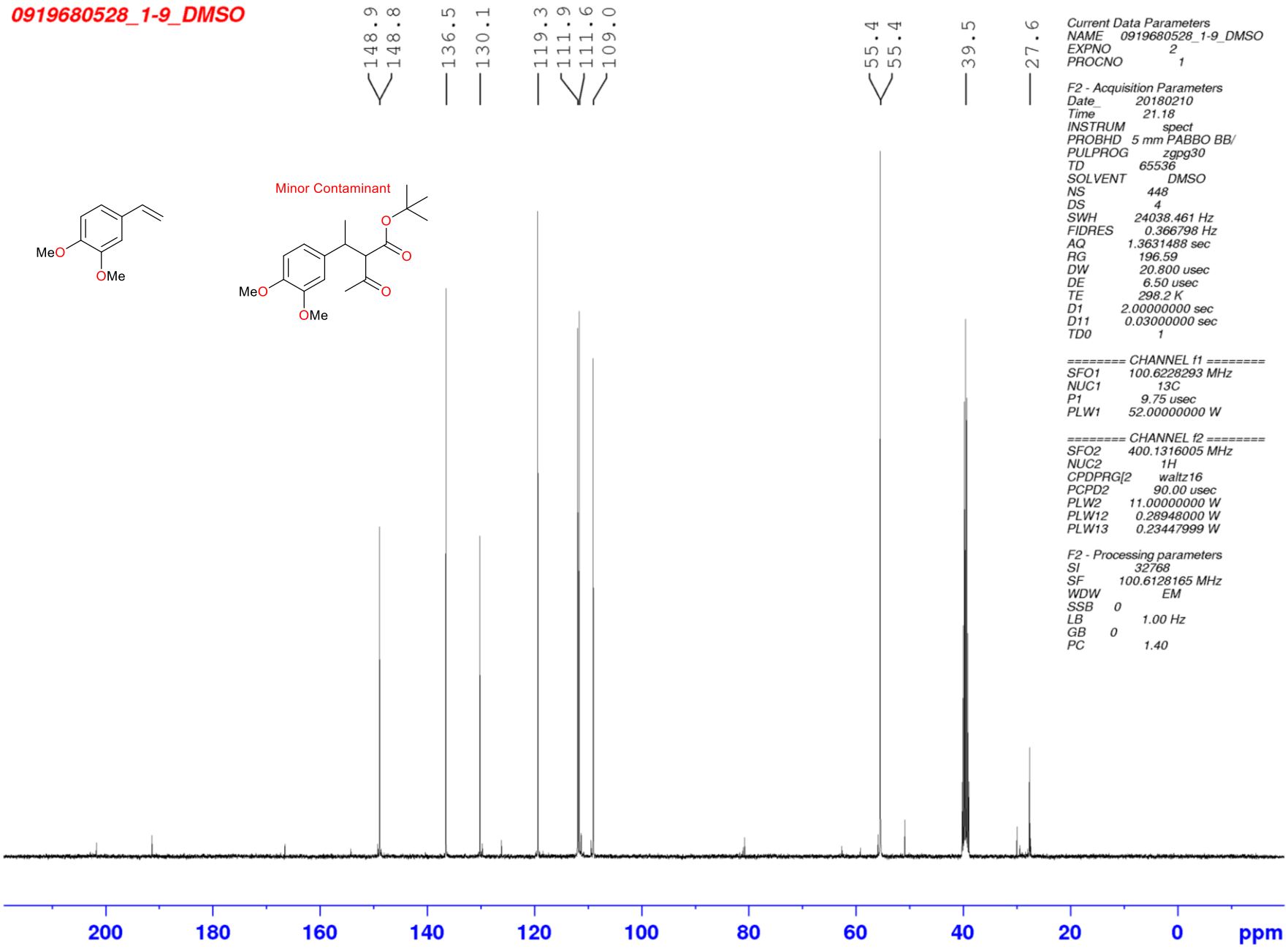


Figure S 66 **4-Vinylveratrole & t-butyl acetoacetate** ^{13}C NMR (DMSO d_6)

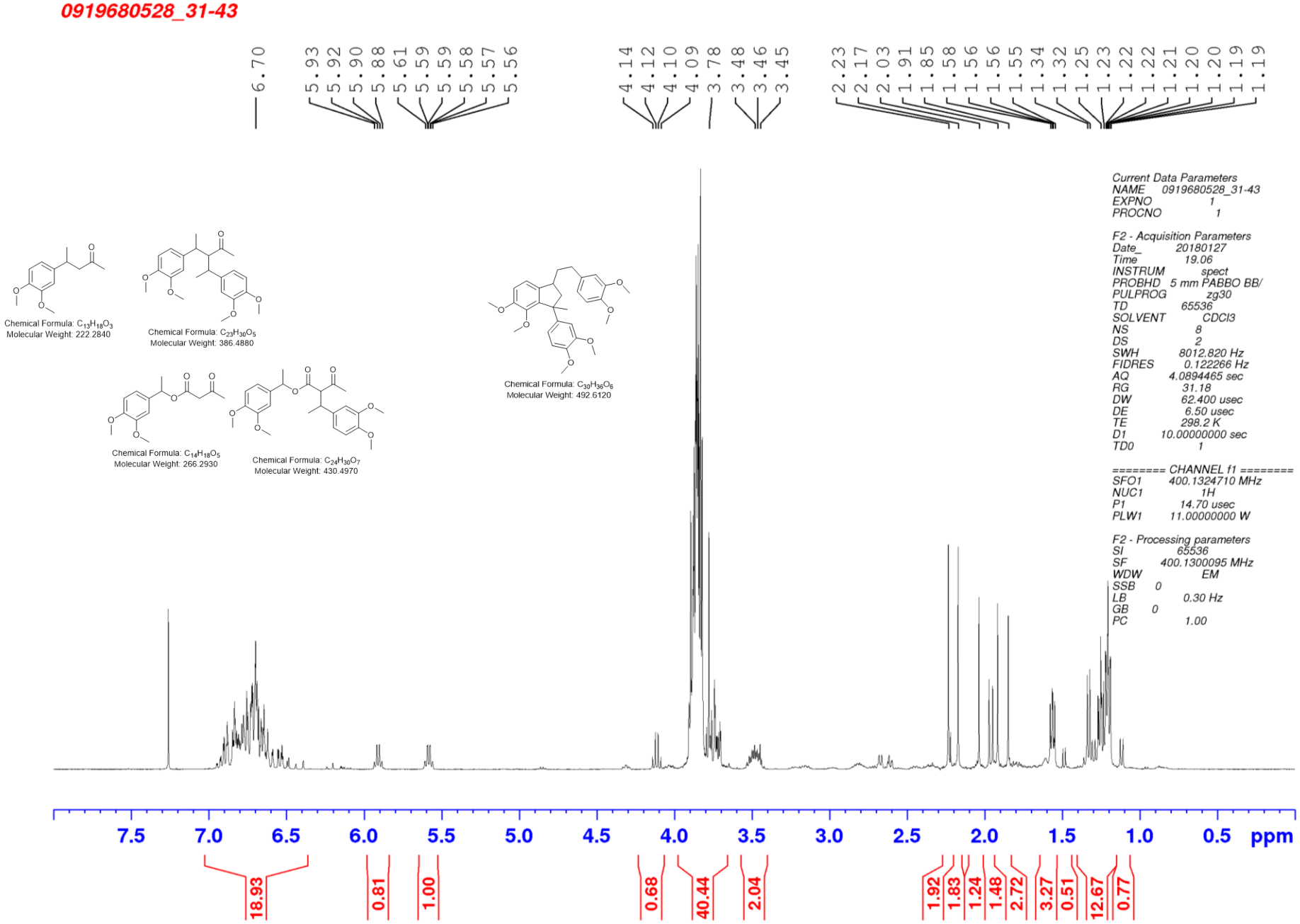


Figure S 67 **Additional degradation products from acetoacetylation of 1-(3,4-dimethoxyphenyl)ethan-1-ol** ^{1}H NMR ($CDCl_3$)

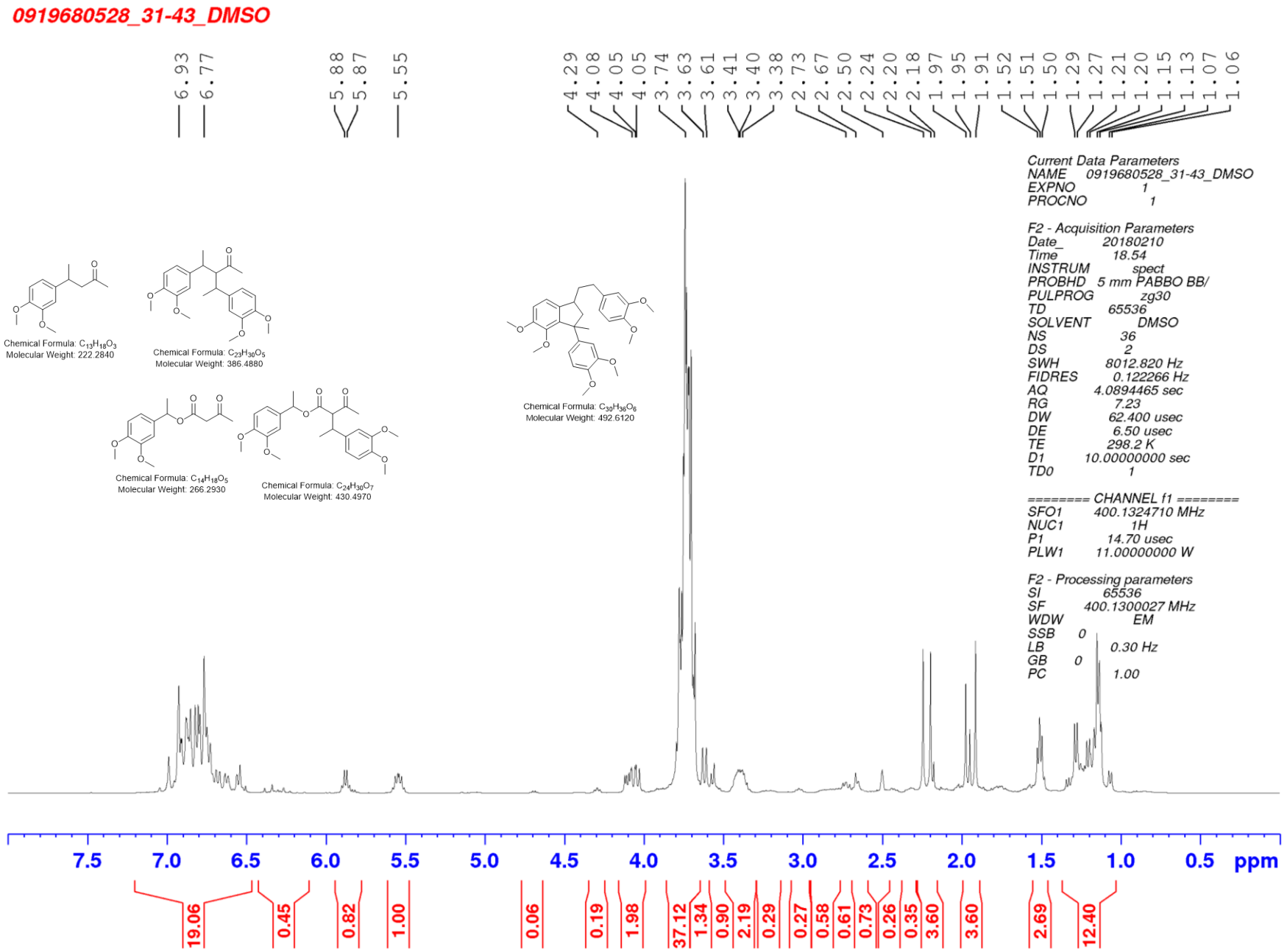


Figure S 68 **Additional degradation products from acetoacetylation of 1-(3,4-dimethoxyphenyl)ethan-1-ol** ^{1}H NMR (DMSO d_6)

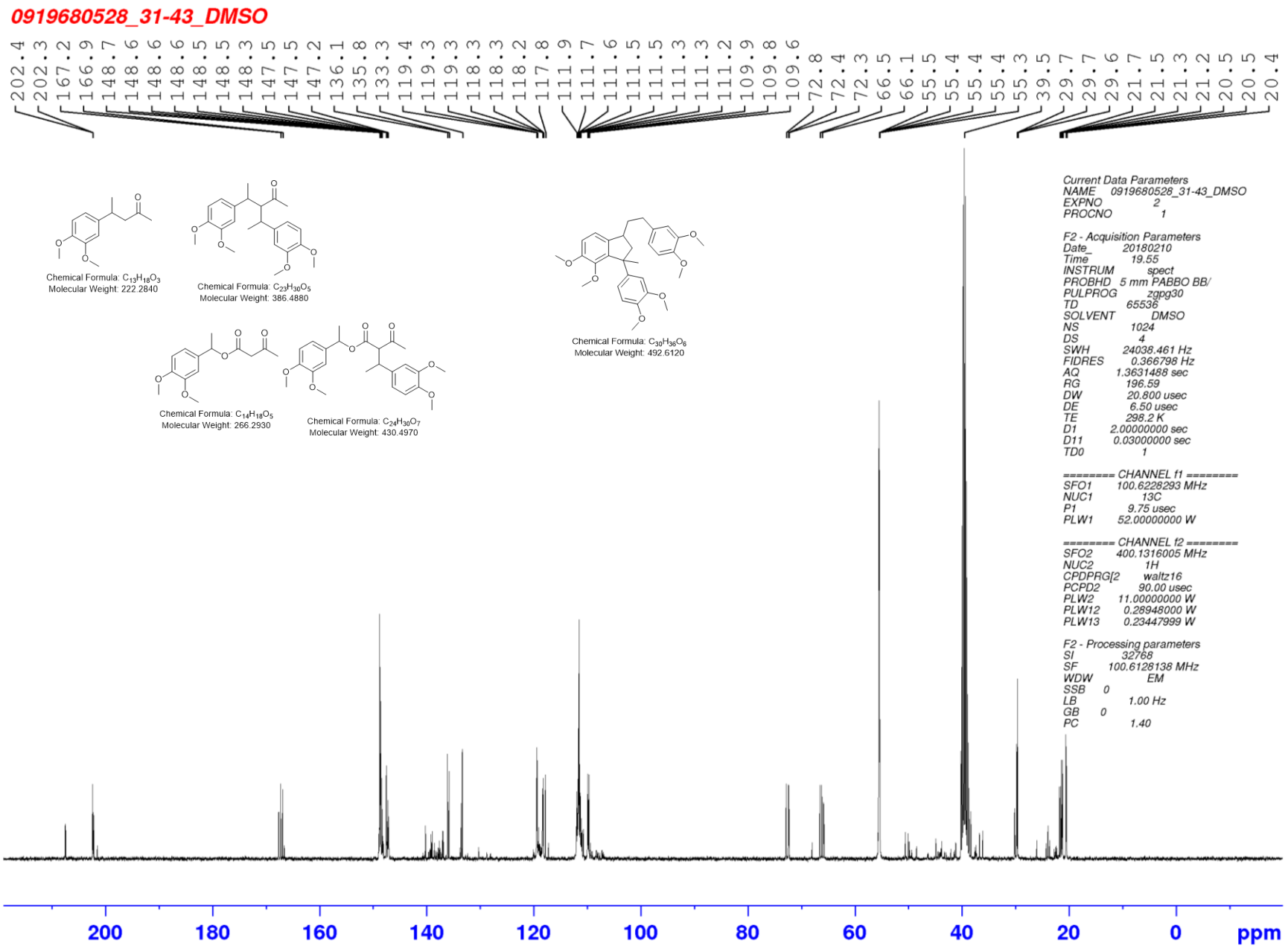


Figure S 69 **Additional degradation products from acetoacetylation of 1-(3,4-dimethoxyphenyl)ethan-1-ol** ^{13}C NMR (DMSO-d_6)

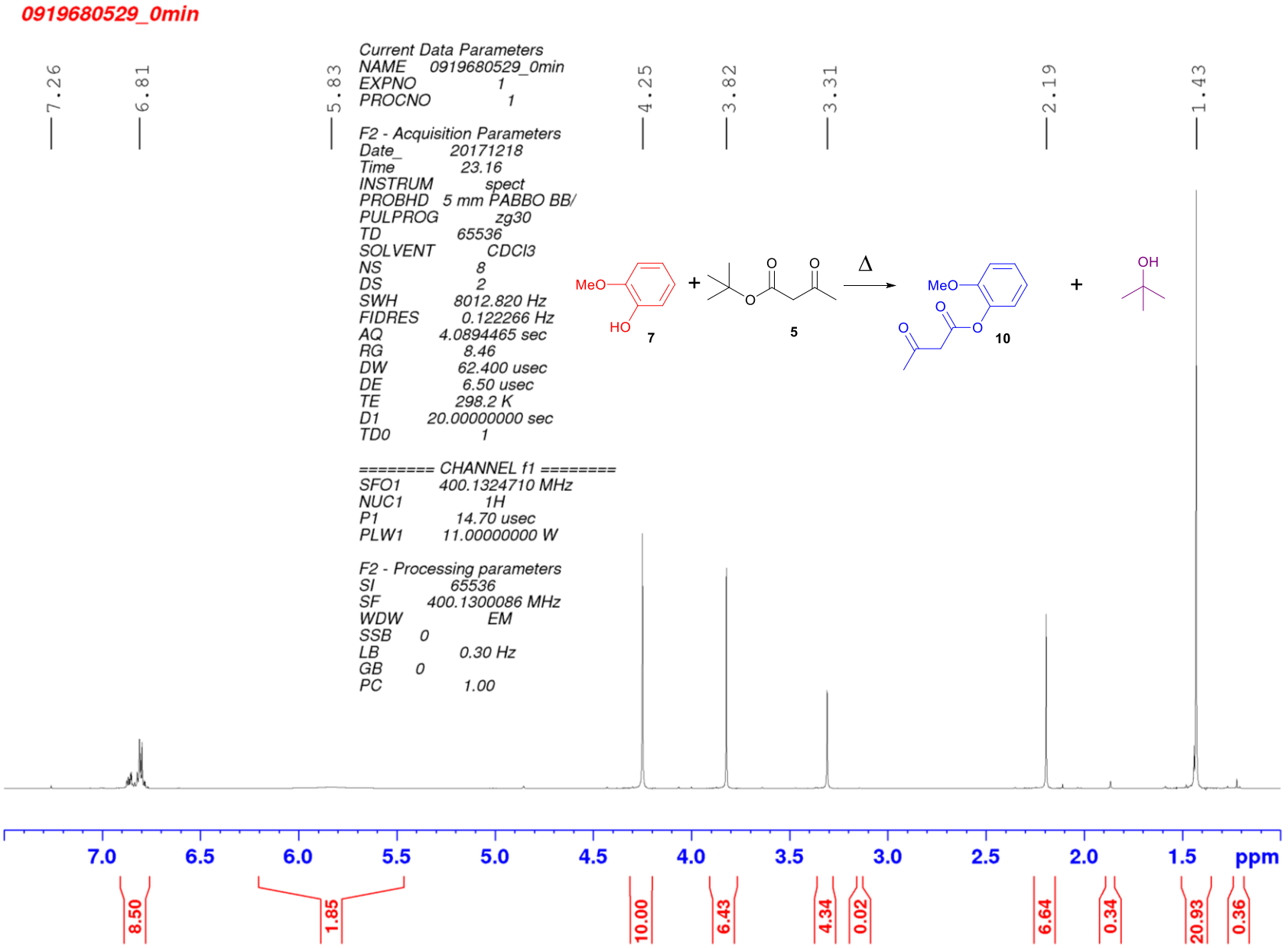


Figure S 70 **Acetoacetylation of guaiacol**: 0 min ($CDCl_3$, ^1H NMR)

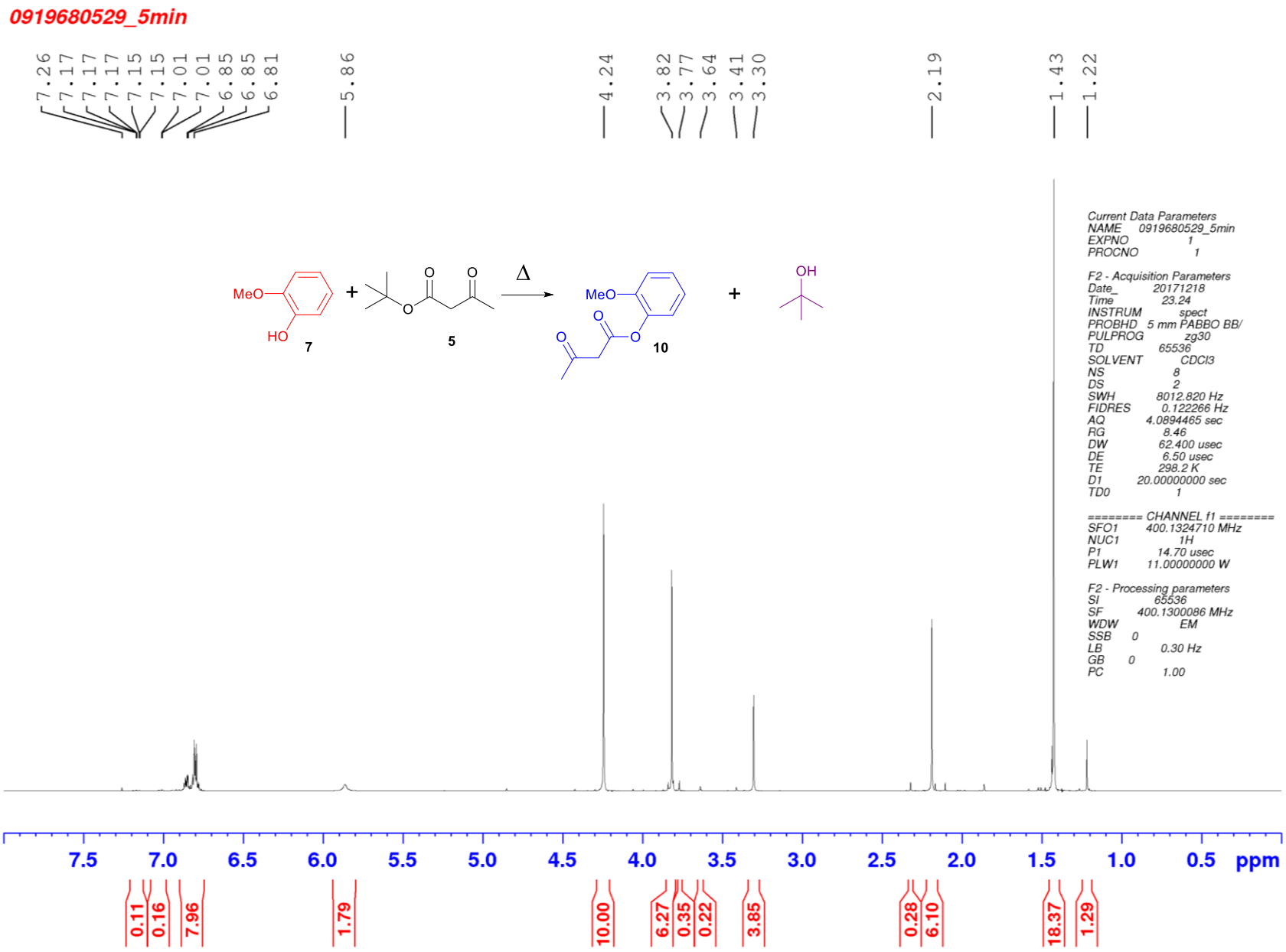


Figure S 71 **Acetoacetylation of guaiacol**: 5 min ($CDCl_3$, ^1H NMR)

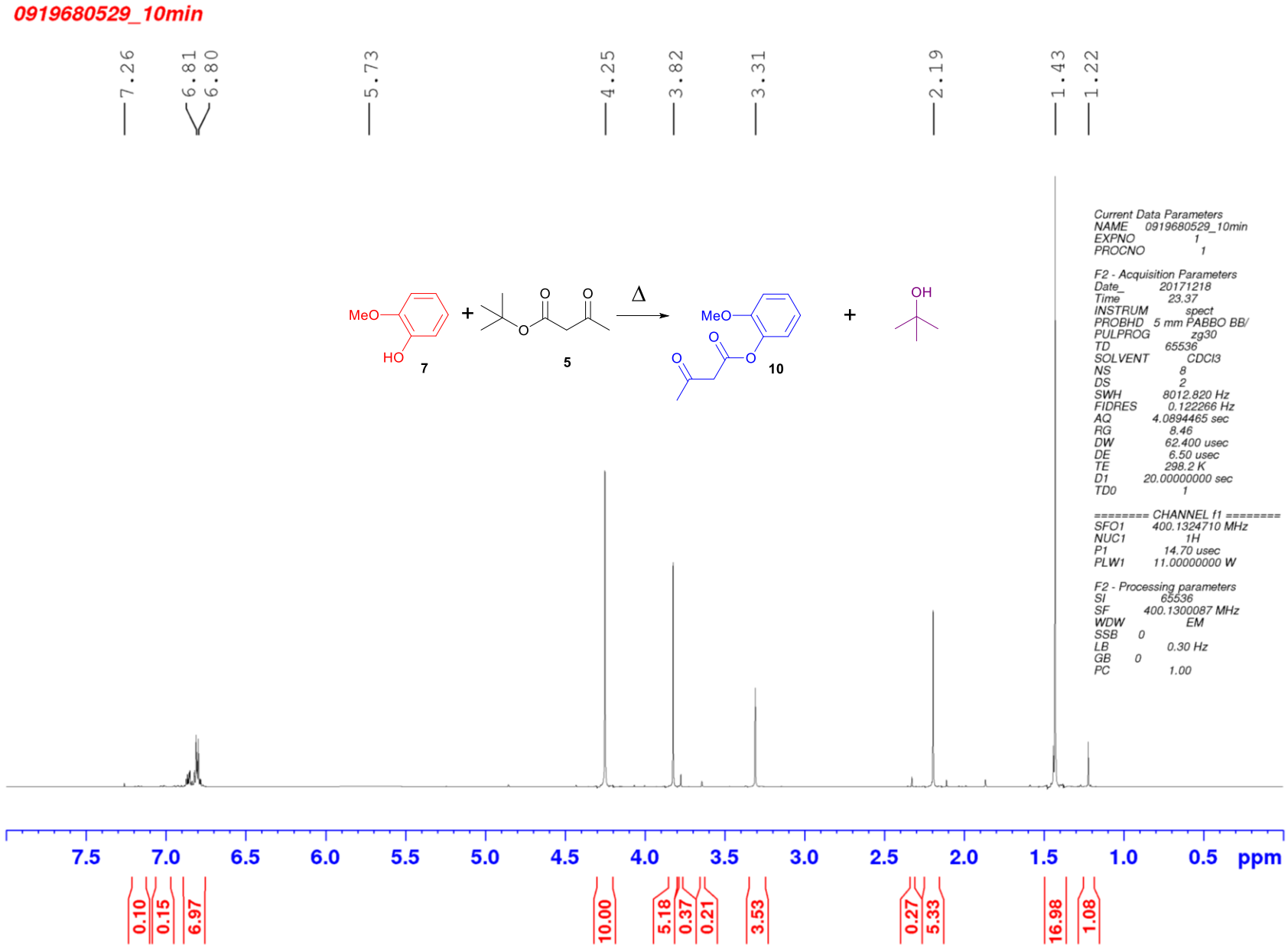


Figure S 72 **Acetoacetylation of guaiacol**: 10 min ($CDCl_3$, ^1H NMR)

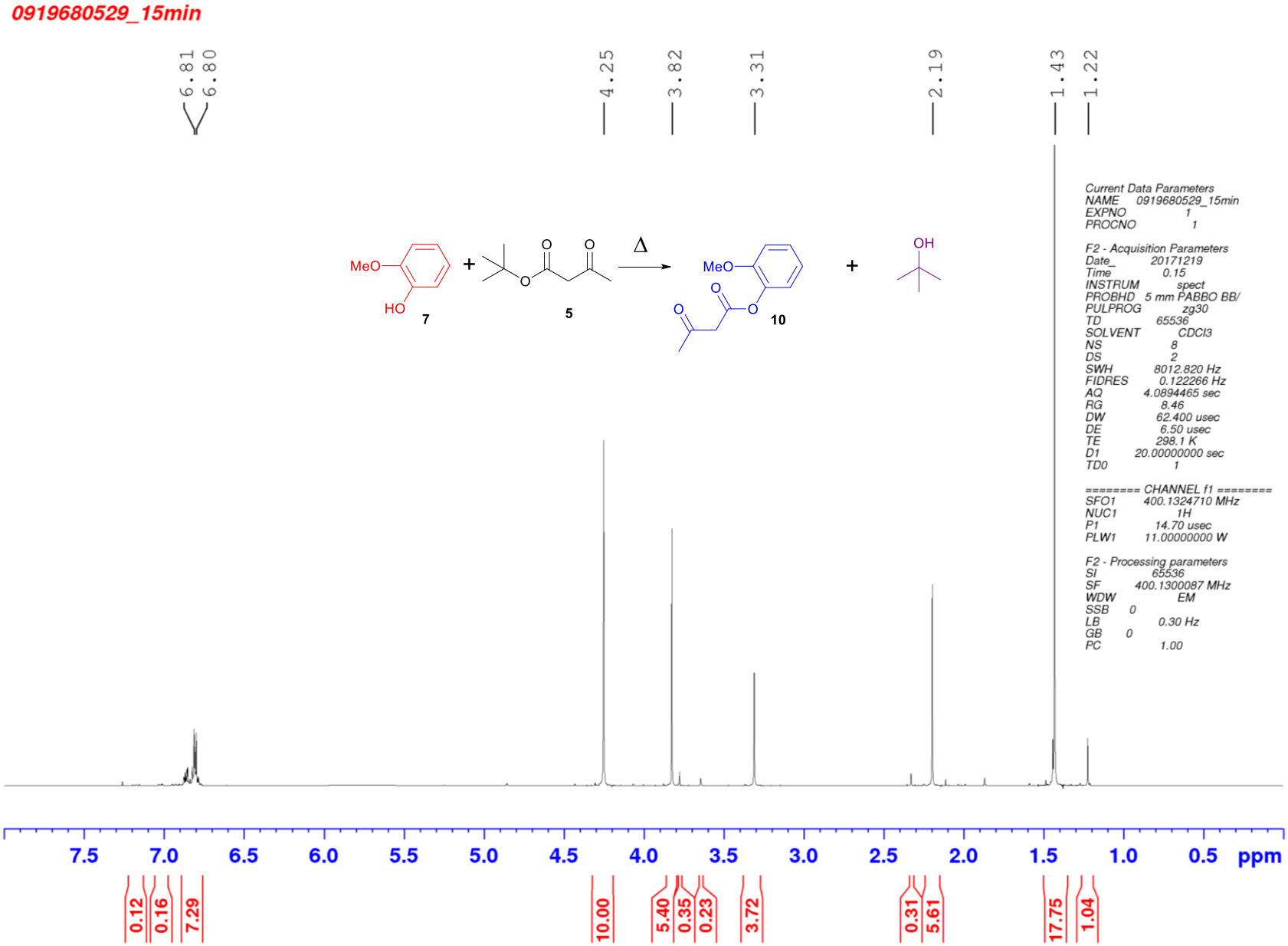


Figure S 73 **Acetoacetylation of guaiacol**: 15 min ($CDCl_3$, ^1H NMR)

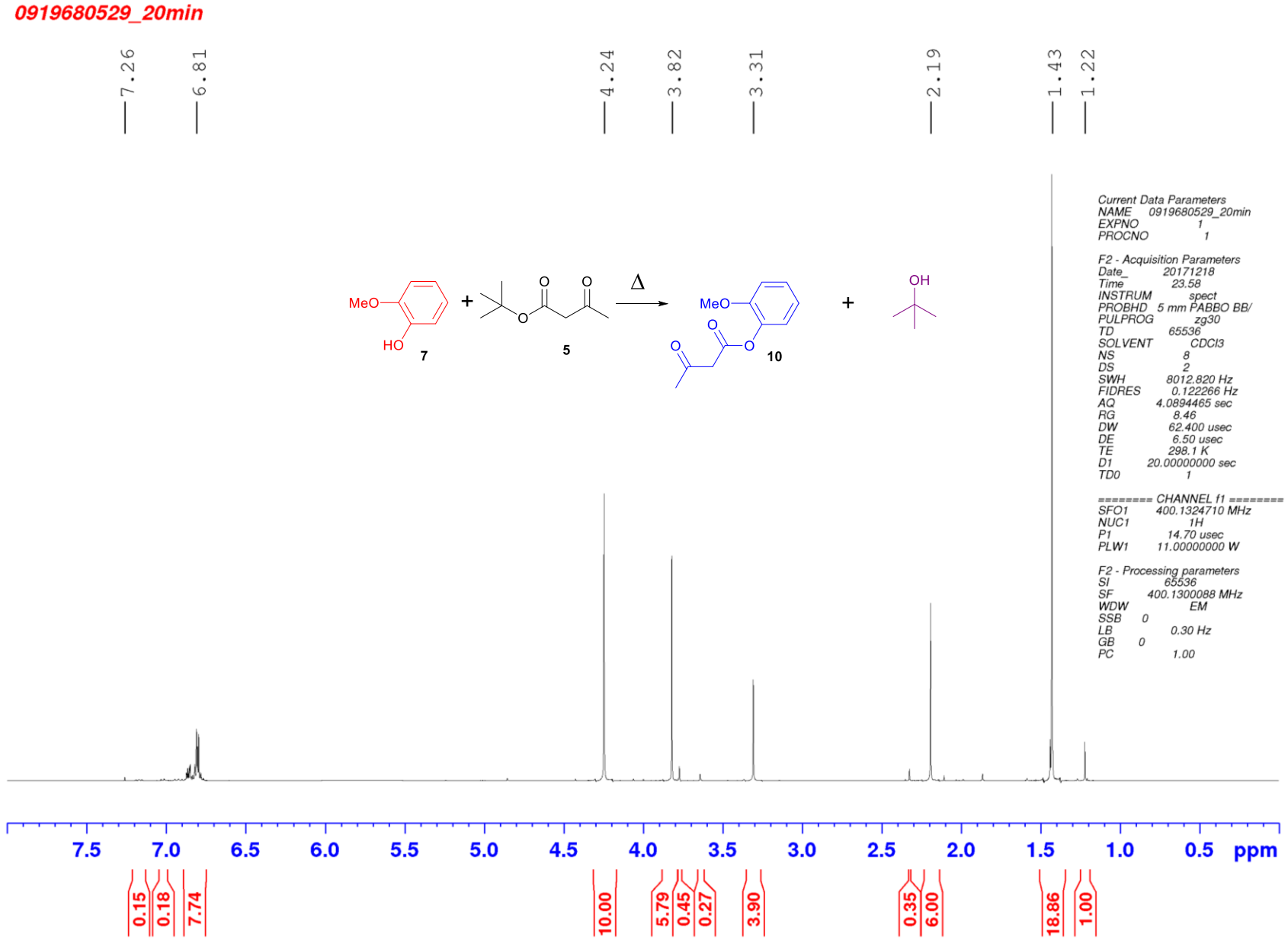


Figure S 74 **Acetoacetylation of guaiacol**: 20 min ($CDCl_3$, ^1H NMR)

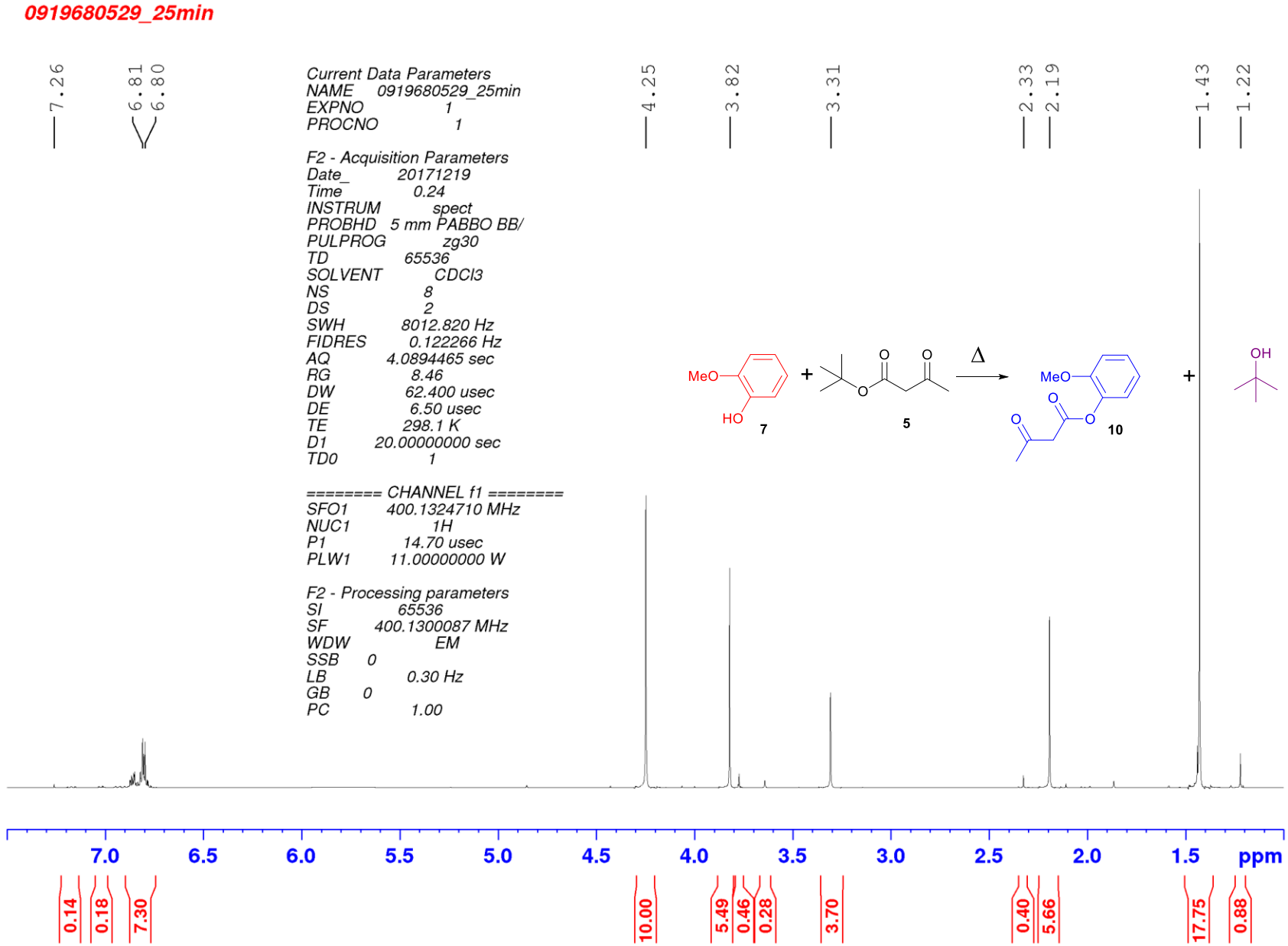


Figure S 75 **Acetoacetylation of guaiacol**: 25 min ($CDCl_3$, ^1H NMR)

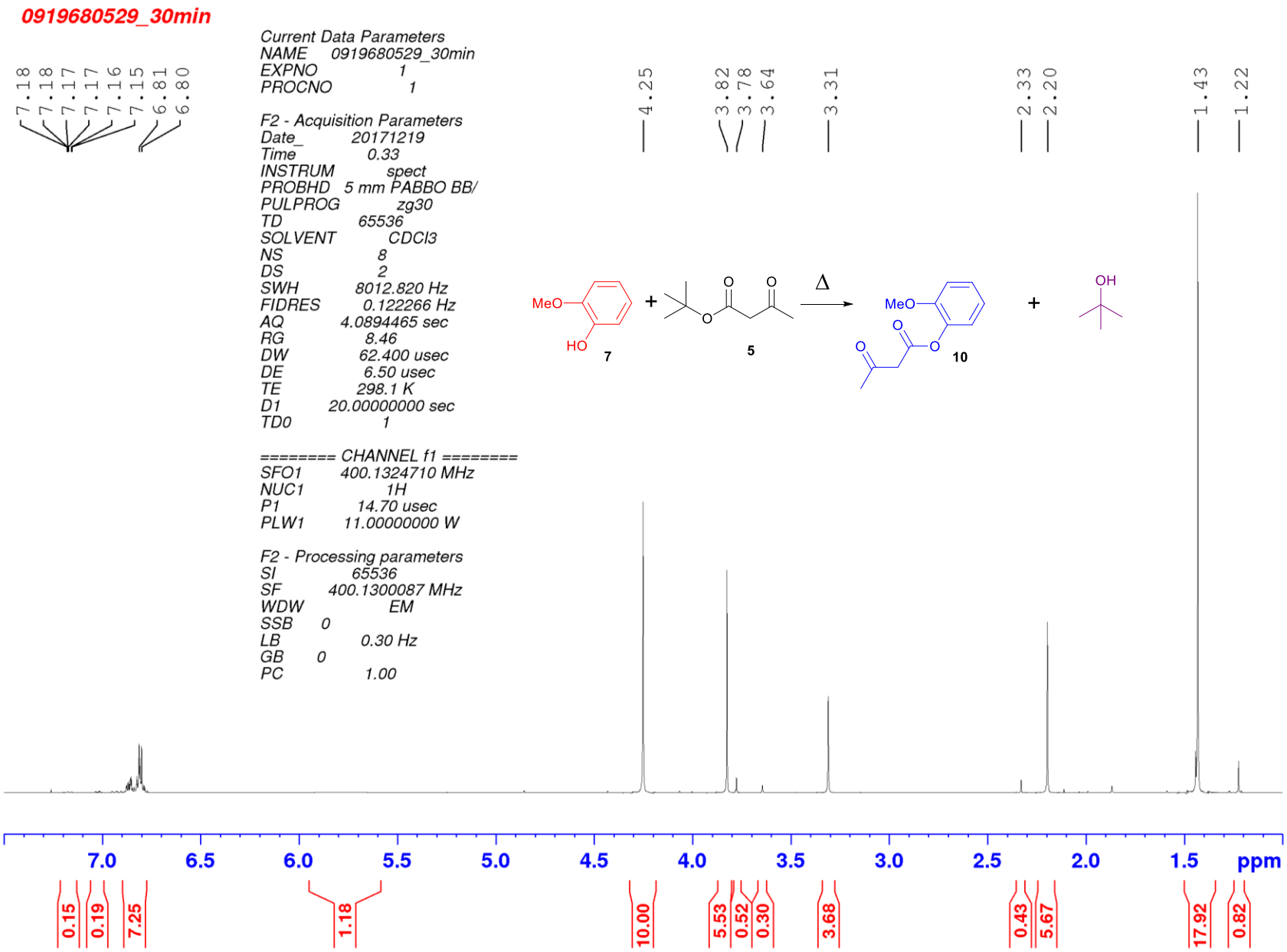


Figure S 76 **Acetoacetylation of guaiacol**: 30 min ($CDCl_3$, ^1H NMR)

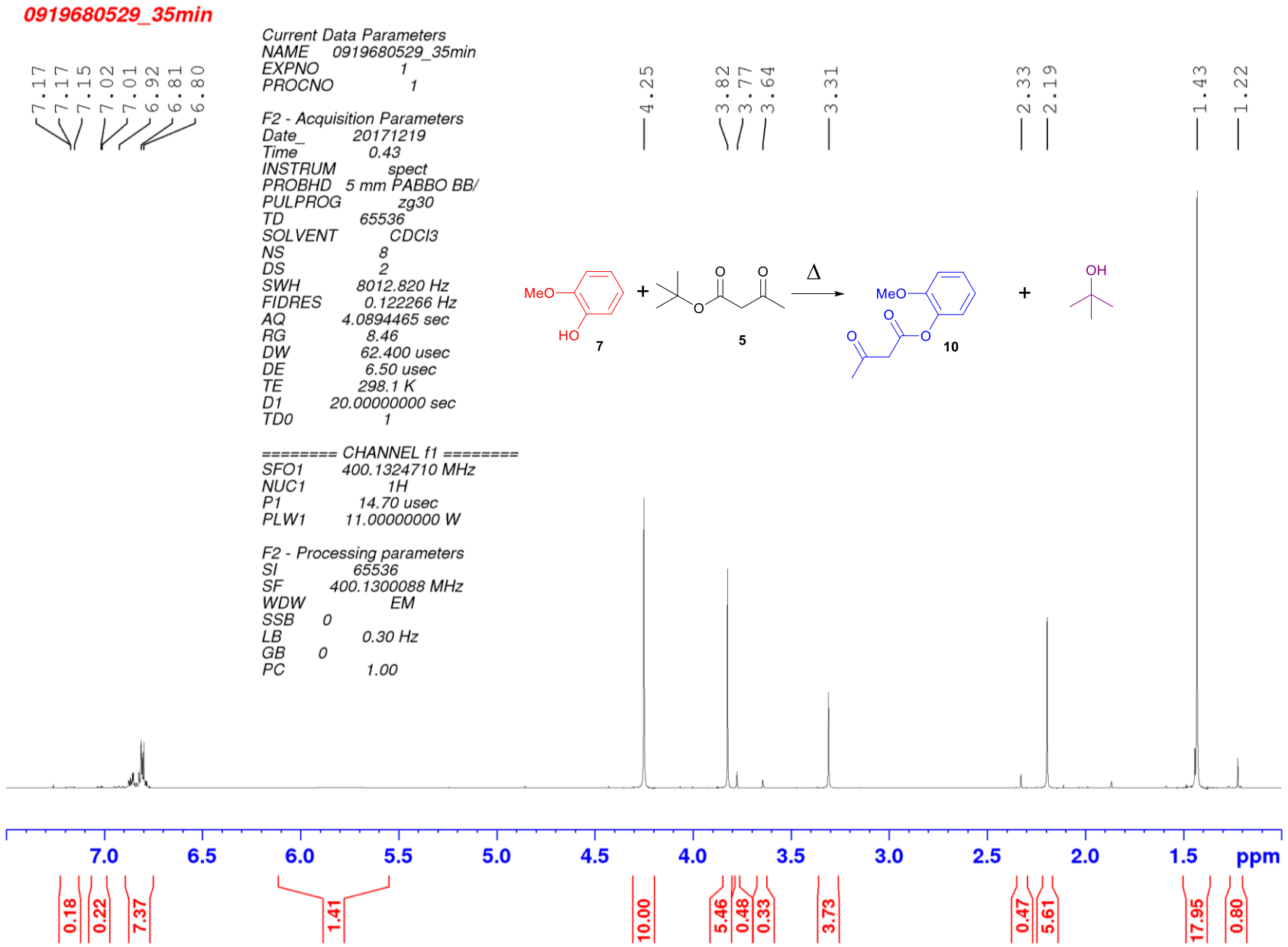


Figure S 77 **Acetoacetylation of guaiacol**: 35 min ($CDCl_3$, ^1H NMR)

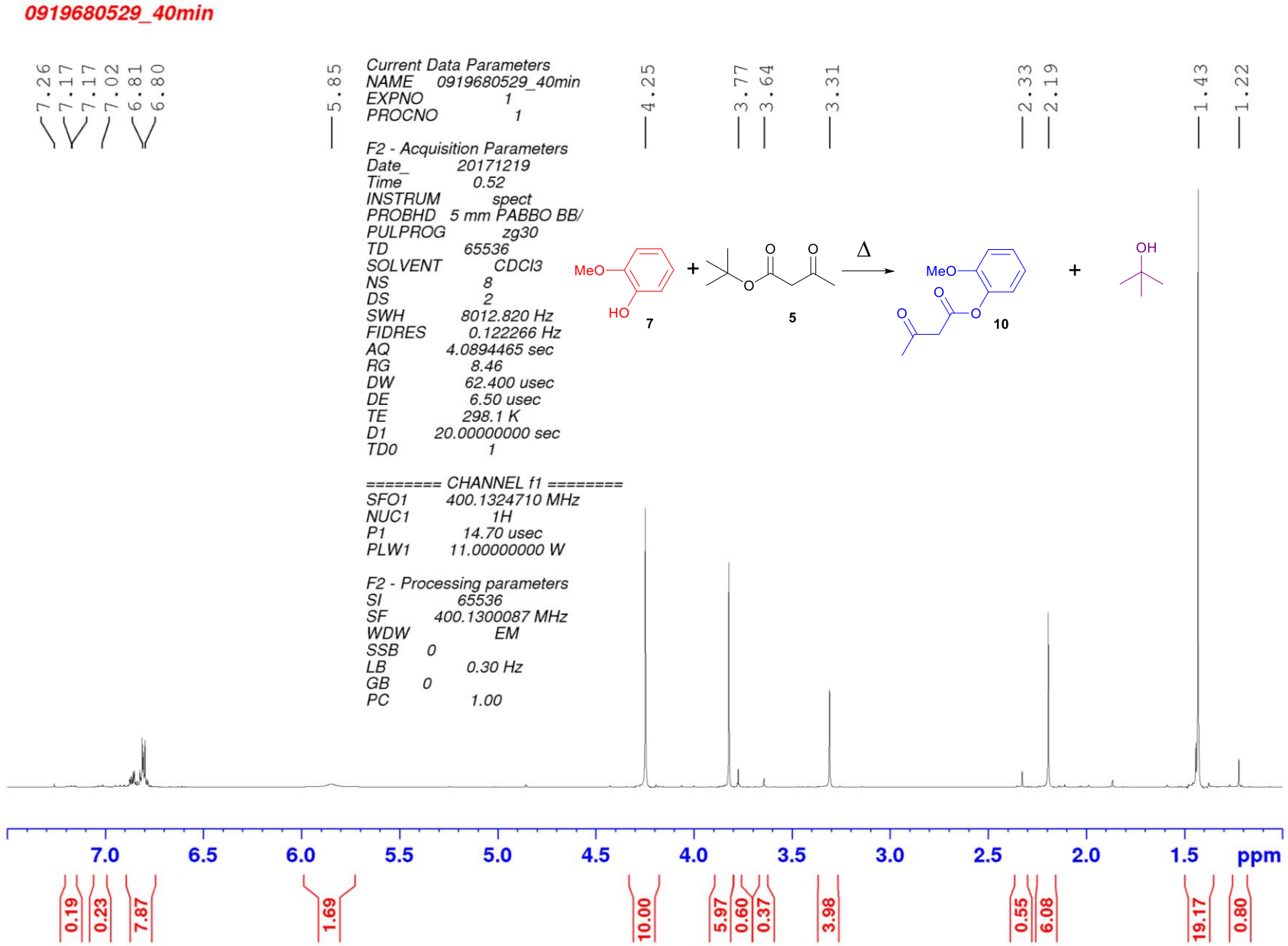


Figure S 78 **Acetoacetylation of guaiacol**: 40 min ($CDCl_3$, ^1H NMR)

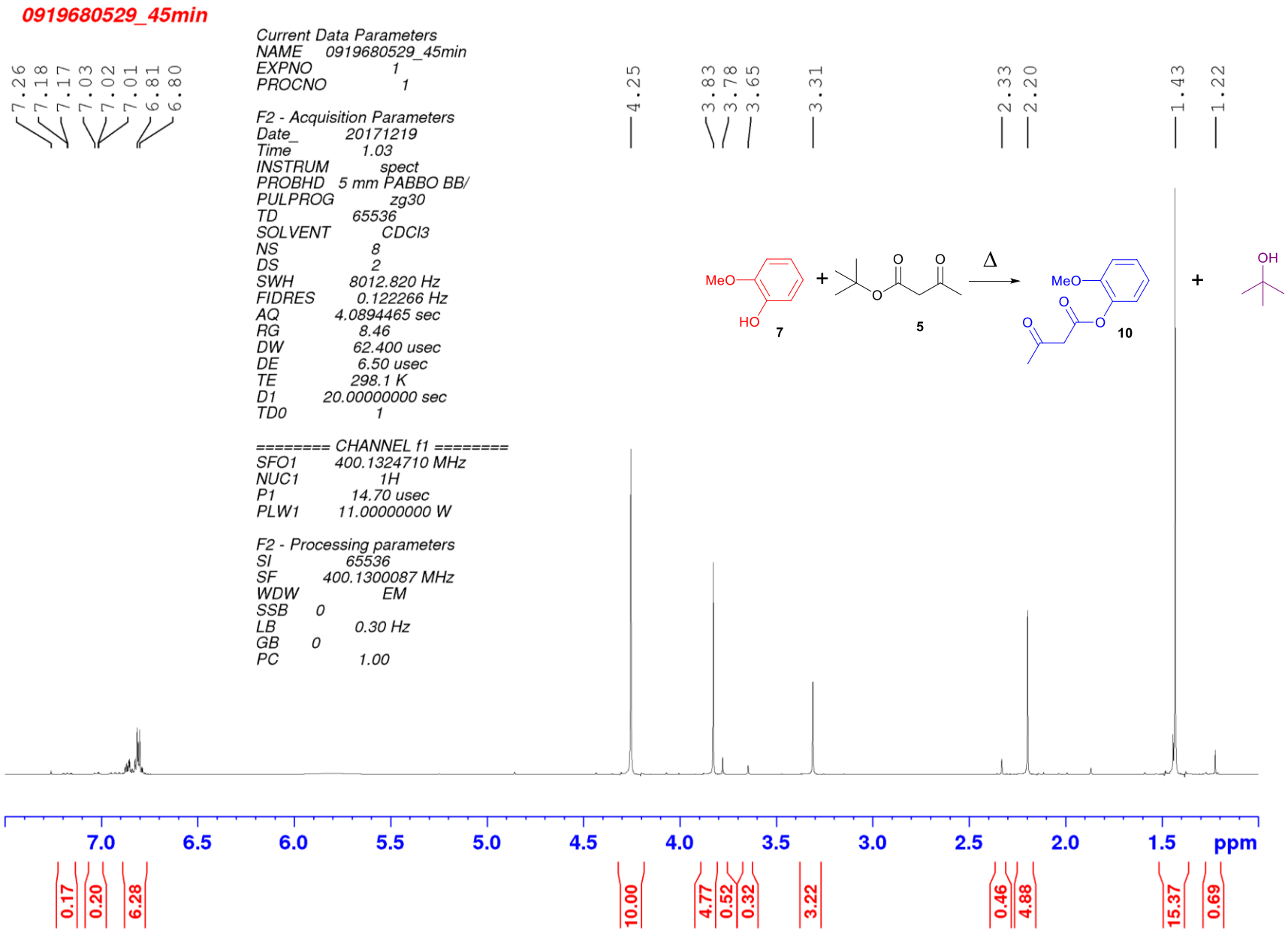


Figure S 79 **Acetoacetylation of guaiacol**: 45 min ($CDCl_3$, ^1H NMR)

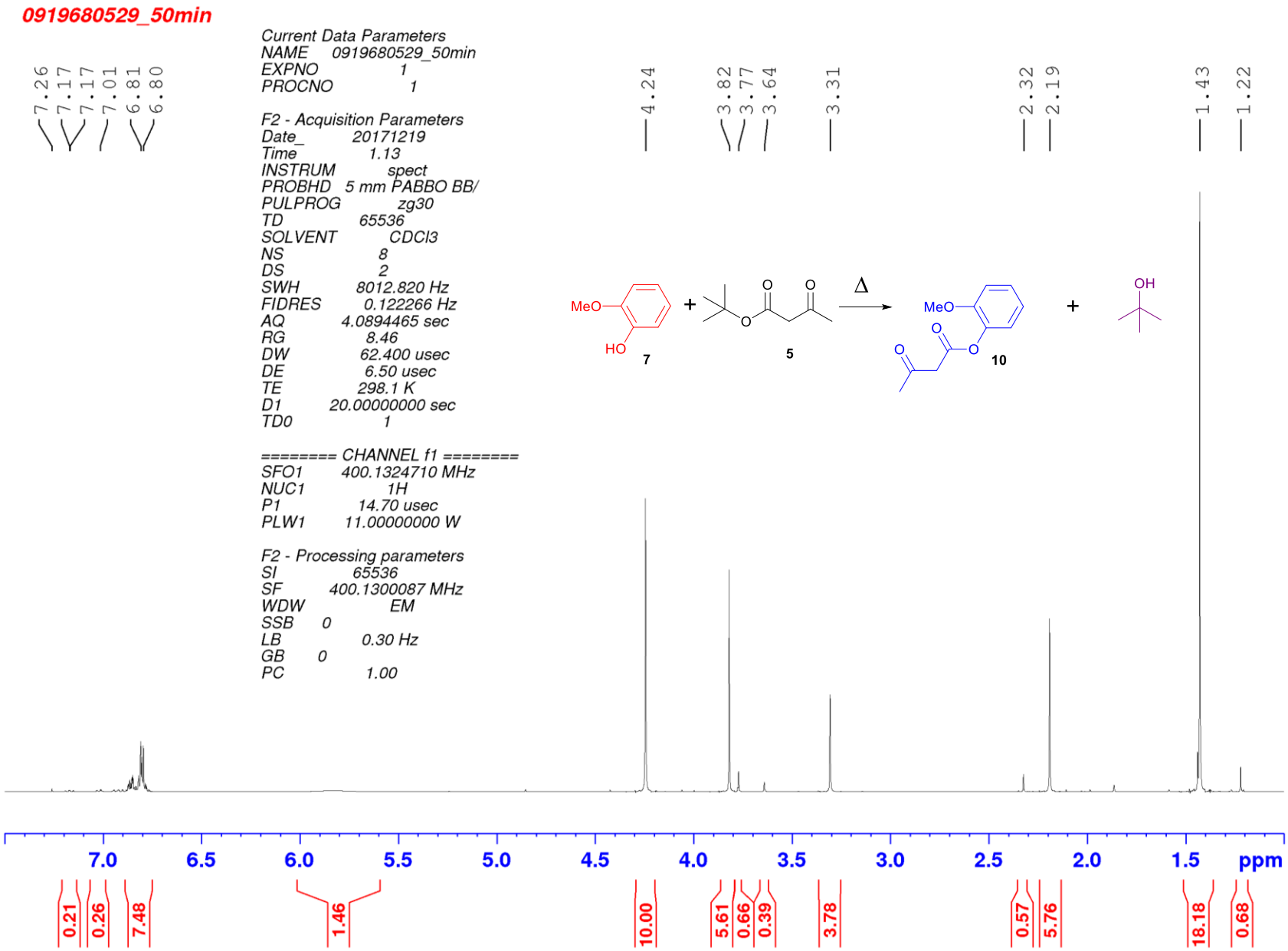


Figure S 80 **Acetoacetylation of guaiacol**: 50 min ($CDCl_3$, ^1H NMR)

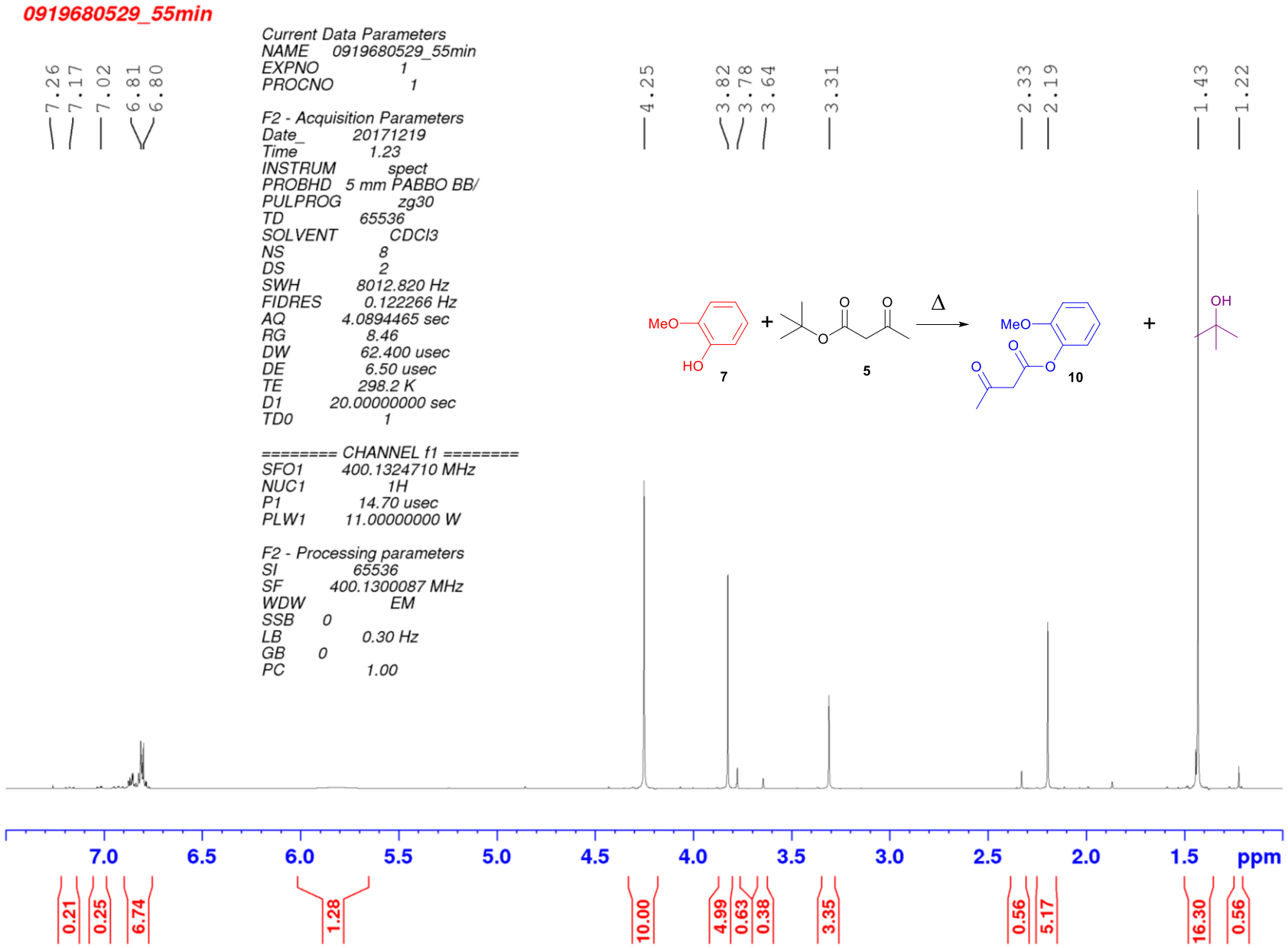


Figure S 81 **Acetoacetylation of guaiacol**: 55 min ($CDCl_3$, ^1H NMR)

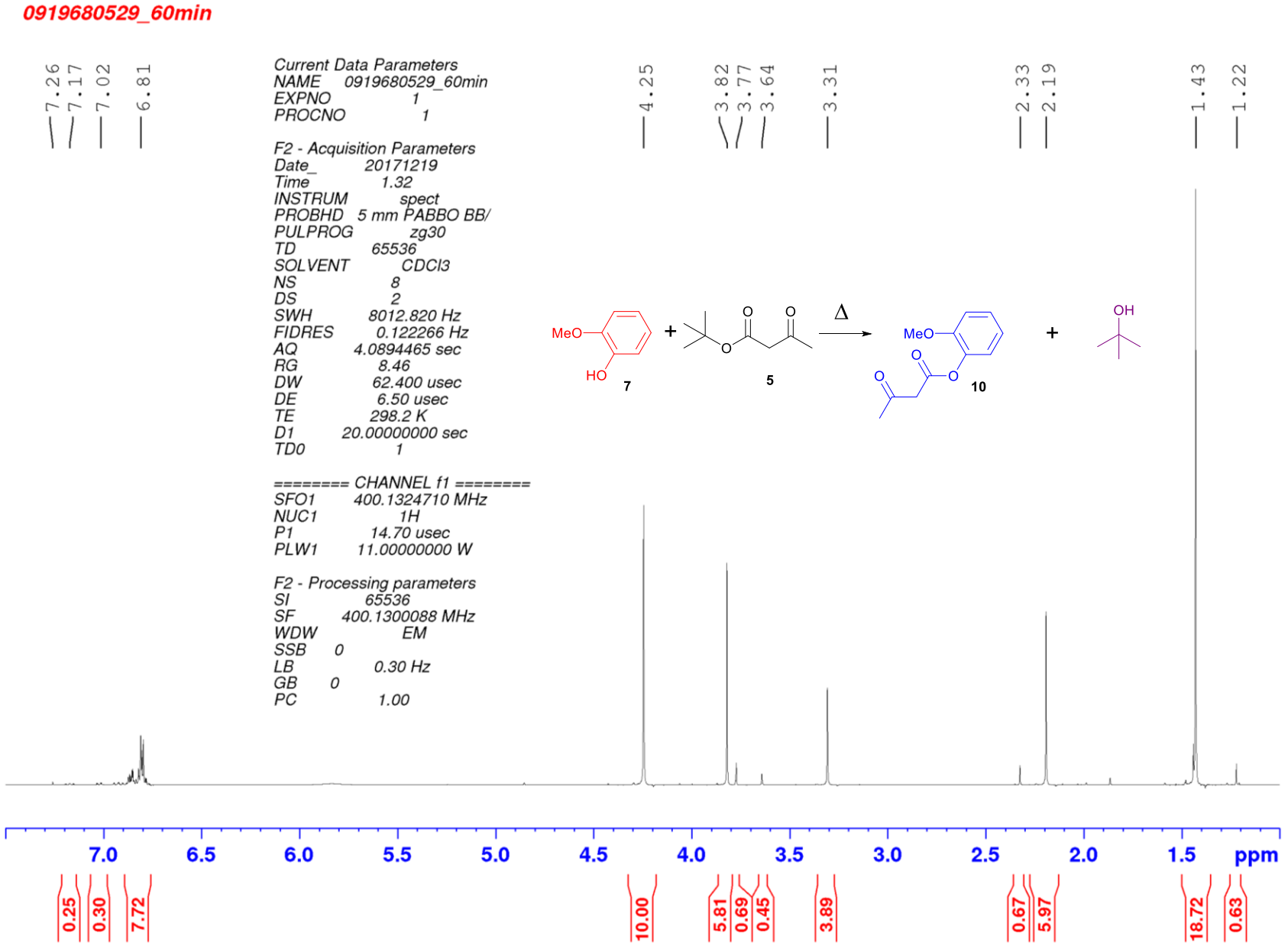


Figure S 82 **Acetoacetylation of guaiacol**: 60 min ($CDCl_3$, ^1H NMR)

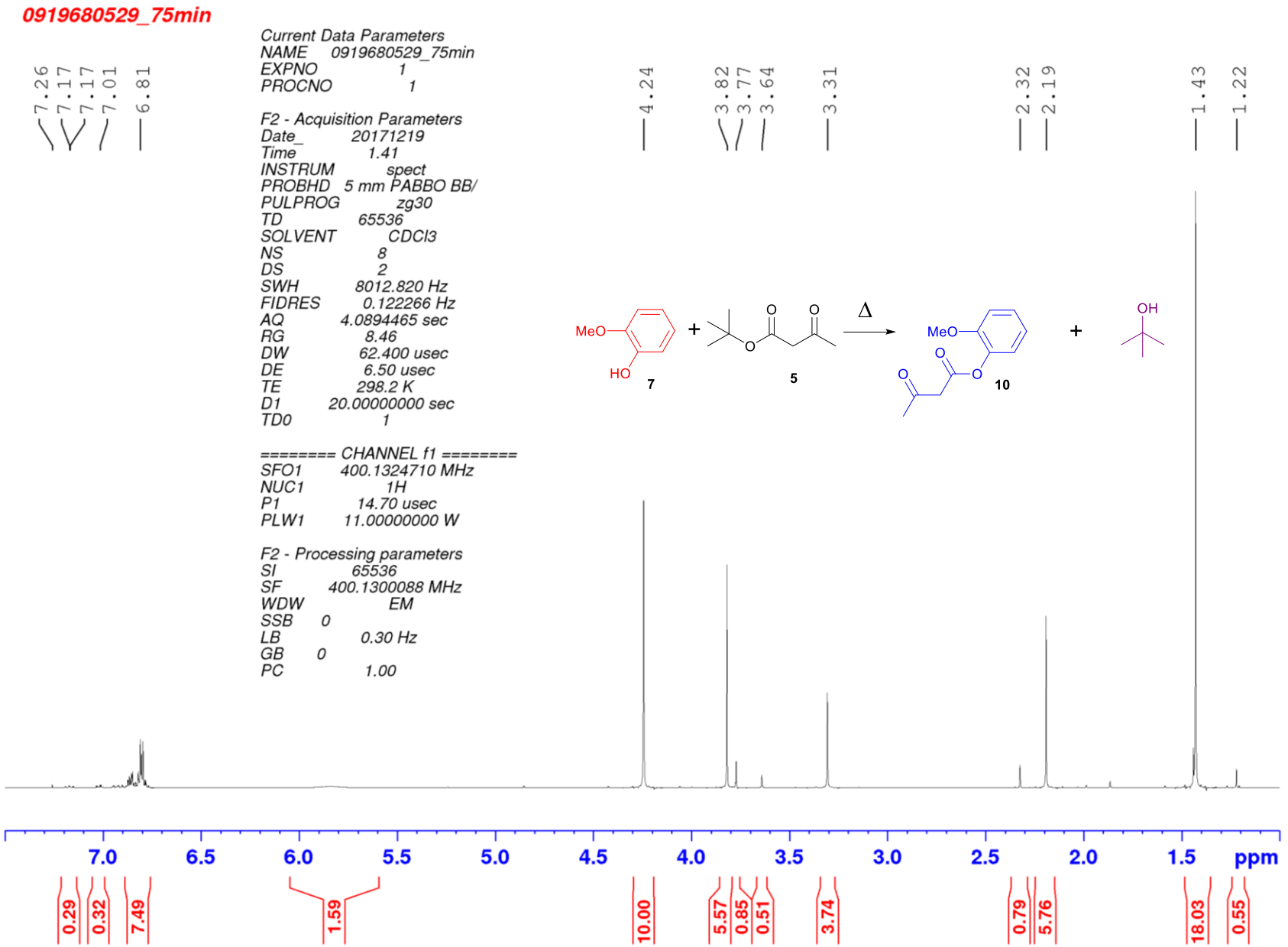


Figure S 83 **Acetoacetylation of guaiacol**: 75 min ($CDCl_3$, ^1H NMR)

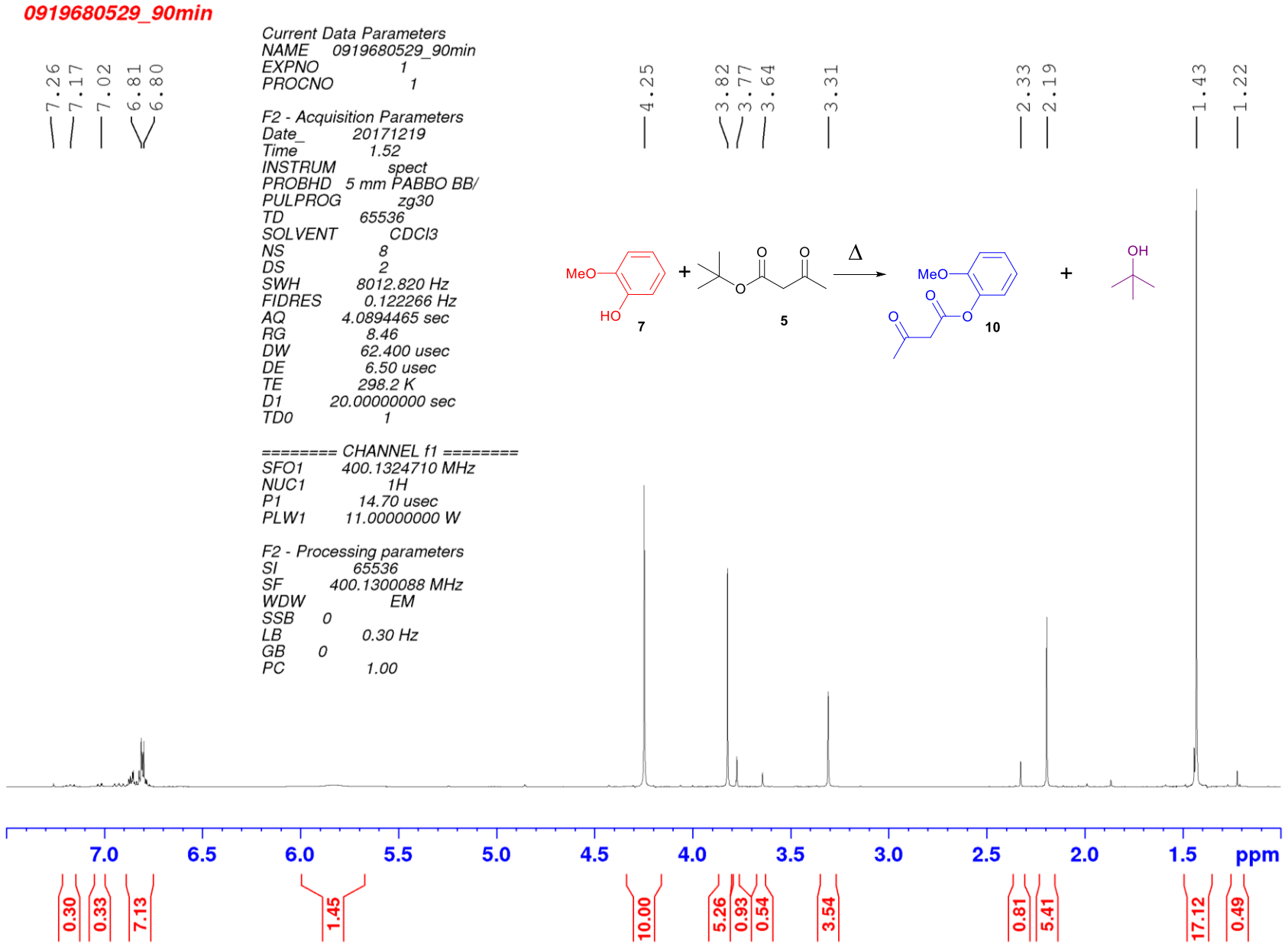


Figure S 84 **Acetoacetylation of guaiacol**: 90 min ($CDCl_3$, ^1H NMR)

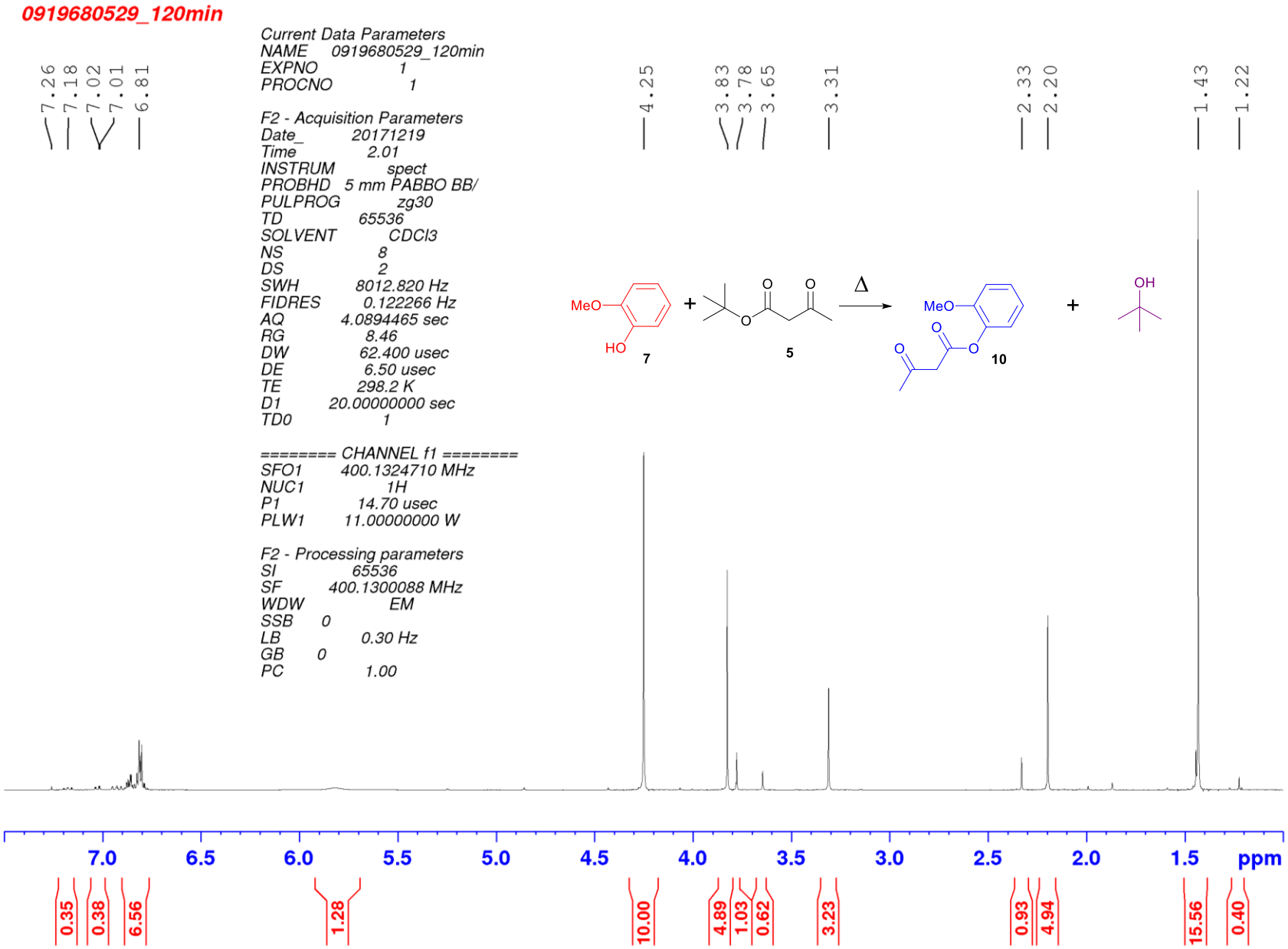


Figure S 85 **Acetoacetylation of guaiacol**:120 min ($CDCl_3$, ^1H NMR)

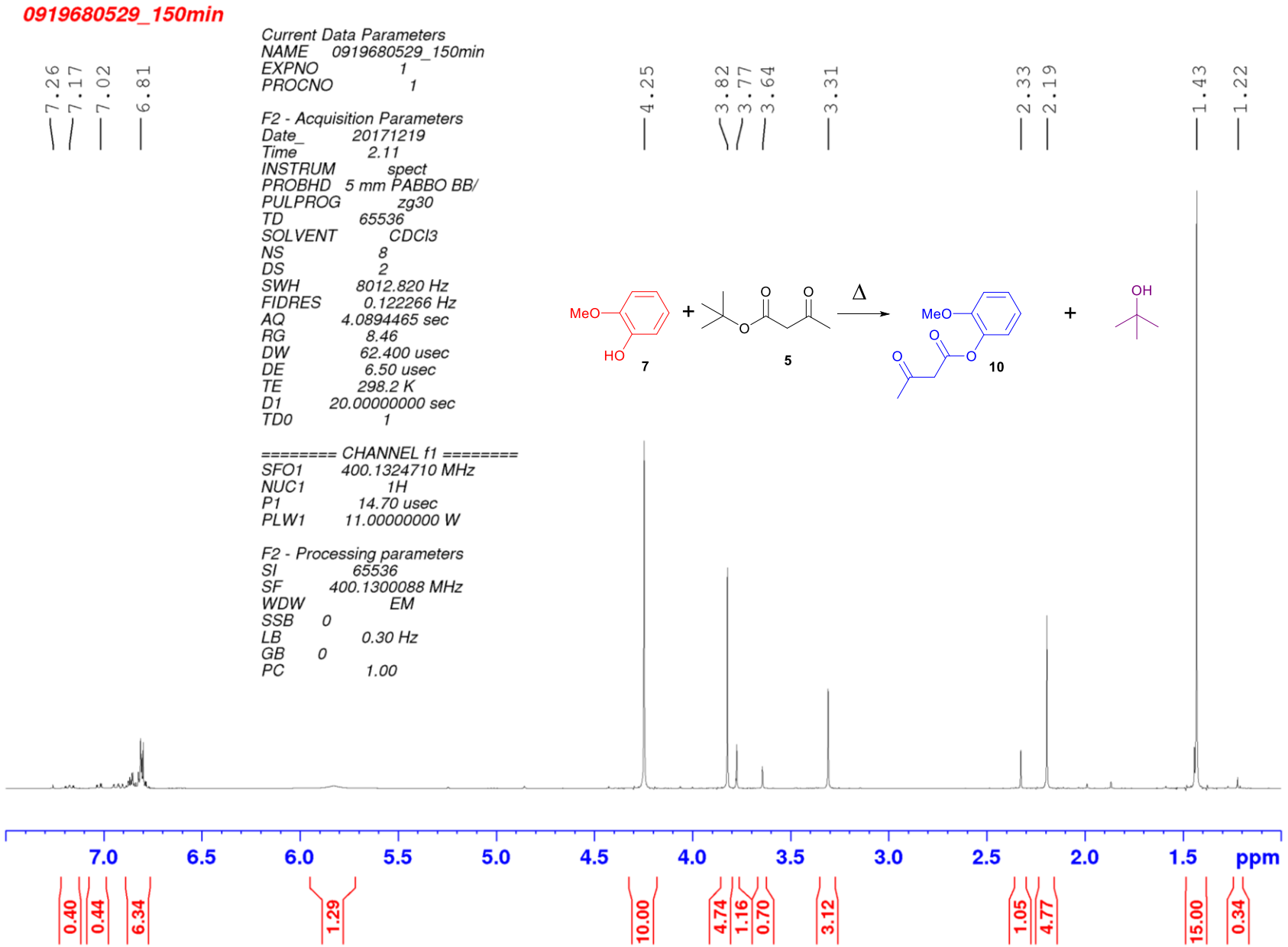


Figure S 86 **Acetoacetylation of guaiacol**: 150 min ($CDCl_3$, ^1H NMR)

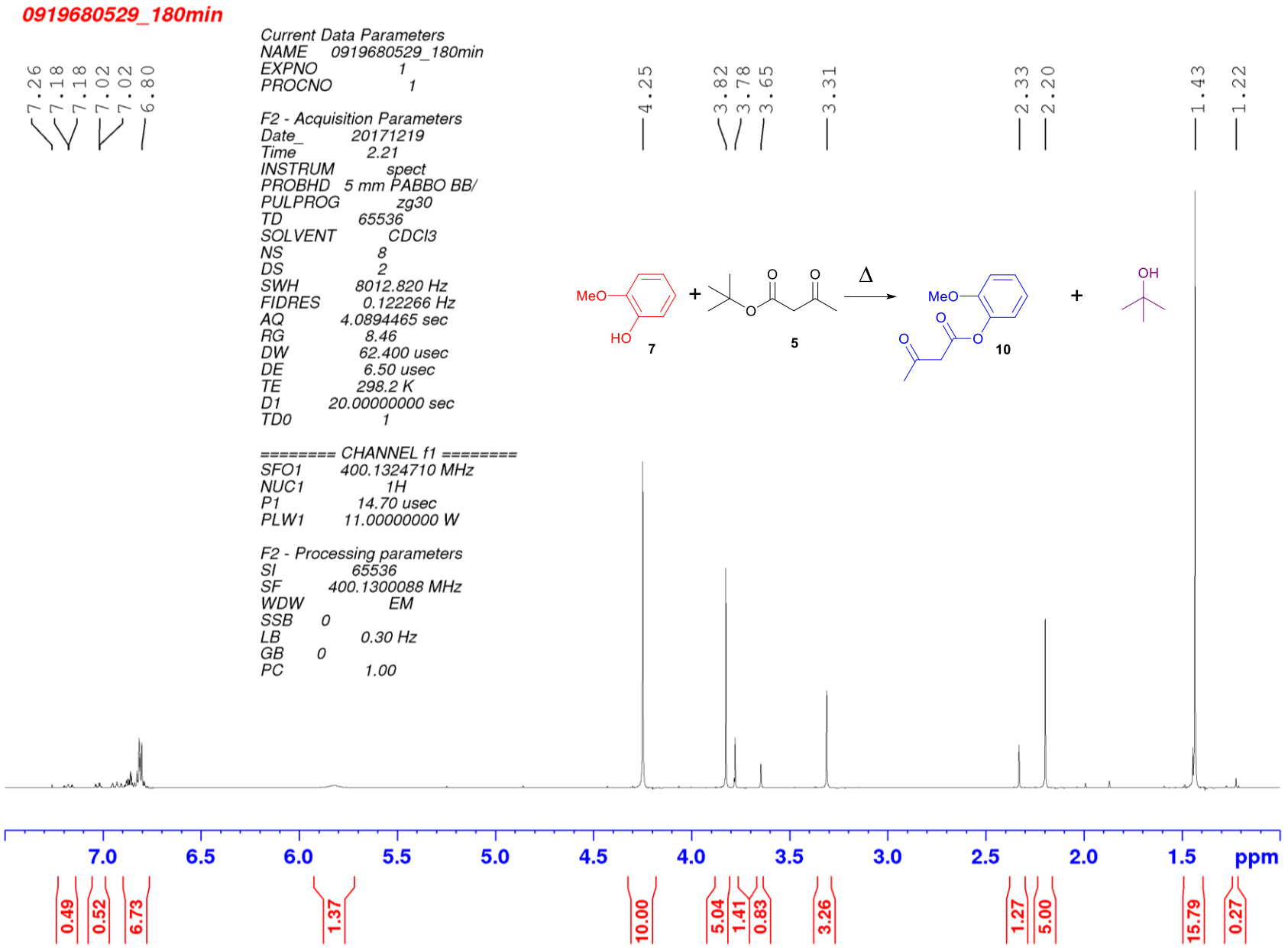


Figure S 87 **Acetoacetylation of guaiacol**:180 min ($CDCl_3$, ^1H NMR)

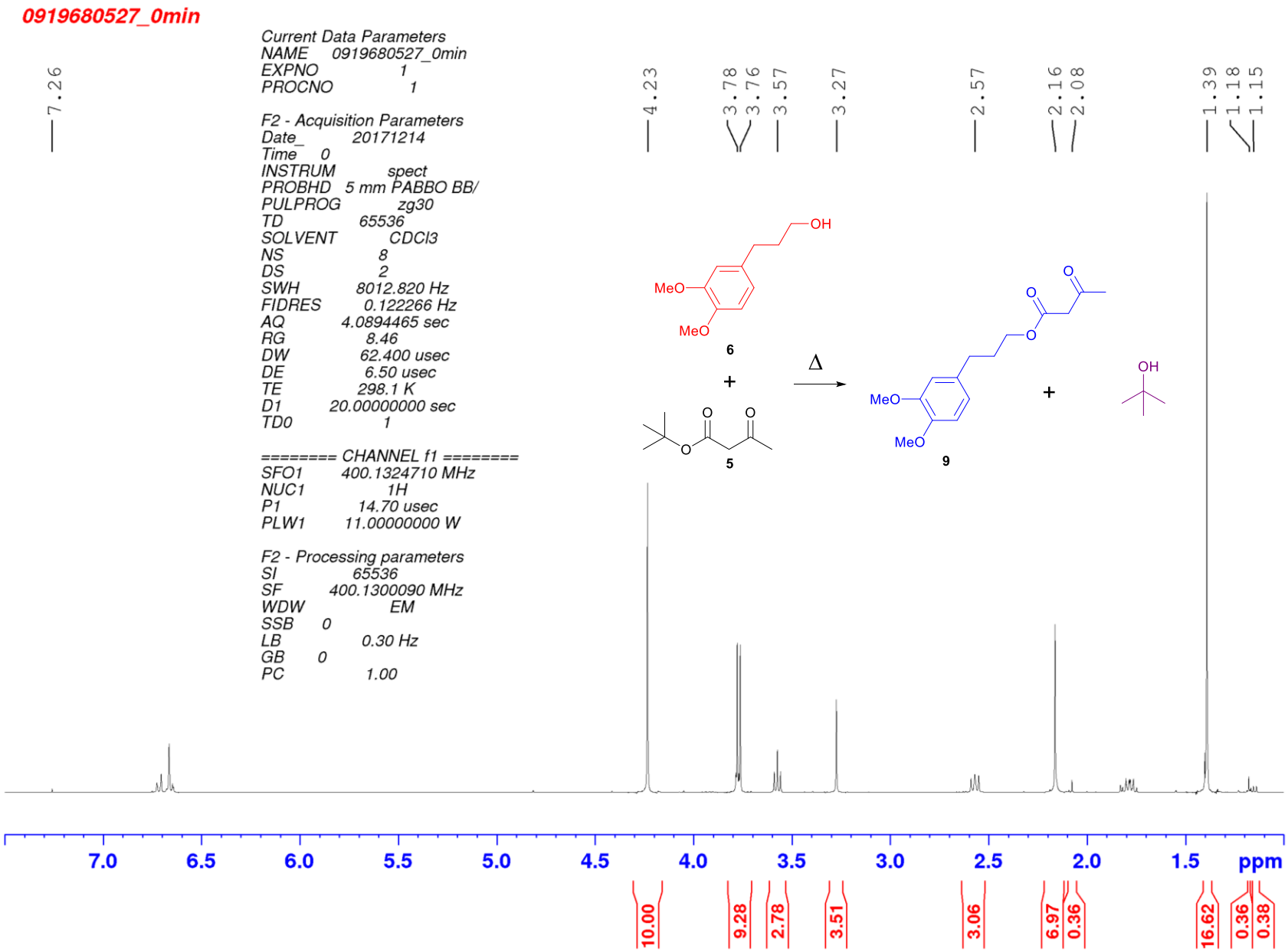


Figure S 88 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 180 min ($CDCl_3$, ^1H NMR)

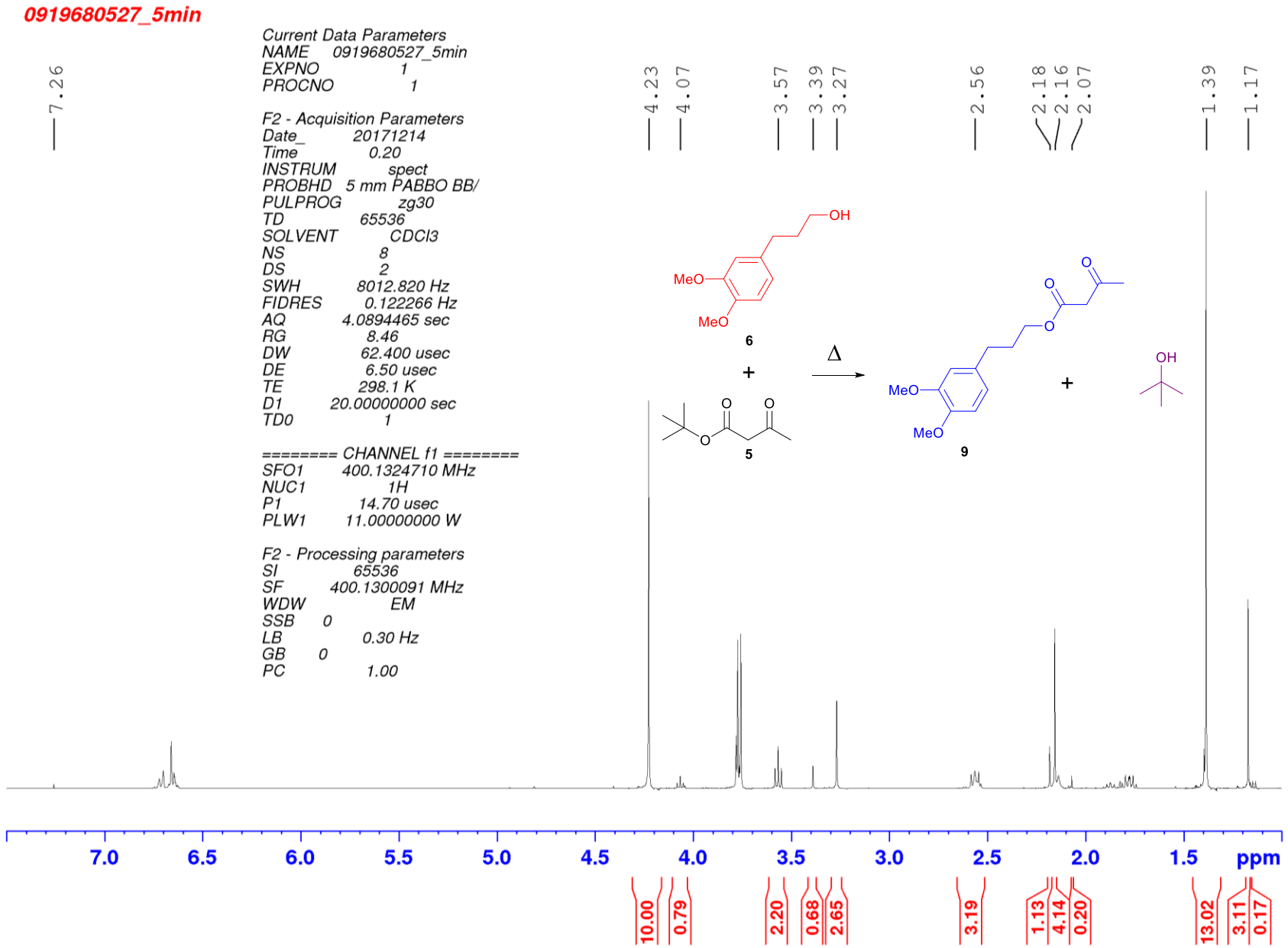


Figure S 89 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 5 min ($CDCl_3$, ^1H NMR)

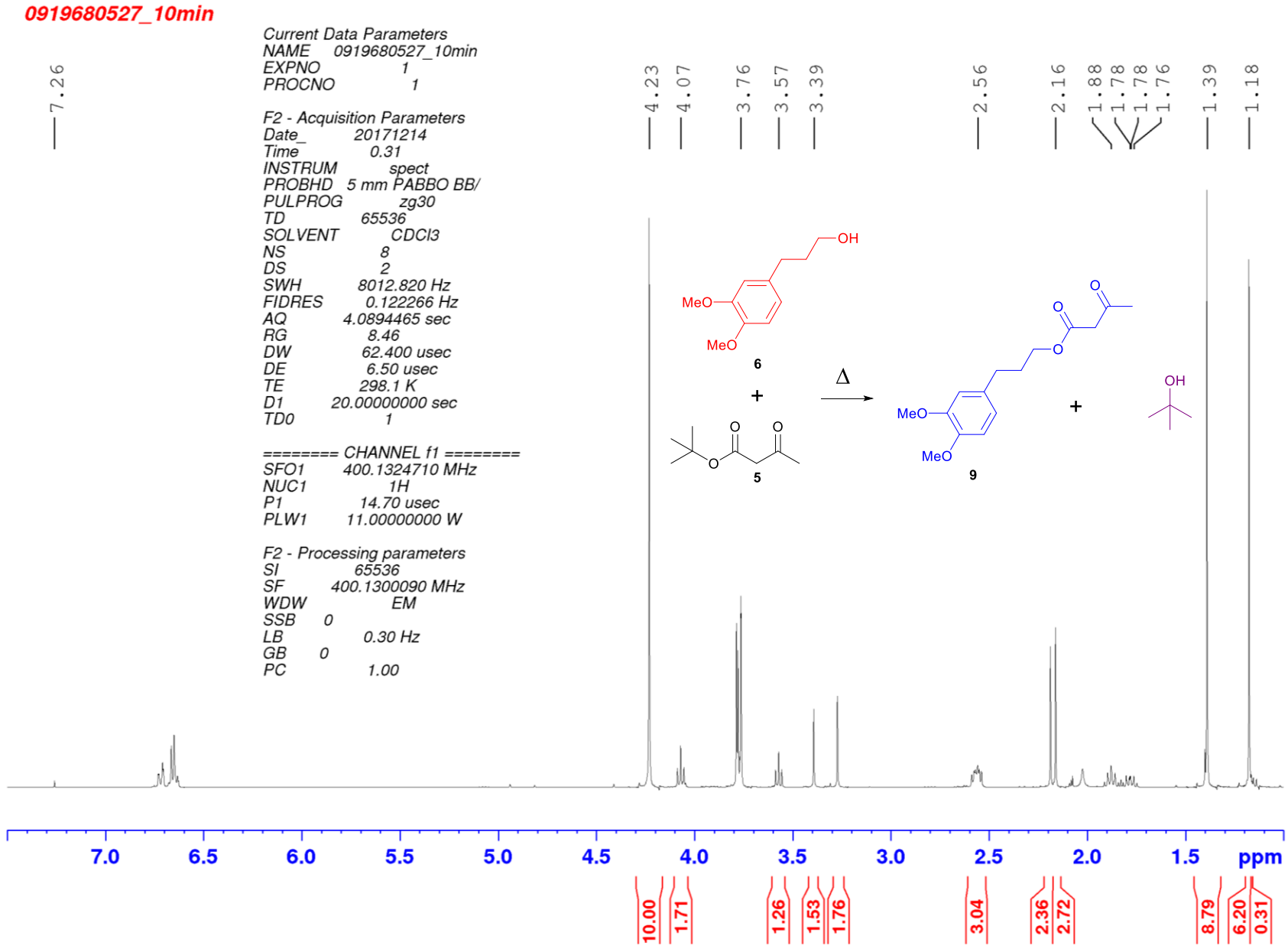


Figure S 90 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 10 min ($CDCl_3$, ^1H NMR)

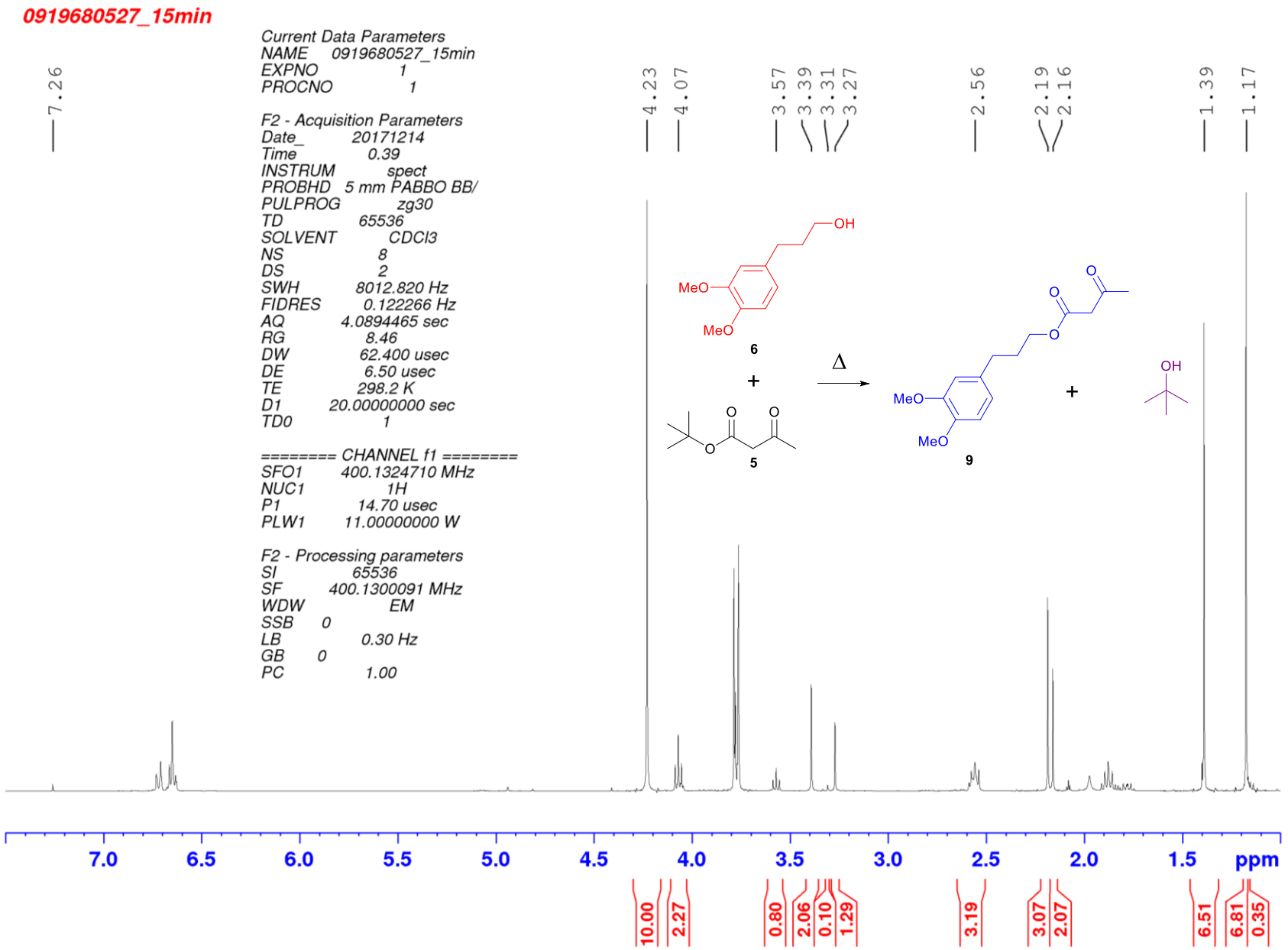


Figure S 91 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 15 min ($CDCl_3$, ^1H NMR)

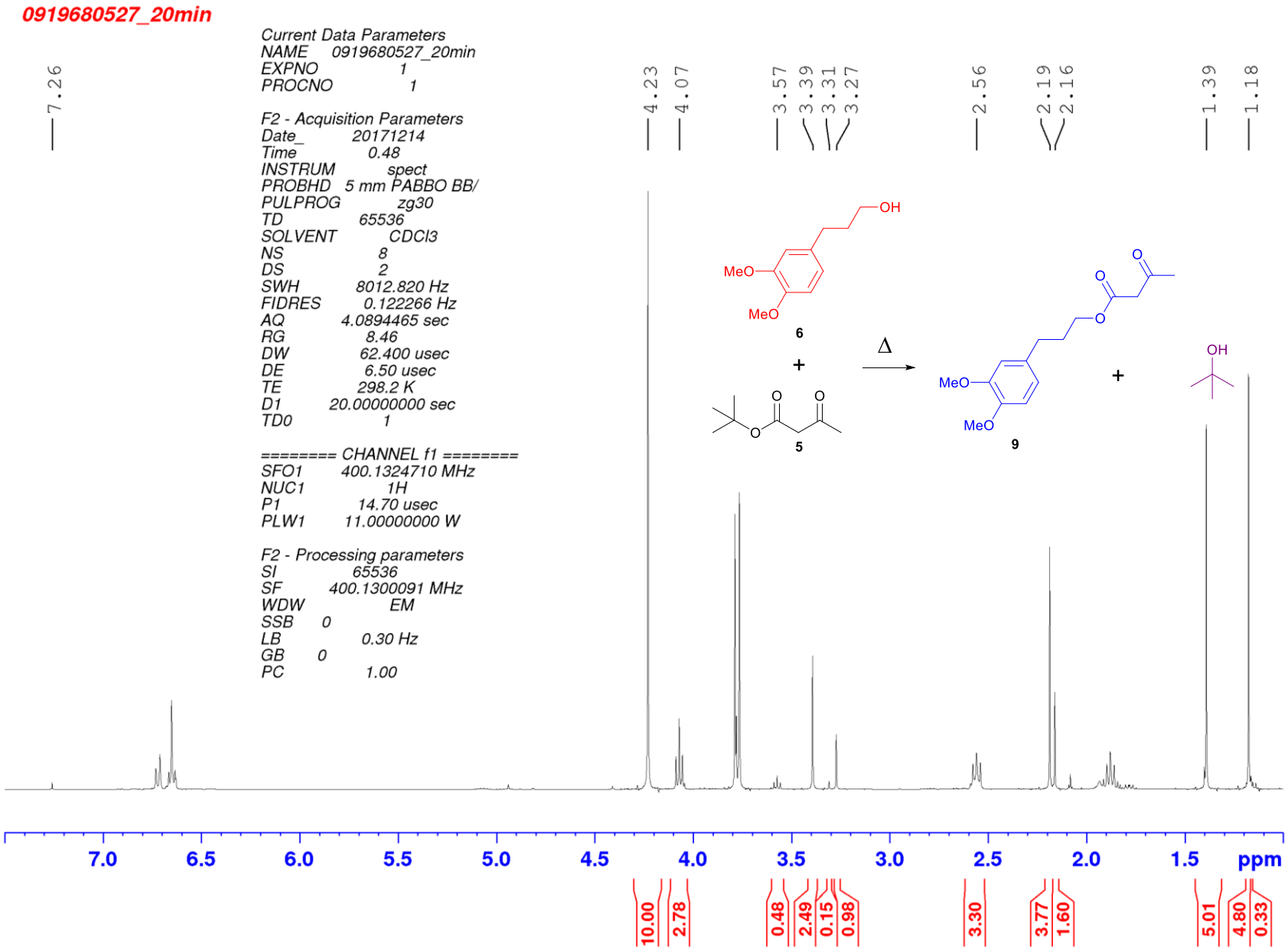


Figure S 92 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 20 min ($CDCl_3$, ^1H NMR)

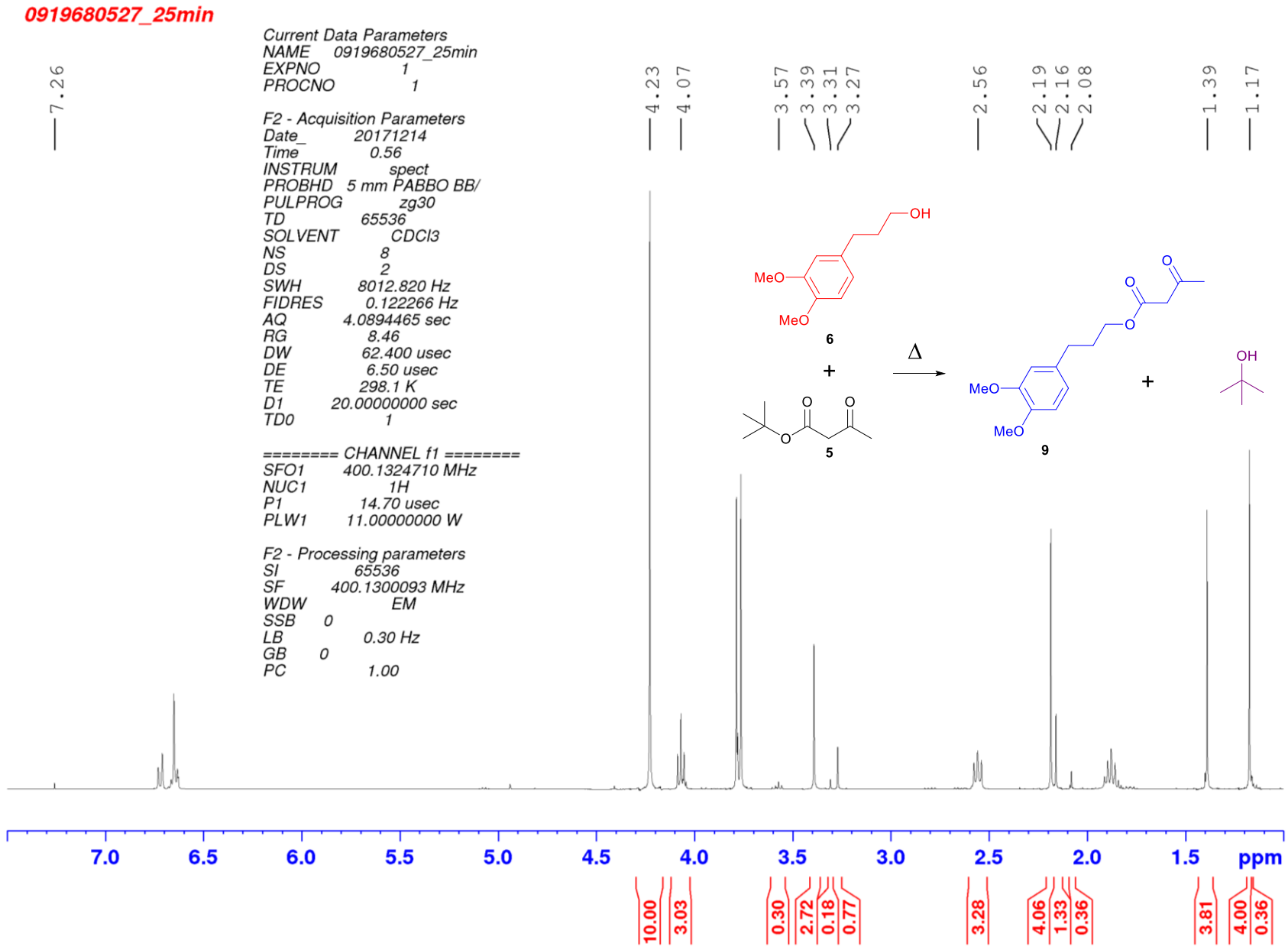


Figure S 93 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 25 min ($CDCl_3$, ^1H NMR)

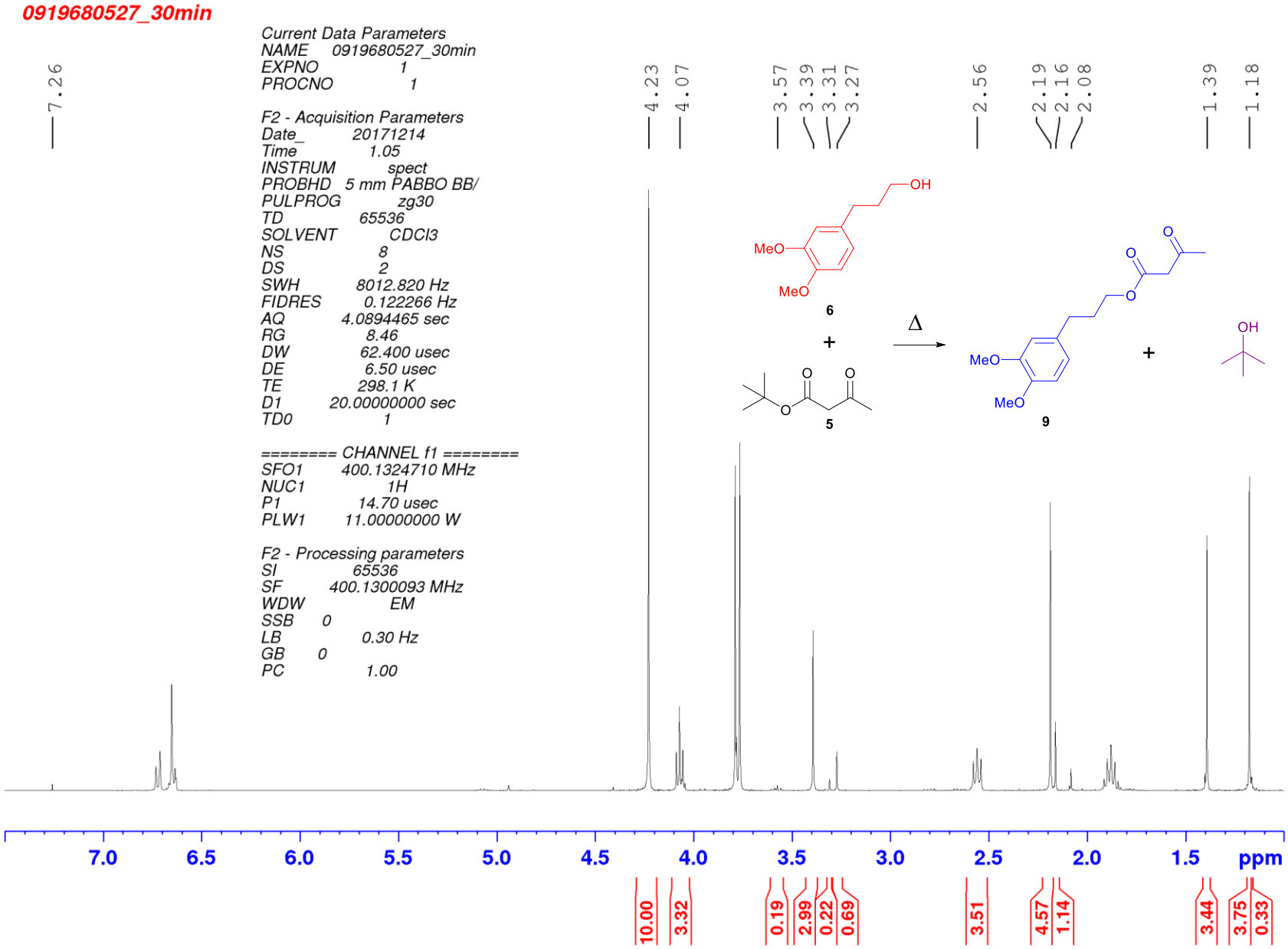


Figure S 94 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**:30 min ($CDCl_3$, ^1H NMR)

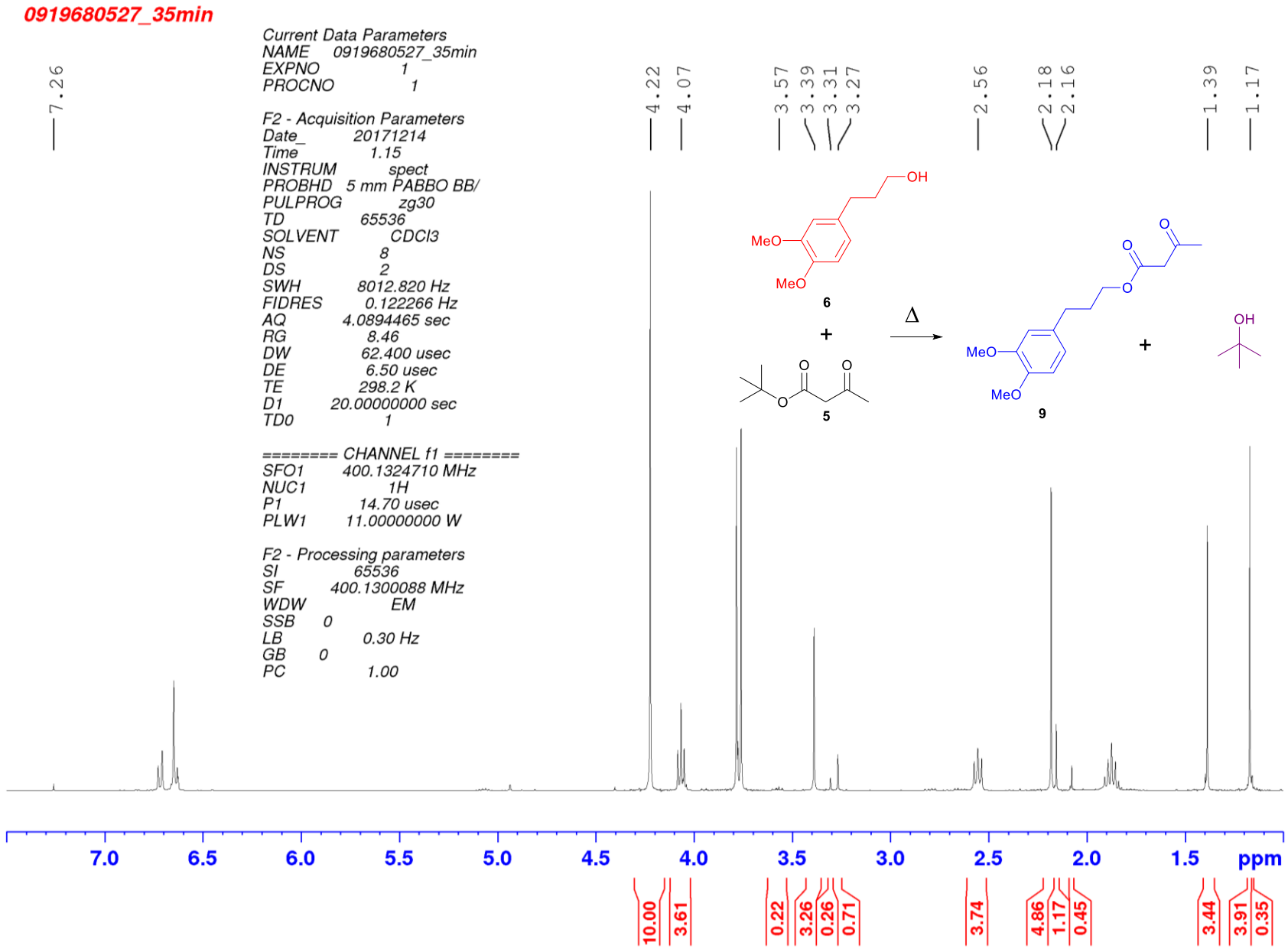


Figure S 95 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 35 min ($CDCl_3$, ^1H NMR)

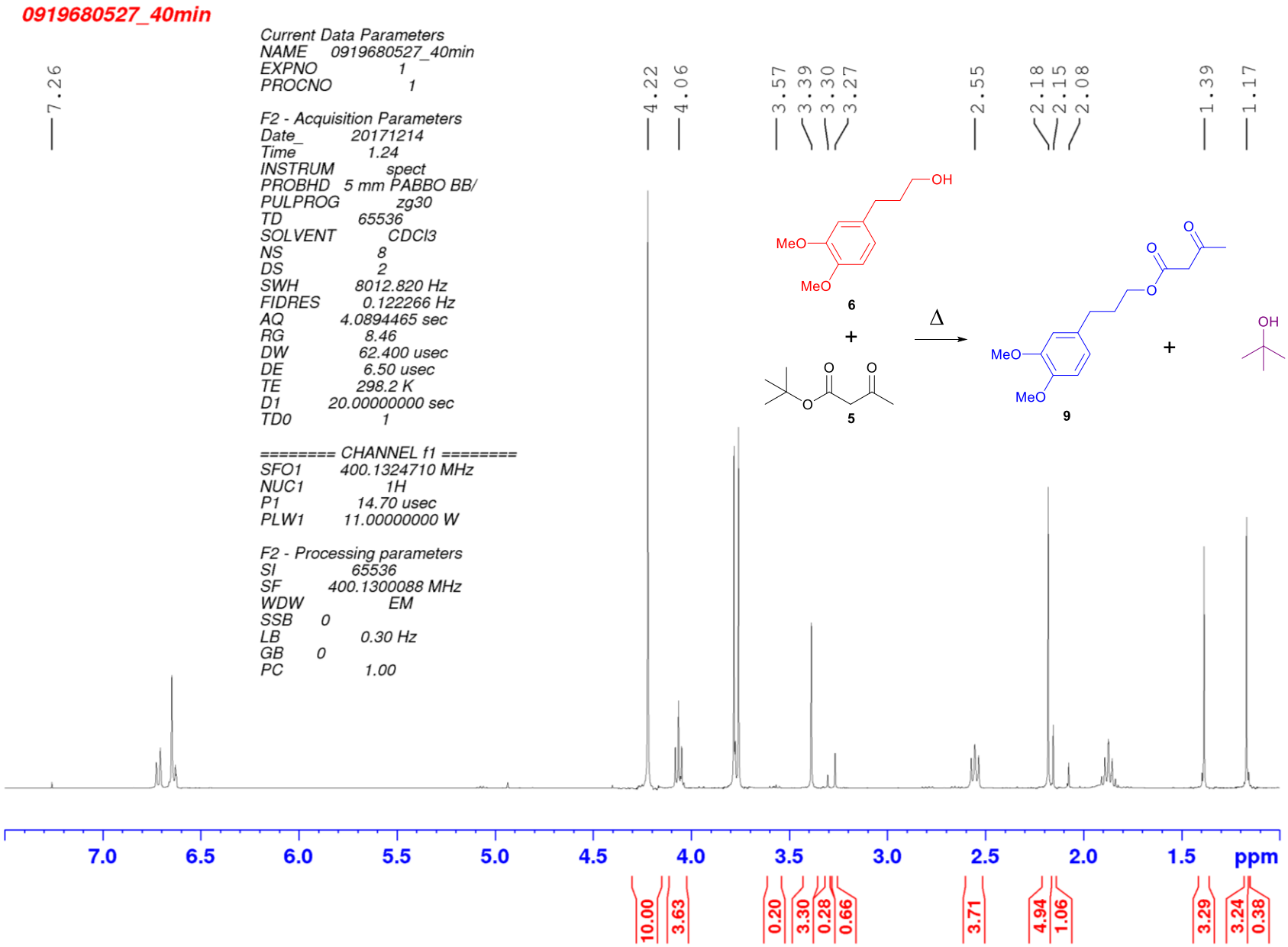


Figure S 96 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 40 min ($CDCl_3$, ^1H NMR)

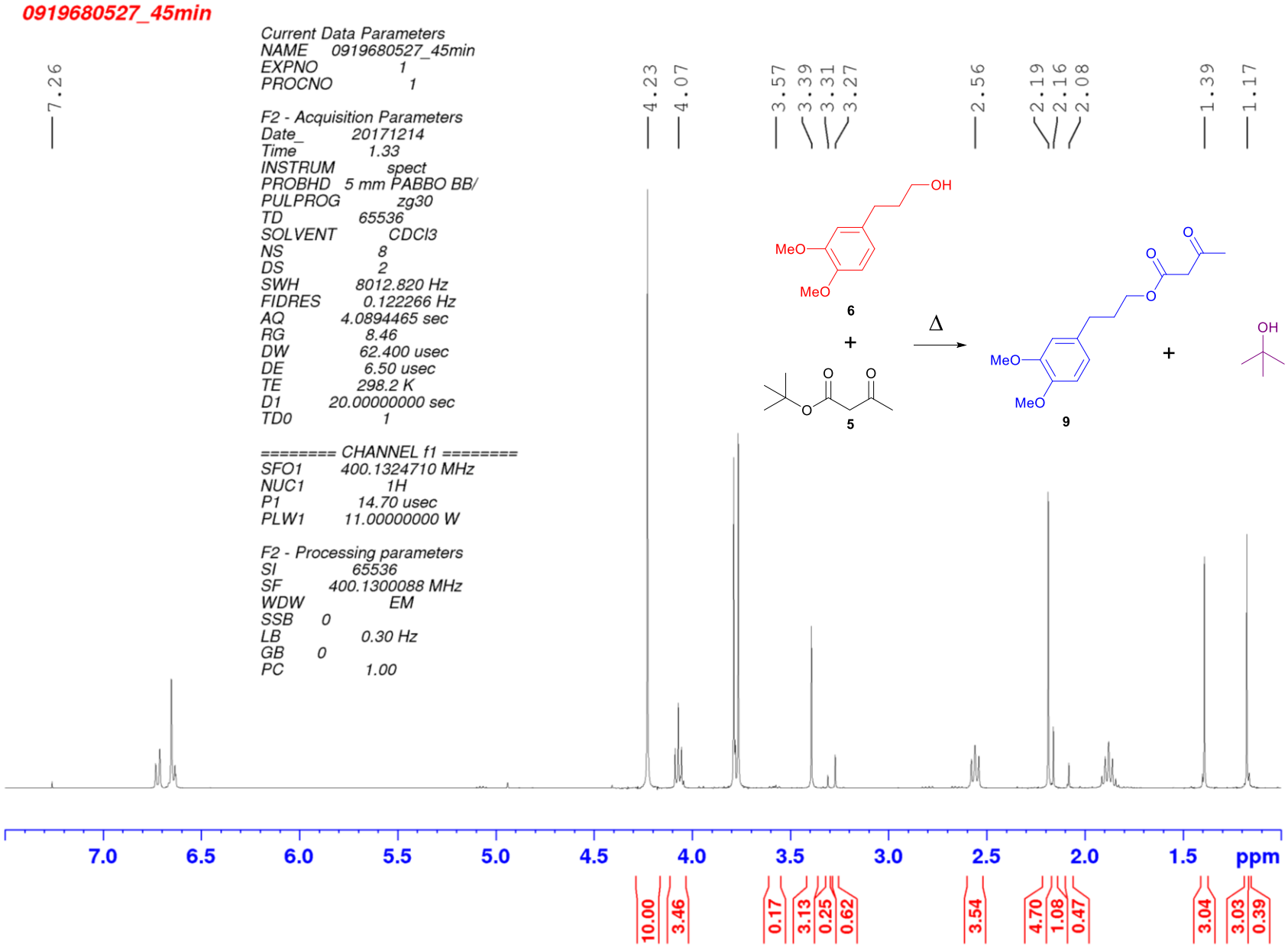


Figure S 97 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 45 min ($CDCl_3$, ^1H NMR)

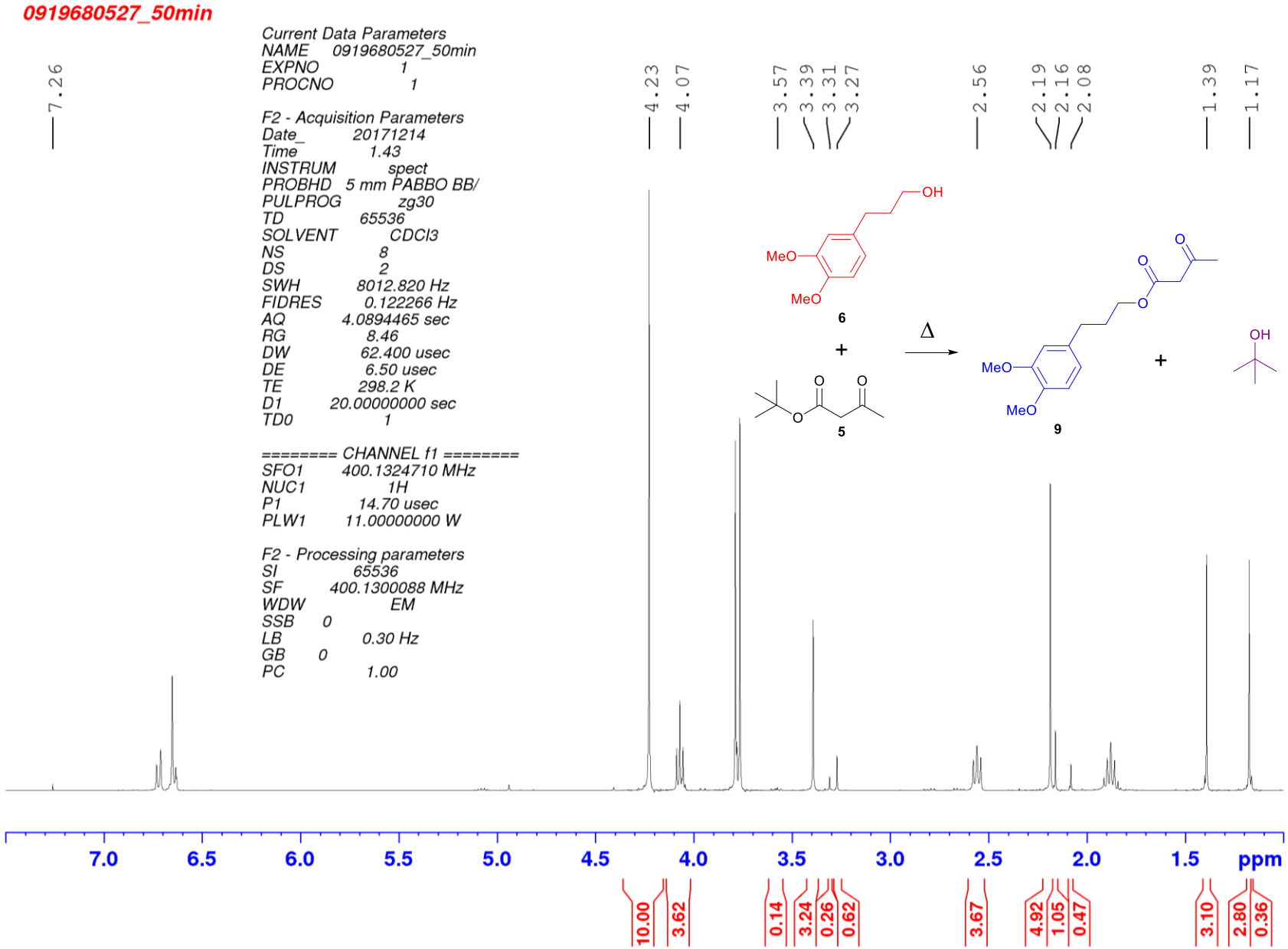


Figure S 98 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 50 min ($CDCl_3$, ^1H NMR)

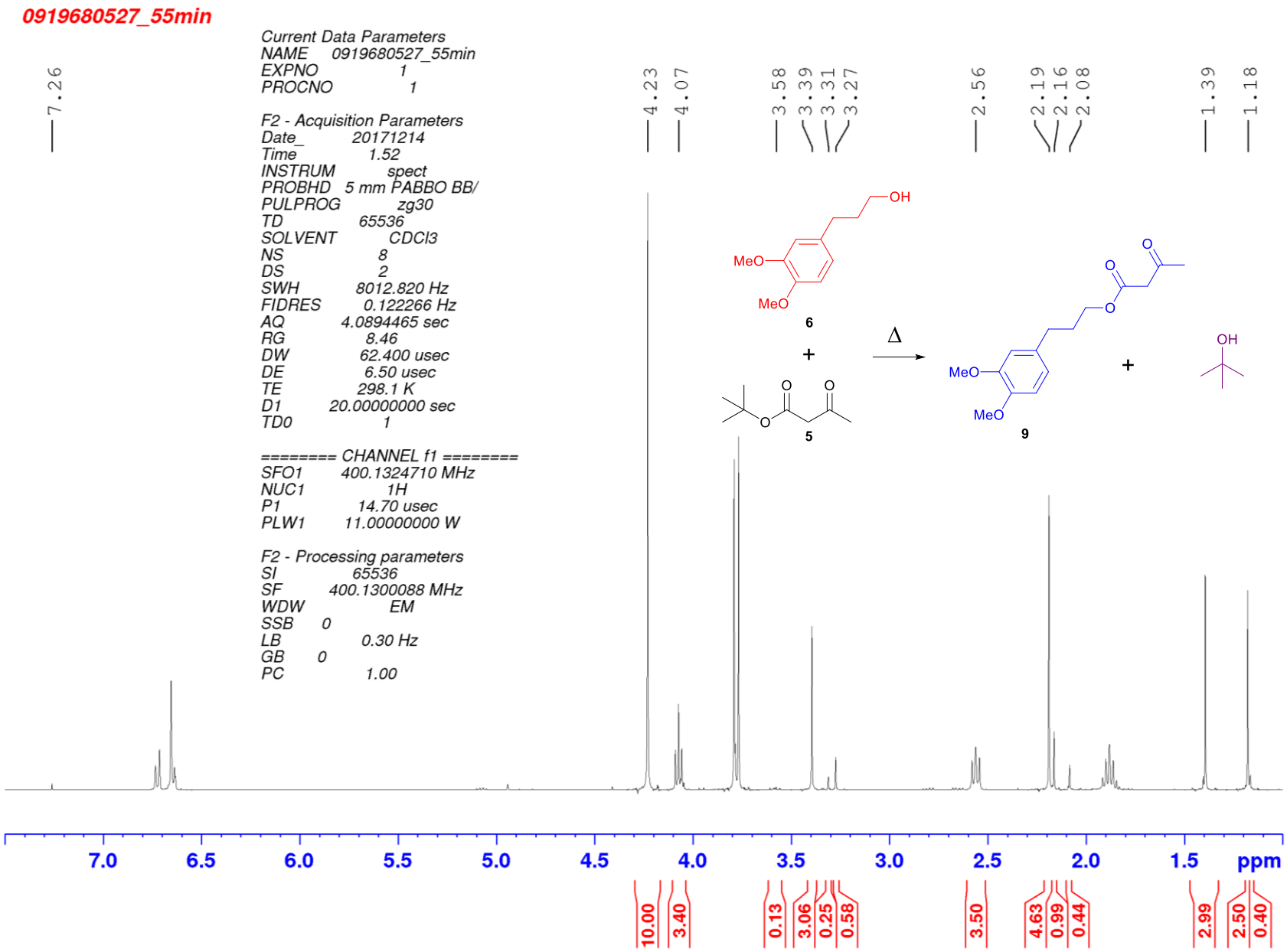


Figure S 99 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 55 min ($CDCl_3$, ^1H NMR)

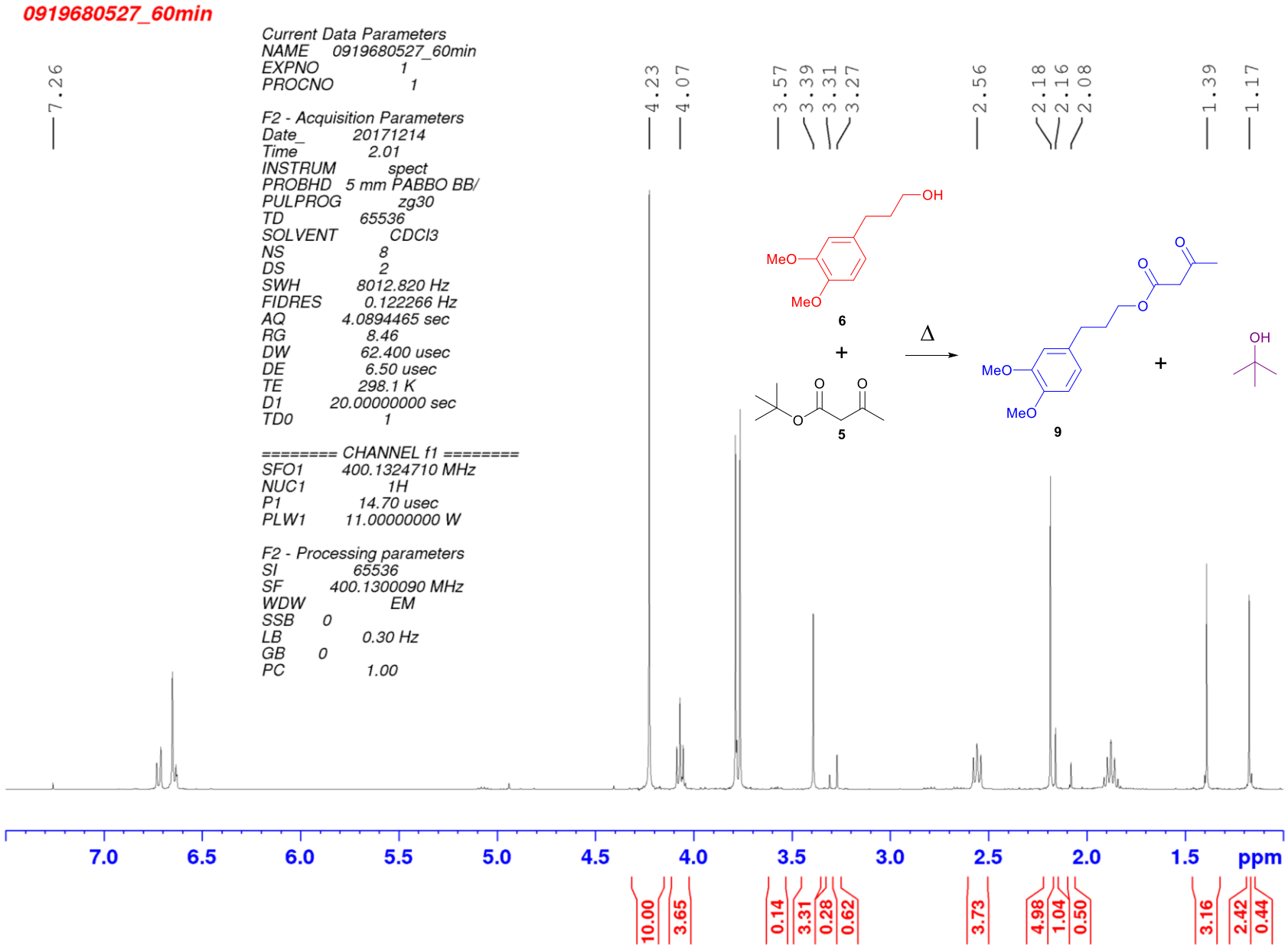


Figure S 100 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 60 min ($CDCl_3$, ^1H NMR)

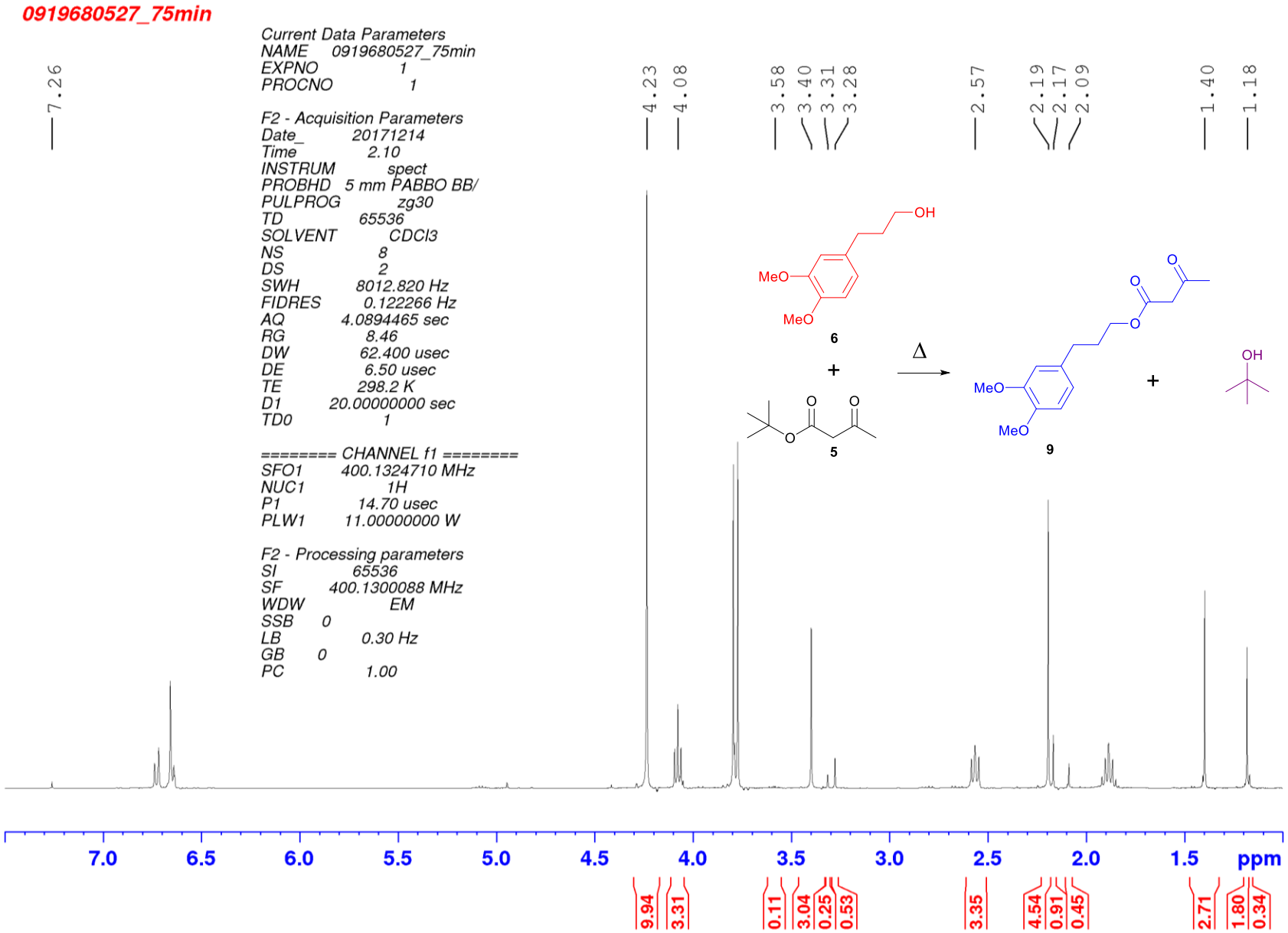


Figure S 101 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 75 min ($CDCl_3$, ^1H NMR)

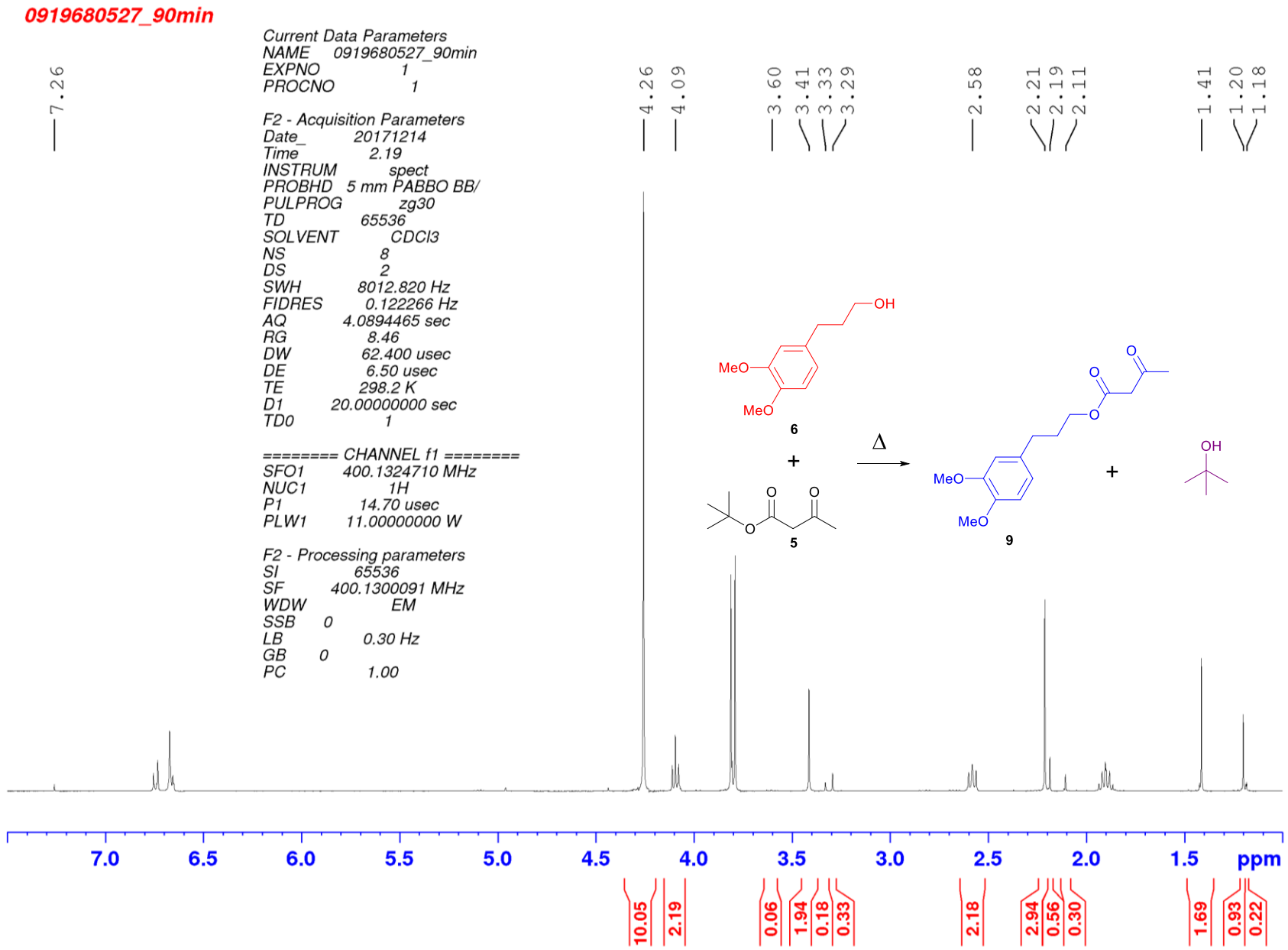


Figure S 102 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 90 min ($CDCl_3$, ^1H NMR)

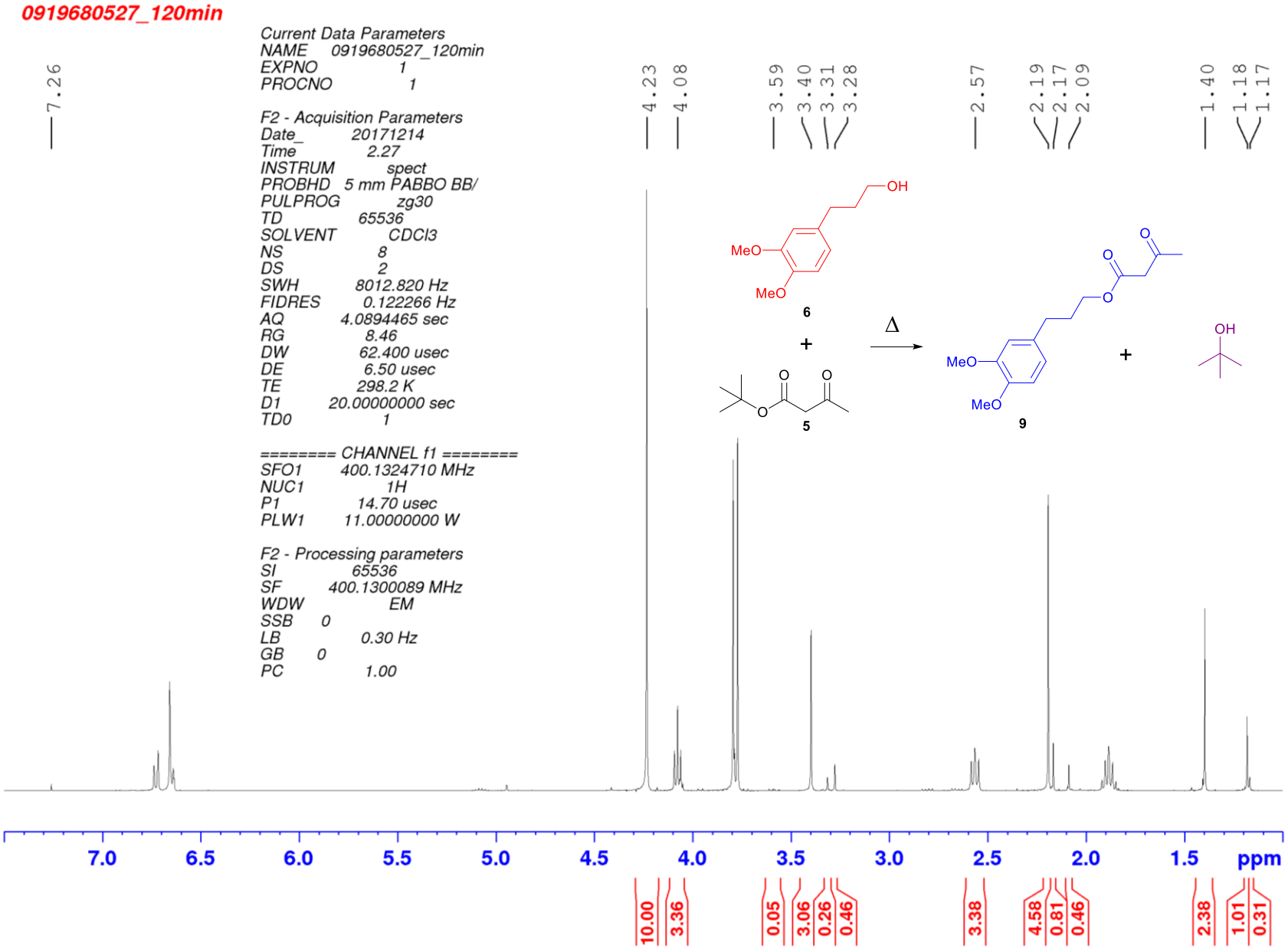


Figure S 103 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 120 min ($CDCl_3$, ^1H NMR)

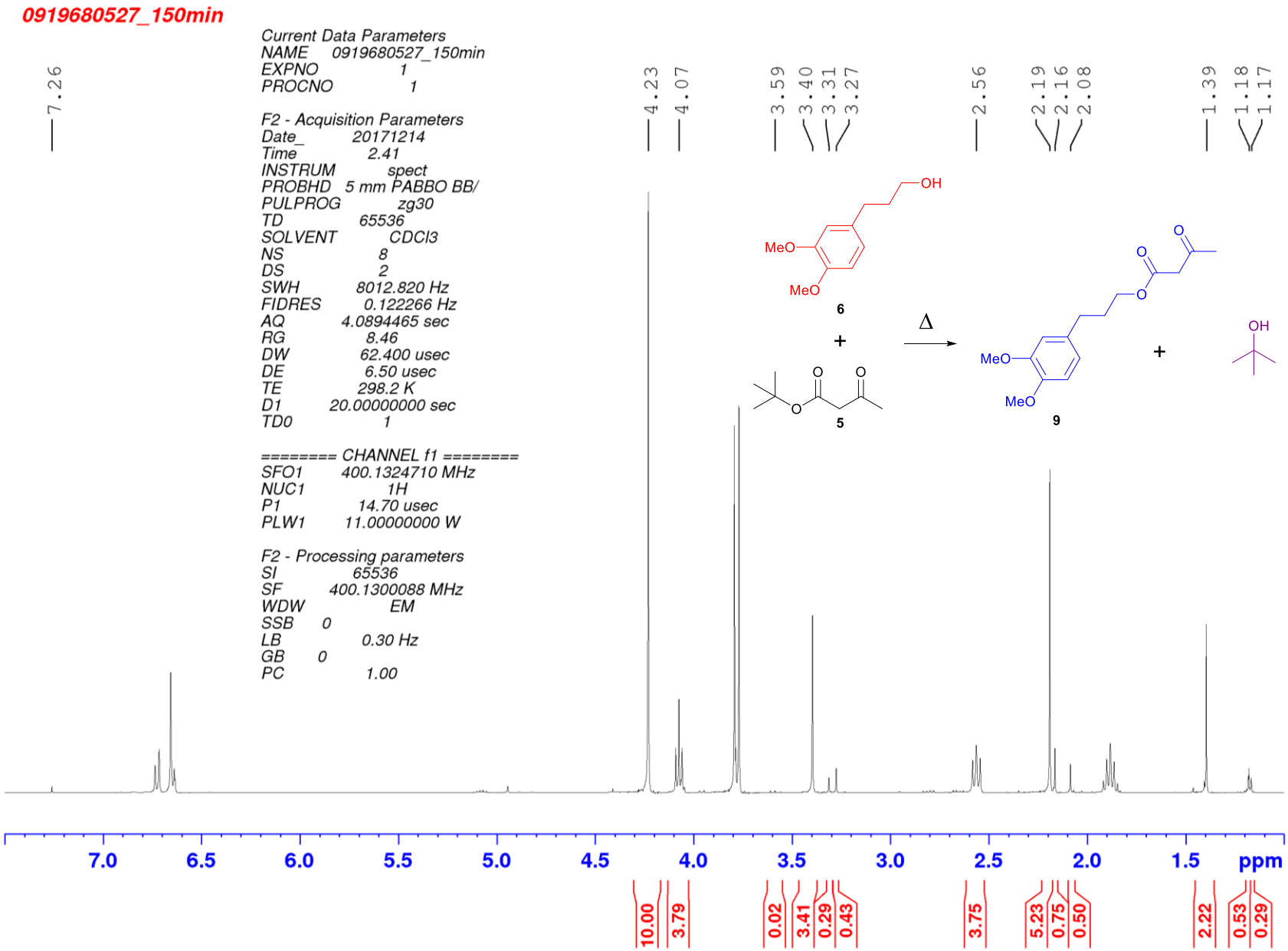


Figure S 104 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 150 min ($CDCl_3$, ^1H NMR)

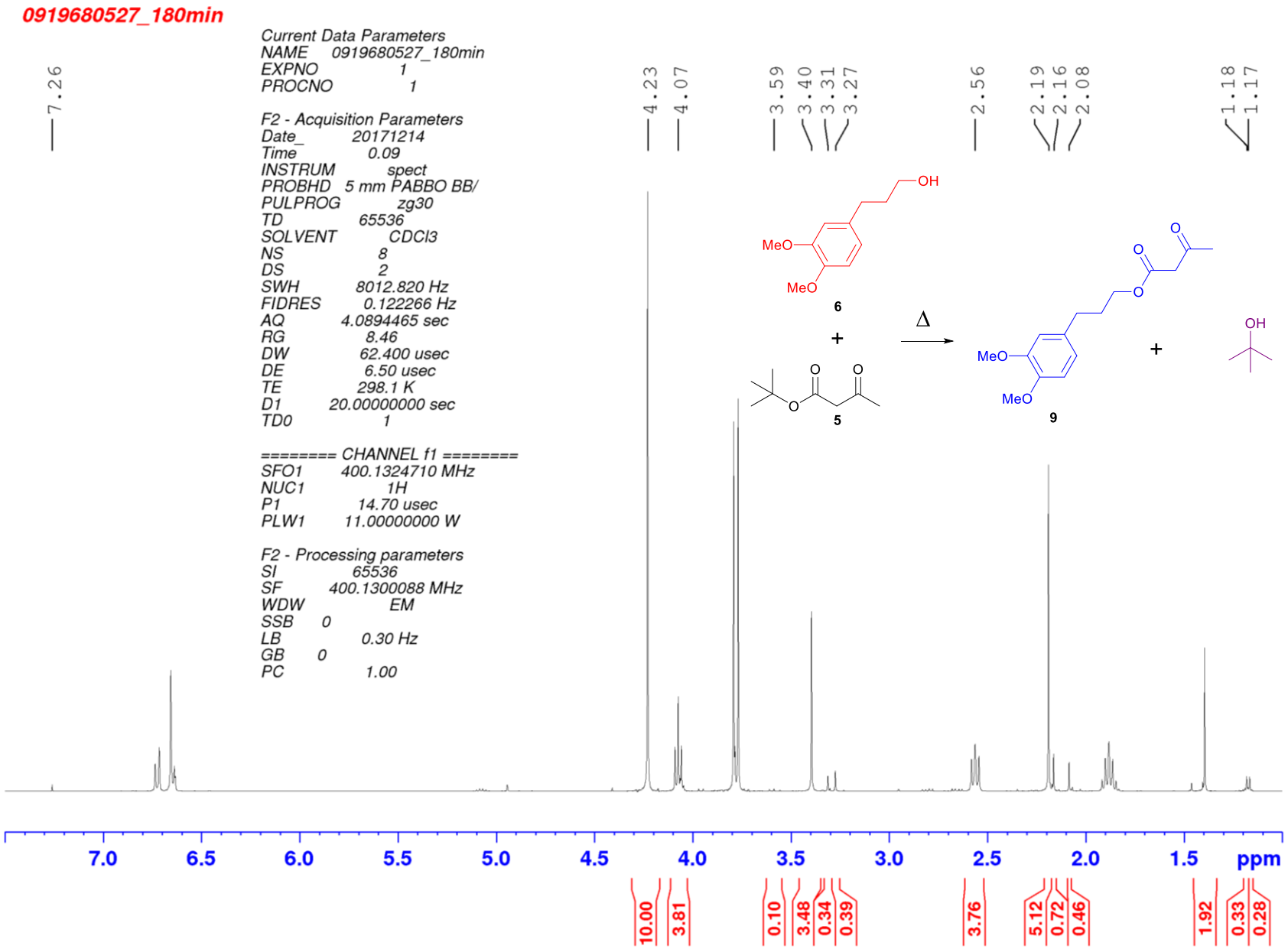


Figure S 105 **Acetoacetylation of 3-(3,4-Dimethoxyphenyl)-1-propanol**: 180 min ($CDCl_3$, ^1H NMR)

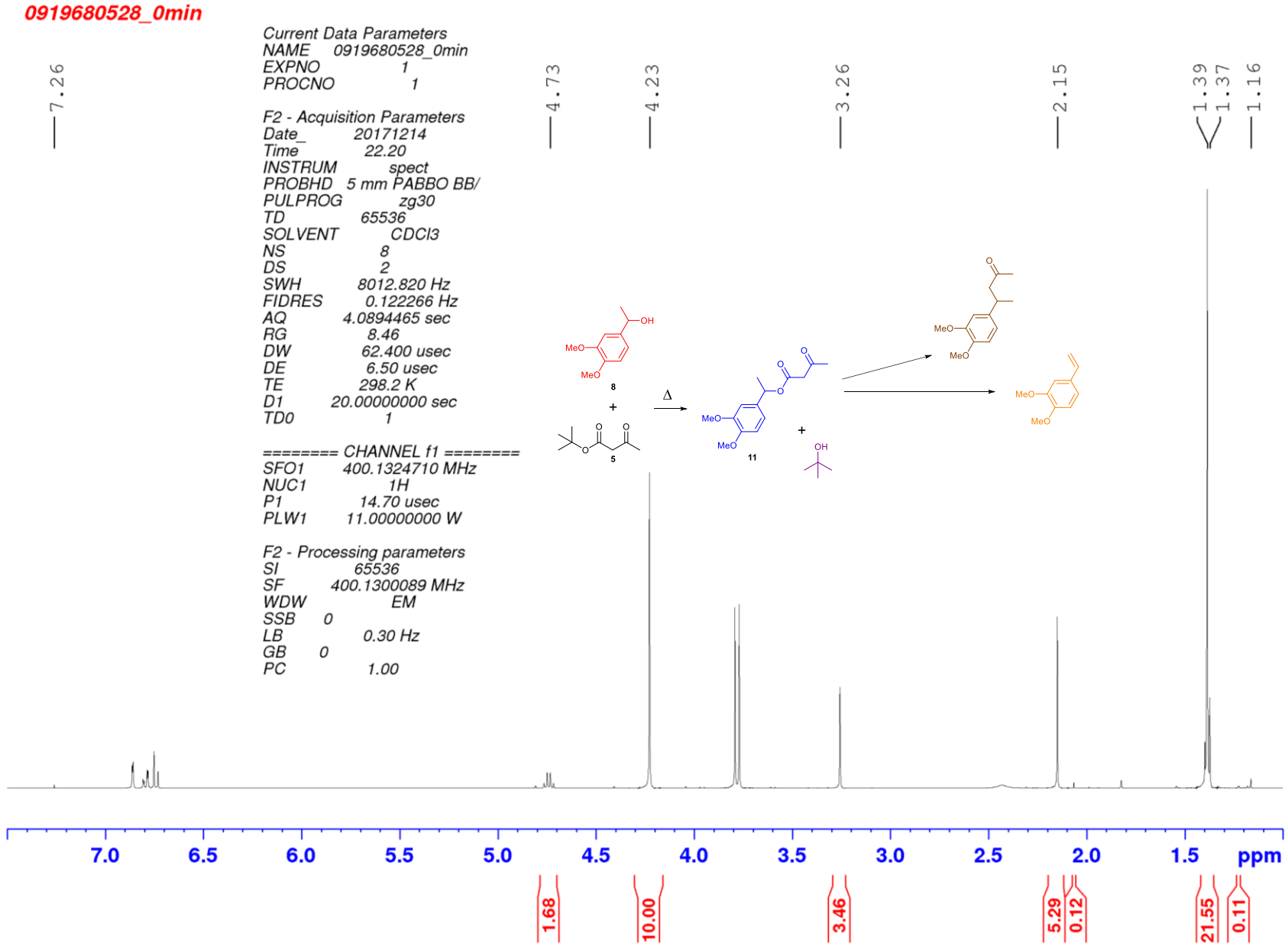


Figure S 106 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 0 min ($CDCl_3$, ^1H NMR)

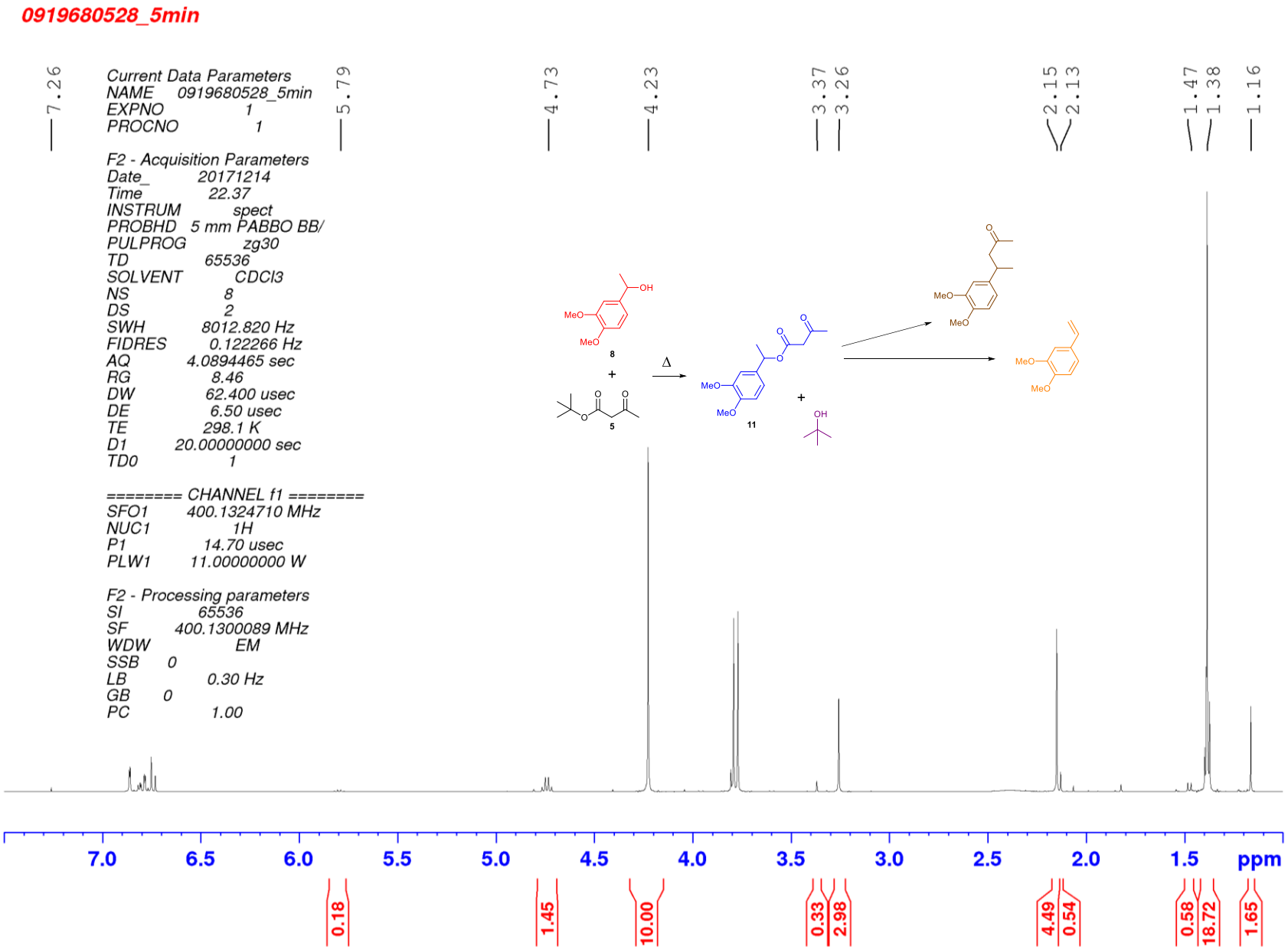


Figure S 107 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 5 min ($CDCl_3$, ^1H NMR)

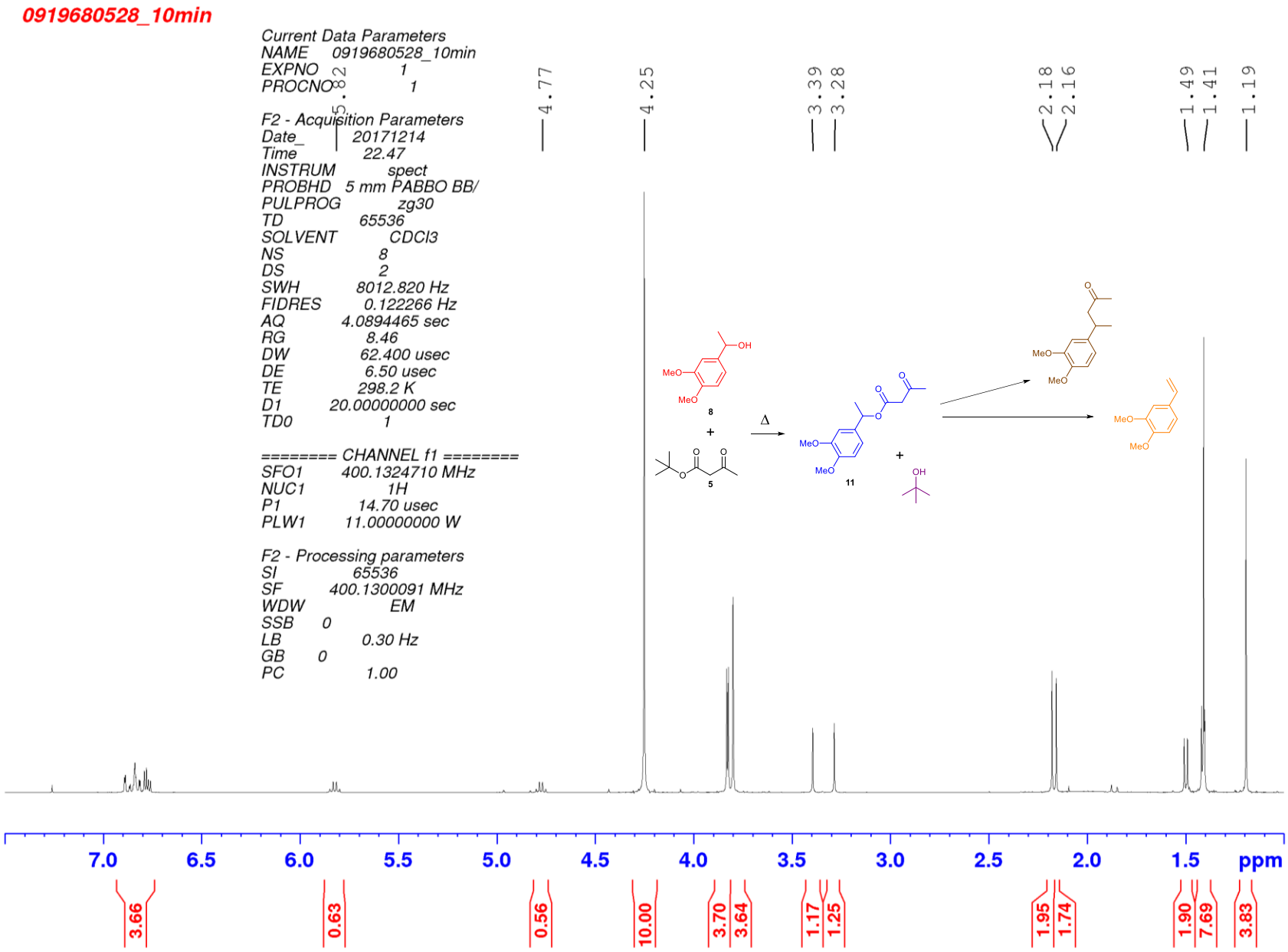


Figure S 108 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 10 min ($CDCl_3$, ^1H NMR)

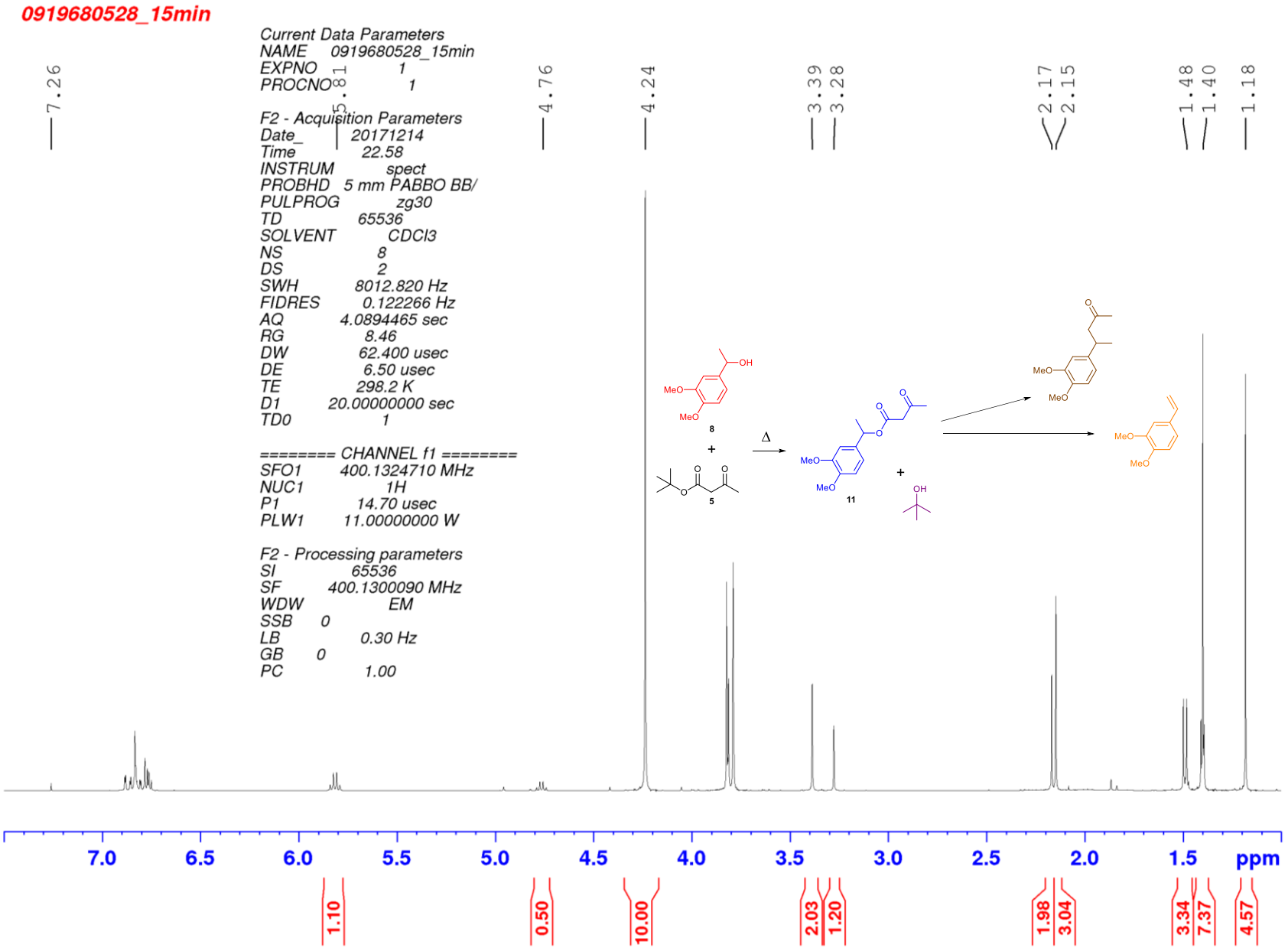


Figure S 109 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 15 min ($CDCl_3$, ^1H NMR)

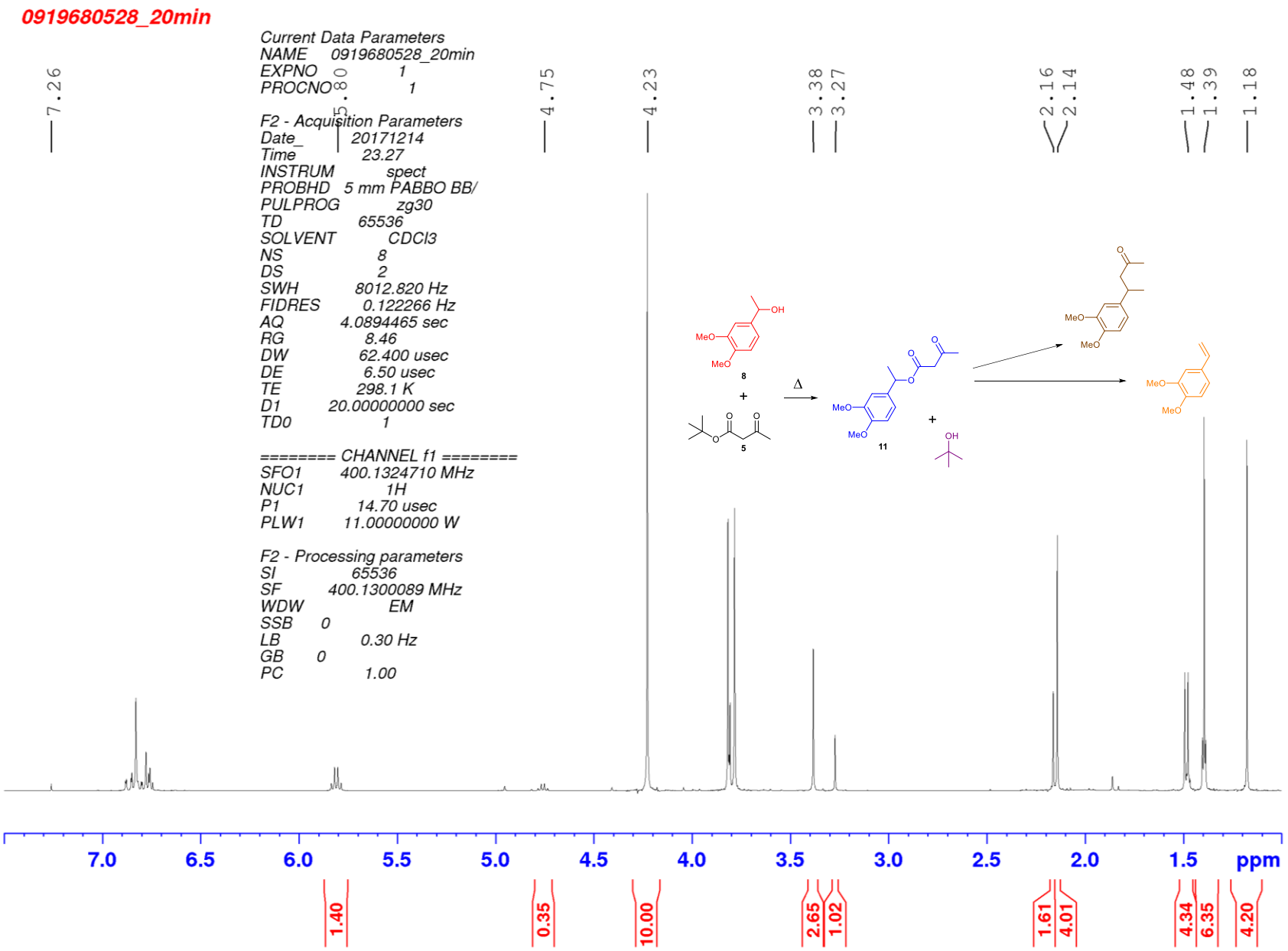


Figure S 110 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 20 min ($CDCl_3$, ^1H NMR)

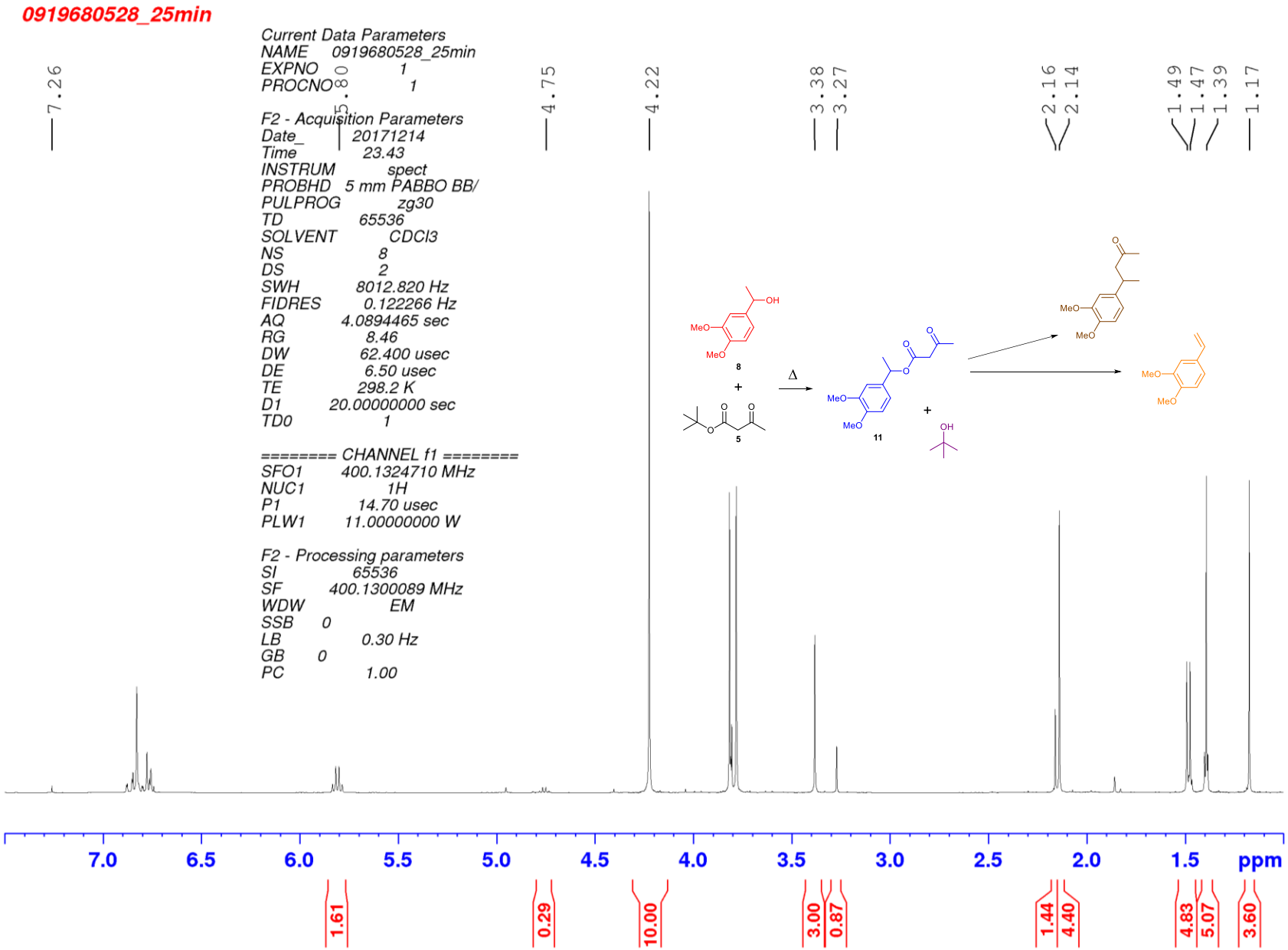


Figure S 111 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 25 min ($CDCl_3$, ^1H NMR)

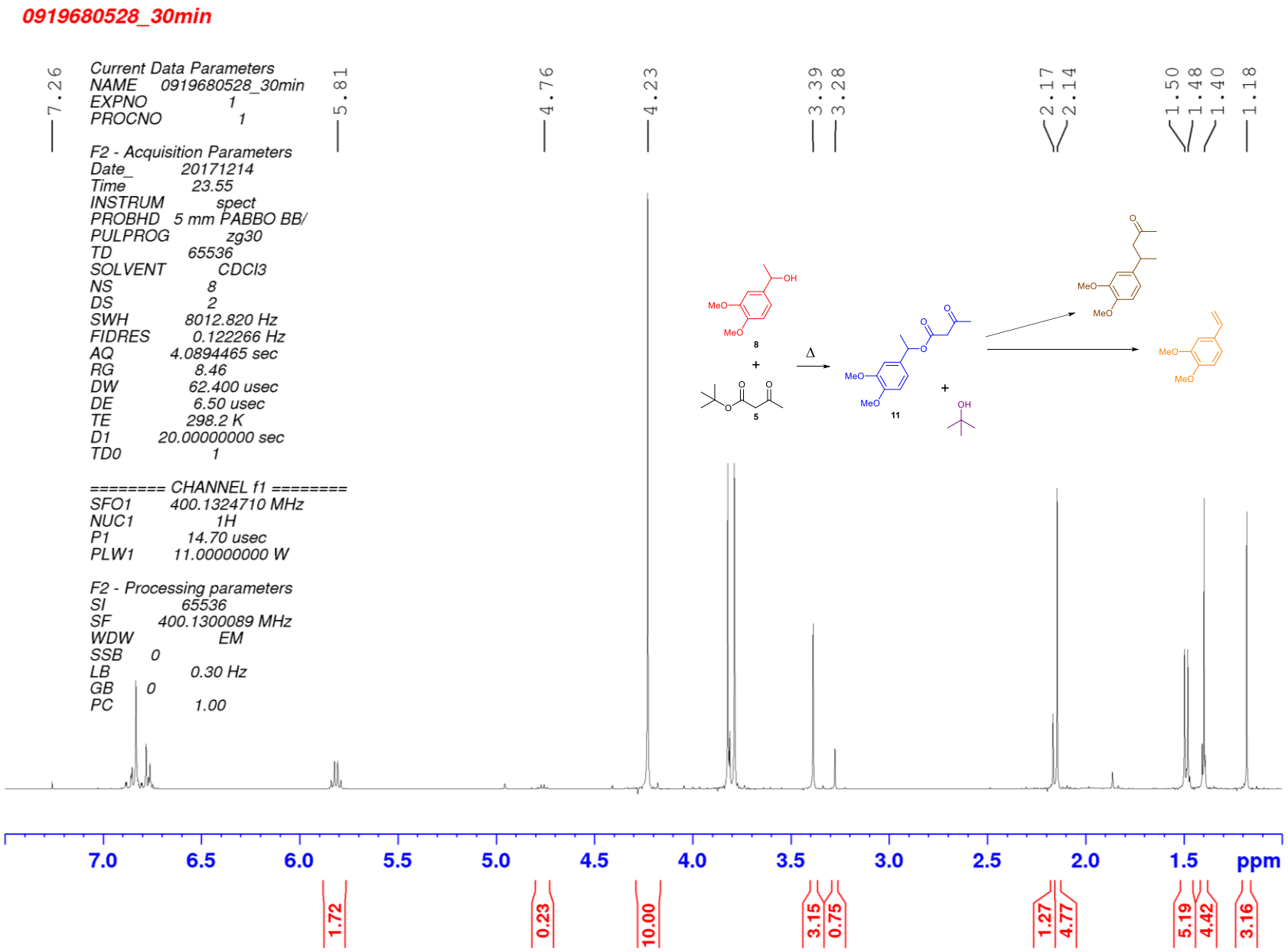


Figure S 112 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**:30 min ($CDCl_3$, ^1H NMR)

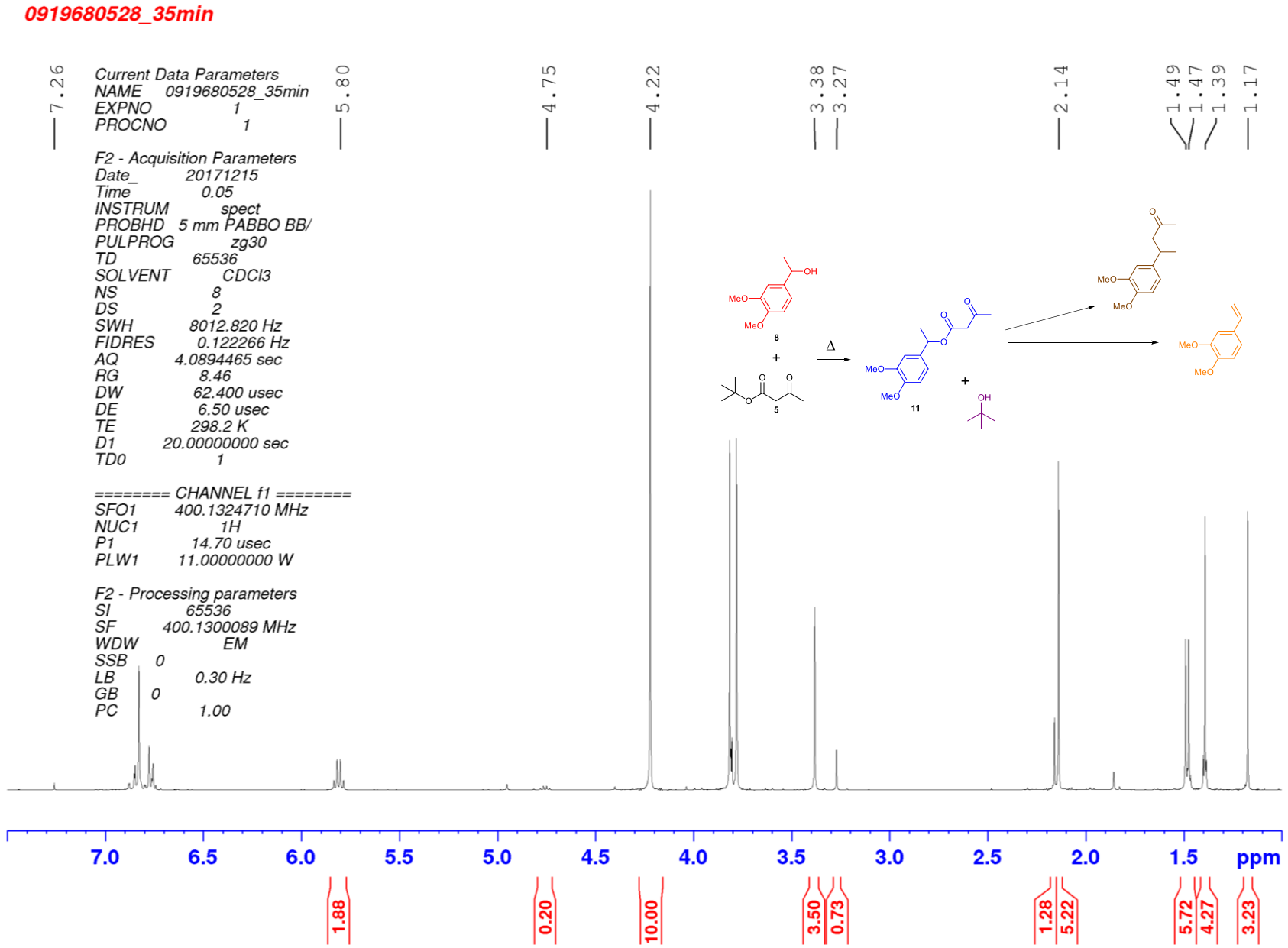


Figure S 113 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 35 min ($CDCl_3$, ^1H NMR)

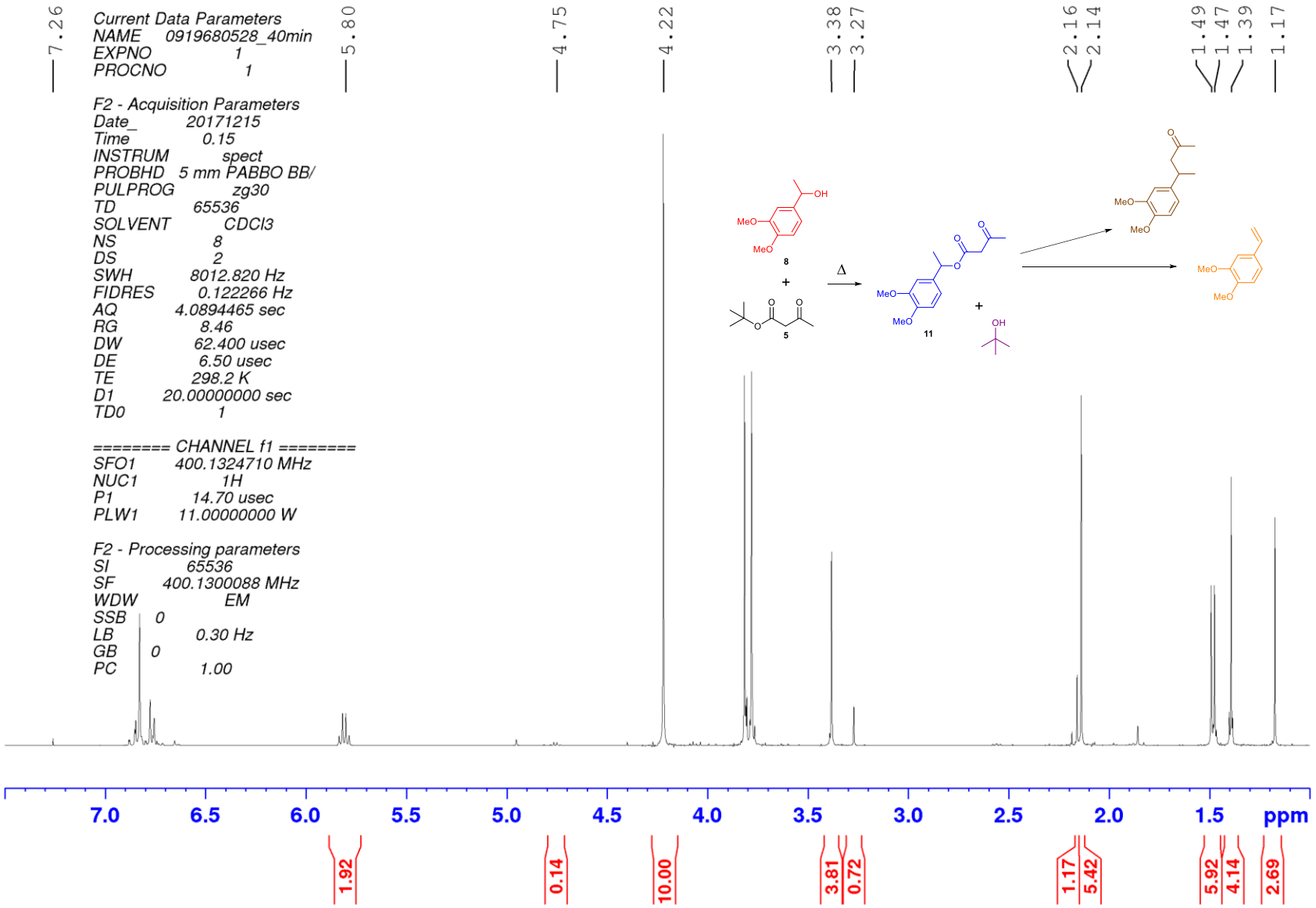


Figure S 114 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 40 min ($CDCl_3$, ^1H NMR)

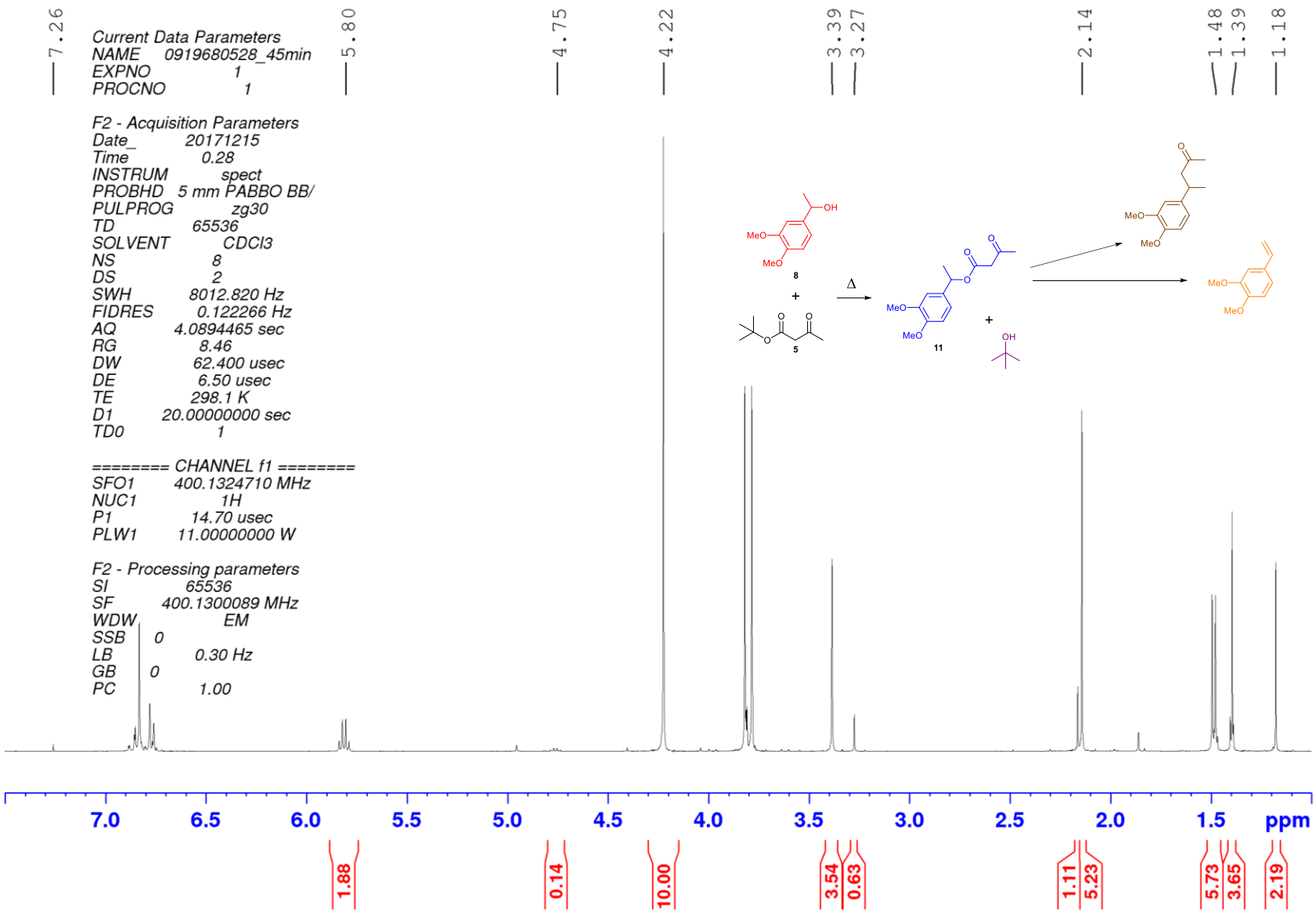


Figure S 115 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 45 min ($CDCl_3$, ^1H NMR)

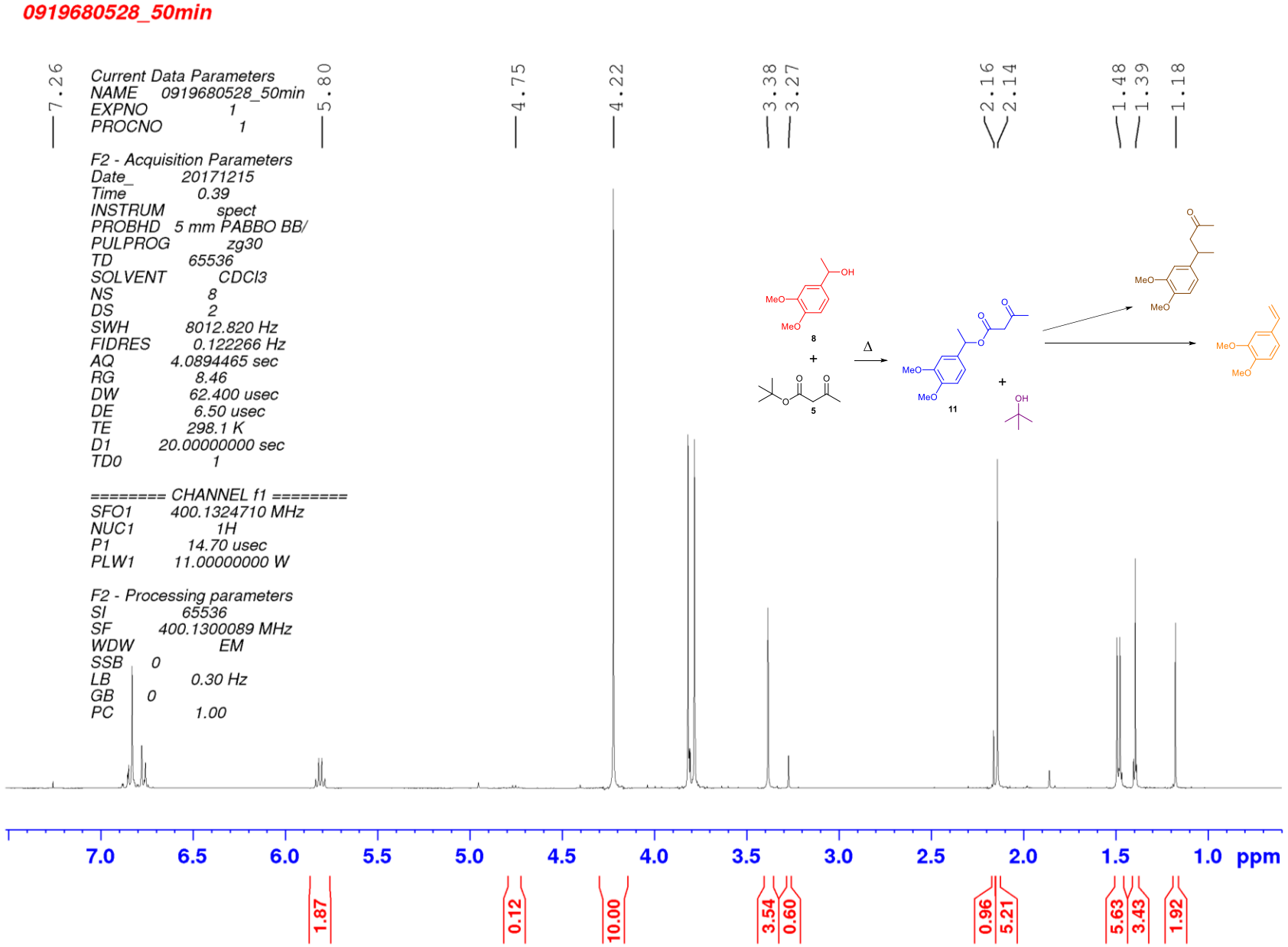


Figure S 116 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 50 min ($CDCl_3$, ^1H NMR)

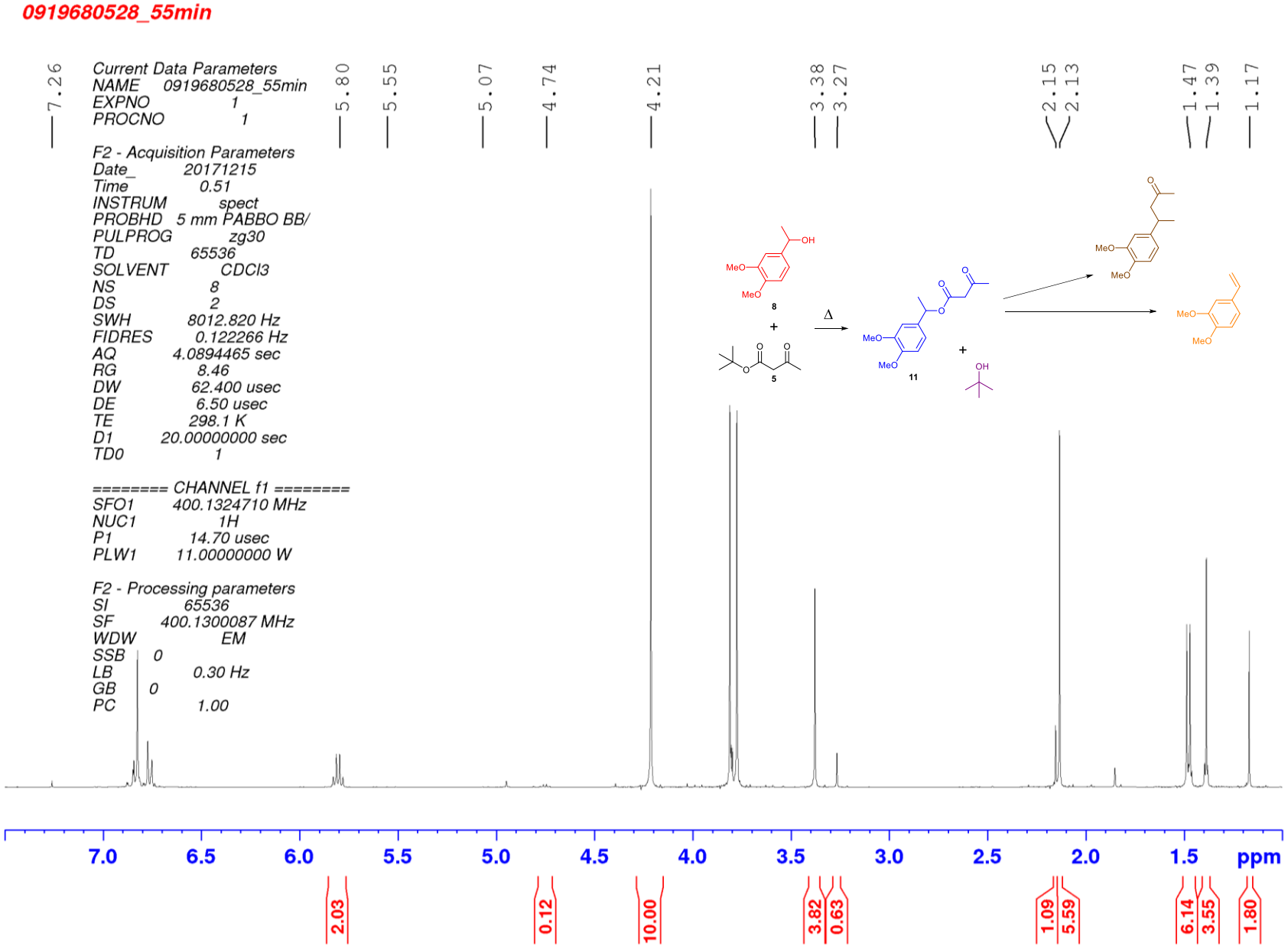


Figure S 117 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 55 min ($CDCl_3$, ^1H NMR)

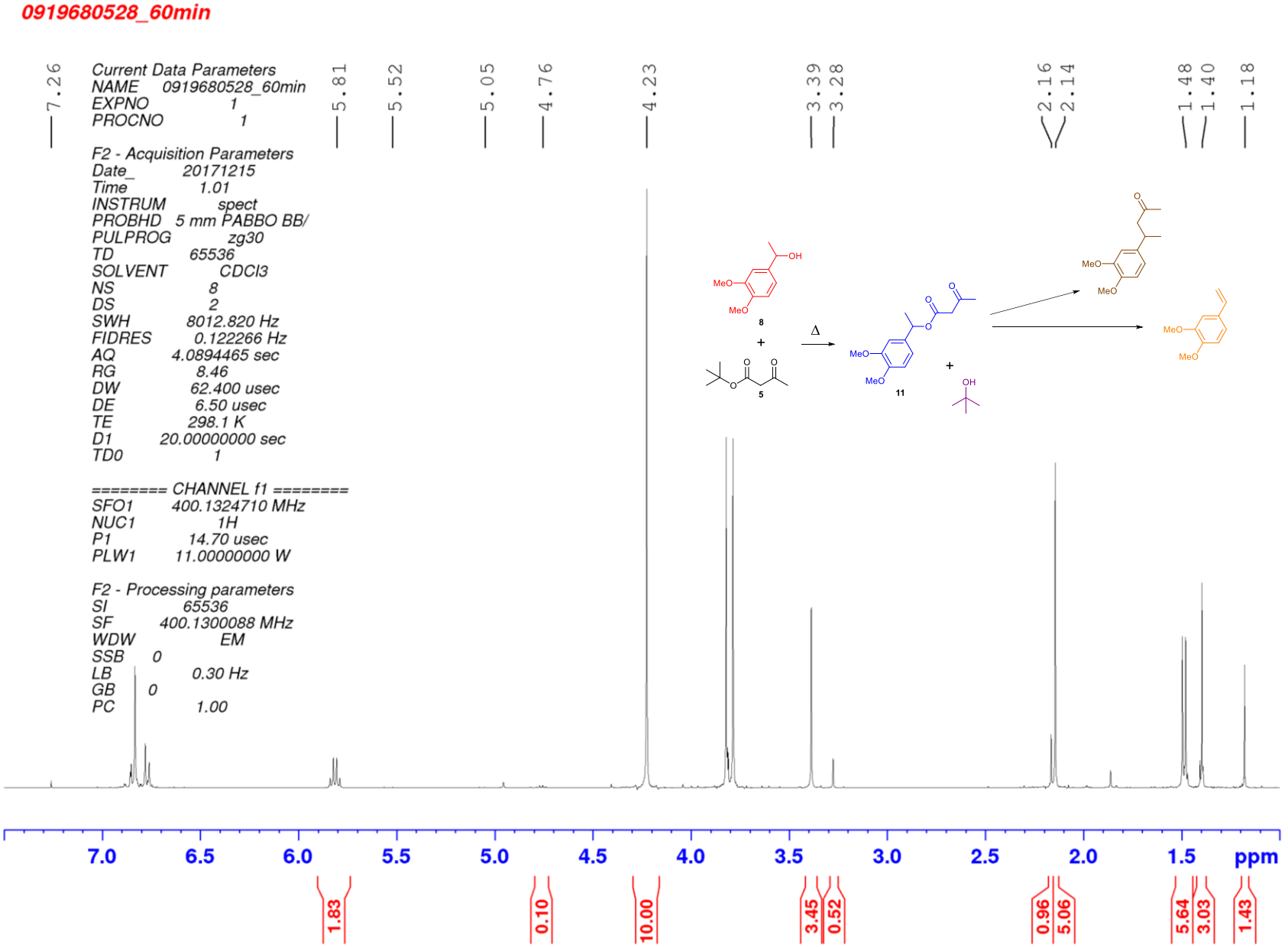


Figure S 118 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 60 min ($CDCl_3$, ^1H NMR)

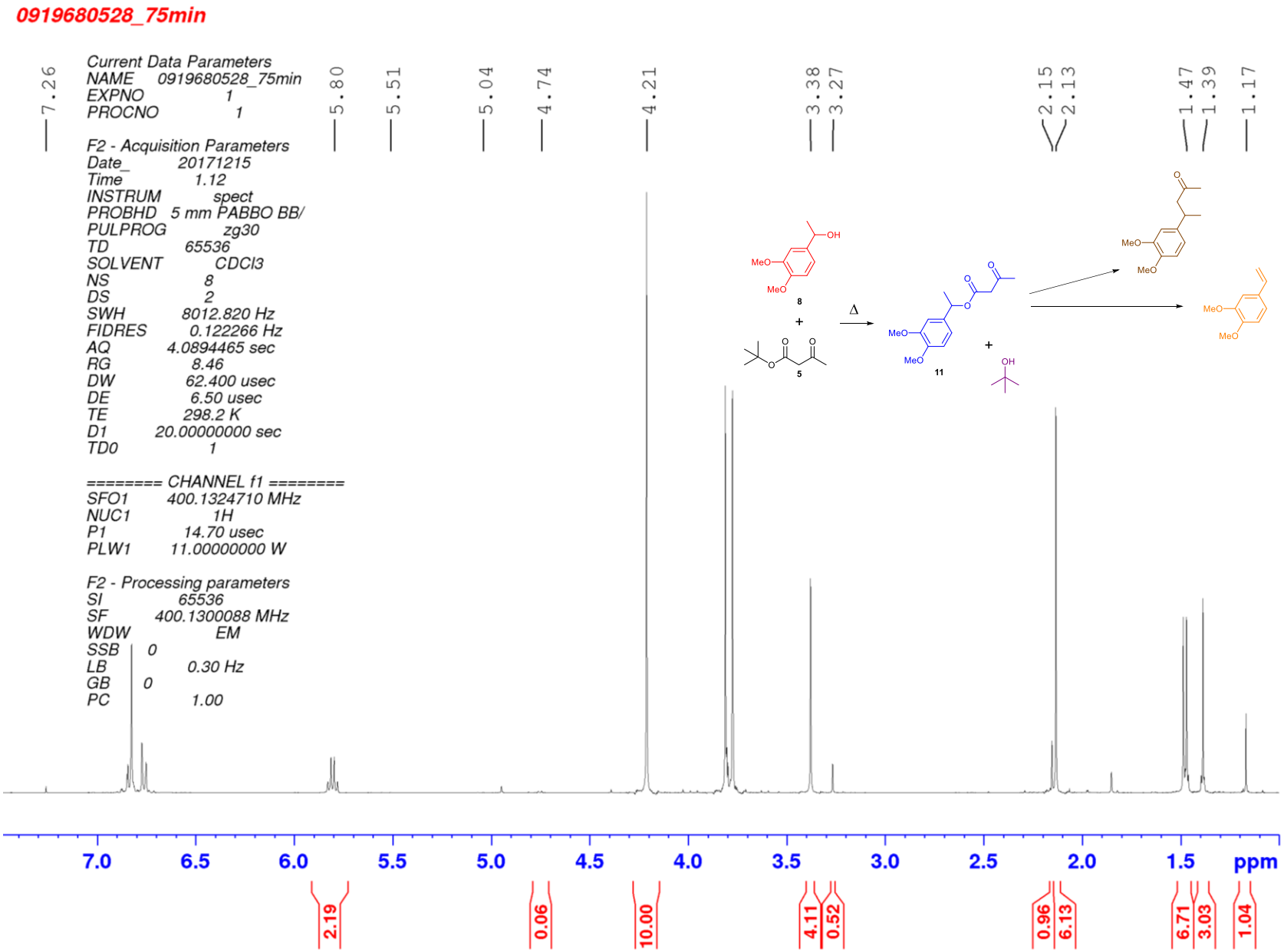


Figure S 119 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 75 min ($CDCl_3$, ^1H NMR)

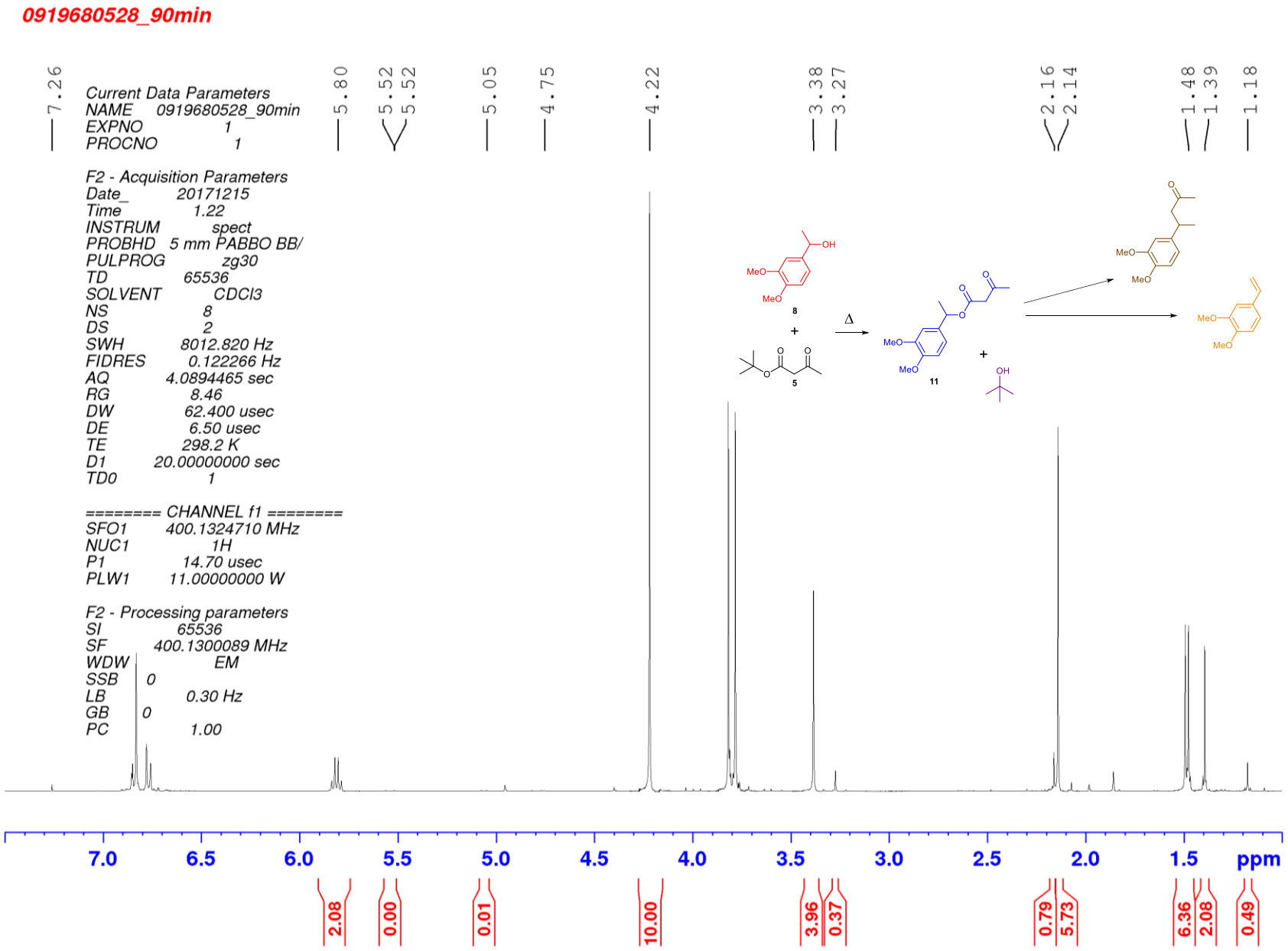


Figure S 120 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 90 min ($CDCl_3$, ^1H NMR)

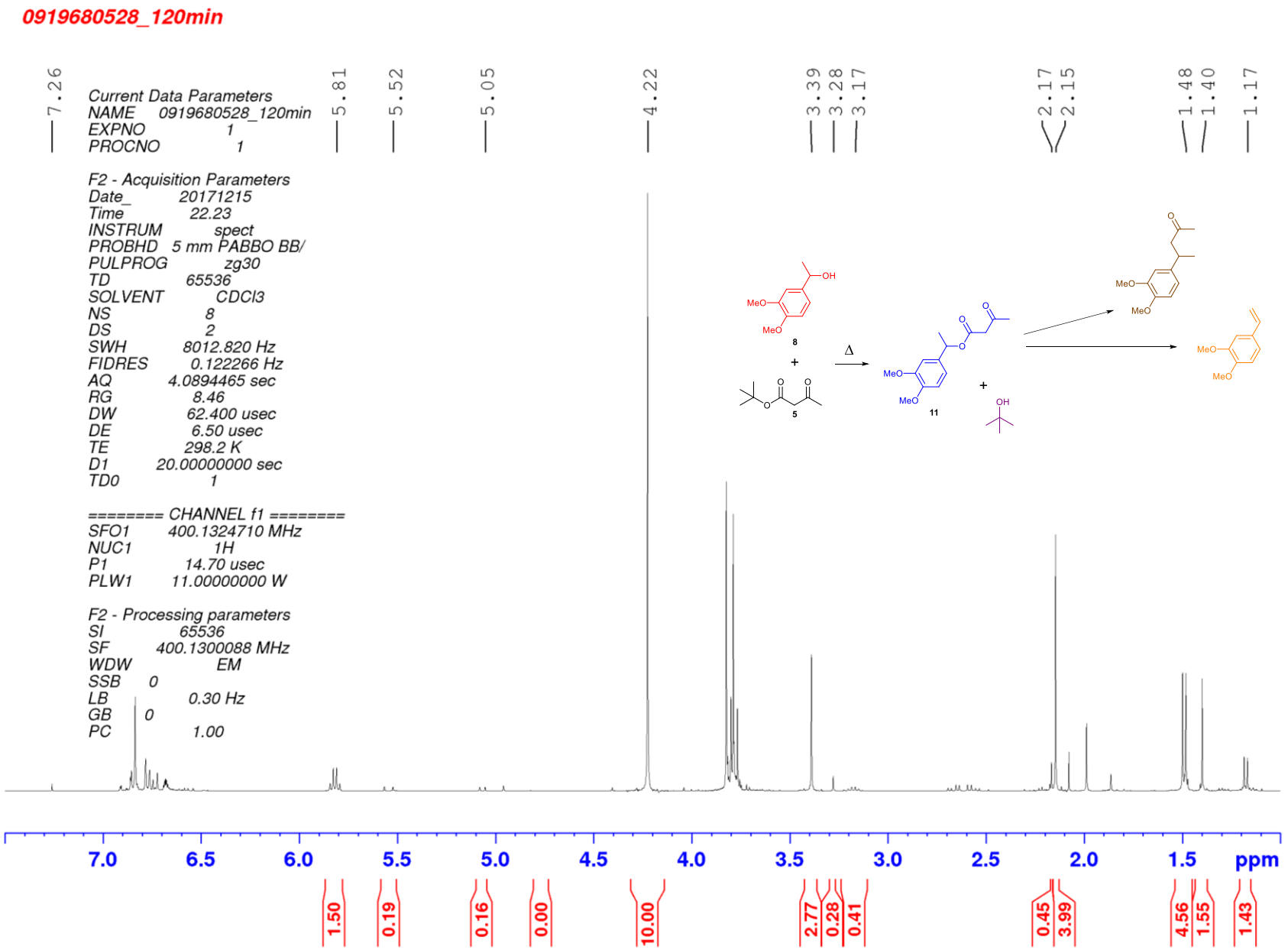


Figure S 121 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 120 min ($CDCl_3$, ^1H NMR)

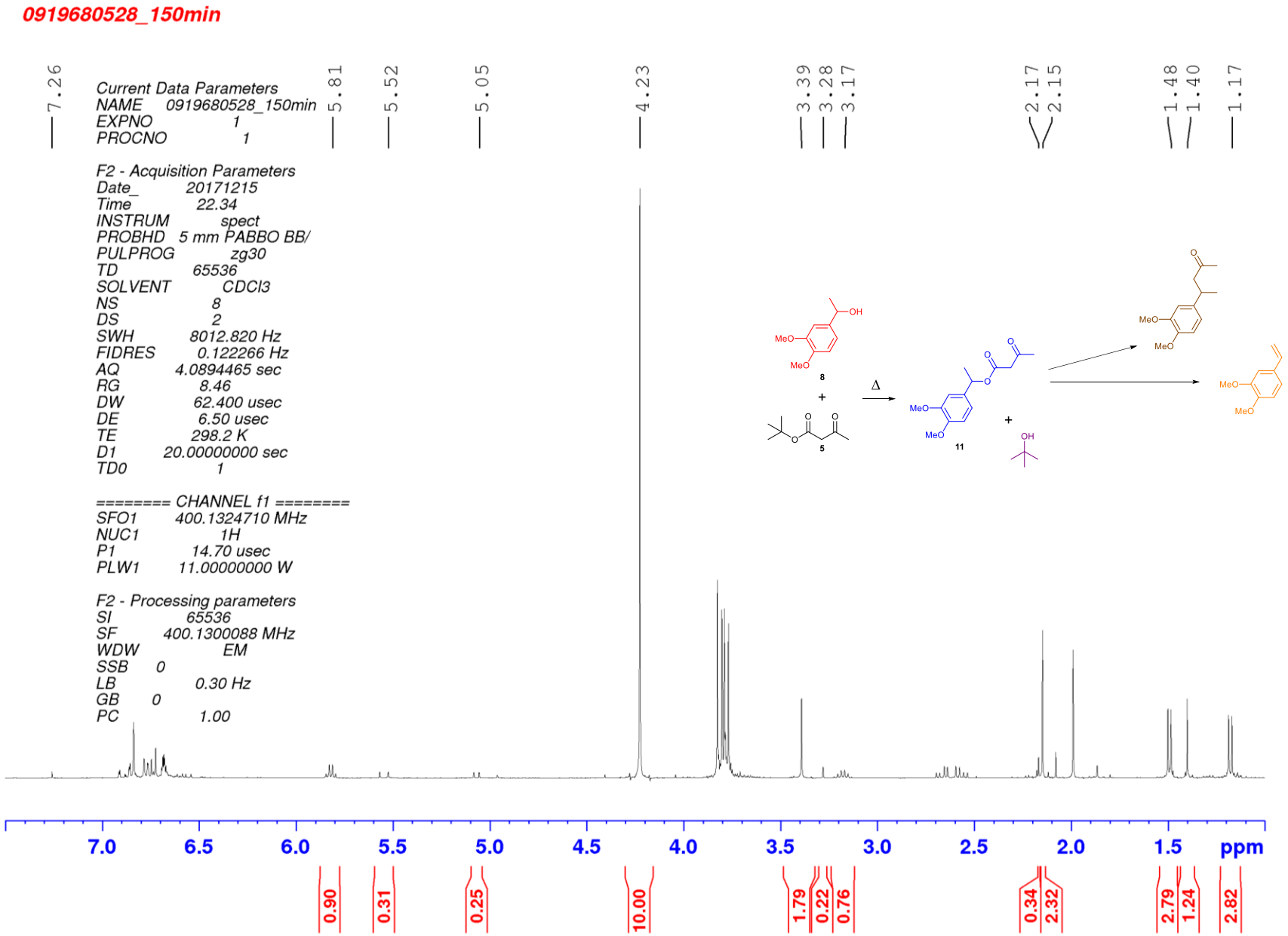


Figure S 122 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 150 min ($CDCl_3$, ^1H NMR)

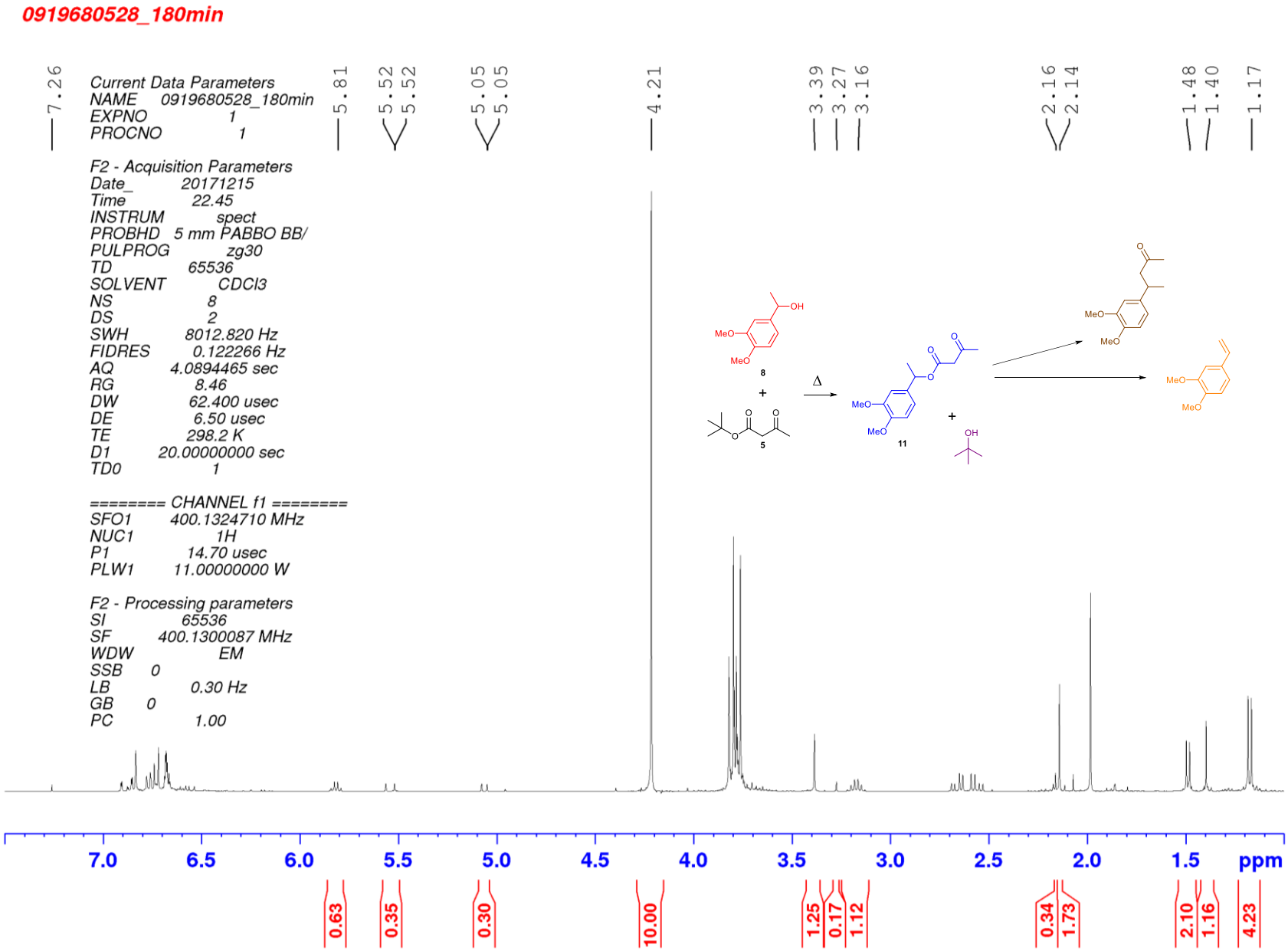


Figure S 123 **Acetoacetylation of 1-(3,4-Dimethoxyphenyl)-1-ethanol**: 180 min ($CDCl_3$, ^1H NMR)