SUPPORTING INFORMATION

for

Characteristic ^{1}H NMR spectra of β-D-ribofuranosides and ribonucleosides; factors driving furanose ring conformations

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Content:

Synthesis Procedures and Results of Analysis

General methods:

Solvents and chemical reagents, including nucleosides **11**-**14**, were purchased and used without further purification. Positive-ion mode MALDI-TOF mass spectra were obtained using a Bruker Biflex III spectrometer with 4-cyano-4-hydroxycinnamic acid or 2,5-dihydroxybenzoic acid matrixes. The IR spectra were recorded as Nujol mulls with a Bruker IFS 66 spectrophotometer. Thin-layer chromatography (TLC) was conducted on aluminium plates coated with E. Merck Kieselgel 60 F_{254} (0.2 mm) using the following eluent systems (v/v): A, 3 : 2 : 1 AcOEt : $CHCl_3$: MeOH; B, 4 : 1 *n*-hexane : AcOEt; C, 2 : 1 toluene : AcOEt; D, 9 : 1 toluene : AcOEt; E, 10 : 1 $CHCl_3$: MeOH. For the detection of compounds the dry plates were sprayed with a 5% aqueous sulfuric acid solution and then heated at 150 ^oC. Column chromatography was performed on MN Kieselgel 60 (<0.8 mm) with one of the above listed eluent systems. Flash column chromatography was conducted using puriFlash 450 Interchim instrument with silica column (SIHP, 50μm) using one of the above-mentioned eluent systems.

General procedure for alkyl 2,3-*O*-isopropylidene-β-D-ribofuranosides (**1**-**5**)

D-Ribose (0.3 g, 2 mmol) and $SnCl_2$ x 2 H_2O (0.45 g, 2 mmol) were dissolved in acetone (6 mL). Then respective alcohol (40 mmol) and catalytic amounts of conc. H_2SO_4 were added and the mixture was stirred under reflux at 40-45 ^oC for 20 h. The course of reaction was monitored by TLC (eluent A). After completion of the reaction, the mixture was cooled to rt and the precipitate was filtered off. The filtrate was neutralized with saturated aqueous $NaHCO_3$ solution and filtered through a Celite pad. The latter was washed with a mixture of acetone and MeOH (1:1). The resulting filtrate was concentrated to an oil, which was dissolved in cold water (100 mL) and extracted with ethyl acetate (5 x 30 mL). The collected organic layers were washed with brine (50 mL), dried with $MgSO_4$, filtered and concentrated in vacuum. The residue was purified using column chromatography (eluent B). The obtained reaction products were straw-colored syrups.

Methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (1)

Reaction of D-ribose with methanol gave **1** (214 mg, 53%); R_f 0.81 (eluent A); IR: ν (cm^{-1}): 3459 (OH), 2988, 2940, 2836 (CH_2); MALDITOF-MS: *m/z* 205.4 $(M+H)^+$, 227.3 $(M+Na)^+$, 243.3 $(M+K)^+$.

Ethyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (2)

Reaction of D-ribose with ethanol gave **2** (197 mg, 45%); R_f 0.84 (eluent A); IR: ν (cm^{-1}):

3452 (OH), 2980, 2939, 2880 (CH_2); MALDITOF-MS: *m/z* 241.1 $(M+Na)^+$.

Propyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (3)

Reaction of D-ribose with propanol gave **3** (243 mg, 53%); R_f 0.88 (eluent A); IR: ν (cm^{-1}): 3453 (OH), 2963, 2938, 2878 (CH_2); MALDITOF-MS: *m/z* 255.1 $(M+Na)^+$.

Isopropyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (4)

Reaction of D-ribose with isopropanol gave **4** (269 mg, 58%); R_f 0.88 (eluent A); IR: ν (cm^{-1}): 3448 (OH), 2977, 2939, 2878 (CH_2); MALDITOF-MS: *m/z* 232.0 $(M)^+$.

Butyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (5)

Reaction of D-ribose with butanol gave **5** (231 mg, 47%); R_f 0.85 (eluent A); IR: ν (cm^{-1}): 3454 (OH), 2958, 2937, 2874 (CH_2); MALDITOF-MS: *m/z* 269.0 $(M+Na)^+$.

General procedure for alkyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranosides (**6**-**10**)

Respective furanoside (**1**-**5**) was dissolved in the mixture of pyridine and acetic anhydride and stirred at rt for 1 h. The course of reaction was monitored by TLC (eluent C). Next, the mixture was poured into ice water and put into the refrigerator for 24 h. After this time it was extracted with $CHCl_3$ (4 x 40 mL). The collected organic layers were washed with 1M HCl (40 mL), with saturated aqueous $NaHCO_3$ until neutral pH and finally with water (40 mL). Then it was dried with $MgSO_4$, filtered and concentrated in vacuum. The residue was purified using column chromatography (eluent D). The obtained reaction products were colorless syrups.

Methyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (6)

Acetylation of ribofuranoside **1** (200 mg, 0.98 mmol) with Ac_2O (2 mL) in pyridine (2 mL) gave **6** (178 mg, 74%); R_f 0.37 (eluent D); IR: ν (cm^{-1}): 2989, 2940 (CH_2), 1746 (C=O), 1240 (CO-O); MALDITOF-MS: *m/z* 269.3 $(M+Na)^+$, 285.2 $(M+K)^+$.

Ethyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (7)

Acetylation of ribofuranoside **2** (190 mg, 0.87 mmol) with Ac_2O (1.9 mL) in pyridine (1.9 mL) gave **7** (169 mg, 75%); R_f 0.39 (eluent D); IR: ν (cm^{-1}): 2980, 2939 (CH_2), 1747 (C=O), 1240 (CO-O); MALDITOF-MS: *m/z* 241.1 $(M+Na)^+$.

Propyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (8)

Acetylation of ribofuranoside **3** (230 mg, 0.99 mmol) with Ac_2O (2.3 mL) in pyridine (2.3 mL) gave **8** (196 mg, 72%); R_f 0.41 (eluent D); IR: ν (cm^{-1}): 2965, 2939 (CH_2), 1747 (C=O), 1240 (CO-O); MALDITOF-MS: *m/z* 297.2 $(M+Na)^+$, 313.2 $(M+K)^+$.

Isopropyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (9)

Acetylation of ribofuranoside **4** (260 mg, 1.1 mmol) with Ac_2O (2.6 mL) in pyridine (2.6 mL) gave **9** (179 mg, 58%); R_f 0.42 (eluent D); IR: ν (cm^{-1}): 2976, 2940 (CH_2), 1747 (C=O), 1241 (CO-O); MALDITOF-MS: *m/z* 297.3 $(M+Na)^+$, 313.2 $(M+K)^+$.

Butyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (10)

Acetylation of ribofuranoside **5** (220 mg, 0.89 mmol) with Ac_2O (2.2 mL) in pyridine (2.2 mL) gave **10** (194 mg, 75%); R_f 0.40 (eluent D); IR: ν (cm^{-1}): 2959, 2937, 2874 (CH_2), 1748 (C=O), 1240 (CO-O); MALDITOF-MS: *m/z* 311.2 $(M+Na)^+$, 327.1 $(M+K)^+$.

General procedure for 2,3-*O*-isopropylidenenucleosides (**15-18**)

Respective nucleoside (**11-14**) (1 mmol) and *p*-toluenesulfonic acid (28 mg, 0,15 mmol) were placed in ampoule where anhydrous DMF (4.4 mL) and roasted molecular sieves were added. This was placed on a shaker until the substrates were completely dissolved. Then, 2,2-dimethoxypropane (0.47 mL, 3.9 mmol) was added and the ampoule was kept at 40 °C until the reaction was completed (TLC, eluent E). Then, the mixture was neutralized with Dowex HO^- and filtered through a Celite pad. The latter was washed with a mixture of $CHCl_3$ and MeOH (1:1). The resulting filtrate was concentrated and purified using Flash chromatography (eluent H) to an oil, which was dissolved in cold water (100 mL) and extracted with ethyl acetate (5 x 30 mL). The products obtained were white solids.

2,3-*O*-Isopropylideneuridine (15)

Isopropylidenation of uridine (**11**, 244 mg) took 36 h and gave **15** (151 mg, 53%); R_f 0.42 (eluent E); MALDITOF-MS: m/z 285.1 $(M+H)^+$, 307.1 $(M+Na)^+$.

2,3-*O*-Isopropylideneadenosine (16)

Isopropylidenation of adenosine (**12**, 267 mg) took 24 h and gave **16** (85 mg, 28%); R_f 0.41 (eluent E); MALDITOF-MS: m/z 308.1 $(M+H)^+$, 330.1 $(M+Na)^+$.

2,3-*O*-Isopropylidenecytidine (17)

Isopropylidenation of cytidine (**13**, 243 mg) took 72 h and gave **17** (78 mg, 28%); R_f 0.2 (eluent E); MALDITOF-MS: m/z 284.1 $(M+H)^+$, 306.1 $(M+Na)^+$, 322.1 $(M+K)^+$.

2,3-*O*-Isopropylideneguanosine (18)

Isopropylidenation of guanosine (**14**, 283 mg) took 48 h and gave **18** (49 mg, 15%); R_f 0.24 (eluent E); MALDITOF-MS: m/z 324.1 $(M+H)^+$, 346.1 $(M+Na)^+$, 362.1 $(M+K)^+$.

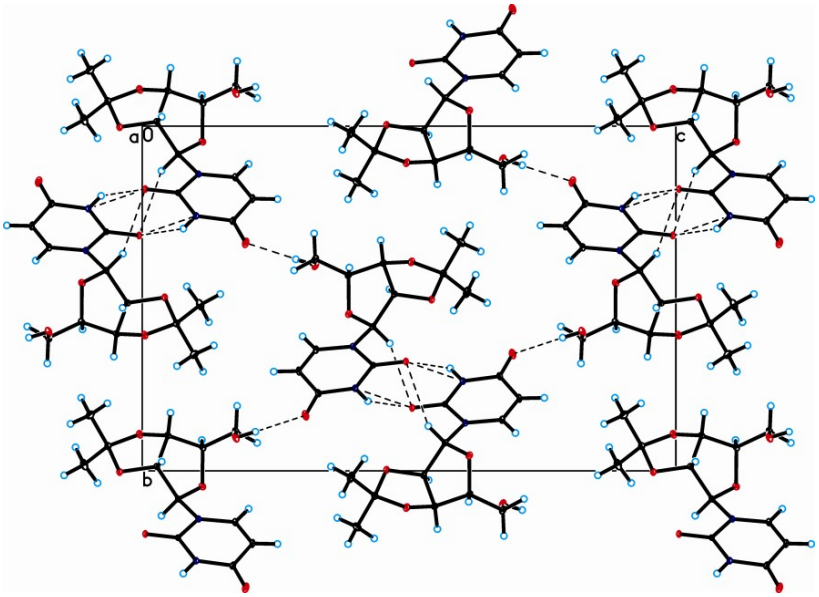

Figure S1. The arrangement of the molecules in the crystal structure of **15** viewed along the *a*-direction. The N–H···O, O–H···O and C–H···O hydrogen bonds are represented by dashed lines.

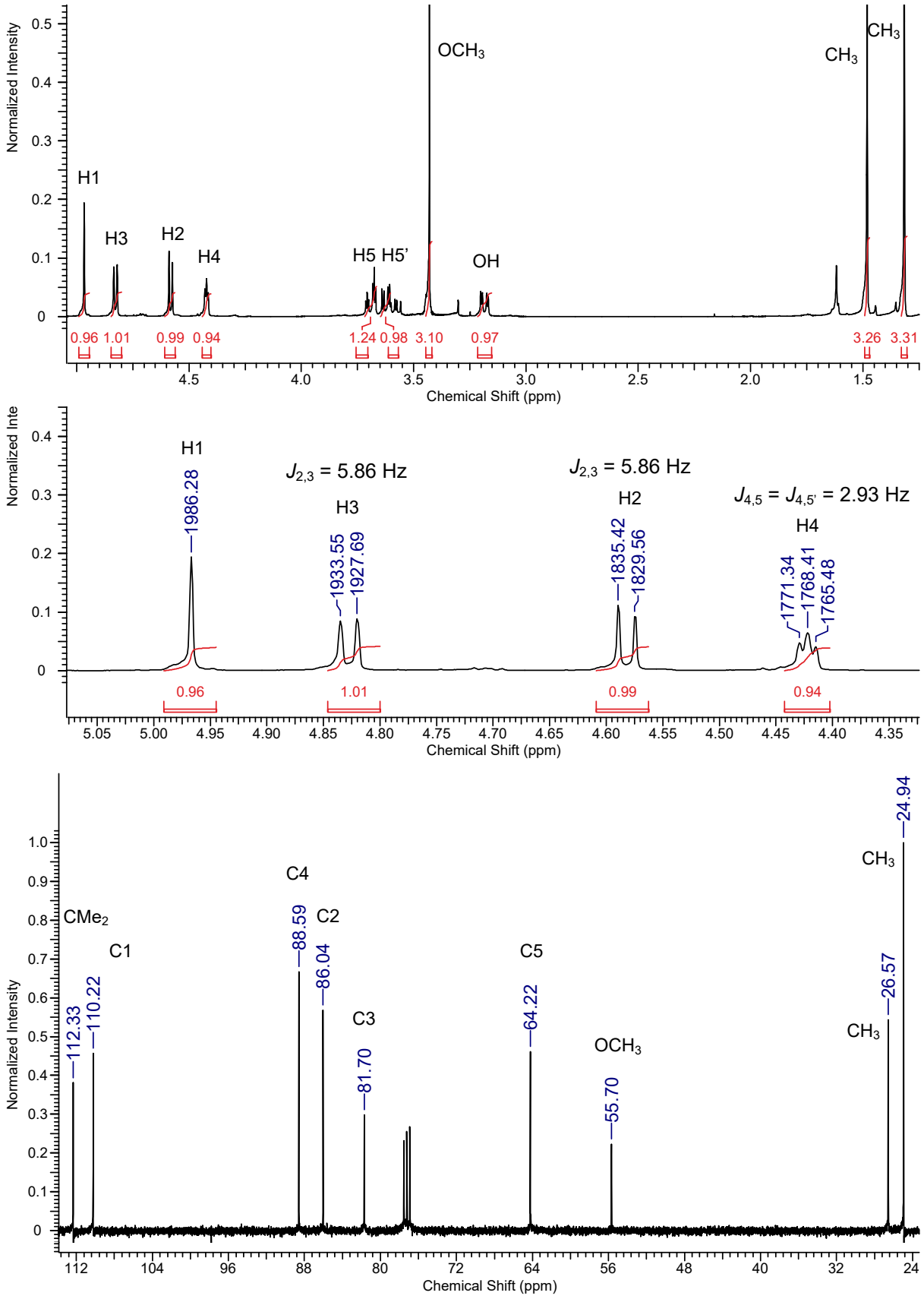

Figure S2. ^{1}H and ^{13}C NMR spectra of **1**.

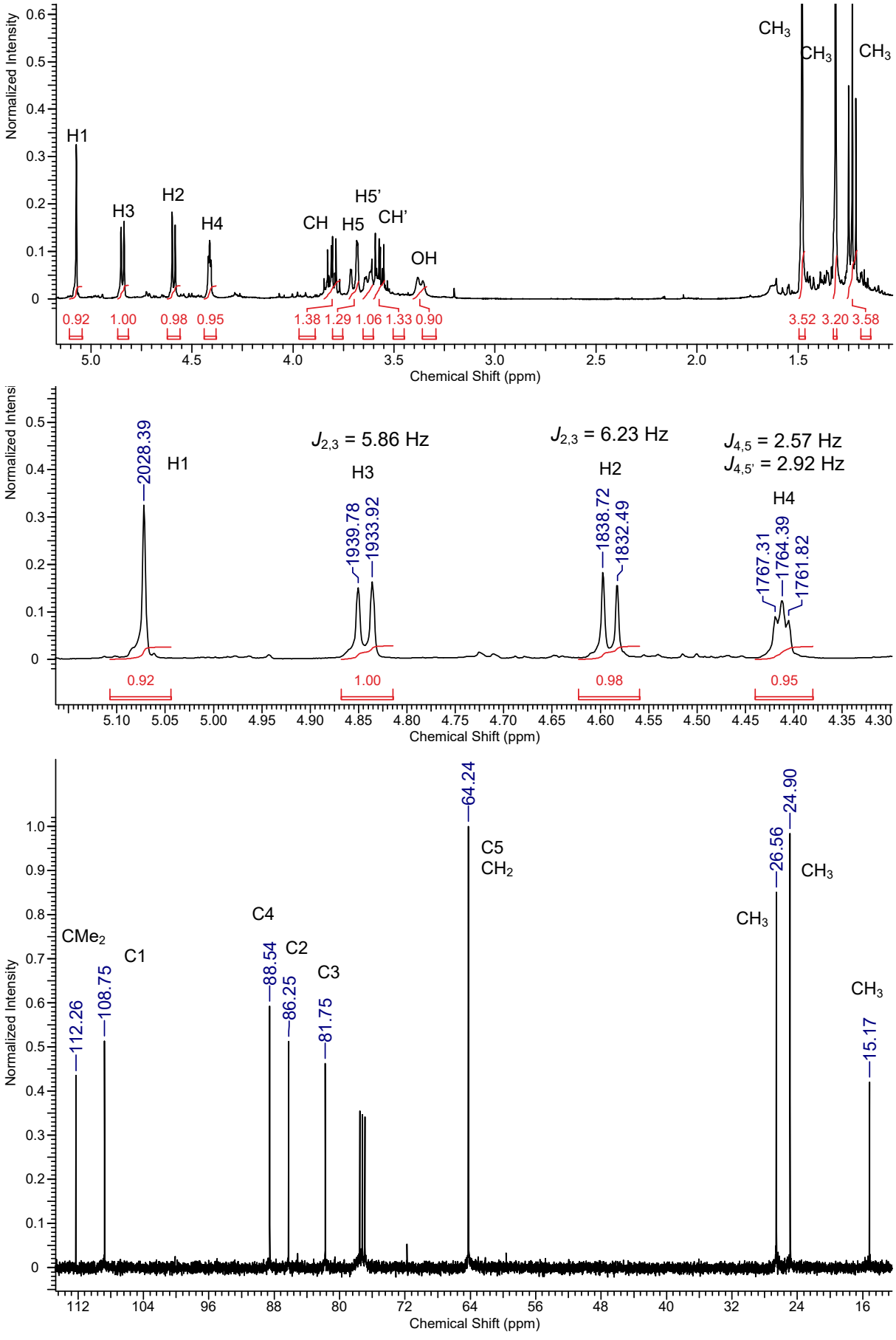

Figure S3. ^{1}H and ^{13}C NMR spectra of **2**.

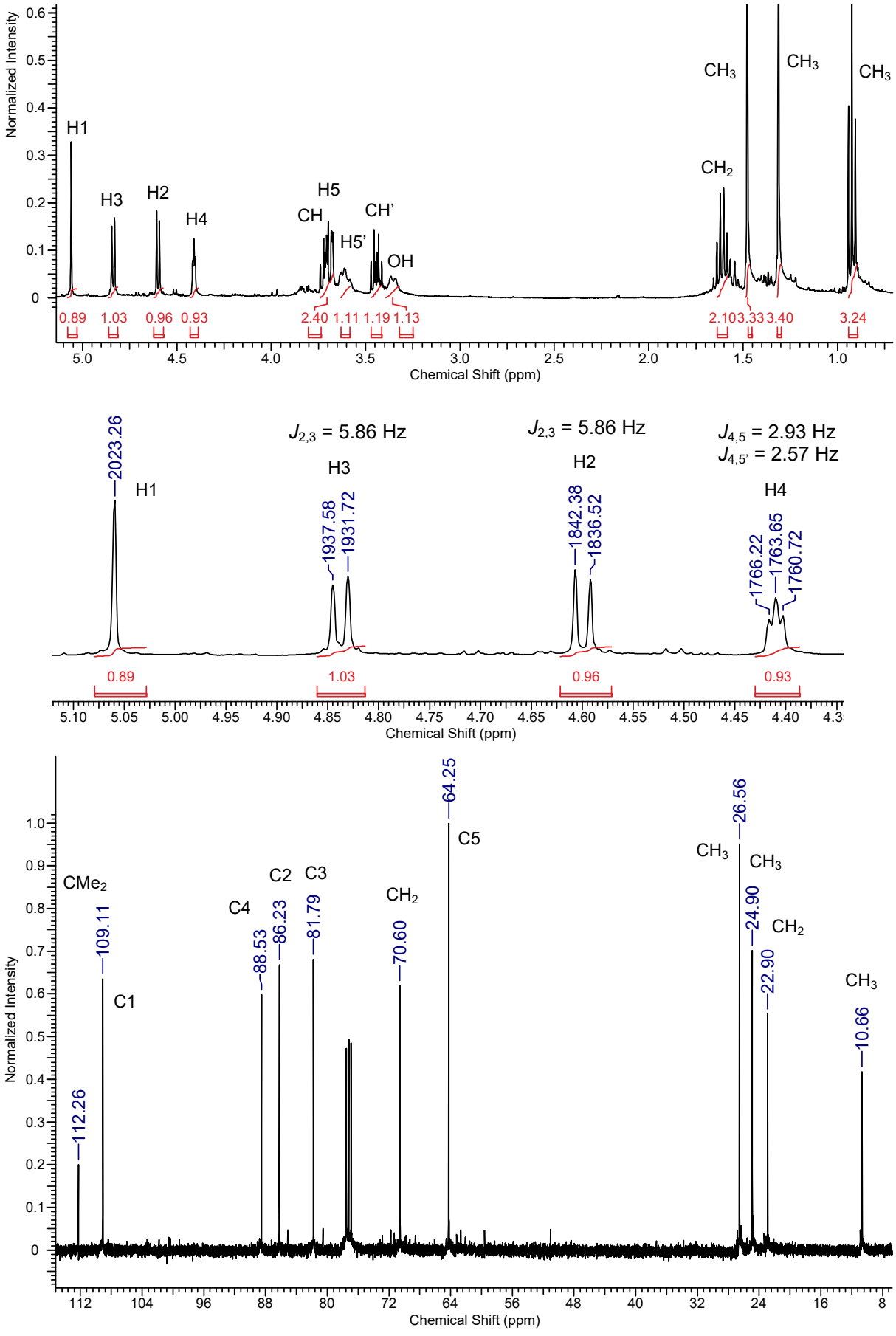

Figure S4. ^{1}H and ^{13}C NMR spectra of **3**.

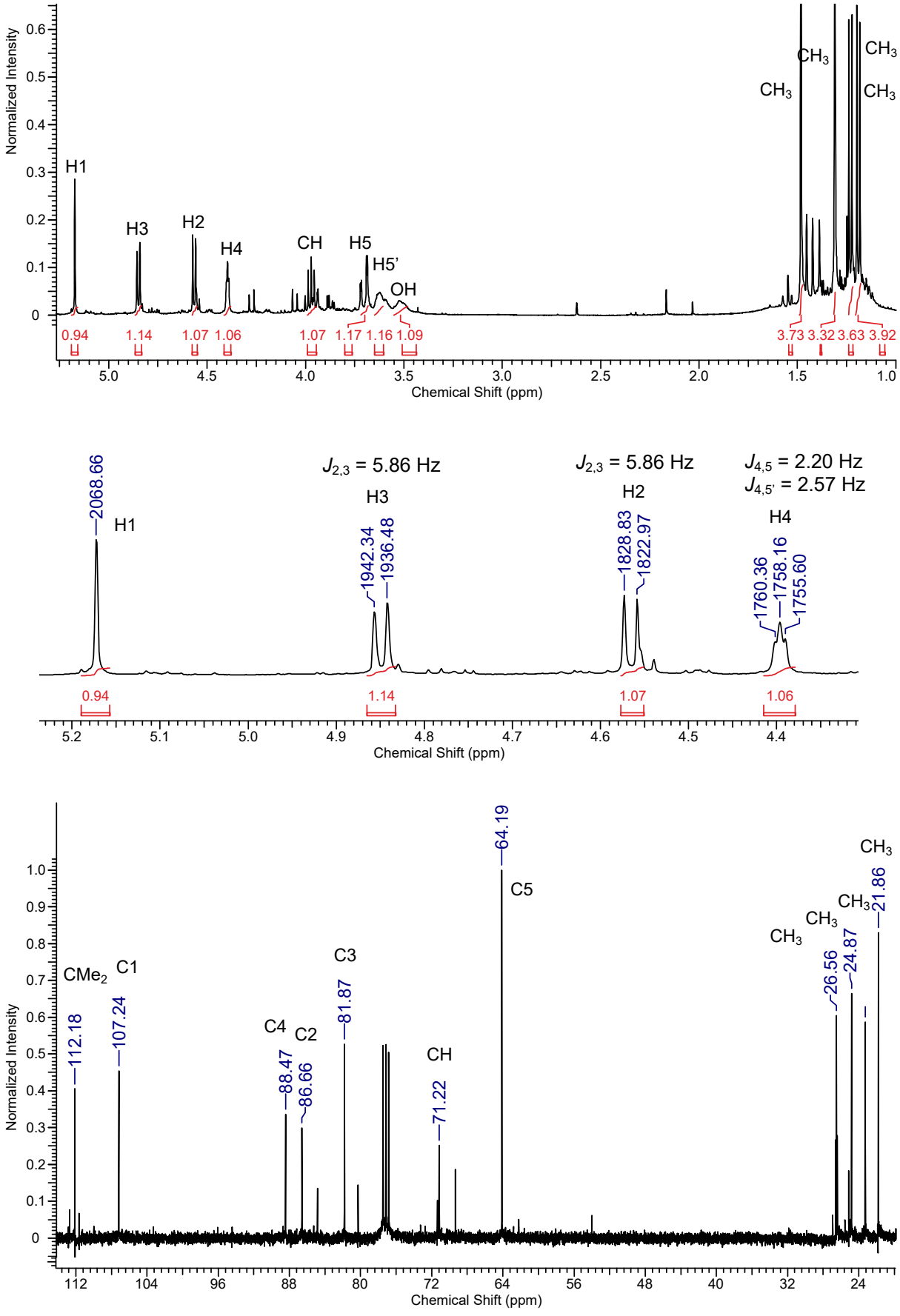

Figure S5. ^{1}H and ^{13}C NMR spectra of **4**.

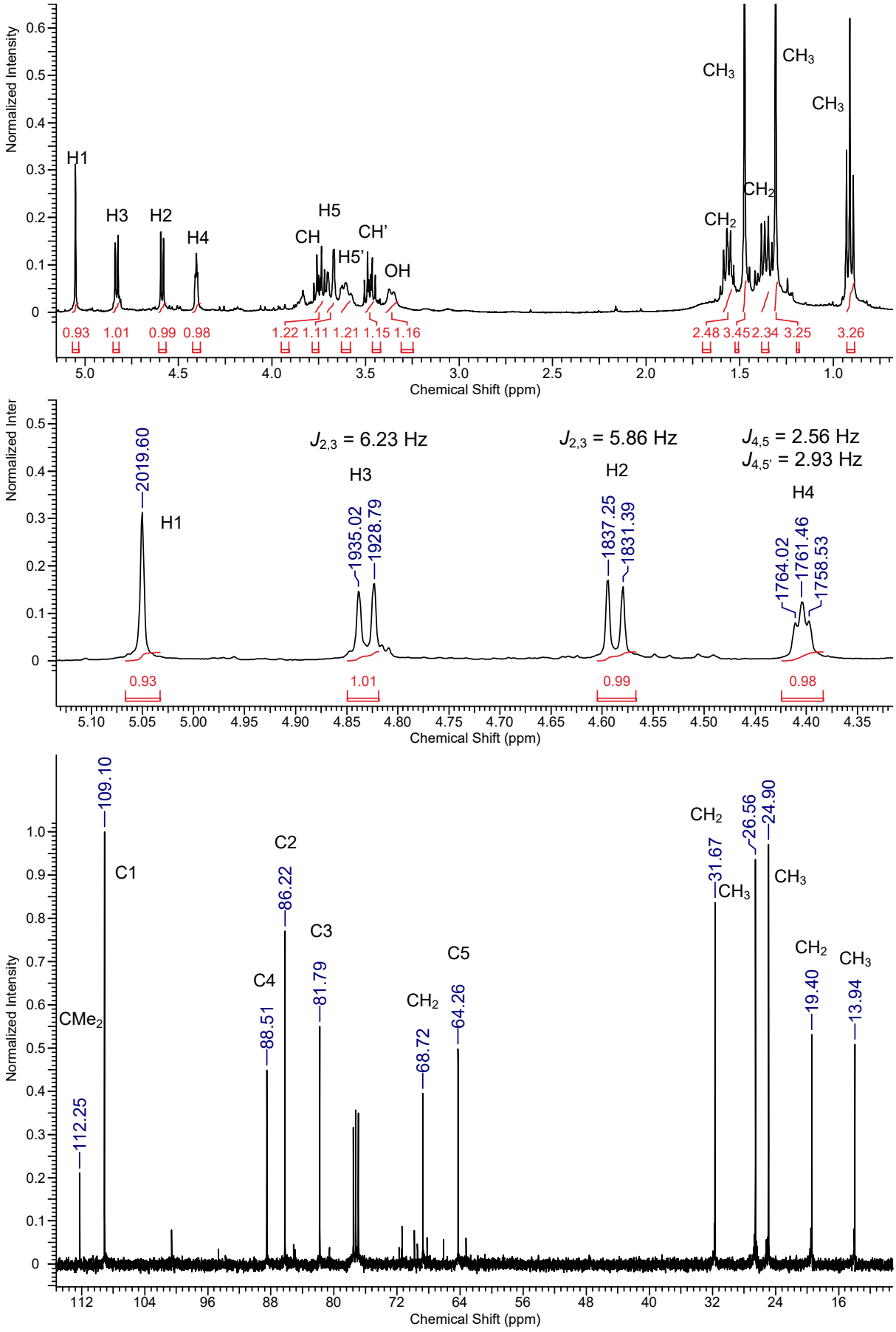

Figure S6. ^{1}H and ^{13}C NMR spectra of **5**.

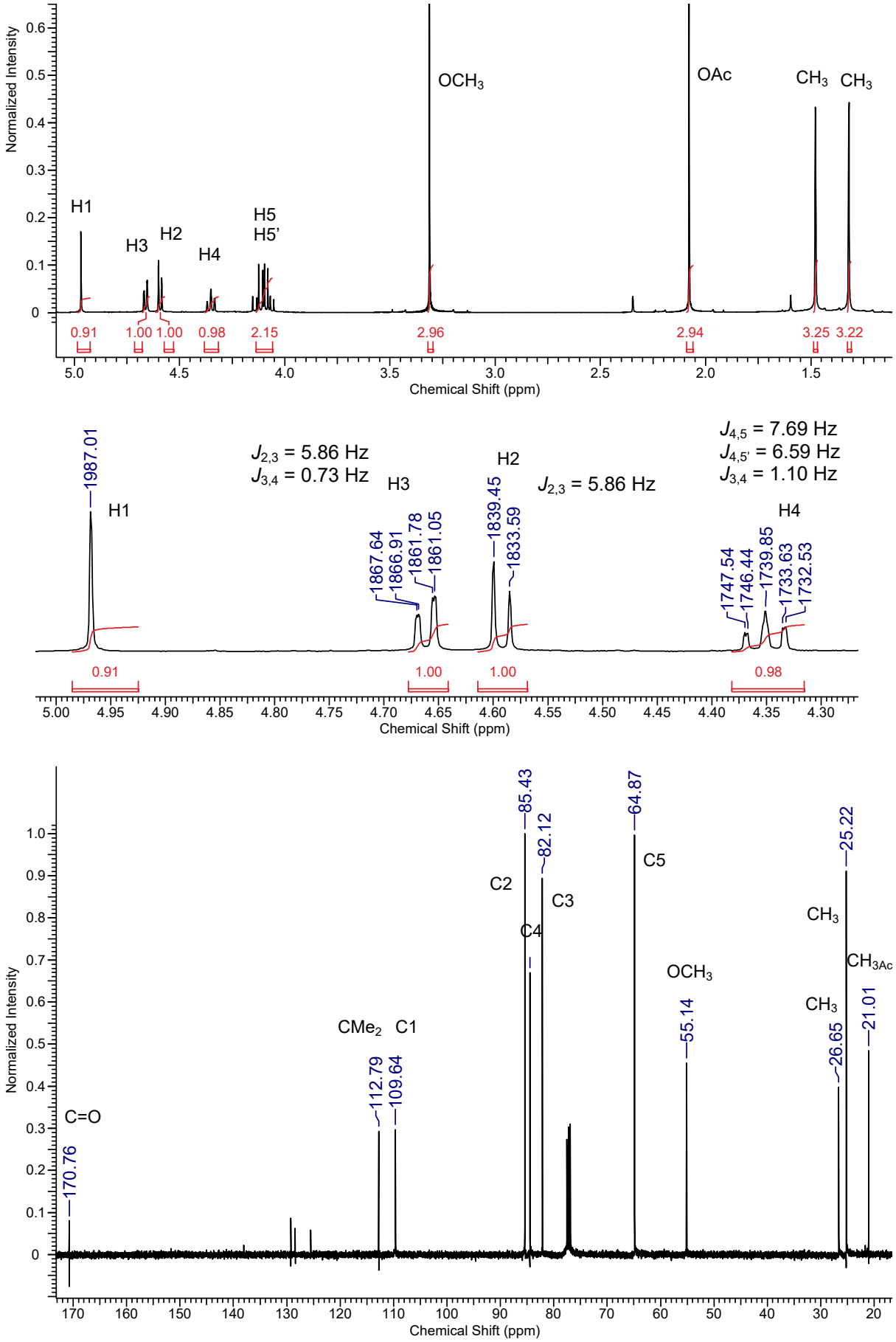

Figure S7. ^{1}H and ^{13}C NMR spectra of **6**.

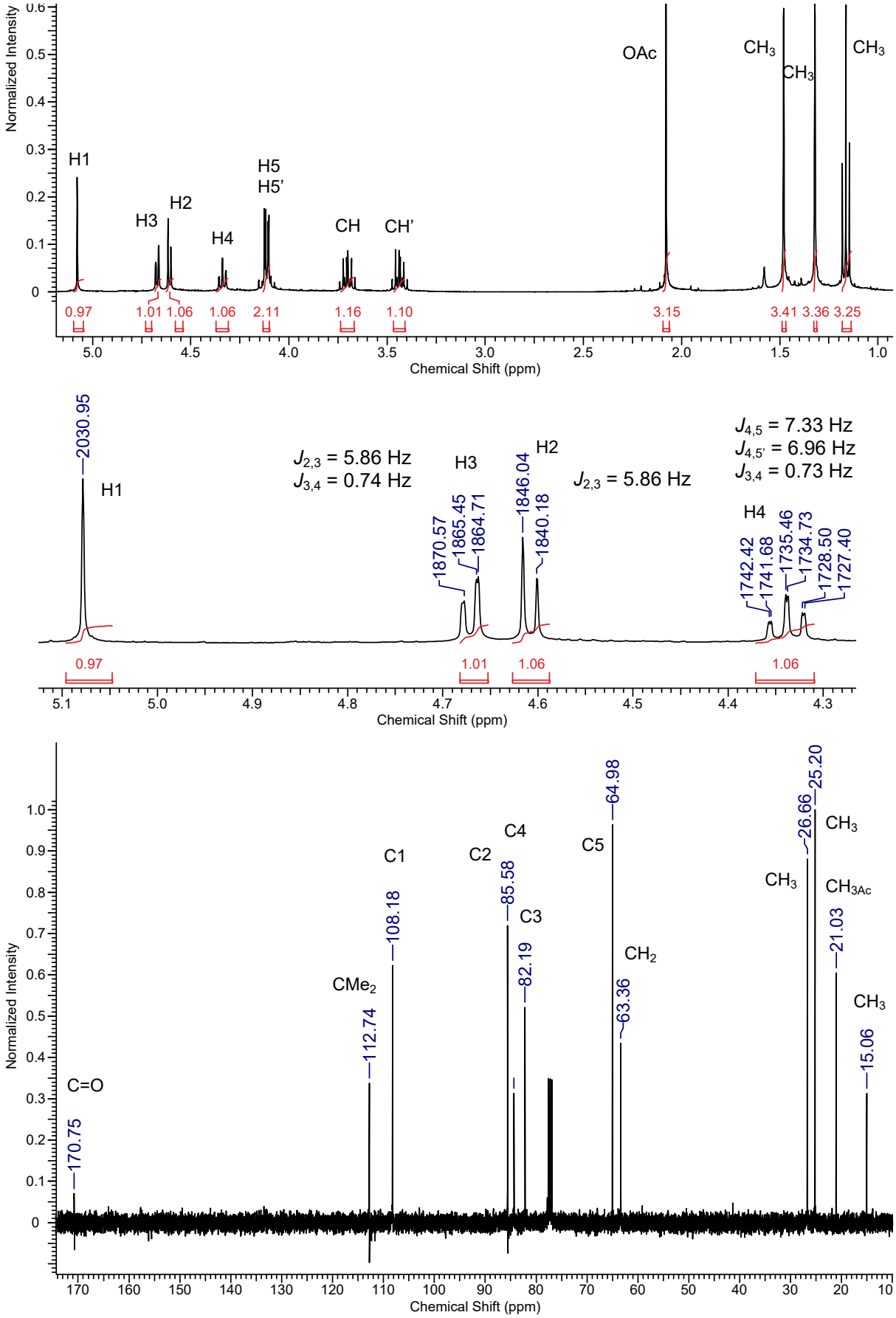

Figure S8. ^{1}H and ^{13}C NMR spectra of **7**.

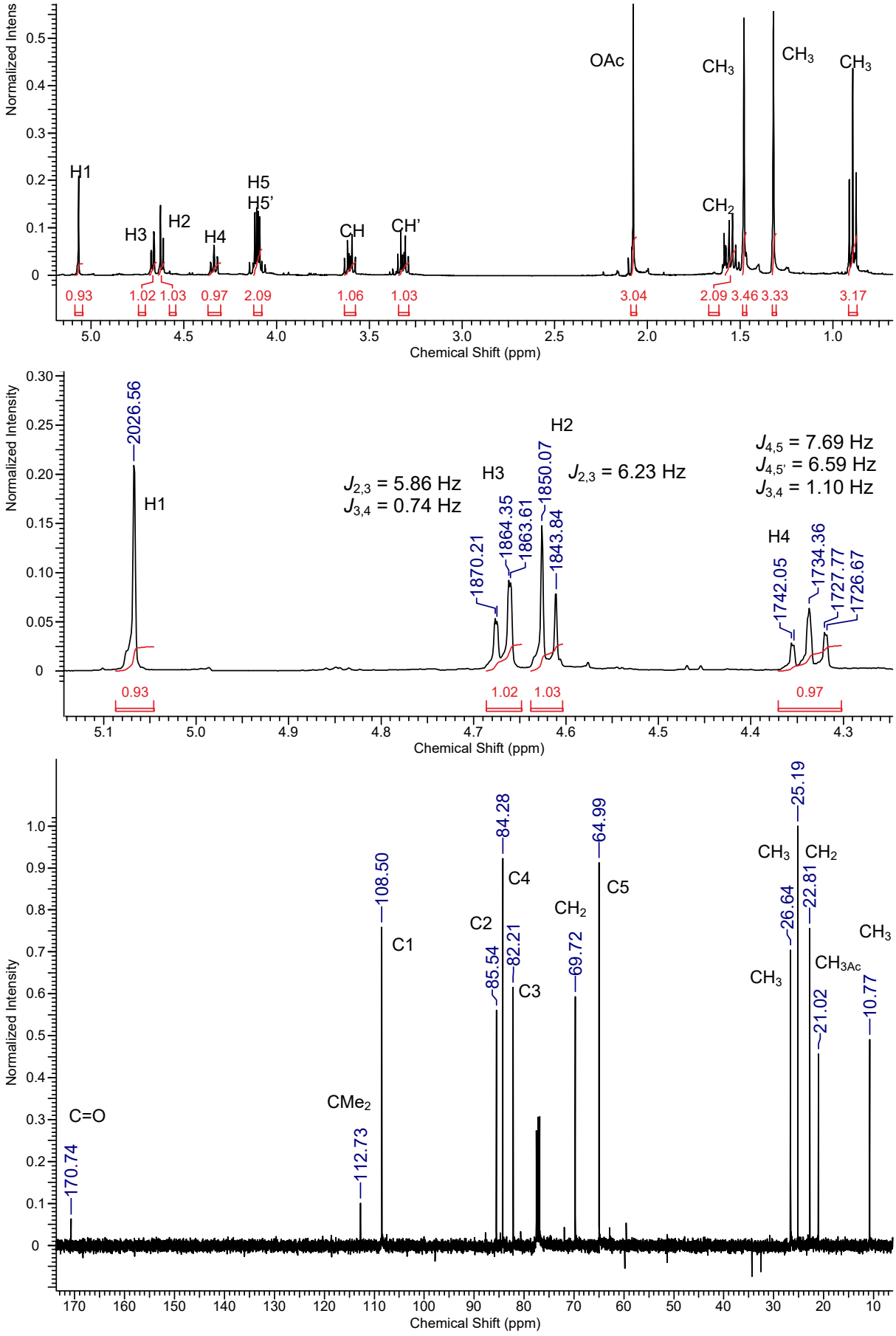

Figure S9. ^{1}H and ^{13}C NMR spectra of **8**.

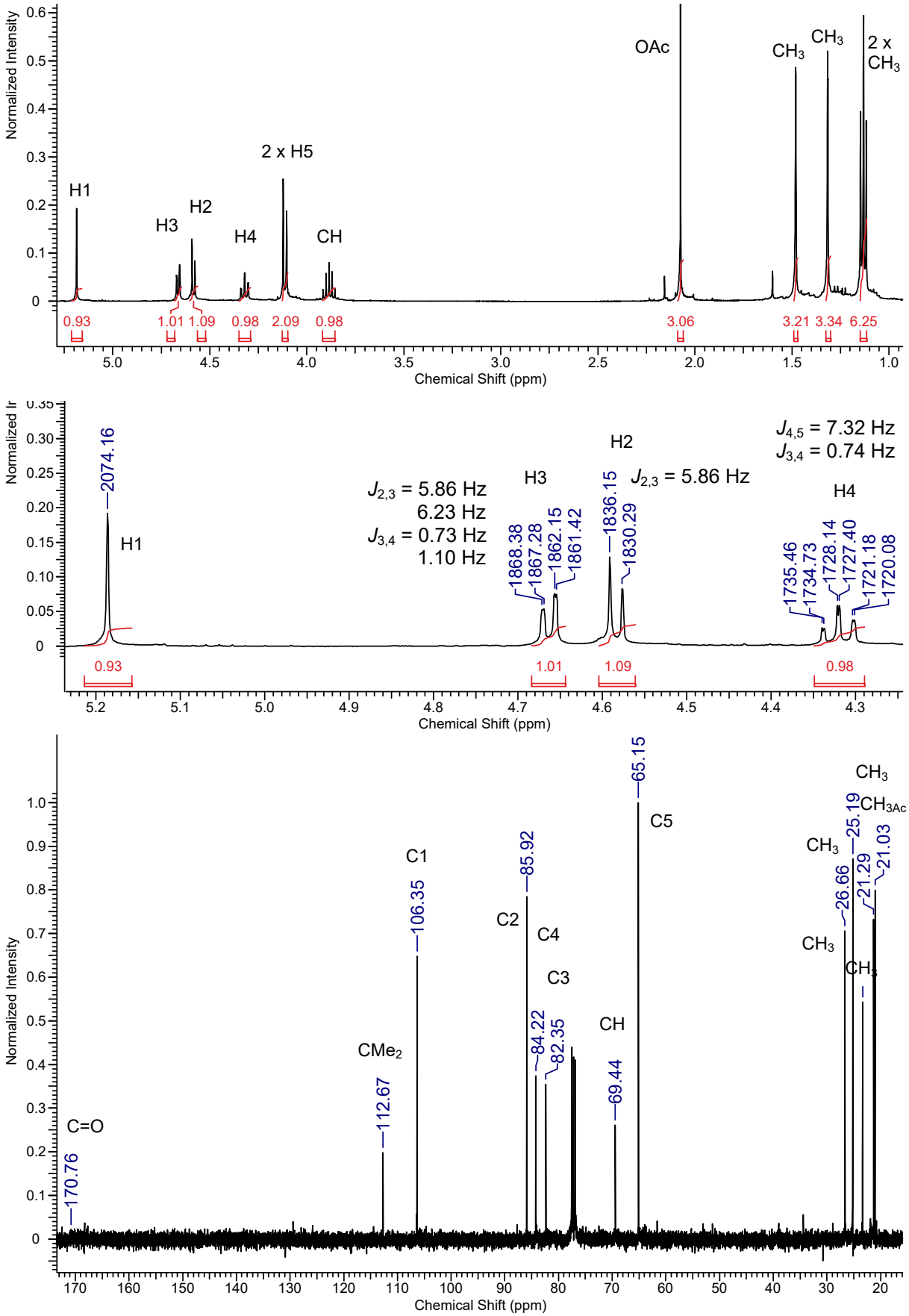

Figure S10. ^{1}H and ^{13}C NMR spectra of **9**.

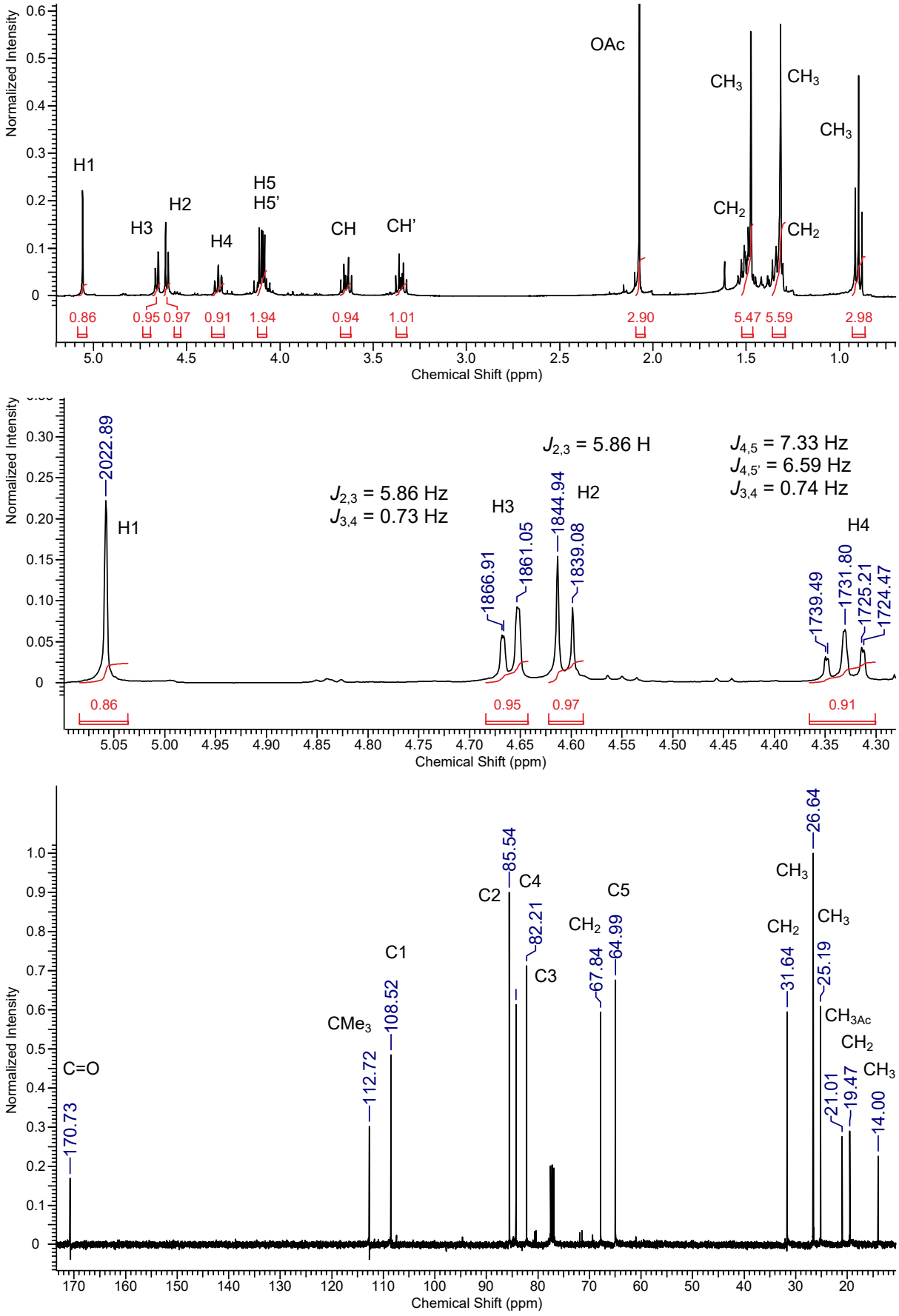

Figure S11. ^{1}H and ^{13}C NMR spectra of **10**.

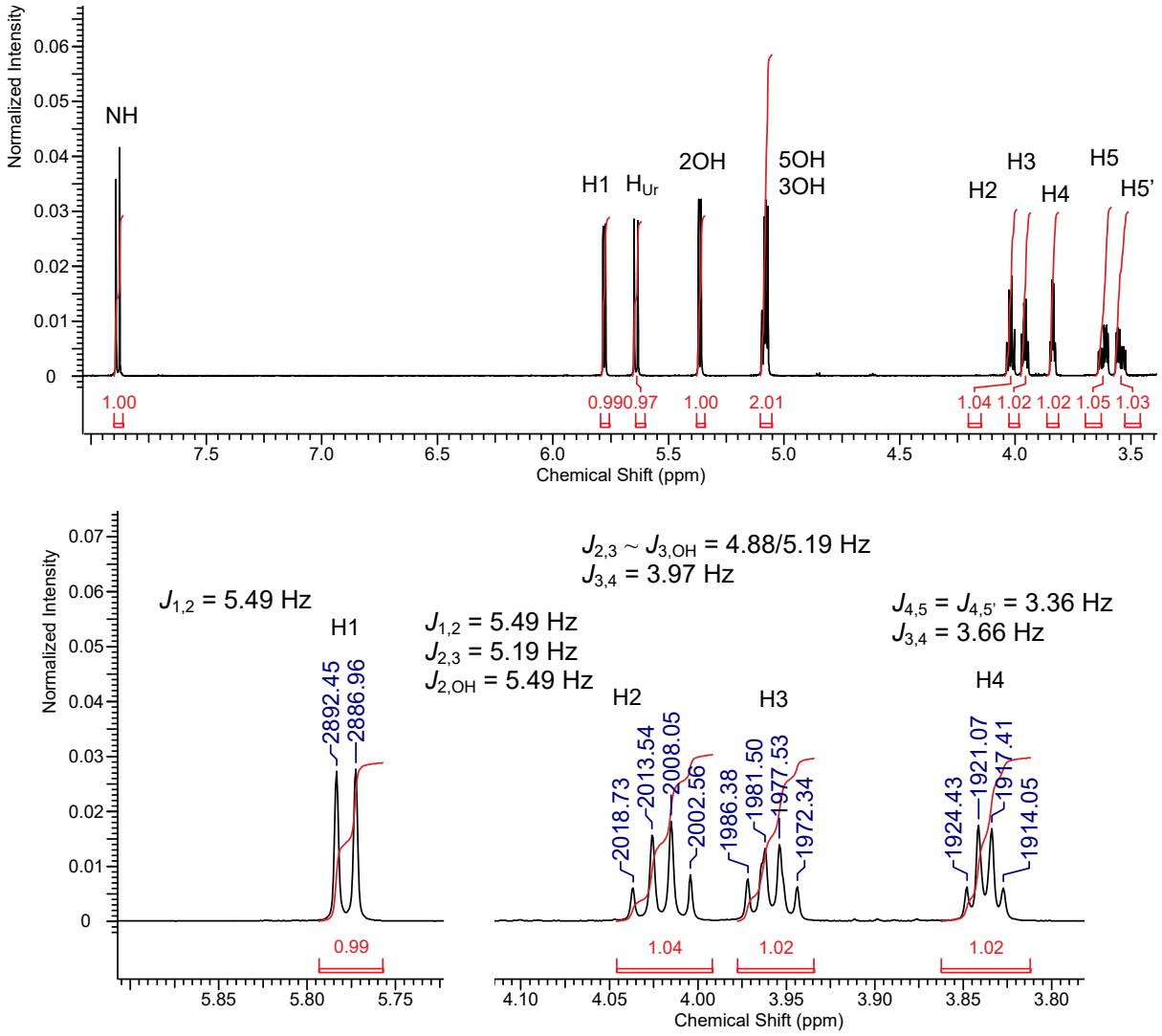

Figure S12. ^{1}H NMR spectrum of **11**.

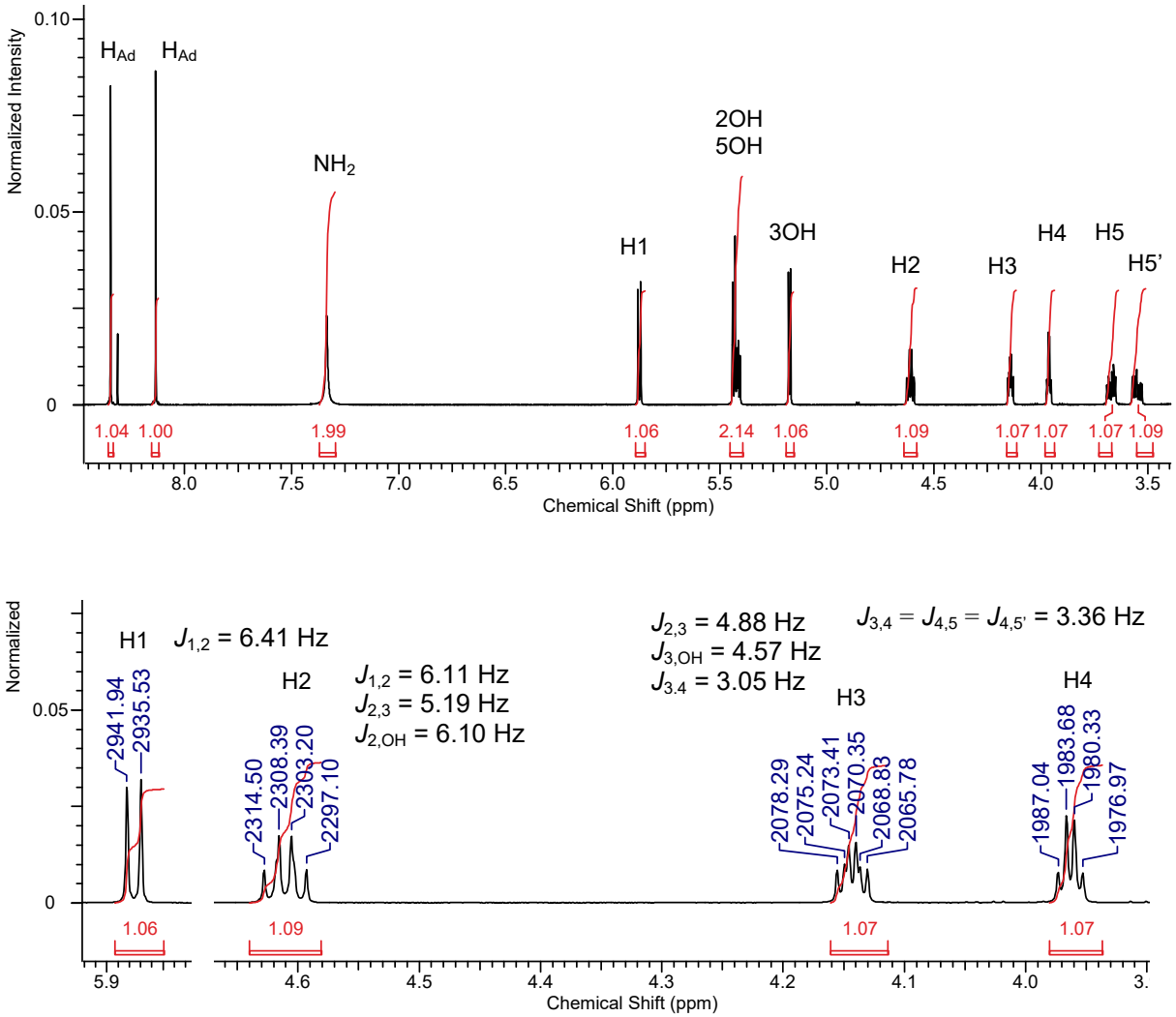

Figure S13. ^{1}H NMR spectrum of **12**.

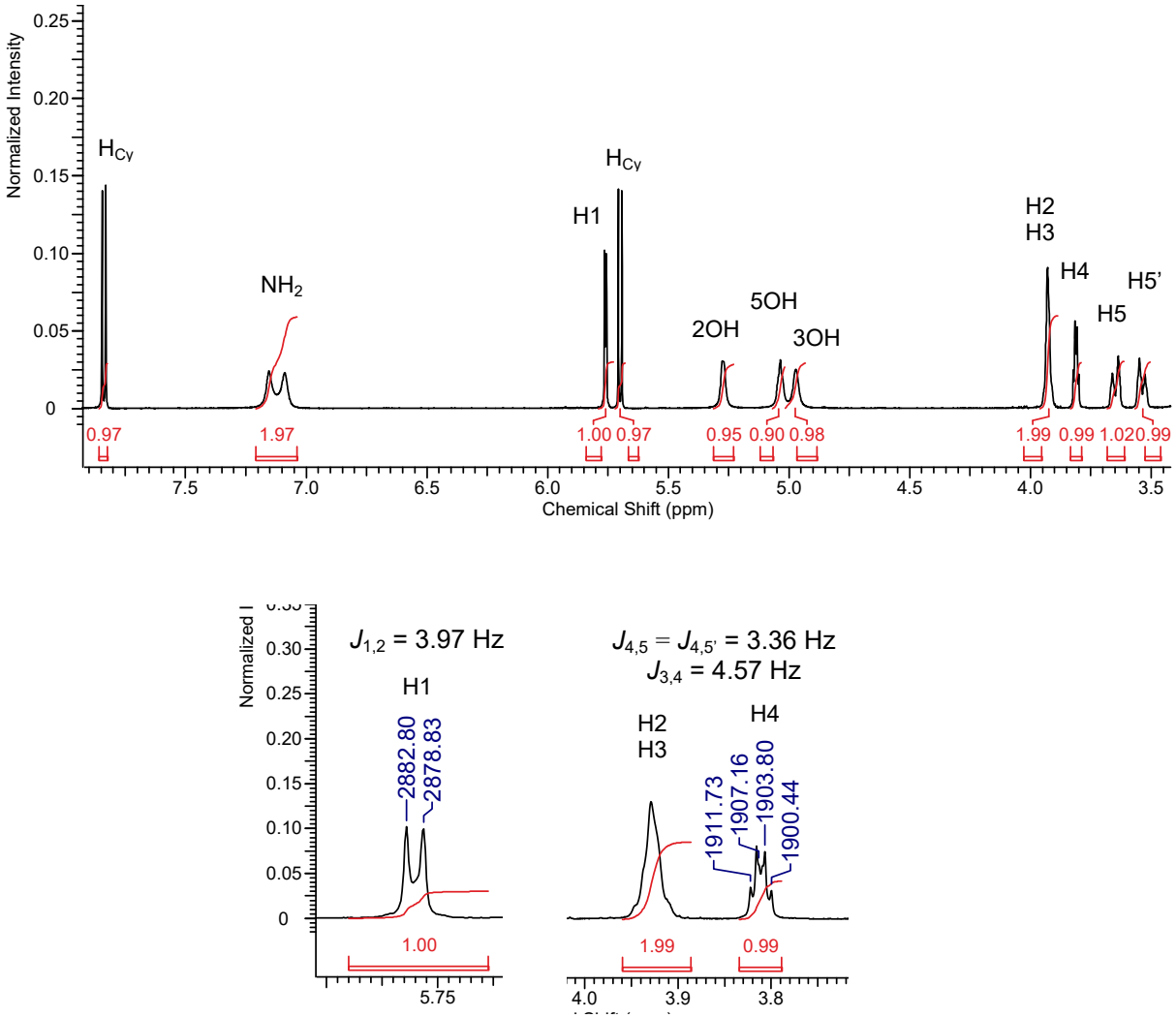

Figure S14. ^{1}H NMR spectrum of **13**.

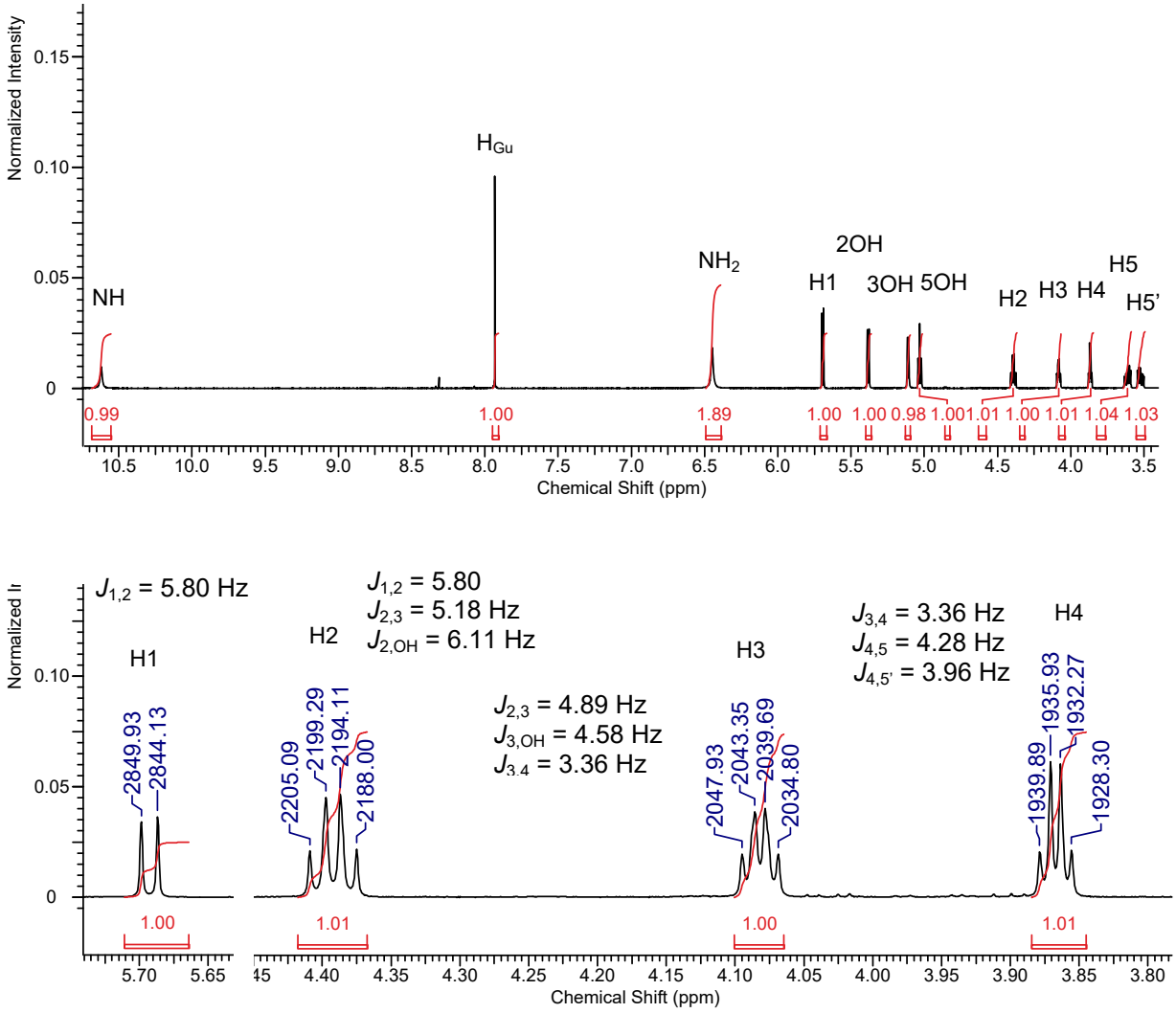

Figure 15. ^{1}H NMR spectrum of **14**.

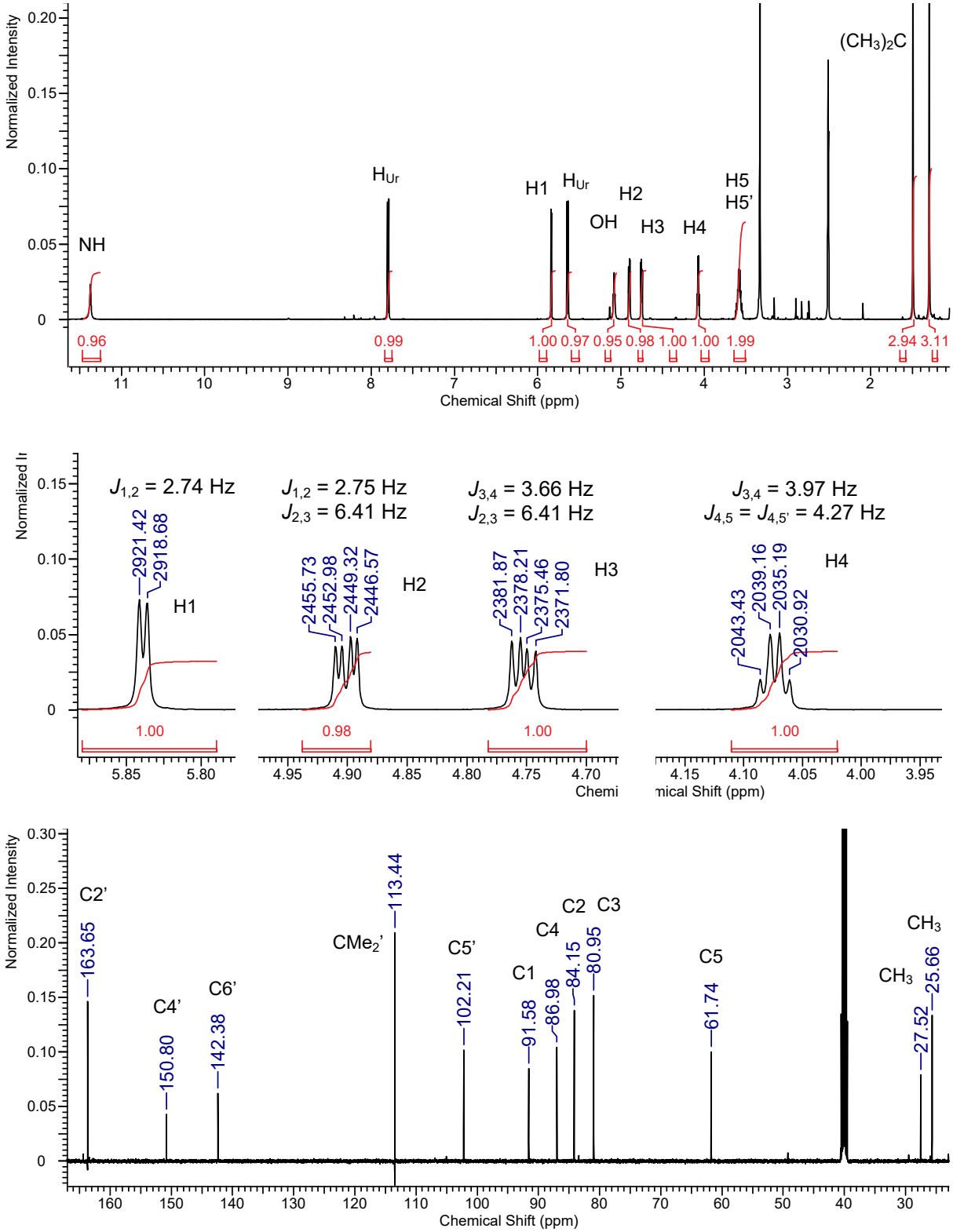

Figure 16. ^{1}H and ^{13}C NMR spectra of **15**.

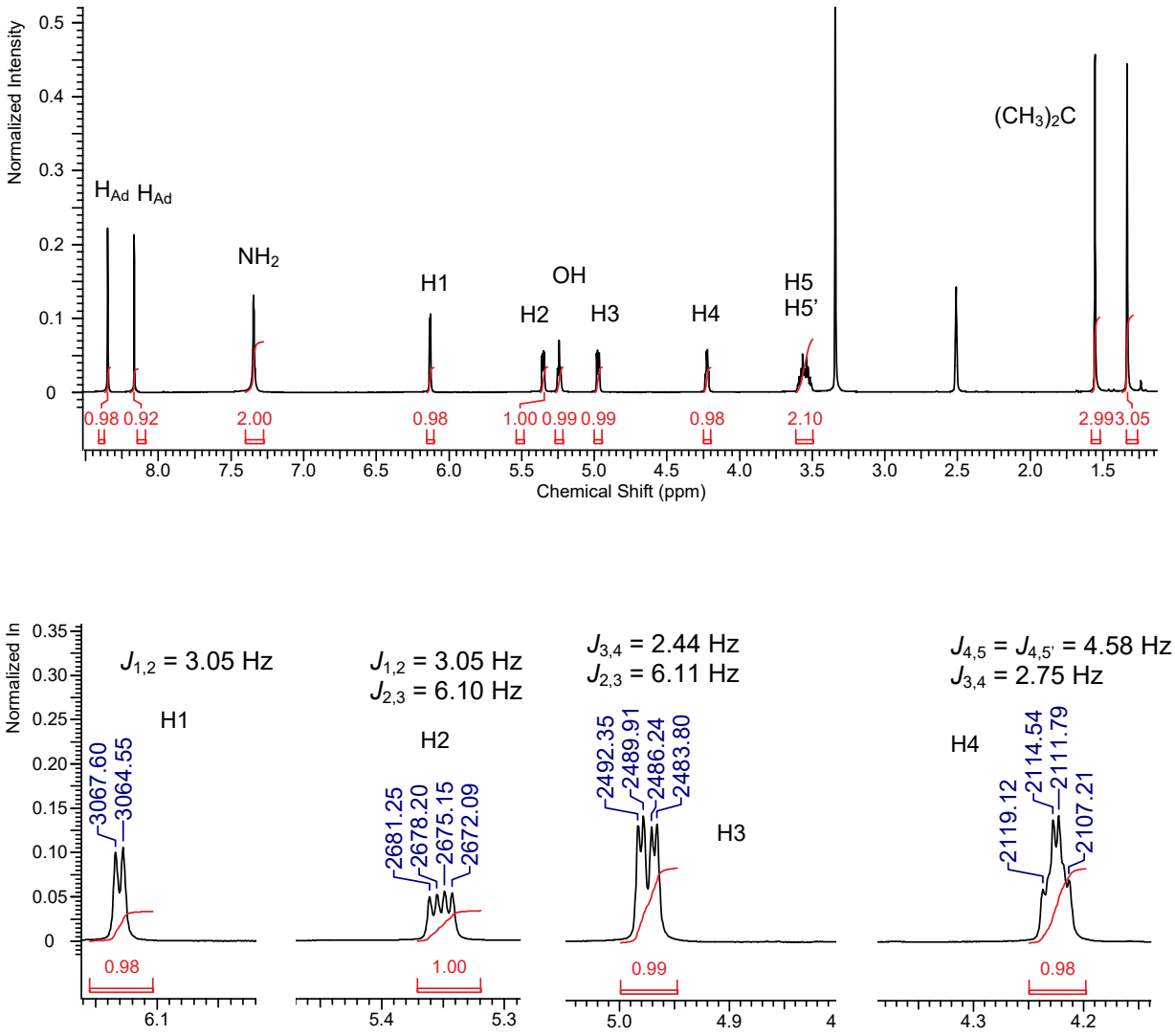

Figure 17. ^{1}H NMR spectrum of **16**.

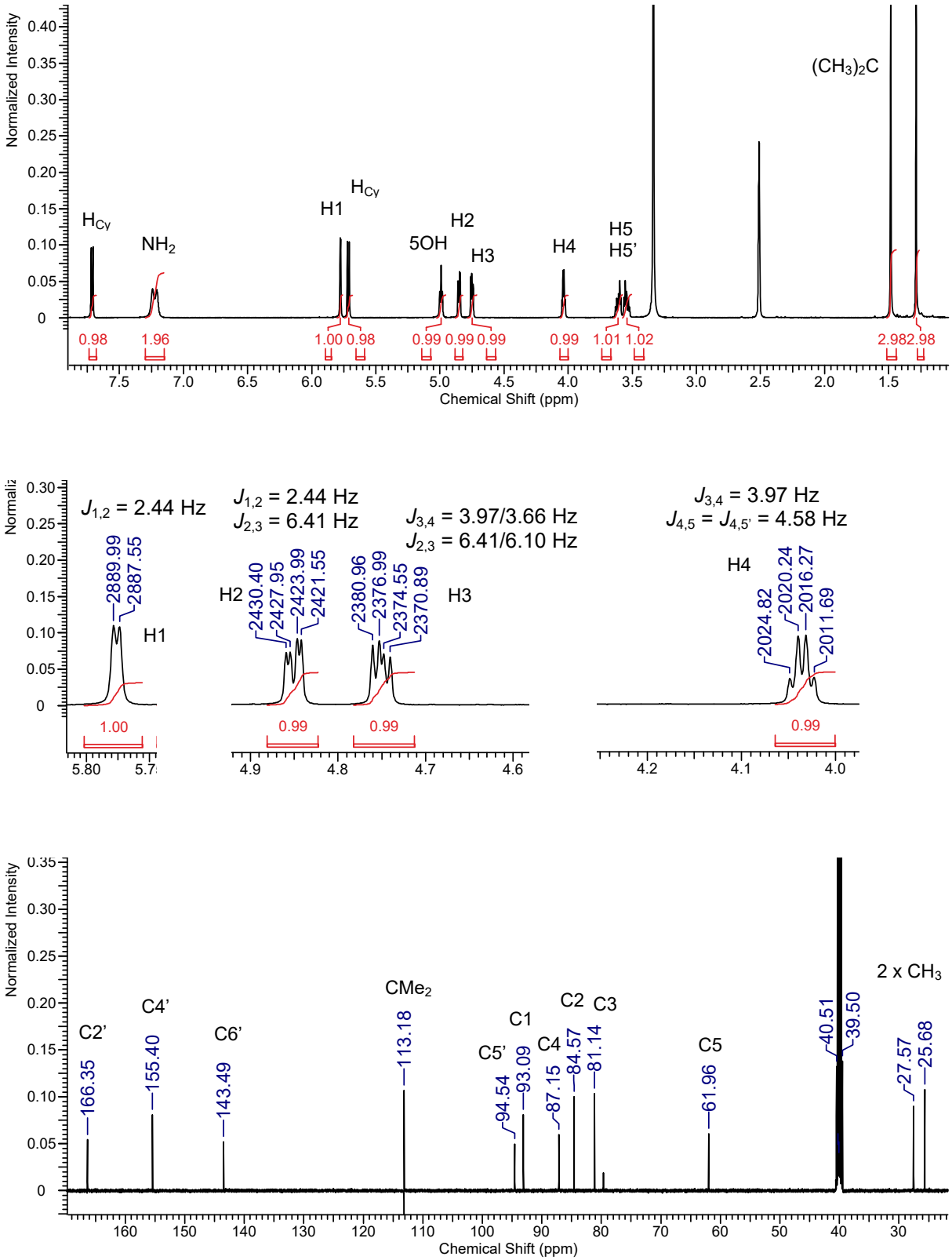

Figure 18. ^{1}H and ^{13}C NMR spectra of **17**.

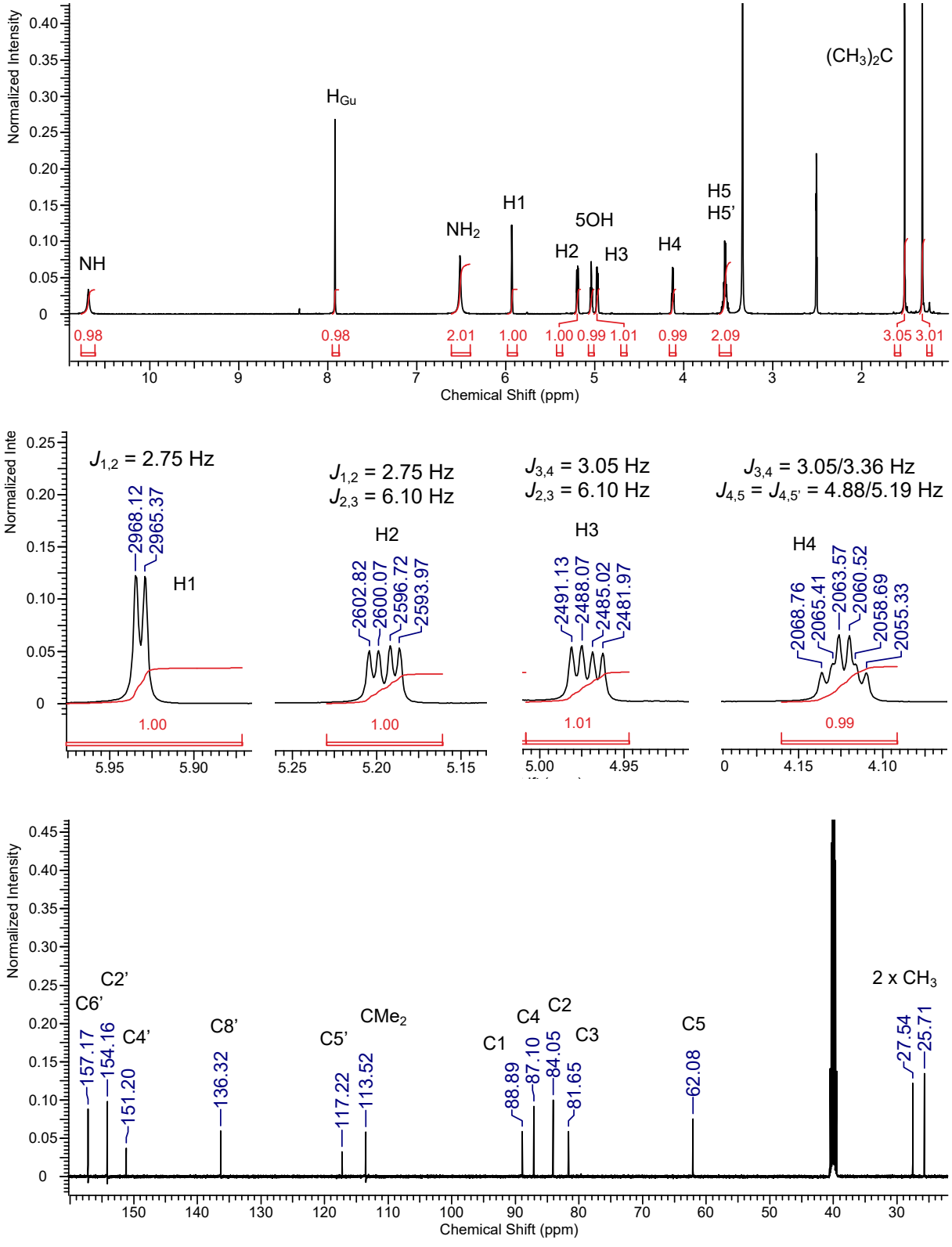

Figure 19. ^{1}H and ^{13}C NMR spectra of **18**.